Supplementary Information for

Role of Nucleation Mechanism on the Size Dependent Morphology of Organic Aerosol

Muhammad Bilal Altaf^a, Andreas Zuend^b, and Miriam Arak Freedman^a* ^aDepartment of Chemistry, The Pennsylvania State University, 104 Chemistry Building, University Park, Pennsylvania 16802, United States ^bDepartment of Atmospheric and Oceanic Sciences, McGill University, 805 Sherbrooke Street West, Montreal, Quebec, Canada

Summary

This supplementary information contains detailed experimental methods for the cryotransmission electron microscopy (cryo-TEM) experiments. We also provide information regarding particle composition, the resolution of the cryo-TEM technique, and the ability to distinguish between liquid-liquid phase-separated and homogeneous particles for the PEG-400/ammonium sulfate system based on electron beam damaging behavior. The histograms for the 60/40 and 45/55 PEG-400/ammonium sulfate systems are also included. In addition, a description of the computed bulk phase diagram and a discussion of the interfacial energy contribution of the aqueous PEG-400/ammonium sulfate system are provided.

Computed Bulk Phase Diagram

In the following, a brief discussion of the computed phase diagram is provided. Figure 1b of the main text shows a phase diagram of the pseudo-ternary system water + PEG-400 + ammonium sulfate at 298.15 K. Figure S1 shows the same phase diagram yet provides additional information on the Gibbs energy difference (color axis) between the (initial) single-phase state (of known composition) and the two-phase, liquid-liquid phase-separated state (if it is the stable equilibrium state). The pink curves in Figs. 1b and S1 mark the solubility limit of ammonium sulfate. At relative humidities below the pink curve (here below ~80 %), a crystalline phase of ammonium sulfate would be in equilibrium with the liquid phases – or as

done in the shown computation, the liquid phases would actually be supersaturated with respect to dissolved ammonium sulfate. The two points where the pink curve intersects with the binodal represent the predicted (dry) compositions of the two coexisting liquid phases in liquid-liquid equilibrium. Similarly, in Fig. 1b, the intersections of isolines of water activity with the binodal indicate the compositions of coexisting phases (this is why they can be considered as tie-lines).¹ The water contents of the coexisting phases are obtained from a related plot (not shown) where the ordinate is mass fraction of water rather than mole-fraction-based water activity.

We note that the computed phase diagram pertains to a bulk system of the three mixture components, i.e., to a system where the surface/volume ratio is tiny and interfacial energies between the liquid phases and of the gas-liquid interface are negligible compared to the energy content of the bulk volume of phases. In other words, the shown phase diagram describes the situation of large droplets (typically for diameters > 200 nm) for which a size effect on phase separation is negligible. Such phase diagrams can be computed based on thermodynamic theory and a model that allows for the computation of the Gibbs energies of different phase compositions. While droplet size effects will slightly alter the exact positions of the binodal and spinodal curves, the bulk phase diagram offers insight into the approximate locations of metastable and unstable single-phase compositions and the expected onset RH of liquid-liquid phase separation (LLPS).

Here we use the thermodynamic group-contribution model called Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC), developed by Zuend et al.^{2,3}, for the calculation of activity coefficients of the different mixture species at given compositions. In contrast to other organic-inorganic systems where the organic molecules do not contain large numbers of repetitive units, an accurate description of oligomers and polymers like PEG in aqueous solutions is rather difficult. For example, it is known that phase equilibria of PEG oligomers are poorly represented by the set of standard functional groups and associated model parameters of the widely-used UNIFAC model^{4,5}, as discussed by Ninni et al.⁶ This limitation also affects the AIOMFAC model, which contains a modified UNIFAC model. Recently, a PEG-specific oxyethylene group (-CH₂-O-CH₂-; the monomer unit in PEG oligomers) was introduced in order to develop a PEG-specific AIOMFAC model parameterization of aqueous PEG solutions and to account for interaction effects of PEG oligomers of various molar masses with ammonium and sulfate ions in solution. A detailed description of this specific AIOMFAC parameterization will be discussed in a separate manuscript. The phase diagram itself was computed based on the liquid-liquid phase equilibrium prediction method by Zuend and Seinfeld⁷ within the modeling framework of Zuend et al.¹

