

The Pennsylvania State University

The Graduate School

INSIGHTS ON PHASE TRANSITIONS IN SUBMICRON AEROSOL PARTICLES

A Dissertation in

Chemistry

by

Theresa Marie Kucinski

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The dissertation of Theresa Marie Kucinski was reviewed and approved by the following:

Miriam Arak Freedman
Associate Professor of Chemistry
Courtesy Faculty Appointment with the Department of Meteorology and
Atmospheric Science
Dissertation Advisor
Chair of Committee

William H. Brune
Distinguished Professor of Meteorology

Paul Cremer
J. Lloyd Huck Chair in Natural Sciences
Professor of Biochemistry and Molecular Biology

Lauren Zarzar
Assistant Professor of Chemistry

Phil Bevilacqua
Co-Director, Center for RNA Molecular Biology
Distinguished Professor of Chemistry and Biochemistry & Molecular Biology
Head of the Department of Chemistry

ABSTRACT

Aerosols are suspended liquid or solid particles that are ubiquitous in the atmosphere. These particles can affect the climate directly by absorbing/scattering radiation or indirectly by helping the formation of clouds. Aerosol particles have an overall net cooling effect, however, there is a large uncertainty associated with the magnitude of cooling. A portion of this uncertainty is due to an incomplete understanding of the chemical and physical properties of particles. Aerosol particles also exist over a large range of sizes which can alter these properties due to size effects, that would require parameterization. Properties that need to be further explored include morphology, phase transitions, and their respective size dependence. This dissertation explores size effects associated with liquid-liquid phase separation (LLPS) and the development of a new method to study phase transitions in submicron particles.

Previously, we found that LLPS is a size-dependent process in submicron particles consisting of an organic compound and a single salt component. The size-dependence produces large particles that phase separate while small particles remain homogeneous. Particles in the atmosphere are complex and can contain hundreds of organic compounds. To expand the size-dependence study to better mimic ambient aerosol, we studied particles consisting of complex organic mixtures and ammonium sulfate. The organic mixtures included: dicarboxylic acids (DCA), complex organic mixtures (COM), and α -pinene secondary organic matter (SOM). We imaged the particles with cryogenic- transmission electron microscopy (cryo-TEM) and all systems displayed size-dependent morphology. Additionally, we observed the presence of three-

phase particles in addition to ‘channel’ morphology. Our results provide further evidence that size-dependent LLPS may be relevant for ambient aerosol.

Studying phase transitions in individual submicron particles proves to be difficult with currently available techniques. We present a new method that flash freezes particles to create snapshots into the phase transition process for submicron particles. This method uses vitrification, which is a technique which cools the sample rapidly such that crystallization is avoided and the humidified properties are retained. A temperature controlled flow tube is used to vitrify the particles at several relative humidity (RH) points followed by imaging with cryo-TEM. The method was verified using efflorescence of potassium salts. Additionally, we demonstrate the ability to image the process of LLPS in submicron particles consisting of 2-methylglutaric acid (2-MGA) and ammonium sulfate.

We applied the flash freeze technique to study the dynamics of LLPS in submicron particles. In particular, we studied separation relative humidity (SRH), which is defined as the RH that separation occurs, for 2-MGA/ammonium sulfate, 1,2,6-hexantriol/ammonium sulfate, and COM/ammonium sulfate. Particles were vitrified and imaged above phase separation, throughout the process of separation, and until LLPS reaches final maturation. We found that the onset of separation is lower for submicron particles than for particles several micrometers in diameter, indicating a potential shift in the phase diagrams. Additionally, the average SRH is significantly lower for submicron particles in the nucleation and growth regime compared to bulk systems. The decrease in SRH indicates a need for new parameterizations to accurately define particles in models. We also found that the dynamics of separation is a random process that is not dependent

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Chapter 1

Introduction

Significance of Studying Aerosol Particles

Aerosols, which are liquid or solid particles suspended in air, are ubiquitous in the atmosphere. Particles in the atmosphere have diverse compositions, sizes, morphologies, and properties. Primary emissions include aerosols directly emitted into the atmosphere from sources such as soot from incomplete combustion to mineral dust from deserts (Figure 1-1).¹⁻³ Secondary emitted aerosols are formed due to volatile organics condensing to form particles. Lifetimes for particles can extend to as long as a week before settling or getting rained out of the atmosphere.⁴ Once in the atmosphere, particles can be transported thousands of miles, for instance mineral dust from African deserts has been detected off the coast of Florida.⁵ Aerosol particles can also undergo transformations such as reactions, uptake, diffusion, and phase transitions.⁶⁻¹⁰

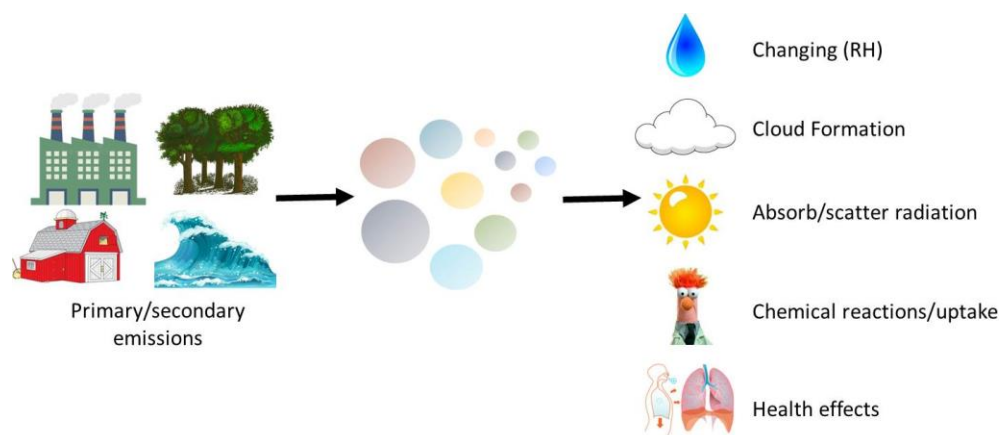


Figure 1-1. Aerosol particles can be emitted into the atmosphere from direct (primary) sources such as industry emissions to indirect sources such as organic compounds that can condense to form aerosols. Particles have a range of compositions, sizes, and properties. Once in the atmosphere, particles can undergo phase transitions due to changing relative humidity (RH), aid in cloud formation, interact with radiation, undergo reactions/reactive uptake, and cause health effects.

Large concentrations of aerosol particles can negatively affect human health due to inhalation. Small particles in the PM_{2.5} range (2.5 μm and smaller) can travel deep into the lungs, entering the alveoli, and can even transverse into the bloodstream.¹¹ Exposure to particles has been shown to increase the risk for cardiovascular and respiratory diseases and also worsens asthma symptoms.¹¹ Locations with high particle concentrations due to pollution are most at risk to experience the respiratory health hazards. Certain countries have agencies, such as the EPA, that sets limit on the particle concentrations. However, many countries lack these guidelines and are experiencing surges in pollution, putting their citizens at risk. The risk is especially prevalent in individuals with pre-existing respiratory diseases. Historical particle pollution events have shown the hazards of extreme pollution events. The Great Smog of London (1952) is an example of an extreme pollution event that was caused by industry emissions and high pressure weather conditions leaving smog surrounding the city for 5 days. During this period, approximately 1.2×10^4 people

were killed due to conditions caused from the smog, and another 1.5×10^5 people were hospitalized.¹²

Aerosol particles can also have a significant impact on climate making them an important component of the atmosphere to study. The climate is directly affected by aerosols by particles absorbing or scattering incoming radiation.¹³ Particles also indirectly affect the climate by acting as nuclei that help form clouds. In turn, the clouds interact with the incoming radiation. The effect of aerosol particles on climate can be measured with radiative forcing. Radiative forcing describes the energy balance of the Earth given by subtracting the outgoing radiation amount from the incoming radiation. The radiative forcing calculated by the IPCC is compared to conditions from the year 1750, which is to represent preindustrial times. The comparison to 1750 indicates the effects of human activity have on the Earth's energy budget and thus climate.¹³ Aerosol particles in particular have an overall cooling effect on climate, however the error associated with this value is quite large. This error is partly due to incorrect parameterization of particles in climate models due to not fully understanding their properties. By studying aerosol particles, we can better understand their processes and accurately include them in models.

Phase Transitions in Aerosol Particles

In the atmosphere, aerosol particles can undergo several phase transitions (Figure 1-2). Efflorescence, which is the process of aqueous particles losing water and crystalizing, occurs with decreasing relative humidity (RH). Deliquescence,

which is the process of crystallized particles uptake water to become aqueous, occurs as RH is increased. Additionally, liquid-liquid phase separation (LLPS) occurs primarily with decreasing RH and is the process of a single phase, homogeneous, particle separating into two liquid phases. LLPS results in a particle with an inorganic rich core and an organic rich exterior. Phase separated particles can have either core-shell (core is enclosed) or partially engulfed (core is partially exposed) morphologies. The resulting morphology of phase transitions can alter particles physical and chemical properties. For instance, particles that have undergone LLPS have been shown to have different viscosities which can alter reactive uptake and diffusion.⁸ The influence of morphology on particle particles requires a thorough understanding of their phase transitions to accurately represent particles in climate models.

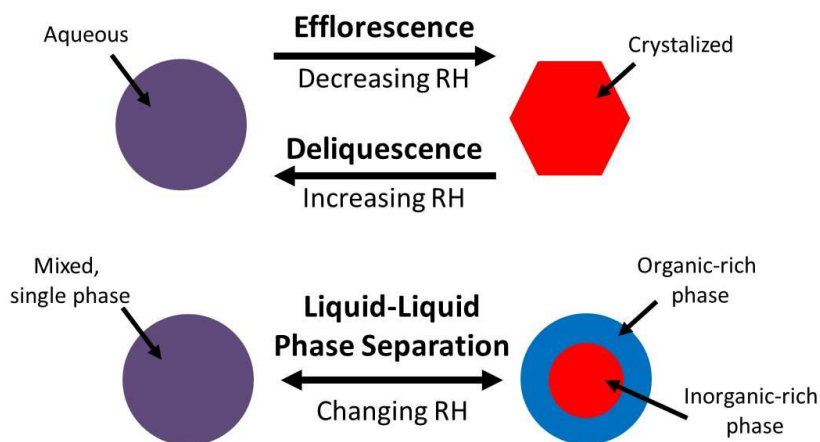


Figure 1-2. Phase transitions present in aerosol particles. Particles can undergo efflorescence, deliquesce, or liquid-liquid phase separation (LLPS) with changing relative humidity (RH). Efflorescence is the process of an aqueous particle crystallizing upon decreasing RH. Deliquescence is a crystallized particle that uptakes water upon an increase in RH. Liquid-liquid phase separation (LLPS) is the process of a mixed single phase particle separating into two liquid phased. LLPS primarily occurs with decreasing RH but can also occur with increasing RH for secondary organic aerosol (SOA).

Effect of Size on Phase Transitions

Properties of submicron particles can differ from bulk properties due to size effects. The Kelvin effect, which states that the vapor pressure over a curved surface is greater than a flat surface, can cause a change in properties for small particles. It has been well-documented that both the efflorescence relative humidity (ERH) and the deliquesce relative humidity (DRH) is lower for submicron particles than for particles several micrometers in diameter.^{14–17} Additionally, our research group found that LLPS is size-dependent for simple systems consisting of a single organic and salt such that small particles remain homogeneous while large particles phase separate.^{18–20} This size dependence was shown to alter properties such as the point at which a particle is activated as cloud condensation nuclei (CCN).²¹

Dissertation Overview

The work presented in this dissertation primarily focuses on understanding the dynamics of phase transitions, and in particular liquid-liquid phase separation (LLPS), of submicron aerosol particles. Studying phase transitions in submicron particles allows us to identify the difference between submicron and bulk systems. Previous studies on LLPS found size-dependent trends however these trends were found in simple systems containing a single organic component and a salt that do not fully represent ambient aerosols which have complex compositions. This dissertation investigates more complex particles to fully understand the LLPS process occurring in submicron ambient aerosol. Additionally, the development of a new methodology

that utilizes flash freezing to study phase transitions in submicron particles is reported. The flash freezing method was used to identify the parameters associated with phase separation in the submicron range. By investigating the phase transition properties of submicron particles, we will be able to create new parameterizations which could help improve the representation of aerosol particles in particle based models.

Chapter 2 discusses the instrumentation and methods used to study phase transitions in submicron aerosol particles. The methods cover particle generation, humidification, drying, and preparation via flash freezing. Instrumentation reviews transmission electron microscopy (TEM) with cryogenic (cryo) capabilities and the condensation particle counter (CPC).

In Chapter 3, the presence of size-dependent LLPS in more complex organic/ammonium sulfate systems is explored. We use 7 complex organic mixtures in the following categories: dicarboxylic acids (DCA), complex organic mixtures (COM), and lab generated α -pinene secondary organic matter (SOM). Particles are imaged with cryo-TEM to determine morphology as a function of size. The presence of new morphologies is also discussed.

Chapter 4 presents a new methodology to study phase transitions in submicron particles. The design of a flash freeze flow tube to vitrify aerosol particles is discussed. Efflorescence of potassium salts is used to verify the method, and 2-methylglutaric acid/ammonium sulfate is used as an example system to showcase the capabilities of imaging the LLPS process.

Chapter 5 builds upon the work discussed in chapter 4. The flash freeze flow tube is used to prepare particles to image the dynamics of LLPS. This study covers the onset of separation, average separation relative humidity (SRH), and insights into the process of separation. Phase separation parameters are determined and suggest the need for new parameterization.

Finally, Chapter 6 summarizes the key points of this dissertation and highlights how it can be applied to the atmospheric community. Future directions for the continuation of these projects are also discussed.

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Chapter 2

Instrumentation and Methods

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique that transmits electrons through a sample to a detector. The produced image reveals submicron details at a significantly higher resolution than optical microscopes. TEM is a powerful technique that is used across many fields including the biological sciences, materials science, and in the atmospheric community. In the atmospheric community, TEM along with its applications can be used to determine size, morphology, phase transition parameters, and elemental composition.

The design of TEM can be thought of similarly to an optical microscope with some differences (Figure 2-1). For comparison, the probing beam in TEM is electrons opposed to light, and electromagnetic lenses are substituted in place of glass lenses to act as the condenser, objective, and projector.¹⁻³ Samples are placed onto TEM grids (usually copper) opposed to slides. TEM also has the presence of a phosphorescent screen that displays the image to the naked eye before imaging. From the beam, the electrons interact with the sample and produce elastically and inelastically scattered electrons that are recorded with a CCD camera. Inelastically scattered electrons contribute to worse resolution in the image and can be filtered out.³ Due to the use of electrons, the entire system is under vacuum to prevent damage to the filament. This also means that the samples are exposed to vacuum conditions, which can we worked

around with an environmental cell that encloses the sample under a gas-controlled environment.^{4,5}

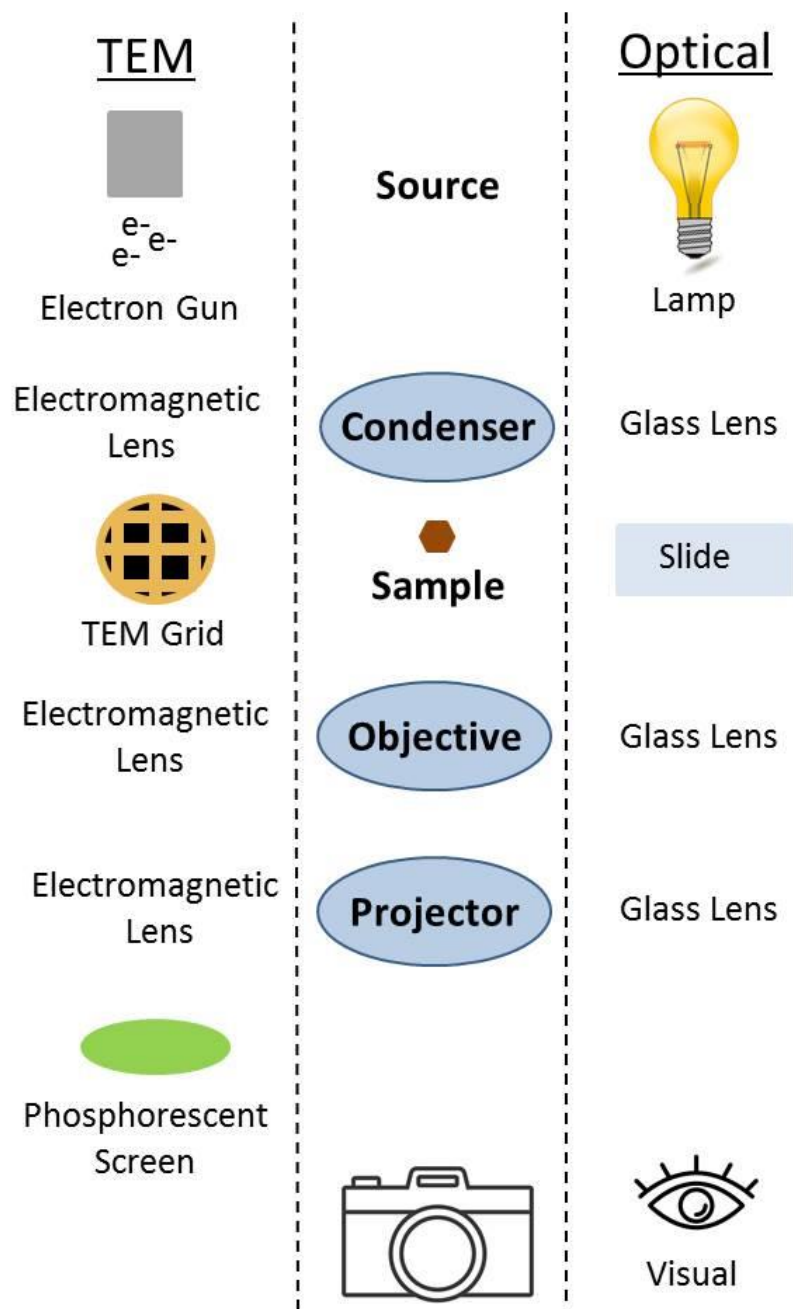


Figure 2-1. The comparison of transmission electron microscopy vs. optical microscopy. The designs are similar however differ in several places. The electron beam is produced from an electron gun comparative to the light source in optical microscopy. In place to glass lenses, are electromagnetic lenses that act as the condenser, objective, and projector. Samples are places on TEM grids, usually made of copper, in TEM. Additionally, a phosphorescent screen is used to display the image. Both methods utilize CCD cameras to capture images, however optical microscopy also has the visual option.

The resolution of the image depends on the energy spread of the electron beam, specimen thickness, and composition, and thus stability, of the sample.² The electron beam is dependent on the instrument itself.² Meanwhile, the specimen thickness and composition can be modified through sample preparation and experimental parameters. A thinner sample will provide better contrast, and composition of the sample can determine its stability under the electron beam.^{2,3} Additionally, specialized specimen holders can be chosen to best fit the needs of the users as mentioned previously with the environmental cell.

In the case of sensitive samples that perform poorly under the harsh electron beam, cryogenic holders can be used to minimize damage.⁶⁻⁸ Cryogenic TEM (cryo-TEM) cools the sample to liquid nitrogen temperatures which help preserve the sample's structure, especially those consisting of organic components. Traditional cryo-TEM vitrifies samples such that they remain in a frozen-hydrated state, which will be explored more in Chapter 4.⁷ Our group does not use vitrification for dry particle analysis, and modifies from the existing technique.⁹⁻¹² In this method, dried samples are transferred into the cryo-holder without previous cooling. Once the cryo-holder, with the loaded sample, is inserted into the TEM and is under vacuum, the setup is then cooled with liquid nitrogen. This method limits ice formation and allows for longer imaging times without the presence of ice. Limiting ice is an important component because the presence of ice can limit the information gathered about the particles. To further prevent the buildup of ice, samples are stored in a desiccator until imaging.

Particle Generation and Collection Methods

Aerosol particles are generated from an aqueous 0.03-0.07 wt % solution through an output atomizer. We use one of two methods to dry aerosol particles to their desired RH value. For fast drying rates, aqueous particles produced from the atomizer are pumped through diffusion dryer to obtain <2% RH with a drying rate of ~99.7% RH/second. To achieve slow drying rates, the particles produced from the atomizer are drawn through a humidifier tube and into a Tedlar bag. Once the bag is filled with particles, dry nitrogen gas is added until the desired RH is reached at drying rates of ~0.005-0.05% RH/second. At this point, the particles are pumped through the diffusion dryer to become fully dried. The benefit of slow drying first is to mimic atmospheric conditions and avoid kinetic effects in phase transitions. For both methods, dry particles are impacted onto a carbon coated copper mesh TEM grids. Methods for imaging humidified samples with vitrification are discussed in detail in Chapter 4.

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Chapter 3

Size Dependent Liquid-Liquid Phase Separation in Atmospherically Relevant Complex Systems

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Abstract

Physical properties of aerosol particles, such as liquid-liquid phase separation (LLPS), have the potential to impact the climate system. Model systems have been shown to have size-dependent LLPS in the submicron regime, however, these systems are an extreme simplification of ambient aerosol, which can include myriad organic compounds. We expand the studies of LLPS in particles consisting of ammonium sulfate and more complex organic mixtures from multiple organic compounds to α -pinene secondary organic matter (SOM). All systems display a size-dependent morphology, with small particles remaining homogeneous while large particles phase separate. Surprisingly, three-phase particles were also observed in some of the systems in addition to a new phase state that we have termed channel morphology, which can arise upon efflorescence. The existence of size-dependent LLPS in complex organic mixtures and SOM provides evidence that this is a relevant

phenomenon for ambient aerosol and should be considered when modeling atmospheric aerosol.

Introduction

Aerosol particles are ubiquitous, complex systems that have a net cooling effect on the Earth's climate.¹ Physical properties including size, shape, morphology, and composition can modify the processes that impact the aerosol-contributed cooling. Recently, several studies report that multicomponent aerosol particles containing inorganic salts and organic compounds can undergo liquid-liquid phase separation (LLPS) with changes in relative humidity.^{2–13} We previously found that submicron particles have size-dependent LLPS where large particles phase separate while small particles remain homogeneous due to the fact that small particles cannot overcome the activation energy to form a new phase.^{14,15} The resulting morphology can impact physiochemical properties of particles including gas partitioning, optical properties, hygroscopic properties, heterogeneous reactivity, and cloud condensation nuclei (CCN) formation activities.^{13,16–21}

Laboratory studies with micron-sized particles show that more complex systems undergo LLPS suggesting that this phase transition is relevant for ambient aerosol.^{22–24} For instance, complex organic mixtures (COM) presented by Song et al., consist of dicarboxylic acids, oxidized aromatic compounds, pinonic and pinolic acid, polyols and levoglucosan, and have been shown to undergo LLPS with optical microscopy when mixed with ammonium sulfate for particles with micrometer

diameters.⁶ Additionally, LLPS in dicarboxylic acid mixtures (DCA) with ammonium sulfate has also been observed.³ You et al. determined that micrometer-diameter particles consisting of the water soluble component of laboratory-generated α -pinene secondary organic material (SOM) with ammonium sulfate undergo LLPS.⁹ Furthermore, SOM free of inorganic salts that includes both water soluble and insoluble components can undergo LLPS with increasing RH, leading to SOM particles with higher CCN activity than previously predicted.^{25,26} These studies suggest that LLPS is present in atmospheric particles, however it remains unclear if this phase transition will have a size dependence.

Previous studies of LLPS in the submicron regime used systems consisting of a single organic compound and an inorganic salt.^{14,15,19,24,27,28} Simplified systems such as these provide a working foundation, but do not necessarily fully represent atmospheric particles which can contain thousands of organic compounds.⁶ Increasing the complexity of representative systems is required to extrapolate physical properties, such as the size dependence of LLPS, of ambient aerosol. In this work, we explore the existence of size-dependent LLPS for complex organic mixtures including the water soluble component of laboratory-generated secondary organic matter (SOM) mixed with ammonium sulfate. We focus on studying a broad range of submicron multicomponent particles with varying degrees of complexity to determine whether size-dependent LLPS is omnipresent in atmospheric particles.

Results and Discussion

Several complex systems mixed with ammonium sulfate were imaged with cryogenic-transmission electron microscopy (cryo-TEM) to probe size dependent LLPS. The systems were classified in three groups, dicarboxylic acids (DCA), complex organic mixtures (COM), and secondary organic material (SOM). Organic mixtures, as defined below in the methods section, included DCA-C5, DCA-C6, DCA-C7, COM-1, COM-3, COM-SA, and α -pinene SOM. All systems were mixed with ammonium sulfate, and are known to phase separate with LLPS as the phase separation mechanism in micron-sized droplets.^{3,6,9} Approximately 100-200 particles were studied for each system to confirm the size-dependence of the morphology. We further characterized the size dependence for two systems by obtaining images for 500-1000 particles and created histograms for mass ratios of 60:40 ammonium sulfate/COM-SA and 80:20 ammonium sulfate/ α -pinene SOM (Figure 3-1). Smaller, homogeneous, particles for each system are shown in Figure 3-1a and 3-1c and larger particles that have undergone liquid-liquid phase separation are shown in Figure 3-1b and 3-1d. For particles consisting of COM-SA, 882 total particles were analyzed (736 phase separated and 146 homogeneous). The smallest phase separated particle was 48 nm and the largest homogenous particle was 148 nm (Figure 3-2). A total of 742 particles containing α -pinene SOM were analyzed (575 phase separated and 167 homogeneous). The smallest phase separated particle was 53 nm and largest homogeneous particle was 90 nm (Figure 3-2). All particles above the transition region, defined as the region where both morphologies occur, are liquid-liquid phase

separated and all below are homogeneous.

The submicron size regime in this study is similar to previous studies of submicron LLPS which also studied particles in the range of tens to hundreds of nanometers.^{14,27} Both systems had a broad transition region which is expected due to the fast drying rate (approximately 99.7% RH/second).²⁷ In contrast, slower drying rates (0.0035-0.08% RH/second) have been seen to produce a smaller overlap region where both LLPS and homogeneous particles exist. Our previous results suggest, however, that a size-dependent morphology that is observed at fast drying rates will remain even at infinitely slow drying rates.²⁷ In drying rate studies, the reduced sizes for the largest homogeneous particles were 35 - 45 nm at the slowest drying rates which remains significant for atmospheric processes such as CCN activation and new particle growth.^{27,29,30} Due to the work by Altaf et al., we know that an observed size-dependence at a fast drying rate will remain even at slow drying rates with the difference being in the sizes for the largest homogeneous and smallest phase-separated particles.²⁷

All phase-separated systems studied in this paper had a size-dependent effect in the submicron regime that produced particles that remain homogeneous at small sizes and phase separated at large sizes (Table 3-1). Interestingly, 50:50 ammonium sulfate/DCA-7 produced only homogeneous particles even though optical microscopy has shown it to phase-separate in this mass fraction range.⁴ This may simply be due to the contrast of the individual components in the electron beam. The presence of size-dependent LLPS for all phase-separated submicron systems adds additional evidence that it is a common phenomenon for complex particles. These results are in agreement

with the literature which shows size dependent phase separation for single organic/salt systems.^{14,15,27} It is unlikely for the observed size-dependence to be due to viscosity of the complex mixtures. A higher viscosity would produce greater amounts of homogeneous particles due to lack of phase separation, however the homogeneous particles are seen at smaller diameters which are known to be less viscous than larger particles.^{31,32} Existence of a size-dependent phase state for more complex organic mixtures and laboratory generated SOM strongly suggests that this is a relevant phenomenon for ambient aerosol particles.

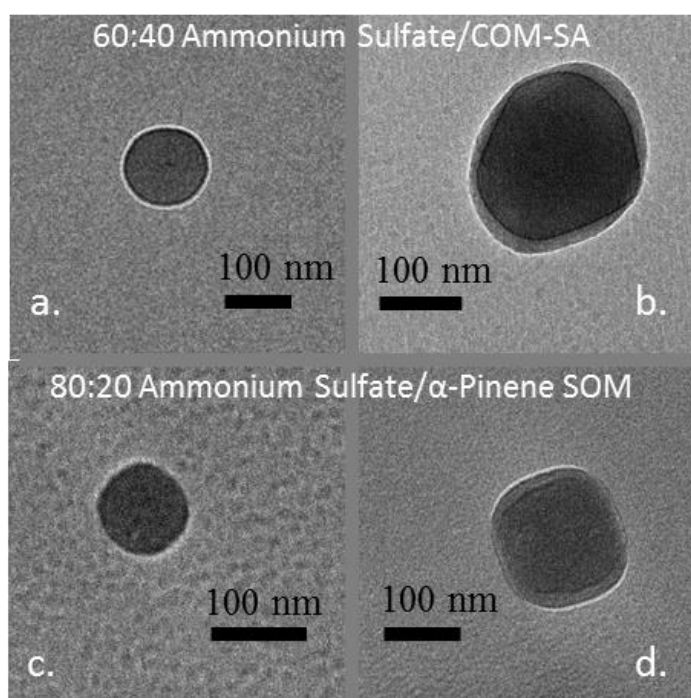


Figure 3-1. Particle morphology for submicron particles observed using cryo-transmission electron microscopy (cryo-TEM) for dry particles composed of 60:40 ammonium sulfate/complex organic mixture-succinic acid (COM-SA) and 80:20 ammonium sulfate/ α -pinene secondary organic matter (SOM). Smaller particles are homogeneous (a & c) whereas larger particles phase separate (b & d). A fast drying rate, at $\sim 99.7\%$ RH/s, was used. The white outline is due to under focusing the electron beam to have optimal contrast to see the phase state. Black line indicates scale bar for each particle.