The dashed contour lines of Gibbs energy difference between a single-phase state and the stable equilibrium state shown in Fig. S1 allow for an estimation of the effect of an activation energy penalty on the onset water activity (or RH) of LLPS due to the energy requirement of the formation of a new interface between two liquid phases. For example, in the case where the additional interfacial energy for a mixture of overall 50/50 PEG-400/ammonium sulfate mass ratio (w_d (salt) = 0.5) would amount to 2 J/mol, the binodal curve would shift to lower water activities and would be represented by the dashed contour line of 2.0 J/mol. That is, this interpretation of the additional information given by the computed phase diagram would mean that the onset RH of LLPS would shift from ~90.3 % to ~87.8 % RH for w_d (salt) = 0.5. However, not included in this estimation is the Kelvin effect accounting for the effect of droplet curvature, which tends to increase the RH of phase separation (due to its effect on droplet water content) and would lead to a smaller effective change in LLPS onset RH, as discussed in the main text.

Generally, for solution droplets of small size (diameters less than ~ 200 nm) a size-dependent phase diagram would be necessary to include both the Kelvin effect and interfacial energy (surface tension) effects accurately.⁸ This also means that the mixture composition of the critical point is essentially both a size- and temperature-dependent quantity.



Figure S1. Computed phase diagram of the water + PEG-400 + ammonium sulfate bulk system at 298.15 K. Shown is the phase diagram in terms of water activity (equivalent to RH at equilibrium with the liquid mixture) versus mass fraction of ammonium sulfate, w_d (salt), in terms of the dry (water-free) mixture composition. The solid white curve is the predicted binodal and the dotted white curve the spinodal. The dashed white curves are contour lines of constant Gibbs energy difference between a (forced) single phase state and the stable (two-phase) state at thermodynamic equilibrium (color axis). The dash-dotted pink curve marks the solubility limit of ammonium sulfate.

Size dependence and effect of the liquid-liquid interfacial energy contribution

The formation of a new liquid phase in an eventually liquid-liquid phase-separated system, here considered for a concentric core-shell morphology of a spherical droplet, introduces a thermodynamic energy barrier associated with the formation and expansion of the interfacial area between the two liquid phases. Based on the computed phase diagram for the bulk system, we discuss here the approximate impact and droplet size dependence of the interfacial Gibbs energy contribution on the phase separation onset RH. The interfacial Gibbs energy contribution is one of the size dependent energy contributions that will affect the locations of the binodal and spinodal curves in a composition-based phase diagram of a small droplet at constant temperature. Thus, an estimate of the interfacial energy contribution allows for an estimate of the shift in onset RH of LLPS (to lower RH). We note that there are other size-dependent effects that will influence the thermodynamic phase behavior for a given droplet size and morphology. These other effects include (i) the Kelvin (curvature) effect on the equilibrium vapor pressure of semivolatile mixture substances (here water) over a curved droplet surface, which increases the concentration of dissolved solutes (here ammonium sulfate and PEG-400), and (ii) the change of surface tension at the gas-droplet interface upon LLPS. Both of these effects typically tend to increase the RH of LLPS onset and therefore partially or fully counteract (and potentially exceed) the effect of an interfacial energy penalty. Thus, knowledge of the interfacial energy contribution alone is not sufficient to accurately determine the droplet size effect on phase separation onset and the deviation of a size-dependent phase diagram from the bulk phase diagram, such as the one shown in Fig. S1. However, the magnitude of the interfacial energy contribution as a function of droplet size allows an estimation of the change in expected LLPS onset RH if this were the dominant size effect. Table S1 lists calculated interfacial energy contributions for the water + PEG-400 + ammonium sulfate system (1:1 mass ratio of PEG-400