Table 3-1. Morphology of dry submicron particles in relation to the ratio of the mass of ammonium sulfate (AS) to the organic component.

Morph./ AS:Org	Homog.	2-phase	3-phase	Channel
<i>α</i>-pinene				
52:48	×	×		×
80:20	×	×		
COM-1				
50:50	×	×		×
66:34	×	×		×
80:20	×	×	×	
COM-3				
30:70	×	×		×
49:51	×	×		×
50.7:49.3	×	×		
61:49	×	×	×	
68:32	×	×		×
COM-SA				
40:60	×	×		×
58:42	×			×
60:40	×	×		
DCA-C5				
50:50	×	×	×	
DCA-C6				
50:50	×	×	×	
DCA-C7				
50:50	×			

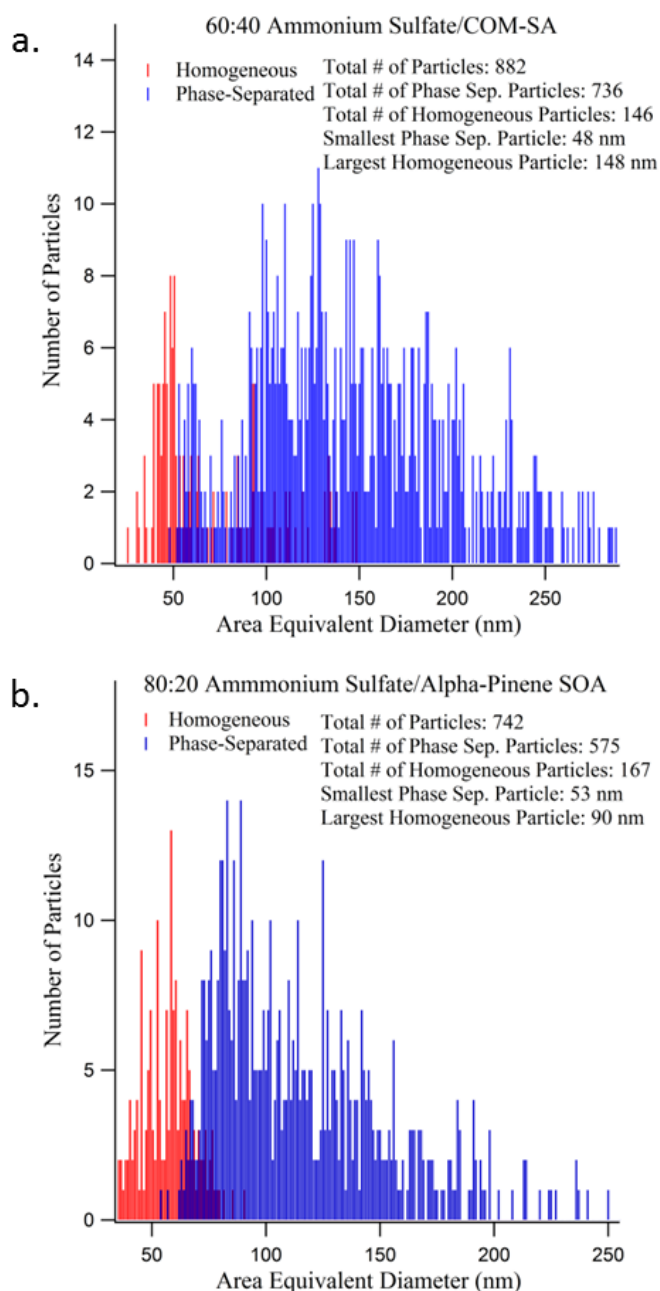


Figure 3-2. Size dependence of liquid-liquid phase separation (LLPS) in dry particles for a) 60:40 ammonium sulfate/complex organic mixture-succinic acid (COM-SA) and b) 80:20 ammonium sulfate/ α -pinene secondary organic matter (SOM). Small particles remain homogeneous while larger particles phase separate.

Surprisingly, we observed the occasional presence of three-phases for 50:50 ammonium sulfate/DCA-5, 50:50 ammonium sulfate/DCA-6, 80:20 ammonium sulfate/COM-1, and 61:49 ammonium sulfate/COM-3 that does not appear to be

dependent on the size of the particles (Figure 3-3). DCA-5, DCA-6, and COM-1 had multiple trials with three-phases present. Both DCA mixtures displayed the presence of three-phases for both fast ($\sim 99.7\%$ RH/s) and slow (~ 0.005 - 0.05% RH/s) drying rates. Aggregation has been ruled out as a possibility for three-phase particles because it persists even when dilute concentrations of the particles are used.. It was unexpected to observe three-phase particles for the DCA and COM mixtures because the organic compounds have at least moderate solubility in the solvent. With this in mind, these particles may not represent the thermodynamic equilibrium state. Determining composition is difficult due to the particles being too fragile to probe with the electron beam and too small for other techniques such as Raman microscopy. To summarize, it appears that three-phases can occur in a subset DCA and COM systems with an inorganic salt, however this phase occurs at a low frequency and does not depend on size.

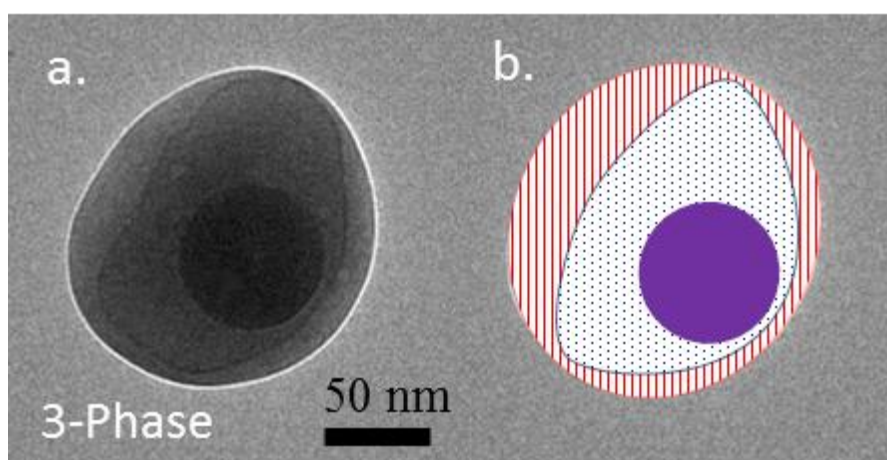


Figure 3-3. a) An example of a 3-phase dried particle observed for the dicarboxylic acid (DCA) – C6 system imaged with cryo-TEM and b) colored image to emphasize phase. A slow drying rate (0.005% RH/s) was used for the DCA-C6 system.

Drying times have been shown to play a significant role in the phase separation process and could also contribute to the resulting morphology of inorganic salts/organic mixtures.²⁷ A slow drying rate (0.008% RH/s) for 80:20 ammonium sulfate/COM-1 produced 32 three-phase particles out of 143 total particles compared to a fast drying rate which produced 12 three-phase particles out of 132 total particles. Moreover, 60:40 ammonium sulfate/COM-SA slow dried at 0.005% RH/s resulted in the three-phase morphology that was not present in fast drying at 99.7% RH/s. It is possible that the three phases are inclusions, although we would then expect the opposite trend in the number observed as a function of drying rate.⁴ That three-phase particles are induced by slow drying rates suggests that inhibition of the formation of three phases during fast drying might be due to particles becoming trapped in a higher energy state morphology.

Additionally, we observed a type of phase separated particle state we refer to as “channel morphology” (Figure 3-4a&b). Channel morphology is present in systems where we also observe two-phase and homogeneous particles. In TEM images of ambient organic-coated sulfate aerosol, Buseck and Posfai found a similar morphology.³³

In addition, molecular dynamic simulations performed by Karadima et al. predicted several mixed phase states including organic-enriched surface with islands or inorganic inclusions for multicomponent aerosol particles that bears resemblance to our observed channel morphology.³⁴

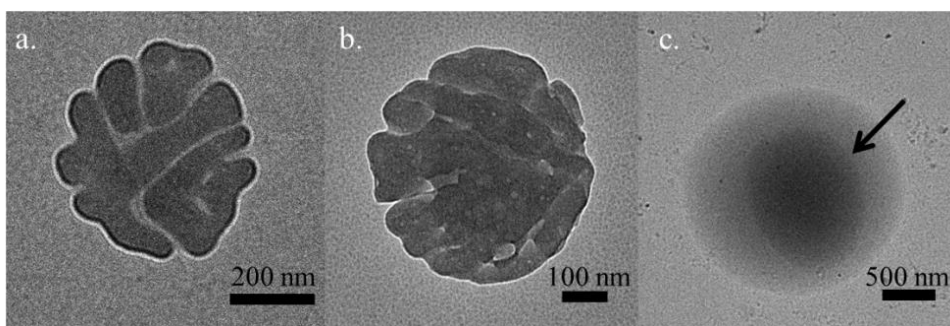


Figure 3-4.. a) Channel morphology for a 50:50 ammonium sulfate/COM-1 dry particle and b) a 50:50 ammonium sulfate/COM-SA dry particle. Channel morphology (a) is more prevalent. c) Liquid-liquid phase separation in 50:50 COM-1/ammonium sulfate particles vitrified at approximately 50% RH. The arrow indicates the new phase. Particles in a) and b) were dried using a fast drying rate and c) was brought down to 50% RH using a slow drying rate (see text for more details).

The occurrence of homogeneous, two-phase, three-phase, and channel morphology in the systems investigated is sensitive to the inorganic/organic ratio, indicating that a phase diagram could be constructed of the different morphologies as a function of organic mass fraction (Table 3-1). For example, 60:40 ammonium sulfate/COM-SA displayed two-phase and homogeneous particles whereas at 40:60 it was channel morphology, two-phase, and homogeneous. Morphology sensitivity to salt concentration was unique for each mixture. For example, the morphology of COM-SA particles changed from two-phase to channel morphology over a smaller range of salt concentrations when compared to other systems such as COM-1. The observed morphology also changes with organic compound mass fractions within COM. Decreasing the mass fraction of pinonic acid from 12.5 to 3.1 and increasing 1,2,7,8-octanetetrol from 3.1 to 12.5 in 50:50 ammonium sulfate/COM-3 was sufficient to induce channel morphology. Considering 1,2,7,8-octanetetrol is approximately ten orders of magnitude higher in solubility than pinonic acid, it is possible that solubility of organic components may contribute to the resulting

morphology. Altering the mass fraction also changes the O:C ratio, however no trend regarding O:C was observed for channel morphology.

The channel morphology is likely occurring at efflorescence and was probed using a new flash freeze method. Particles equilibrated at a specific RH value underwent flash-freezing to produce vitrified particles that keep their phase characteristics and were collected for imaging in cryo-TEM. Particles consisting of 50:50 ammonium sulfate/COM-1 were vitrified at approximately 55 and 50% RH and were imaged to see morphology above efflorescence but below the RH at which LLPS occurs. This technique will be detailed in a separate manuscript and is based off of vitrification techniques common in bioscience.³⁵⁻³⁸ The 50:50 ammonium sulfate/COM-1 system has an efflorescence relative humidity (ERH) of 42.2% and a separation relative humidity (SRH) of 83.3% from optical microscopy measurements on droplets ~100 micrometer in diameter.^{4,6} A 50:50 inorganic/organic composition was chosen due to the presence of channel morphology upon drying. Particles vitrified at these RH values existed in two-phase and homogeneous morphologies after the onset of LLPS, confirming that channel morphology is an efflorescence phenomenon (Figure 3-4c). Based on these results, channel morphology should be considered for arid environments with low RH where effloresced particles are present.

Differing physical properties between organic compounds in the particle such as hydrophobicity, viscosity, surface tension, and solubility can limit the spatial orientation of components and lead to inclusions upon the removal of water.^{34,39,40} It was recently suggested the nucleation of crystals in efflorescing aerosol particles

begins at the surface and creates an internal concentration gradient.⁴¹ It is possible that this event can result in the formation of channels during the crystallization process due to a concentration gradient among the organic compounds within the particle. Molecular dynamic studies show that organic compounds congregate to the surface, thus highlighting the importance of the particle surface for the organic fraction in particles.^{34,42} From our study, channel morphology appears to occur at the onset of efflorescence for organic mixtures and is dependent on functional groups, inorganic/organic ratio, and possibly viscosity as well as solubility.

Size-dependent LLPS was present for all systems and was further characterized for ammonium sulfate/COM-SA and ammonium sulfate/COM-SA. These results confirm that size-dependent LLPS is a relevant phenomenon for ambient aerosol. A size-dependent morphology was seen for every system with complex organics including SOM, which indicates consequences for multicomponent particles and their impact on atmospheric processes such as cloud formation and heterogeneous reactivity. The observed size-dependence is expected to remain even at slower drying rates, although the size of the largest homogeneous and smaller phase-separated particle would be expected to change.²⁷ In our investigation, we additionally discovered three-phase systems and a new phase, channel morphology, which is a consequence of efflorescence that occurs below SRH. Three-phase particles exist among two phase and homogeneous populations and appear in greater quantities in particles that have been dried slowly. Channel morphology has been predicted through molecular dynamics simulations and our results help elucidate the parameters. From our study, we conclude that these results provide further evidence

that a size-dependent morphology needs to be taken into account when considering ambient aerosol.

Methods

Solution Preparation and α -Pinene SOM Generation.

Organic mixtures with increasing levels of compositional complexity were combined with ammonium sulfate to produce aqueous solutions used for particle generation. Specifically, we used organic mixtures designed by Song et al. including mixtures of dicarboxylic acids (DCA), labeled as C5, C6, and C7, and complex organic mixtures (COM) 1 and 3.^{3,4} DCA mixtures contain three carboxylic acids with a carbon count corresponding to the mixture number (Table 3-2). COM contains ten organic compounds with various functionalities to represent the diversity found in atmospheric organic compounds (Table 3-2). The compound 1,2,7,8-octanetetrol was replaced with 1,4,5,8-octanetetrol due to availability. An additional COM was generated and referred to as COM-SA that is compositionally similar to COM-3 but contains succinic acid (Sigma Aldrich, 99%) in place of malonic acid to produce an overall O:C ratio of 0.67. All compounds were the highest purity available, consisting of reagent grade or higher (>97%).

Table 3-2. Composition of organic mixtures

Mixture	COM-1		COM-3		COM-SA		DCA-C5	DCA-C6	DCA-C7
Average O:C	0.63		0.70		0.67		0.80	0.67	0.57
Components	O:C	M _f (%)	M _f (%)	M _f (%)	M _f (%)	M _f (%)	M _f (%)	M _f (%)	M _f (%)
1,4,5,8-octanetetrol	0.50	12.5	12.5	12.5	12.5				
2,2-dimethylsuccinic acid	0.67							33.3	
2-methylglutaric acid	0.67	12.5	12.5	12.5	12.5			33.3	
3,3-dimethylglutaric acid	0.57								33.3
3,5-dihydroxybenzoic acid	0.57	12.5	12.5	12.5	12.5				
3-hydroxybenzoic acid	0.43	6.25	6.25	6.25	6.25				33.3
3-methyladipic acid	0.57	12.5	12.5	12.5	12.5				
3-methylglutaric acid	0.67							33.3	
Diethylmalonic acid	1.75	12.5							33.3
Dimethylmalonic	0.80						33.3		
Glutaric acid	0.80						33.3		
Levogluconan	0.83	12.5	12.5	12.5	12.5				
Malic acid	1.25	12.5	12.5	12.5	12.5				
Malonic acid	1.33		12.5	12.5					
Methylsuccinic acid	0.80						33.3		
Pinolic acid	0.11	3.125	3.125	3.125	3.125				
Pinonic acid	0.30	3.125	3.125	3.125	3.125				
Succinic Acid	1.00				12.5				

Additionally, α -pinene secondary organic material (SOM) was generated using a Potential Aerosol Mass (PAM) flow reactor to mimic ambient organics.⁴³⁻⁴⁵ SOM was produced using 15 ± 2 ppm ozone with an α -pinene (Sigma Aldrich) mixing ratio of 125 ± 15 ppbv and hydroxyl exposure of $1.5 \times 10^{12} \pm 0.3 \text{ cm}^{-3} \text{ s}$ which is equivalent to 11.6 ± 2.5 days. Sample was collected on a QR-200 quartz fiber filter and extracted in HPLC grade water (Fisher Chemical). A total of 0.0324 grams of α -pinene SOM was produced. A more detailed experimental procedure for the PAM reactor has been discussed previously.⁴³⁻⁴⁵

Aerosol Particle Generation and Imaging.

We generated aerosol particles from aqueous solutions ranging from 0.03-0.07 wt% of solute. To generate particles, aqueous solution was passed through an output atomizer and dried using a diffusion dryer (drying rate ~ 99.7 % RH/second) for collection on copper 200 mesh TEM grids with a continuous carbon coating using a cascade impactor (PIXE) as described previously.^{14,15,27} Faster drying rates were generally used for systems with high SRH values that fell within $\sim 15\%$ of the RH at particle generation. Particles collected from DCA-C5, DCA-C6, and DCA-C7 solutions were all dried at a slow drying rate where the particles are initially dried using a Tedlar bag (drying rates ~ 0.005 - 0.05% RH/second) to $\sim 10\%$ RH below separation relative humidity (SRH), followed by quick drying as outlined above.²⁷ Samples were imaged using a cryogenic TEM (cyro-TEM) holder at approximately -170 °C to minimize electron beam damage.^{28,46} Size information was analyzed using ImageJ (NIH).

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Chapter 4

Flash Freeze Flow Tube to Vitrify Aerosol Particles at Fixed Relative Humidities

This chapter has been adapted from: Theresa M. Kucinski, Emily-Jean E. Ott, Miriam Arak Freedman, “Flash Freeze Flow Tube to Vitrify Aerosol Particles at Fixed Relative Humidities”, *Analytical Chemistry*, 2020, 92, 5207-5213.

Abstract

Development of methods to measure the phase transitions and physical properties of submicron atmospheric aerosol particles is needed to better model these systems. In this paper, we present a new method to flash freeze submicron particles to measure phase transitions as a function of relative humidity (RH). Particles are equilibrated at a fixed RH, vitrified in a temperature-controlled flow tube, and imaged with cryogenic transmission electron microscopy (cryo-TEM). We demonstrate the use of the technique for measuring the efflorescence relative humidity (ERH) of potassium sulfate and potassium chloride aerosol as well as the separation RH for a multicomponent organic/inorganic system that undergoes liquid-liquid phase separation (LLPS). The location of phase transitions can shift between the micrometer and nanometer size regimes and particles in a given population may have a range of RH over which a phase transition occurs. This technique addresses these requirements by allowing for characterization of the phase transitions for individual particles in a population on the submicron scale.

Introduction

Development of analytical techniques to characterize aerosol particles is crucial in understanding their effects on Earth's climate and weather. In The Future of Atmospheric Chemistry Research report, The National Academies of Sciences, Engineering, and Medicine lists "the development of analytical instrumentation, measurement platforms, laboratory, theory, and modeling capabilities" as part of the infrastructure needed to fulfil priority science areas.¹ Furthermore, they specify that the development of tools to understand composition, morphology, and phase need to progress over a broad size range from nanometer to micrometer size regimes.¹

While numerous studies of the physical properties of aerosol particles are performed on model micrometer particles, most aerosol particles in the atmosphere are in the submicron size regime. Characterization of particles in the nanoscale size regime is essential because they can have different properties from their bulk (micrometer) counterparts due to finite size and surface effects.²⁻⁴ Literature shows that efflorescence and deliquescence occur at different relative humidity (RH) values on the nanoscale due to the Kelvin effect.^{5,6} Additionally, particles do not always reach thermodynamic equilibrium due to processes such as diffusion, uptake, and changing temperature/pressure during transport/uplift that can create physical and chemical changes to aerosol which leads to size dependence effects due to kinetics. Particles in the nanometer regime have been difficult to characterize due to limitations in available methods. To gain the best representation of the atmosphere, submicron particles need to be as well characterized as their micrometer

counterpoints over a range of RH values, requiring development of new methodology. Particle morphology has been well documented on the micrometer scale with the use of optical microscopy that images aerosol particles over a range of RH values, along with several other characterization techniques such as FTIR and Raman.⁷⁻¹¹

Accessing phase state information in relation to RH is essential for understanding the chemistry and physics of aerosol particles in the atmosphere. With cycling humidity levels in the atmosphere, aerosol particles can undergo efflorescence, deliquescence, and liquid-liquid phase separation (LLPS).^{12,13} The resulting phase state can alter hygroscopic behavior, cloud condensation nuclei activity, reactive uptake, and several other properties that can affect aerosol impacts on climate.¹⁴⁻¹⁷ Limiting phase state studies to the micrometer scale fails to account for the broad size range of atmospheric aerosol and nanoscale effects. For instance, nanometer sized particles that undergo LLPS have been shown to have a size-dependence, such that large particles phase separate and small particles remain homogenous.¹⁸⁻²⁰ Additionally, theory shows that efflorescence and deliquescence can differ on the nanometer scale due to particle size effects.^{5,6}

Currently, there are several microscopy techniques employed to study submicron aerosol particles. Atomic force microscopy (AFM) has been used for analysis of atmospherically relevant particles.²¹⁻²³ Various types of electron microscopy (EM), such as environmental transmission electron microscopy (ETEM), are commonly used to study phase changes of submicron particles.^{24,25} Transmission electron microscopy (TEM) in general provides information on morphology and size

and is advantageous due to its ability to readily achieve images for large numbers of particles.^{19–24,30–31} ETEM can be used to study phase transitions of aerosol particles by exposing particles on the TEM substrate to water vapor.³² Similar to TEM, scanning electron microscopy (SEM), has also been used to study submicron aerosol particles.^{33–36} In addition to the above techniques, scanning transmission x-ray microscopy with near edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) can resolve the organic/inorganic components in an internally mixed particle and can be used to study liquid-liquid phase separation (LLPS) at high RH levels.^{29,37,38} Note that in addition to microscopy techniques, hygroscopic tandem differential mobility analyzer (H-TDMA) analysis has been widely used to investigate efflorescence relative humidity (ERH) and deliquescence relative humidity (DRH) of submicron aerosol particles.³⁹ H-TDMA is used to measure ERH and DRH for ensembles of particles rather than individual particles.

In this study, we introduce a new method that allows for imaging of multicomponent submicron particles at specific RH with minimal damage using a vitrification flow tube. The system is based on the freeze-drying aerosol particles method published by Adler et al.⁴⁰ We have previously dried aerosol particles before collection and imaging, which avoids the use of a substrate during the phase transitions, but neglects critical information about the aqueous particle state.^{19,20,26–28} Our new method vitrifies or “flash freezes” particles equilibrated at a chosen RH. Particles are subsequently imaged using cryogenic-TEM (cryo-TEM). Vitrification is a common technique in the biosciences that allows for TEM imaging of biological specimens with minimal damage.^{41,42} It is an inexpensive cryopreservation technique

used to preserve biological matter due to improved recovery of viable samples while retaining their initial morphology.⁴³⁻⁴⁵

Vitrification freezes a cryopreservant (solvent) around a sample which immobilizes and maintains the solute structure thus creating a snapshot of a liquid locked in place.^{41,46,47} The technique uses fast cooling rates that increase the viscosity of the system to the point that nucleation and crystal growth of water is hindered. The resulting phase is highly viscous and becomes a glass, which is a stable non-equilibrium phase.^{48,49} Transitioning to the glassy state becomes easier to achieve in multicomponent systems due to solute molecules creating a structural barrier for ice formation.^{49,50} The vitrified samples can then be imaged using cryogenic EM using a cold stage that permits imaging without dehydration and minimal damage.^{41,51,52} Aerosol particles can be similarly vitrified with the use of a temperature-controlled flow tube. Temperature-controlled flow tubes have been used previously to study particle freeze-drying, phase changes, as well as to measure freezing curves of aerosol droplets.^{38,51,53} Our technique utilizes a temperature-controlled flow tube in combination with vitrification to produce a new technique to study nanometer particles over a range of RH values. Particles can be imaged at specific relative humidity points thus creating snapshots of the phase transition processes.

Experimental

Particle Generation and Drying

Aerosol particles are generated using an atomizer from a 0.05-0.07 wt% solution. A Tedlar bag (approximately 500 L) is filled with the generated particles (~98% RH). Particle count and RH is measured using a TSI condensation particle counter (CPC) model 3752 and Vaisala HMP110 RH and temperature probe. The probe has an uncertainty of $\pm 1.5\%$ RH. Particles are slowly dried (0.3-0.5% RH/minute) with ultra-purified N₂ (g). On average, the particle concentration ranges from 3×10^3 to 1.4×10^4 particles per cm³. The size distributions of particles before and after vitrification is provided in Figure 4-S1 of the Supporting Information

Flash Freezing and Temperature Controlled Flow Tube

The flash freeze flow tube (Figure 4-1) consists of two concentric stainless-steel tubes.⁴⁰ Nitrogen gas is chilled through a copper coil submerged in liquid nitrogen and is flowed into the outer tube which acts as a jacket to cool the system. The system is covered with 1" flexible foam rubber insulation to maintain temperature throughout. Teflon tubing that can withstand temperatures down to -240 °C is used to transport particles to the flash freeze flow tube. Aerosol particles pass through the chilled inner tube at a port in the start of the flow tube. Particles, now vitrified, exit a second port at the end of the flow tube for collection. The flow rate exiting the tube is 2.5×10^3 sccm. The Reynold's number for the initial and final temperatures are both below 1×10^3 , indicating laminar flow throughout. The residence time of particles is approximately 0.9 seconds. The time needed for a

particle of a given size to reach equilibrium at a given RH was calculated using the method from Chenyakin et al. and was on the order of several minutes.⁵⁴ In comparison, freezing occurs in less than a second. It is then reasonable to assume that the particles stay equilibrated to the bag surroundings with little to no change during freezing. The efflorescence relative humidity (ERH) of ammonium sulfate has been shown to stay approximately constant between 293 K and 233 K.⁵⁵ The ERH of citric acid/ammonium sulfate particles was also found to be approximately constant down to temperatures of 233 K for organic mass fractions of 0.1 and 0.15, but is temperature dependent below 250 K for higher organic mass fractions (0.20 and 0.25).⁵⁵ Meanwhile, the ERH of palmitic acid and ammonium sulfate particles was insensitive to temperature changes down to 235 K.⁵⁶ Additionally, the separation relative humidity (SRH) for ten types of organic/ammonium sulfate particles has been shown to not be a strong function of temperature over a range of 244 to 290 K and varied less than 9.7% RH for all systems studied.¹¹

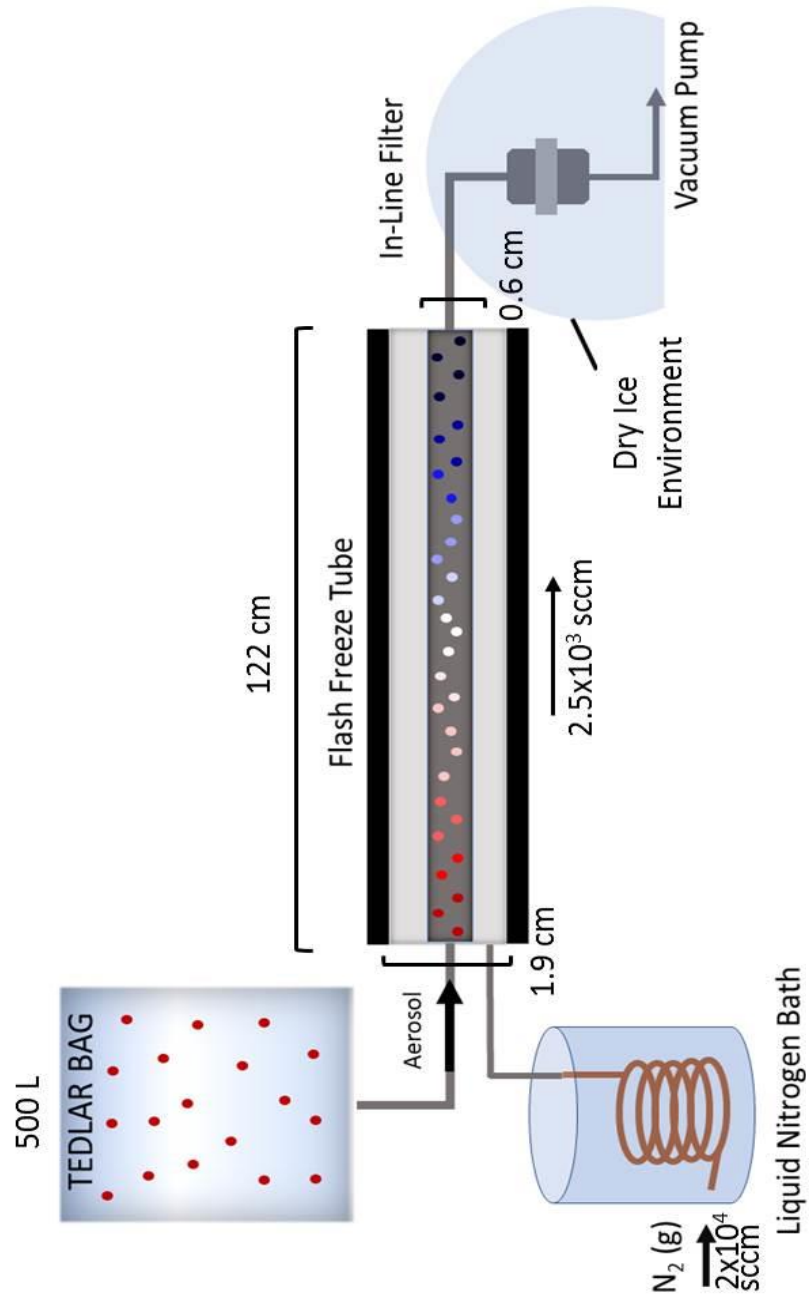


Figure 4-1. Schematic of the flash freeze technique. Aerosol particles are created with an atomizer that flows into the Tedlar bag where they are dried to a specific RH value. A vacuum pump pulls the particles through the flash freeze tube which has been cooled with chilled nitrogen gas. The vitrified particles are impacted onto a TEM grid using an in-line filter within a dry-ice environment.