to ammonium sulfate) for a selection of droplet sizes ranging from 1 µm to 10 nm in diameter. The given values are calculated based on measured solution densities and surface tensions by Song et al. and other mixture properties and assumptions given in Table S2.⁹ Combining the phase diagram information shown in Fig. S1 for the bulk system with Table S1 shows that the interfacial energy contribution leads to a shift of the onset water activity (equivalent to the onset RH at bulk conditions) of phase separation to a lower RH value. This is seen from the location of the dashed white curves in Fig. S1, which are contour lines of constant Gibbs energy difference between a (forced) single phase state and the stable (two-phase) state at thermodynamic equilibrium. The interfacial energy penalty to be overcome for LLPS in a small droplet means that this energy barrier to separation needs to be compensated by a reduction in the system's Gibbs energy due to phase separation, which is achieved with a reduction in equilibrium water activity of the droplet. For example, with the interfacial tension of 1.07×10^{-3} J/m², a droplet of 90 nm diameter is predicted to have an interfacial energy contribution of ~ 2 J/mol, which can be compared to the molar Gibbs energy shown in Fig. S1. Such a droplet will undergo LLPS at a RH approximately 2.5 % lower than the corresponding bulk solution (both with a 1:1 mass ratio of PEG-400 to ammonium sulfate). Taking, for comparison, the lower range of the interfacial tensions given by Song et al. as 0.08×10^{-3} J/m²,⁹ the 90 nm diameter droplet would experience an interfacial energy contribution of ~ 0.15 J/mol and a shift in LLPS onset of approximately 0.7 % RH. In conclusion, Table S1 shows that the interfacial energy contribution increases with a decrease in droplet size and overcoming this energy barrier for phase separation therefore requires a reduction in the onset RH of LLPS, typically of less than 10 % RH even for rather small droplets. As mentioned above, other droplet size effects tend to counteract this reduction in onset RH of LLPS. We note that the interfacial energy contribution calculated in this section for

a certain droplet size relates to the equilibrium thermodynamic state of that system and is different from an activation energy for nucleation and growth of a new phase that starts as a critical cluster of distinct composition within a homogeneous droplet, because the size of a critical cluster will be different from the size of the core or shell phases of the droplet at equilibrium.

Droplet diameter [nm]	Droplet volume [m ³]	Substance amount in droplet volume [mol]	Core phase surface area [m ²]	Interfacial energy ^(a) [J/mol]
1000	5.236E-19	1.151E-14	1.979E-12	0.184
800	2.681E-19	5.892E-15	1.267E-12	0.230
600	1.131E-19	2.486E-15	7.125E-13	0.307
400	3.351E-20	7.365E-16	3.167E-13	0.460
300	1.414E-20	3.107E-16	1.781E-13	0.613
200	4.189E-21	9.206E-17	7.916E-14	0.920
150	1.767E-21	3.884E-17	4.453E-14	1.227
100	5.236E-22	1.151E-17	1.979E-14	1.840
90	3.817E-22	8.389E-18	1.603E-14	2.045
80	2.681E-22	5.892E-18	1.267E-14	2.300
70	1.796E-22	3.947E-18	9.697E-15	2.629
60	1.131E-22	2.486E-18	7.125E-15	3.067
50	6.545E-23	1.439E-18	4.948E-15	3.680
40	3.351E-23	7.365E-19	3.167E-15	4.600
30	1.414E-23	3.107E-19	1.781E-15	6.134
20	4.189E-24	9.206E-20	7.916E-16	9.201
10	5.236E-25	1.151E-20	1.979E-16	18.401

Table S1. Calculated droplet size dependence of the interfacial energy contribution to the system's Gibbs energy.

^(a) This is the interfacial energy contribution per overall molar amount of substance in the phase-separated droplet based on a value of 1.07×10^{-3} J/m² for the interfacial surface tension and the given assumptions about the volume ratio and average density of the droplet phases.