A Sterlitech LS 25 Gas Line Holder (25mm, stainless steel) is used as an inline filter to collect vitrified particles onto copper TEM grids. The inline filter is contained in a dry ice environment that both chills at -78.5 °C and provides a CO₂ enriched environment to minimize water exposure. Particles reach the inline filter already vitrified, avoiding chance of acidification.

Imaging

TEM grids remain in the dry ice environment until transfer to a Gatan TEM cryo-holder. The cryo-holder is precooled using a cryo-transfer station and the grid is transferred in a liquid nitrogen environment. Imaging is performed at approximately -170 °C and 200 kV, at a spot size selected to avoid damage to the samples from the electron beam. The spot size, which is size of the beam on the sample, ranged from 4 to 6 (arb. units) for minimal damage and depended on the system. The cryogenic temperatures prevent the particles from damaging for tens of seconds while under the electron beam. Size information is gathered using the ImageJ software (NIH).

Theoretical Temperature and Cooling Rates

Temperature as a function of radius was determined by modeling conduction in one direction through multiple layers in cylindrical geometry assuming steady state conditions. The following equation was used to estimate the temperature throughout the radius of the flash freeze flow tube

$$T = T_1 + \frac{S}{4k}(R^2 - r^2)$$

where T is temperature at radial position r , T_1 is temperature at furthest radial point measured at the end of the flow tube, S is heat generation rate per unit volume

dependent on material, k is thermal conductivity of the material, and R is the maximum radius.⁵⁷ The physical parameters are listed in Table 4-S1 and a plot of temperature as a function of radius is in Figure 4-S1 of the Supporting Information. The calculated temperature gradient shows that the outer tube, which contains the chilled nitrogen gas, has the lowest temperature of 218 K, and that temperature increases towards the center of the flow tube where it reaches 227 K. The outermost layer reaches the coldest temperature, and cools the internal components consisting of the stainless steel exterior and the nitrogen contained within the inner tube.

The cooling rate of individual particles in the flash freeze flow tube was calculated as a function of particle diameter. We applied the following equation, which describes cooling rate for falling particles in drop tube, to the particles in our system

$$v_c = \frac{6}{\rho C_p D} [\varepsilon_h \sigma_{SB} (T_{part}^4 - T_o^4) + h(T_{part} - T_o)]$$

where v_c is the cooling rate, ρ is the density of the droplet, C_p is the specific heat, D is droplet diameter, ε_h is surface emissivity, σ_{SB} is the Stefan-Boltzmann constant, h is thermal transfer coefficient of the droplet, T_{part} is particle temperature, and T_o is the flash freeze temperature.^{58,59} Particle temperature is assumed to be equilibrated with ambient air temperatures prior to flash freezing. The flash freeze temperature refers to the temperature of the chilled nitrogen gas within the inner tube. Physical parameters of the particles were assumed to be equivalent to water and are listed in Table 4-S1 of the Supporting Information. The cooling rate rapidly increases with decreasing particle diameter, as expected (Figure 4-2).⁵⁸ Particles will reach

equilibrium with the flash freeze temperature within subnanoseconds to nanoseconds depending on particle diameter, producing vitrified particles.

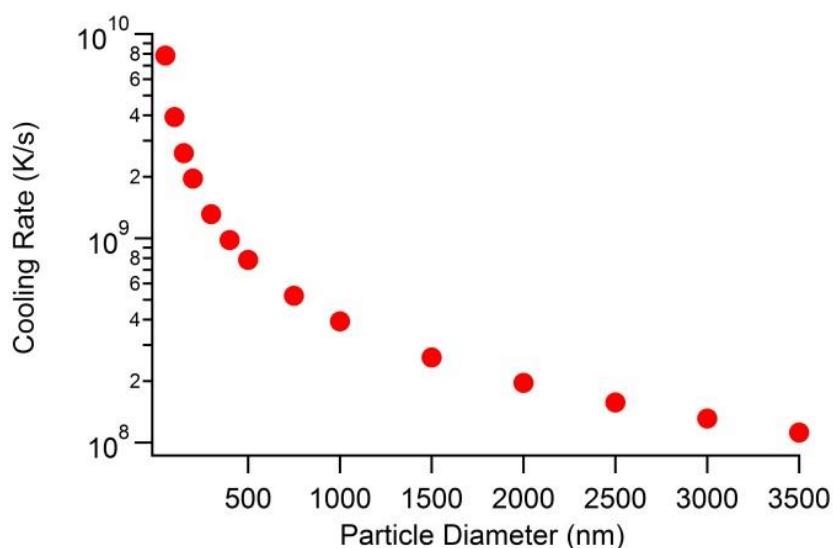


Figure 4-2. Calculated cooling rate (K/s) as a function of particle diameter. Smaller particles are expected to have a faster cooling rate compared to larger particles.

Results and Discussion

Imaging Efflorescence and Liquid-Liquid Phase Separation with Flash Freeze

The vitrification flow tube method was verified using two salts, potassium sulfate (K_2SO_4) and potassium chloride (KCl). Efflorescence and deliquescence of K_2SO_4 and KCl have been characterized for submicron particles previously using environmental TEM by Freney et al. and we verified RH by comparing to these previously published results.⁴⁴

The characterization of these salts at the nanoscale is significant to this work due to the size dependence of efflorescence in inorganic salts. For instance, ERH of ammonium sulfate and sodium chloride decreased with decreasing dry

particle size in particles as large as tens of micrometers down to 50 nm.^{60,61} Working in the same size regime as Freney et al.,²⁵ we were able to verify our method by measuring the ERH values for K₂SO₄ and KCl. Both systems were imaged above and just below efflorescence, in 2-3% RH increments. We found that the particles look empirically different prior to efflorescence compared to the effloresced salt. Above efflorescence, particles have low contrast, appearing as light grey (Figure 3). With decreasing RH, the contrast darkens, centralized at the core. Upon efflorescence, particles have high contrast appearing as a dark grey-black. At this point, reducing the electron beam onto the particle creates a diffraction pattern due to the crystal structure of the particle. Wise et al. identified the phase change of ammonium sulfate and potassium bromide using changes in particle diameters.²⁴ We compared the average particle sizes across RH levels and saw a decrease indicating the loss of water and ERH. The average particle size for KCl at 57% RH was $4 \times 10^2 \pm 2 \times 10^2$ nm and it decreased to $3 \times 10^2 \pm 1 \times 10^2$ nm at efflorescence (52% RH). Similarly, the average particle size for K₂SO₄ was $1.8 \times 10^3 \pm 600$ nm at 68% RH and $1.6 \times 10^2 \pm 50$ nm at efflorescence (61% RH). The provided average size is to give a sense of the amount of water loss, however, we must point out that each listed RH indicates a different experiment and does not track the same group of particles. K₂SO₄ and KCl particles have reported ERHs of $60 \pm 1\%$ and $56 \pm 2\%$ respectfully.²³ The experimental ERHs from this study are $61 \pm 3\%$ and $52 \pm 4\%$ RH for K₂SO₄ and KCl, respectfully. Studies show that ERH tends to decrease when transitioning between micrometer to submicron particles until approximately 40 nm when the Kelvin effect causes an increase in ERH.^{55,57}

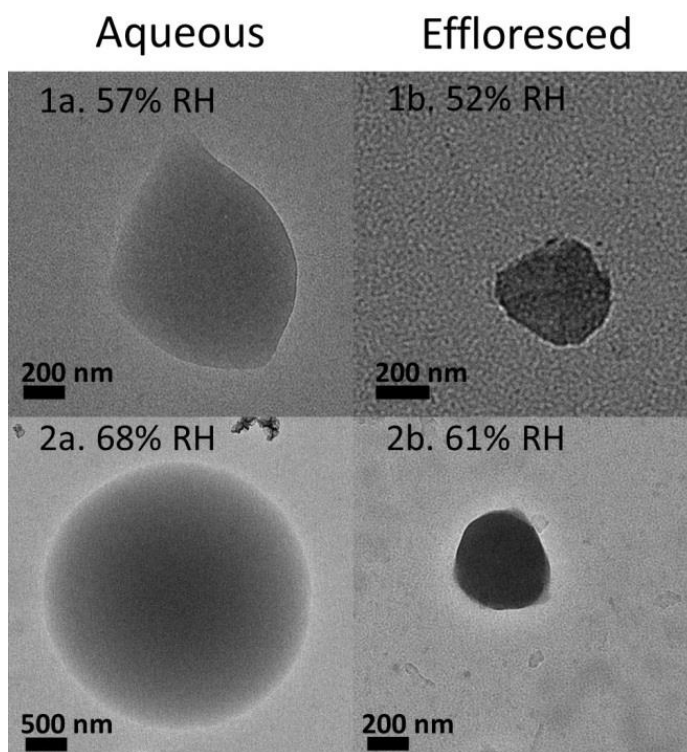


Figure 4-3. Progression of particle phase state for potassium chloride (1a-b) and potassium sulfate (2a-c) with RH. Potassium chloride effloresced at 52% RH (1b) and potassium sulfated effloresced at 61% RH (2b). The white halo around particles is due to under focusing the electron beam to produce optimal contrast.

Additionally, the vitrification flow tube can be used to determine the relative humidity at which liquid-liquid phase separation occurs. 2-Methylglutaric acid mixed with ammonium sulfate in a 2:1 ratio was imaged in approximately 5% RH increments as an example of the capabilities of this method to measure phase changes in multicomponent aerosol (Figure 4-4). Song et al. reports the SRH of 2:1 2-methylglutaric acid/ammonium sulfate as 75% RH for micrometer-sized particles.⁶³ 2-Methylglutaric acid/ammonium sulfate particles were imaged at several points above SRH until the RH at which LLPS was observed. Particles above SRH have light and uniform contrast showing no signs of phase separation. At the onset of SRH

(65% RH for the particle in Figure 4-4) particles have a lighter contrast shell with a darker contrasted spherical core that indicates that phase separation has occurred. Core darkening with the appearance of a defined semi-circular core is the indication that the particle has undergone LLPS and is not present above SRH. Upon decreasing RH further (62% and 56% RH), phase separation becomes more defined with a decrease in overall average particle area and a pronounced reduction in size of the outer shell indicating a decrease in water content. Particles are core shell at the onset of LLPS and progress to become partially engulfed with decreasing RH. This change in morphology has previously been observed with decreasing RH in micrometer diameter particles contained in an optical trap^{64,65}

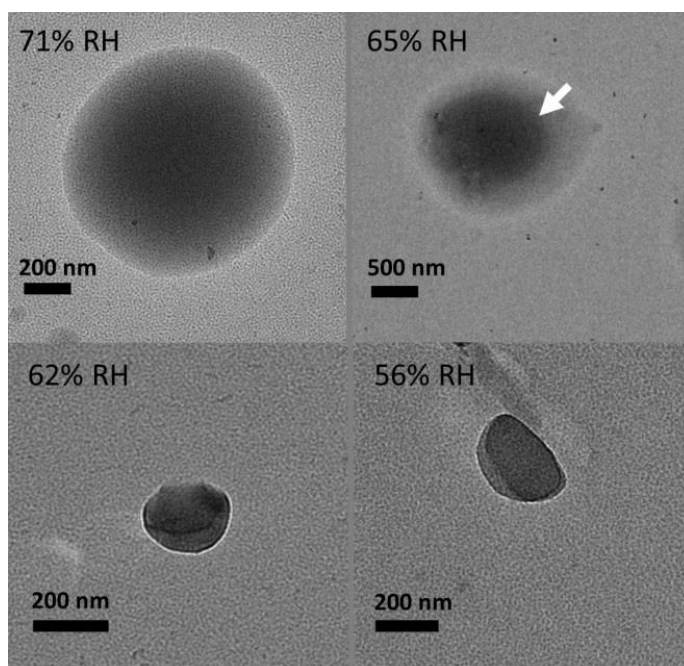


Figure 4-4. Progression of 2-methylglutaric acid (2-MGA) and ammonium sulfate (AS) particles with decreasing RH. At 71% RH, particles are uniform and have no clear indication of a secondary phase. At 65% RH, a new phase appears characterized by the distinct contrast difference (white arrow) indicating LLPS has occurred. At 62% and 56% RH, the morphology further develops.

We expect that SRH and ERH will be lower in submicron systems compared to supermicron droplets. Literature ERH values for inorganic salts including sodium chloride and ammonium sulfate are 5-15% lower for nanometer diameter particles compared to measurements of particles with micrometer diameters.^{60,62} Additionally, the ERH and DRH of multicomponent particles have also been shown to change between 100 nm and 6 μ m sized particles due to morphology.⁶² We compared our flash freeze submicron ERH and SRH values to bulk values to determine size trends. Optical microscopy was used to determine the bulk ERH of K_2SO_4 and KCl.^{9,66} From this study, we determined that K_2SO_4 has a bulk ERH of $73.3 \pm 5.4\%$ RH and KCl has a bulk ERH of $65.3 \pm 3.5\%$ RH (Table 4-1). These bulk values are significantly higher than previously published values for submicron to few micron diameter droplets that are listed in Table 4-1.^{25,67} From the flash freeze data, we see that ERH decreases more than 10% RH in submicron particles when compared to supermicron droplets (Table 4-1). Efflorescence occurs at approximately the same RH for most of the particles, and as a result, the size dependence of ERH cannot be assessed. Our lower overall submicron ERH values are consistent with previous results for inorganic salts and we expect that SRH will follow a similar trend. We compared submicron and bulk SRH values for 2-methylglutaric acid/ammonium sulfate (2:1). The published bulk SRH value for this system is $75.3 \pm 2.8\%$ RH.¹² This study calculated submicron SRH by averaging the RH at which individual particles phase separate. The submicron SRH for 2-methylglutaric acid/ammonium sulfate ($60 \pm 4\%$ RH) is 12-15% RH lower than the reported values for micrometer-sized particles. A lower SRH for submicron systems could potentially

impact future particle-resolved modeling when it accounts for the SRH of phase-separated particles.

Table 4-1. Efflorescence Relative Humidity (ERH) and Separation Relative Humidity (SRH) Values Compared to Literature

System	Particle Size	ERH (%)	Source
potassium sulfate	20-200 μm	73 $\pm$ 5	This work
	$\sim$ 0.5-5 μm^*	60 $\pm$ 2	Freney et al. ²⁵
	100 nm – 2 μm	61 $\pm$ 3	This work
potassium chloride	20-200 μm	65 $\pm$ 4	This work
	$\sim$ 0.5-5 μm^*	56 $\pm$ 1	Freney et al. ²⁵
	20 μm	56	Cohen et al. ⁶¹
	100-500 nm	52 $\pm$ 4	This work
System	Particle Size	SRH (%)	Source
2-MGA/AS	28-34 μm	75.3 $\pm$ 2.8	Song et al. ¹²
	100 nm-1 μm	60 $\pm$ 4	This work

* Particle size estimated from the scale bars in the TEM images provided by Freney et al.²⁵

Limitations

Incorrect flash freeze preparation can be observed in cryo-TEM. Two possible errors in particle preparation are warming before imaging and not creating the correct cooling environment to sufficiently flash freeze the particles. K_2SO_4 particles that were warmed after vitrification and cooled again for cryo-TEM show the wrinkled appearance (Figure 4-5a) compared to a K_2SO_4 particle that remained chilled throughout the duration of the experiment (Figure 4-5c). Cooling the flash freeze flow tube to the incorrect temperature or having the incorrect flow rate can lead to insufficient cooling rates. In this case, particles, especially those with large diameters,

will not have completed the flash freeze process and remain somewhat fluid such that they rupture during impaction onto the TEM grids. A phase-separated 2-methylglutaric acid/ammonium sulfate particle in Figure 4-5b was prepared in a flash freeze flow tube that was insufficiently cooled. The arrow in Figure 4-5b indicates the region where the particle burst due to impaction. A vitrified phase-separated 2-methyl glutaric acid/ammonium sulfate particle shows no points of rupture and remains spherical (Figure 4-5d). Proper flow rates and post-vitrification handling methods can prevent these flash freeze preparation errors.

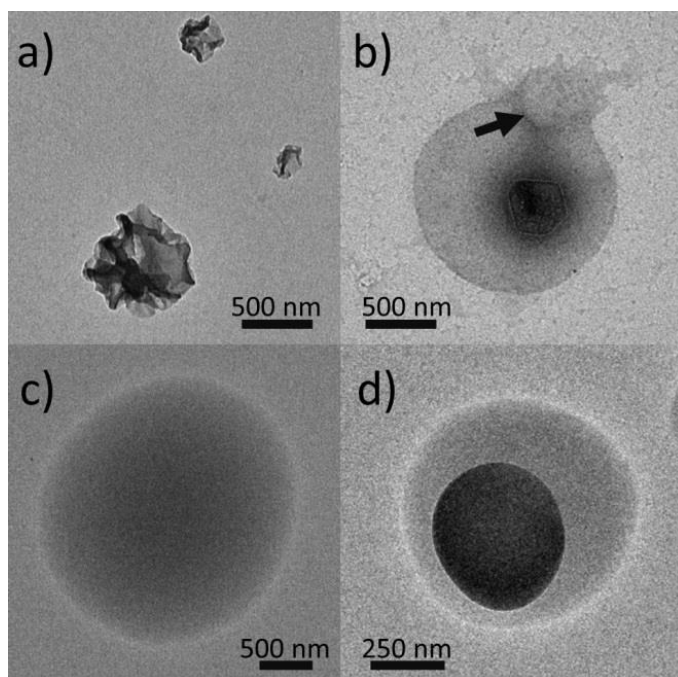


Figure 4-5. Example cryo-TEM images of particles with unsuccessful vitrification (top) and successful vitrification (bottom). Image a) shows potassium sulfate particles that have been vitrified and then warmed up prior to imaging in cryo-TEM and c) is a successfully vitrified particle that remained frozen the entire duration. Image b) is a phase separated particle that was prepared in an insufficiently cooled flash freeze flow tube causing it to rupture and d) is a successfully vitrified phase separated particle.

The flash freeze flow tube was constructed to be used in conjunction with cryo-TEM and is most suitable to image particles approximately 20 to 1×10^3 nm in

diameter. Particles are not expected to expand to the same degree as traditional freezing which produces crystallization. Vitrified water can be expected to expand by approximately 2% whereas frozen water can expand by approximately 10% of initial volume.^{68–70} In the case of lower particle concentration, collection time will need to be increased which increases the risk of water contamination that can produce ice during cryo-TEM imaging. Phase state also affects imaging with cryo-TEM. Particles that have higher water content at the time of flash freezing appear with less contrast and require more underfocusing in the TEM, which creates the bright halo around the particle.

Conclusion

We describe the development of a vitrification flow tube that allows for the imaging of nanometer sized particles over a range of RH with the use of cryo-TEM. We verified the vitrification flow tube using potassium salts by comparing it to the results published previously that measured ERH of these systems on the submicron scale²⁵ Particles of 2-methylglutaric acid and ammonium sulfate were vitrified and imaged to showcase the practicality of this technique as a way to probe SRH for submicron multicomponent particles. This method proved to be successful in preparing particles to be imaged with cryo-TEM to capture efflorescence and LLPS. We anticipate the use of the vitrification flow tube technique as a way to gain further size-resolved information on the phase transitions of submicron aqueous particles and

characterize LLPS at the submicron scale. This future work will parameterize submicron phase separation which can be used to improve particle-based models.

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Supplementary

Summary:

The contents include the theoretical radial temperatures for the flow tube calculated to cylindrical geometries. The physical parameters used in this calculation as well as cooling rate as a function of particle diameter are listed here. Also include are particle size distributions for particles prior and post flow tube with and without vitrification.

Flow Tube Temperature as a Function of Radius

Temperature as a function of radius is displayed in Figure 4-S1. Temperature is lowest (218 K) in the outer tube which contains the chilled nitrogen gas and

increases towards the center of the tube. The temperature gradient for the flash freeze flow tube is logarithmic, which is expected for cylindrical geometries.

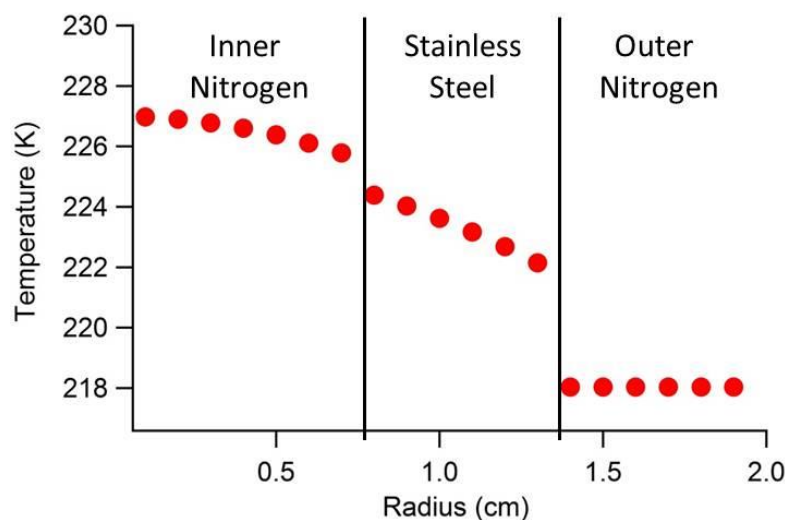


Figure 4-S1. Temperature gradient as a function of radius for the flash freeze flow tube. The plot represents the outer tube containing chilled nitrogen gas, the stainless steel wall of the inner tube, and then the nitrogen gas within the inner tube. The temperature increases with decreasing radius due to heat exchange.

Particle Size Distribution

The particle size distribution for potassium chloride was measured using a scanning mobility particle sizer (SMPS) before and after vitrification (Figure 4-S2a). Red represents the humidified particles equilibrated to 72% RH before vitrification, and blue represents the particles after vitrification. Both distributions look similar; however there is particle loss in the vitrified particles. The particles prior to entering the flow tube have a mean of 117 ± 2 nm and a total concentration of 1.9×10^6 and the particles post flow tube have a mean of 121 ± 2 nm and a total concentration of 1.2×10^5 . Note that the transfer function, which determines the size distribution of particles transmitted through the differential mobility analyzer, depends on temperature. The cold airflow in the vitrified sample could therefore shift the

distribution. Figure 4-S2b compares the size distribution of potassium chloride particles equilibrated to 68% RH before (red) and after (blue) entering the flow tube without cooling/vitrification. The particles prior to entering the flow tube have a mean of 117 ± 2 nm and a total concentration of 1.9×10^5 and the particles post flow tube have a mean of 121 ± 2 nm and a total concentration of 1.2×10^5 . Particle loss is expected from loss to the flash freeze flow tube and the tubing walls. Additionally, particle loss is expected to be size-dependent such that there is a greater loss to small particles and a minimum in wall loss for particles 500-1000 nm in diameter.¹ This may explain the shift in mean between the two distributions. A greater particle loss was seen for particles post vitrification compared to loss to the flow tube without cooling.

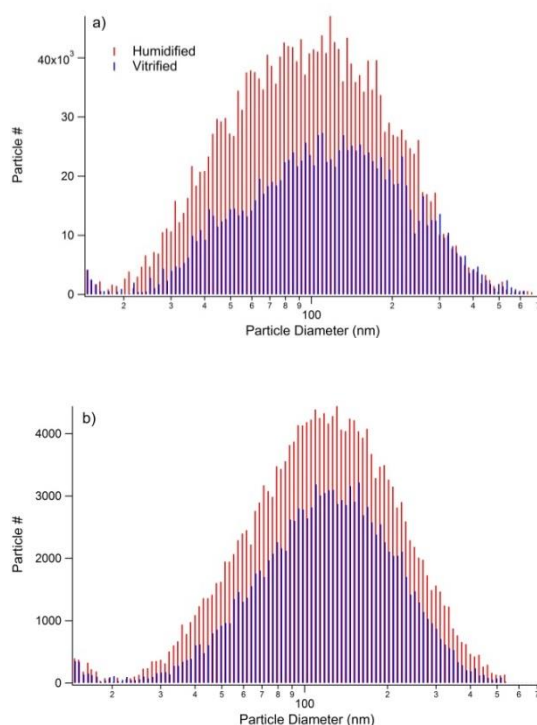


Figure 4-S2. a) Particle size distribution before vitrification (red) and after vitrification (blue). b) Particle size distribution before flow tube (red) and after flow tube (without vitrification/cooling).

Note that the initial humidified size distributions (red) in (a) and (b) are different because these are separate experiments.

Physical Parameters used in Theoretical Temperature and Cooling Rate

The physical parameters used to calculate the temperature as a function of temperature and the cooling rate as a function of particle diameter are listed in Table 4-S1.² The thermal transfer coefficient (h), used in the cooling rate calculation, was calculated with the following equation.

$$h = \frac{\lambda}{D} \left[2 + 0.6 \left(\frac{\nu D \rho_{air}}{\eta_{air}} \right)^{\frac{1}{2}} \left(\frac{c_{p(air)} \eta}{\lambda} \right)^{\frac{1}{3}} \right]$$

where λ is the thermal conductivity coefficient, η_{air} is dynamic viscosity, ρ_{air} is the density, and $C_{p(air)}$ is the specific heat of air. D is diameter of the flow tube and ν is relative velocity.³

Table 4-S2. Parameters for radial temperature and cooling rate calculations

Symbol	Number	Units
$c_{P(\text{air})}$	1000	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
$c_{P(\text{water})}$	4217	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
D	1.00×10^{-8}	M
h	4.24×10^6	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}$
k_n	2.2×10^{-2}	W/mK
k_{ss}	13	W/mK
T	230	K
T_1	218	K
T_{air}	230	K
T_{part}	295	K
v	1.5	$\text{m}\cdot\text{s}^{-1}$
ε_h	9.93×10^{-1}	
η_{air}	1.59×10^{-5}	$\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$
λ	2.098×10^{-2}	$\text{J}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$
ρ_{air}	1.51	$\text{kg}\cdot\text{m}^{-3}$
ρ_{water}	1000	$\text{kg}\cdot\text{m}^{-3}$
σ_{SB}	5.67×10^{-8}	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$

Supplementary Information References

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Chapter 5

Dynamics of Liquid-Liquid Phase Separation in Submicron Particles

Abstract

The properties of nanoscale materials, such as phase transitions, can differ when compared to their bulk components. Liquid-liquid phase separation (LLPS) is a phase transition process that is significant in the fields of atmospheric, biological, and material chemistry, and systems of interest for these fields are often on the submicron scale. In aerosol particles, LLPS is tracked as a function of particle water content. The relative humidity (RH) at which separation occurs (separation RH; SRH) was probed for three organic/inorganic systems. Particles were vitrified after equilibration at various RH and imaged with cryogenic transmission electron microscopy (cryo-TEM). Our findings indicate that SRH for submicron particles is lower than the SRH measured for micron-sized droplets, suggesting a need for the development of new parameterizations for atmospheric models. Additionally, the process of separation occurs over a large RH range ($> 10\%$ RH) which is hypothesized to be due to the activation energy involved in forming a new phase. The onset of phase separation over this range is not dependent on particle size, except at the smallest diameters, which remained homogeneous throughout. This random behavior at the onset of separation is time-dependent, and the number of phase separated particles increases with increasing equilibration time. This behavior is not seen for systems that undergo

spinodal decomposition, indicating the random nature of the onset of separation may be due to the nucleation process. Size dependent morphology, such that large particles phase separate and small particles remain homogeneous, occurs at the full maturation of LLPS. These findings provide insights into the fundamental process of phase separation.

Significance Statement

Liquid-liquid phase separation (LLPS) is a significant process in atmospheric, biological, and materials chemistry and can display different behavior at the nanoscale compared with bulk measurements. The onset of LLPS was found to occur randomly over a large relative humidity range resulting in lower average values of the separation relative humidity (SRH) than previously reported, suggesting the need for parameterization of SRH in submicron particles.

Introduction

Liquid-liquid phase separation (LLPS), the process in which dissimilar liquid components demix, is an important process in the biological, materials, and atmospheric sciences. In particular, LLPS has been well-documented in atmospherically relevant particles (1–12). Particles consisting of organic and salt components can phase separate into multiple liquid phases with decreasing relative humidity (RH); meanwhile, secondary organic aerosol (SOA) has been shown to

undergo LLPS with increasing RH due to differences in the solubility of the components (1, 2, 4, 5, 12, 13). The presence of LLPS in ambient aerosol can affect physical and chemical properties such as reactive uptake, gas partitioning, hygroscopicity, ice nucleation, and cloud condensation nuclei (CCN) activity (14–19).

Some of the earliest studies of LLPS consisted of polymer systems including solutions of a solvent and a polydisperse polymer as well as more complicated multicomponent polymer solutions (20–26). More recent studies have shown that LLPS exists in biological systems, such as in purified protein solutions, and the current theory is that LLPS results in the formation of membraneless compartments (27–34). Additionally, supersaturated aqueous drug solutions have been observed to undergo LLPS, which could affect drug delivery (35–38). In materials science, emulsions are systems consisting of multiple liquid phases and can include Janus particles (39–41). These complex emulsions have been developed in recent years to have controllable morphologies with applications in drug delivery, sensors, tunable lenses, among other implementations (37, 42). It is easy to see the importance in characterizing LLPS due to its application to many fields.

LLPS can occur through two different mechanisms; nucleation and growth, and spinodal decomposition. Spinodal decomposition occurs without an activation barrier whereas nucleation and growth must overcome an energy barrier. The formation of a nucleus itself is known to be a random event (43–46). Studies on classical nucleation theory have indicated that the nucleation rate is greater for larger volumes due to kinetics (47–50). Correlation plots from the study of crystallization of

poly(ethylene oxide) in an amorphous matrix indicated that large droplets nucleate faster than small droplets due to the greater volume and thus probability of nucleation in the larger droplet (47). Further studies on nucleation of polymers in confined spaces showed that the probability of the appearance of a nucleus scales with volume (51). In contrast, the crystallization rate of simulated water nanoparticles was shown to be not very sensitive to particle size, however the temperature at which the rate is maximum decreases with decreasing size (52). From these studies, it remains unclear if the process of separation in particles will be dependent on larger particles having more volume and thus a greater probability in forming the critical nucleus for LLPS.

Investigating LLPS in particles is important to fully understand the role of aerosol in the atmosphere. Our previous studies have investigated the size-dependence of LLPS in submicron particles consisting of atmospherically relevant mixtures (10–12, 14, 53). These studies show that for systems that undergo LLPS in supermicron diameter particles, a size dependence is observed in the submicron regime in which large particles phase separate while small particles remain homogeneous (10–12, 53). This size-dependent LLPS has been observed using transmission electron microscopy (TEM) in particles that have undergone LLPS in the aqueous state and then are dried prior to imaging. Additional information about the process of LLPS, such as SRH values, could be gained from the study of aqueous, humidified samples. Note that hygroscopic tandem differential mobility analyzer (H-TDMA) is a technique that has been used to characterize the efflorescence RH and deliquescence RH in submicron particles, but cannot be applied to LLPS. We applied a newly developed technique that flash-freezes submicron particles to monitor phase

transitions in cryogenic transmission electron microscopy (cryo-TEM) (54). With this method, we can extend the study of LLPS in submicron particles to track separation relative humidity (SRH). Defining SRH for submicron systems will allow us to refine current parameterizations to help resolve discrepancies between observations and model predictions (55). Additionally, identifying the role of the nucleation and growth mechanism on the behavior of phase separation at the onset provides insights into the fundamental process of phase separation.

Results

Three organic/inorganic systems consisting of 2-methylglutaric acid (2-MGA)/ammonium sulfate, 1,2,6-hexanetriol/ammonium sulfate, and complex organic mixture 1 (COM-1)/ammonium sulfate were investigated. COM-1 is a ten-component organic mixture as described in the methods section that was used to represent systems with increased complexity in composition. We tracked the SRH for particles between approximately 20 nm to 3 μ m. Submicron particles were prepared using a flash freeze flow tube and imaged with cryo-transmission electron microscopy (cryo-TEM). Particles were generated at RH above 90% and the RH was reduced to induce LLPS. Phase state (separated or homogeneous) was recorded along with diameter and RH to determine any size trends.

Approximately two hundred to three hundred particles are imaged for each of these systems. Particles are imaged starting at sufficiently high RH that all particles are homogeneous, and until LLPS has reached full maturation and phase

separation is size dependent, which is when large particles are phase separated and small particles remain homogeneous. Separation is tracked for each of these systems. Figure 5-1 shows an example of the process of phase separation for the COM-1/ammonium sulfate system. At 83% RH, all particles in the system are homogeneous and phase separation begins to occur at 66% RH. The average SRH for the particles studied is calculated by averaging individual particles over the separation range. Average SRH for submicron particles was also calculated for particles less than 1 μm . The onset of phase separation was first observed at 65% RH for 2:1 2-MGA/ammonium sulfate and at 76% RH for 2:1 1,2,6-hexanetriol/ammonium sulfate. Average SRH is calculated to be $59\pm 4\%$ RH for 2-MGA/ammonium sulfate and $68\pm 5\%$ RH for 1,2,6-hexanetriol/ammonium sulfate whereas literature values for SRH of supermicron droplets of the respective systems are 75 and 76% RH, respectively (2). The onset of phase separation for a 1:1 ratio of COM-1/ammonium sulfate was observed at 66% RH, the average SRH is calculated to be $59\pm 5\%$ RH, and the literature value for SRH of supermicron droplets is 83.3% (56). The smallest particles for each system remained homogeneous through the range of tested RH values. Above this point, phase separated and homogeneous morphologies were both present without a size-dependence for 2-MGA/ammonium sulfate at 65, 63, 57, and 55% RH, for 1,2,3-hexanetriol/ammonium sulfate at 76 and 65% RH, and for COM-1/ammonium sulfate at 66, 57, and 52% RH (Figure 5-2a-c). Size-dependent LLPS, where large particles phase separate and small particles remain homogeneous, was observed at 47% RH for 2-MGA/ammonium sulfate, 56% RH for 1,2,6-hexanetriol/ammonium sulfate, and at 44% RH for COM-1/ammonium sulfate. Size-

dependent separation is not visible before this point and occurs at random. Most particles begin as core-shell morphologies and develop into partially engulfed as RH continues to decrease.

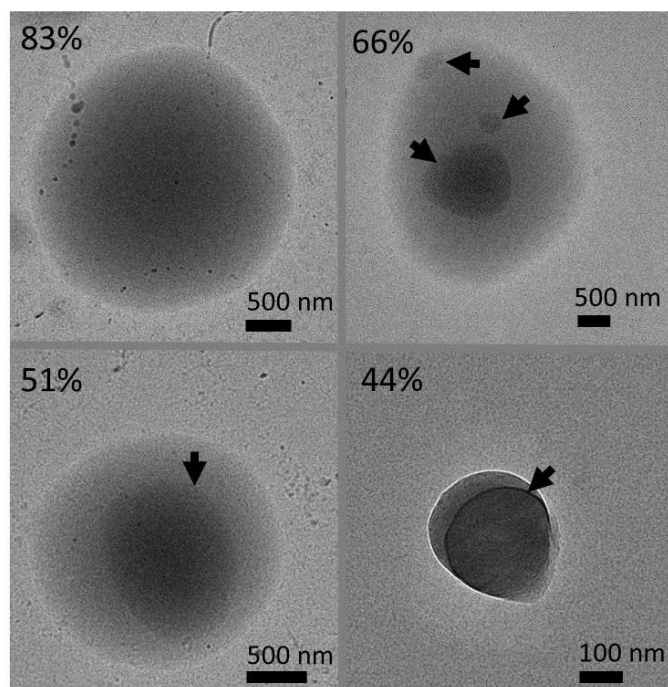


Figure 5-1. Phase separation process for 50:50 complex organic mixture 1 (COM-1) and ammonium sulfate particles. Particles begin as all homogeneous at 83% RH, and undergo the separation process as shown at 66%, 51%, and 44% RH. The black arrows point to the line separating the two liquid phases. Particles begin primarily as core-shell and develop into partially engulfed with decreasing RH.

A plot of particle morphology based on diameter in nanometers at the imaged % RH shows that the onset of separation morphology is random excluding the smallest of imaged particles which remain homogeneous at all RH values studied (Figure 5-2a-c). The random behavior of the onset of SRH may be indicative of a first order phase transition with the phase separation mechanism governed by nucleation and growth. The randomness we observe may be due to the influence of nucleation,

which is a random event, on LLPS. To test this, we explored the effects of equilibration time and phase separation by spinodal decomposition.

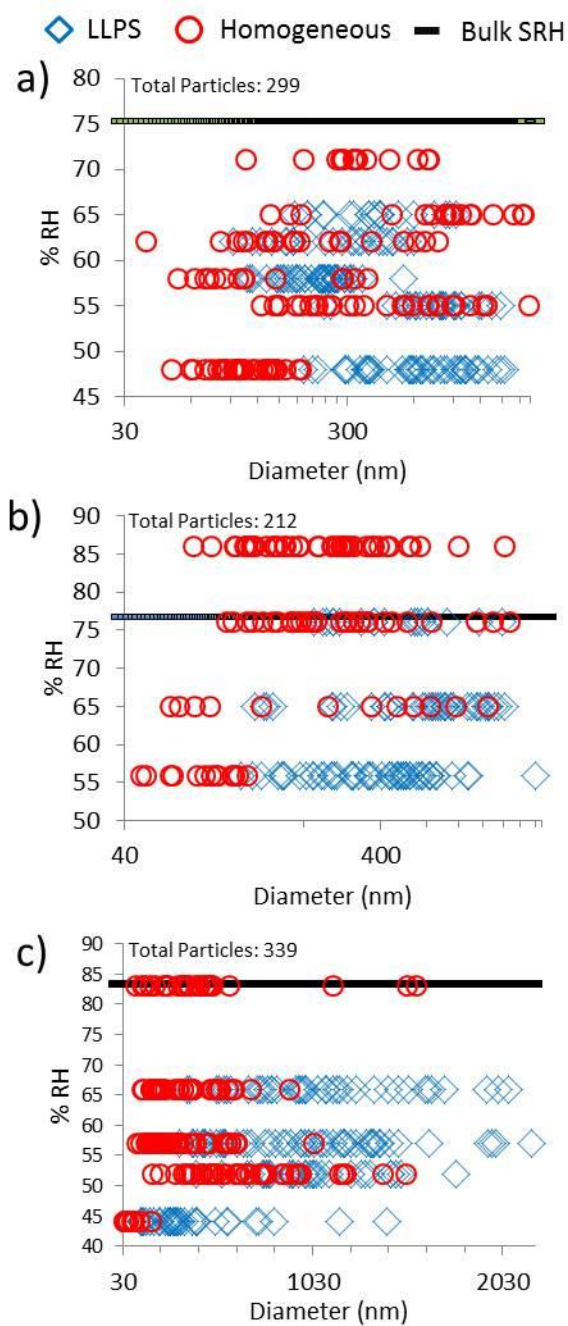


Figure 5-2 Relative humidity (RH) vs. particle diameter for a) 2:1 2-methylglutaric acid (2-MGA) and ammonium sulfate, b) 2:1 1,2,6-hexanetriol and ammonium sulfate, and c) 1:1 complex

organic mixture-1 (COM-1) and ammonium sulfate. Particles that underwent liquid-liquid phase separation (LLPS) are plotted as blue diamonds and homogeneous particles are plotted as red circles. Each point correlates to a single particle. The black line represents the SRH for particles 10s of micrometers in diameter.

To explore the time dependence of phase separation process, we performed further studies for 2-MGA/ammonium sulfate to determine the effects of the length of time that particles are allowed to equilibrate. We equilibrated the particles at $65\pm3\%$ RH for 5, 20, and 75 minutes to determine how the phases develop over time. We found that particles phase separate at random for all of the particle equilibration times (Figure 5-3), however the 75 minute equilibration time produces significantly more phase separated particles indicating a time dependence. 56% of particles are homogeneous for the 5 minute equilibration time, 47% of particles are homogeneous for the 20 minute equilibration time, and only 24% of particles are homogeneous for the 75 minute equilibration time. From these data, we can see that more particles phase separate when they equilibrate longer at the set RH, indicating that phase separation process is time dependent.

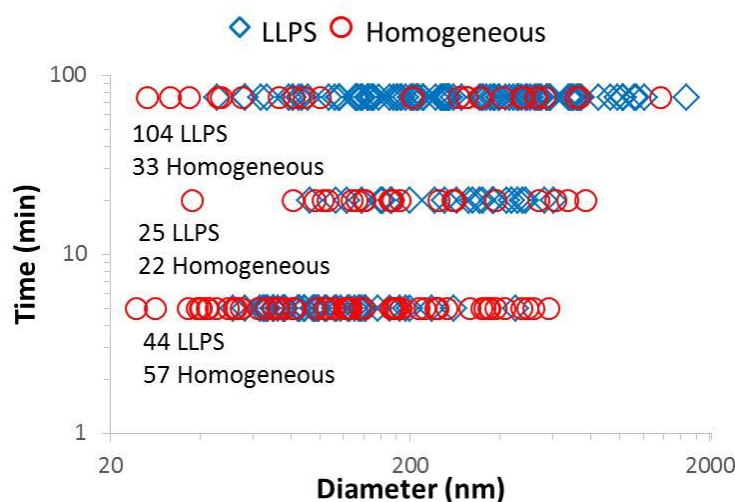


Figure 5-3. Time (minutes) vs. diameter for 2:1 2-methylglutaric acid (2-MGA) and ammonium sulfate particles. Particles were allowed to equilibrate to the set RH (65%) for 5, 20, and 75 minutes. Both equilibration times displayed random behavior at the onset of the separation relative humidity (SRH). Particles that were equilibrated for 5 minutes produced more homogeneous particles, compared to the 20 and 75 minute equilibration time which produced more phase separated particles. The 75 minute equilibration time produced the most phase separated particles.

We also observed the results when 2-MGA/ammonium sulfate system phase separated by spinodal decomposition to investigate the origin of the random behavior. The critical point, where the spinodal and binodal curves on the phase diagram intersect, was determined by imaging with cryo-TEM (53). Because the activation energy goes to zero at the critical point, all particles phase separate when LLPS occurred by spinodal decomposition, and lack a size dependent morphology (53). All particles of all diameters imaged were phase separated at the 55:45 organic to inorganic composition ratio indicating this ratio corresponds to the composition at the critical point or in the very close vicinity that can be imaged with TEM (53). The average SRH for the spinodal decomposition system is $80 \pm 2\%$ RH. The onset of phase separation occurs over a short RH range, displaying nearly spontaneous behavior as expected for spinodal decomposition. Seven particles greater than $1 \mu\text{m}$ remain homogeneous at 81% RH. The SRH of supermicron droplets was found to be $78.8 \pm 0.6\%$ RH, measured with optical microscopy.

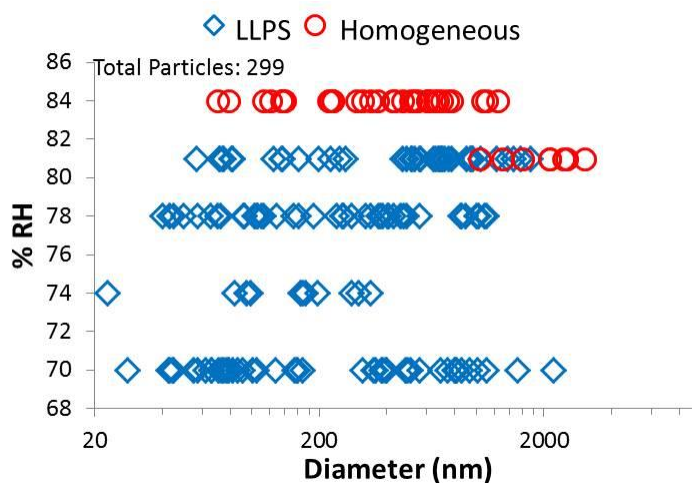


Figure 5-4. Relative humidity (%) vs. diameter (nm) for 55:45 2-methylglutaric acid (2-MGA) and ammonium sulfate particles. Blue diamonds indicate particles that are phase separated and red circles represent homogeneous particles. At 55:45 2-MGA/ammonium sulfate is the system at or near the critical point where there is no energy barrier to LLPS. LLPS occurs rapidly, as expected for spinodal decomposition and does not follow the same random behavior as nucleation and growth systems.

The onset of SRH was also observed in bulk micrometer sized particles for 2-MGA/ammonium sulfate and 1,2,6-hexanetriol/ammonium sulfate using optical microscopy. At the completion of LLPS, all particles were phase separated. Phase separation for these particles appears to also be random but occurs over a much smaller RH range than the submicron studies. LLPS occurs rapidly for particles with diameters of 10s to 100s of micrometers and is more difficult to track compared to submicron LLPS, which occurs over a larger RH range.

Discussion

Our results show the process of phase separation for three systems: 2-MGA/ammonium sulfate, 1,2,6-hexanetriol/ammonium sulfate, and COM-1/ammonium sulfate (Figure 5-1). From this study, we determined the start of SRH,

defined as the point we began to observe separation in particles, and the end of SRH, defined as the point in which LLPS reaches full maturation (Table 5-1). The average SRH was found to be significantly lower for all systems in the binodal region (Table 5-1). The onset of SRH for 2:1 2-MGA/ammonium sulfate and 1:1 COM-1/ammonium sulfate was lower than the bulk onset. The change in the onset of SRH for some systems may be indicative of a shift in the binodal curve for the phase diagram of submicron systems. Near the critical point, the average SRH for 2-MGA/ammonium sulfate (1.2:1) agrees within error of the SRH of supermicron droplets. This provides evidence that the SRH at the critical point for submicron systems may be the same as for bulk systems. Meanwhile, the composition at the critical point can be slightly different (53). Using an individual particle average to calculate SRH can introduce error if the separation range is imaged over too large of RH intervals. Decreasing the number of intermediate RH points used to calculate average SRH and the associated error could potentially change their values. For instance, changing from three to two intermediates that encompasses the highest and lowest RH over the separation range for 2-MGA/ammonium sulfate and COM-1/ammonium sulfate increases the error but not the associated average SRH (59 ± 5 and 59 ± 7 , respectively). Alternatively, calculating average SRH from the highest and lowest RH during separation provides a clearer picture of the magnitude of the separation range.

Table 5-3. Submicron and bulk SRH for the systems studied.

Organic component	Org:Inorg	Regime	Start of SRH	End of SRH	Average SRH	Submicron SRH	Super micron SRH	Source for Supermicron SRH
2-methylglutaric acid	2:1	Nucleation	65	55	59±4	59±4	75.3±2.8	You et al. (2013)
2-methylglutaric acid	1.2:1	Near critical point	84	78*	80±2	81	78.8±0.6	This study
1,2,6-hexanetriol	2:1	Nucleation	76	65	68±5	68±5	76.7±2.5	You et al. (2013)
COM1	1:1	Nucleation	66	52	59±5	59±6	83.3	Song et al. (2013)

*Particles below 1 μm all phase separated by 81% RH. The 78% RH accounts for particles including $>1 \mu\text{m}$ that phase separated at this point.

The process of SRH occurred over a large range that spans an average of 12% RH for systems in the nucleation and growth regime (Table 5-1). This range for the onset of SRH was significantly larger than the range of RH over which supermicron droplets phase separate and could be due to the activation energy required for nucleation. Furthermore, the average SRH was lower for the submicron systems than for droplets 10s of micrometers in diameter for all systems undergoing LLPS through a nucleation and growth mechanism. The large range of phase separation and the significantly lower SRH values could have an effect on the chemical and physical properties of particles.

To further study the random behavior, we looked at the influence of time during equilibration, as well as a system near the spinodal decomposition point. We observed the onset of phase separation for particles equilibrated at 5, 20, and 75 minutes. A larger fraction of particles phase separated when they are equilibrated for 75 minutes compared to the 20 minute and 5 minute equilibration times (Figure 5-3). Similarly, a larger fraction of phase separated particles were observed for 20 minute compared to the 5 minute equilibration time. Overall, we saw an increase in the number of phase separated particles with increasing equilibration time. This result provides evidence that the onset of separation is a random process due to the energy barrier of forming a nucleus and undergoing a first order phase transition. A longer equilibration time provides a greater probability of the nucleation event occurring. Unlike nucleation, spinodal decomposition occurs without an energy barrier to impede the phase separation process (57). The results for the system near the critical point (1.2:1 2-MGA/ammonium sulfate) lacked the random behavior that was

observed for the systems in the nucleation and growth regime (Figure 5-4). The lack of random behavior supports the claim the time-dependent randomness is due to nucleation and is thus kinetically controlled, consistent with previous results from nucleation studies (47–49).

From this study, we gained insight into the dynamics of the phase separation process. The large range over which the onset of phase separation occurs suggests a shift in submicron phase diagrams which has implications for aerosol properties. A reduction in average SRH for submicron systems suggests a need for a new parameterization for accurate representation when modeling particles. This study has also shown that the onset of LLPS is a random process that is time-dependent and that a size-dependent morphology exists once the full maturation of LLPS is reached. The potential shift in submicron phase diagrams compared with the bulk and the decrease in SRH will also affect the way LLPS is approached in the biological and material sciences. The new insights provided on LLPS can potentially be applied to synthesis process of controlled emulsions to helping understand the role of phase separation in biological material.

Materials and Methods

Particle Generation and Equilibration

Aerosol particles are generated from a 0.03-0.07 weight percent solution through an atomizer. The aerosol particles are pumped through a humidifier tube into

a Tedlar bag (500 L) at approximately 98% RH. Particle count is measured with a condensation particle counter (CPC; TSI 3752) and the RH and temperature are measured with a Vaisala HMP 110 probe. Particles are dried with ultra-purified nitrogen gas at a rate of approximately 0.5% RH per minute. The particles sit at a set RH value for approximately 30 minutes to allow for equilibration with the surrounding RH levels unless otherwise specified. On average, the final particle concentration is 5000-10000 particles per cm³.

Flash Freeze Flow Tube

Particles are vitrified at a specific RH value using a flash freeze flow tube which has been described previously (54). A concentric flow tube is cooled with chilled nitrogen gas through the outer jacket. Aerosol particles are pumped through the inner tube at a rate of 2500 sccm and are impacted onto 200 copper mesh transmission electron microscope (TEM) grids through a Sterlitech LS 25 Gas Line Holder which acts as an inline filter. The inline filter is contained within a dry ice environment which keeps the samples frozen and provides a CO₂ rich environment to minimize water exposure.

Imaging with Cryogenic Transmission Electron Microscopy

The TEM grids are transferred to a Gatan cryo-holder using a cryogenic transfer station under liquid nitrogen. Imaging is performed with a FEI Tecnai Lab6 TEM at approximately -175°C with a 200kV beam.

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Chapter 6

Conclusions and Future Directions

Conclusions

In this dissertation, we explored the size-dependence of LLPS in particles containing complex organic mixtures and ammonium sulfate. Seven systems were imaged with cryo-TEM to characterize morphology as a function of diameter. We observed the presence of size-dependent morphology, such that large particles phase separate while small particles remain homogeneous, for all systems that underwent phase separation. This provides further evidence that size-dependence may be relevant for ambient aerosol. In addition to size-dependence, we also observed three-phase and channel morphologies. The presence of these new morphologies appeared to be dependent on composition. Furthermore, channel morphology was found to be a phenomenon of efflorescence that occurs after phase separation. Our results indicate that size-dependent morphology may be an important parameter to consider when modeling ambient aerosol.

We also created a new method to study phase transitions in submicron aerosol particles. The new technique uses a temperature controlled flow tube that flash freezes humidified aerosol particles. Once vitrified, the particles that have been equilibrated at several different RH values are imaged with cryo-TEM. Vitrification allows for the properties of the humidified particles to be retained thus creating snapshots of the phase transition process. We verified this method with the

efflorescence of potassium salts which have been previously characterized on the submicron scale. Imaging the process of LLPS for 2-MGA/ammonium sulfate was also demonstrated. Overall, flash freezing particles provides a new method to monitor phase transitions in individual particles at the submicron scale.

We applied the flash freezing method to study the dynamics of LLPS in the following systems: 2-MGA/ammonium sulfate, 1,2,6-hexanetriol/ammonium sulfate, and COM-1/ammonium sulfate. Particles were vitrified and images at several RH values in 3-5% RH increments that started above phase separation and stopped once the full maturation of LLPS was reached. From this study, we determined the onset of SRH, average SRH for submicron particles, and the dynamics of phase separation. The onset of phase separation was lower for submicron particles in the nucleation and growth regime than the onset of separation for particles several microns in diameter. A decrease in the onset of SRH potentially indicates a shift in the binodal curve for submicron phase diagrams. Meanwhile, the onset of SRH for 2-MGA/ammonium sulfate near spinodal decomposition remains consistent for both submicron and bulk systems, which may indicate that they may share a critical point. The average SRH was significantly lower for submicron particles. A lower SRH suggests the need for a new parameterization of phase separation in submicron systems. Additionally, we found that the separation process is random and is not dependent on size above the smallest particle diameters, which remain homogeneous throughout.

The presence of size-dependent LLPS in submicron particles composed of complex organic mixtures and ammonium sulfate further indicates that this is relevant to ambient aerosol. A size-dependent morphology has previously been shown to

affect CCN activation, and may impact other properties such as uptake and diffusion. A decrease in SRH for submicron particles indicates the requirement for new parameterizations of submicron properties. Furthermore, our results provide evidence for a shift in the phase diagram for submicron systems. An accurate understanding of phase transitions in submicron aerosol particles can help better constrain their contribution to climate change. New parameterization of SRH and the phase diagram would allow for a more accurate representation of particles in models. This dissertation provides new insights into the phase transition process in submicron aerosol particles.

Future Directions

Our work provides key insights into the phase separation process of submicron aerosol particles; however, more systems need to be parameterized to develop a full picture of the process. In particular, organic/inorganic particles that represent species in the atmosphere need to be studied to create a database that encompasses trends that can be used to broadly describe common systems. Atmospherically relevant organics need to be selected to represent commonly found functional groups such as alcohols, carboxylic acids, and esters. Additionally, different salts can be utilized in these systems to broaden the new parameterizations further. Salts can also be expanded, and can include sodium chloride, which is present in sea salt aerosol. The onset of SRH and average SRH for submicron particles needs to be measured for these additional systems to accurately represent these parameters in particle-based models. Furthermore, these parameters need

to be determined for additional organic:salt ratios to create submicron phase diagrams. Further parameterization of submicron SRH will allow for accurately predicting aerosol particles impact on cloud activation, optical properties, and reactions/diffusion.

In addition to further parameterization of submicron SRH, the flash freeze method can be applied to imaging ambient aerosol. Preparing ambient aerosols through vitrification would allow us to see the natural state of atmospheric particles in their native RH while eliminating the need for alternative preparation methods (such as drying and collecting) that can alter morphology or size. Studying vitrified ambient aerosol particles will provide insight into the humidified morphology of the complex particles that exist in the atmosphere. Investigating ambient aerosol will expand our studies beyond laboratory generated particles.

VITA

Theresa Marie Kucinski

EDUCATION

Pennsylvania State University	Ph.D. in Chemistry	August 2016 - August 2020
Drew University	B.A. in Chemistry, <i>Magna cum laude</i>	September 2014 - May 2016
Sussex County Community College	A.S. in Chemistry	September 2012 – May 2014

PRESENTATIONS

Kucinski, T.M., Dawson, J.N., Freedman, M.A. (2019). Size Dependence in Liquid-Liquid Phase Separation of Atmospherically Relevant Complex Systems, Abstract 516406 presented at 2019 Fall Meeting, AGU, San Francisco, CA, 9-13 Dec.

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PUBLICATIONS

The Dynamics of Liquid-Liquid Phase Separation in Submicron Particles **Theresa M. Kucinski**, Emily Ott, Miriam Arak Freedman; *In preparation*

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