Table S2. Component and system parameters used to determine the interfacial energy contribution as a function of size in Table S1.

System or component property	Numeric value and unit
Molar mass of water	0.018015 [kg/mol]
Molar mass of PEG-400	0.400000 [kg/mol]
Molar mass of ammonium sulfate	0.132139 [kg/mol]
Average molar mass (estimated for a system with PEG-400 and ammonium sulfate	0.054143 [kg/mol]
mixed 1:1 by mass and a water content of 80 mol-%)	
Overall solution density ^(a)	$1190 \ [kg/m^3]$
Average molar density of solution (droplet)	$21978.9 \text{ [mol/m}^3\text{]}$
Core/shell volume ratio of the phases	1.0 [-]
Interfacial surface tension ^(b)	$1.07 \ [mN/m]^{(c)}$

^(a) Value based on data given in Table 2 of Song et al. (2013) for this system.

^(b) Song et al. (2013) list a range of values for the interfacial tension between 0.08 and 1.07 [mN/m] at different water activities (i.e. different RH levels). Here the largest measured value is taken, which applies to conditions at 82 % RH.

^(c) An interfacial surface tension of 1 mN/m is equivalent to 10^{-3} J/m².

Experimental Methods: Aerosol Particle Generation and Cryogenic-Transmission Electron Microscopy

Solution preparation and aerosol particle generation

Aerosol particles composed of ammonium sulfate (> 99.0%, EMD) and poly(ethylene glycol) 400 (PEG-400; BioUltra, Sigma-Aldrich) were generated from aqueous solution without further purification. Aqueous solutions with 0.015 wt.% to 0.0625 wt.% solute were prepared for the mixtures of PEG-400 with ammonium sulfate at either a 80/20, 60/40, 52/48, 50/50, or 45/55 mass ratio of PEG-400/ammonium sulfate. These solutions were prepared using ultrapure water (high-performance liquid chromatography grade). Aerosol particles were generated at a high relative humidity (RH \geq 96%) from the aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN). Nitrogen flow through the atomizer was approximately 1.5 L/min. The wet aerosol particles were dried to less than 2% RH (with a drying rate of 87.2% RH/s and at a temperature of 295 K) using a diffusion dryer filled with molecular sieves (13X mesh size, Sigma Aldrich). The dry aerosol particles were collected onto TEM grids for imaging.

Cryogenic-Transmission Electron Microscopy (cryo-TEM)

To prepare samples for imaging, a cascade impactor (PIXE International Corp., Tallahassee, FL) was used to collect dry aerosol particles onto 200 mesh copper TEM grids coated with continuous carbon (Electron Microscopy Science, Hatfield, PA). The impactor was backed by a mechanical pump to provide a flow rate of 1.0 L/min. The particles were imaged using cryo-TEM at an accelerating voltage of 120-200 kV. Prior to imaging, the samples were transferred to a cryo-TEM holder and cooled in the microscope to approximately 93 K using liquid nitrogen. Cryogenic conditions were used to minimize electron beam damage to the samples.¹⁰⁻¹²

Collected TEM images were analyzed using ImageJ (National Institutes of Health, Bethesda, MD). The areas of thousands of particles were determined for each sample. Assuming the particles are spherical, the calculated area is converted to an area equivalent diameter. The total number of particles at each area equivalent diameter can be used to plot the distribution of particle sizes as a function of their morphology.

Particle Composition Information

Due to the procedure by which the aerosol particles are generated, we assume that the overall chemical composition of homogeneous and phase-separated particles is the same for a given organic/inorganic mass ratio. We have used energy dispersive X-ray spectroscopy (EDS) to obtain composition information for the particles studied and have shown that regardless of particle size and morphology, the overall composition is uniform. Although the particles undergo electron beam damage even at cryogenic temperatures (93 K), we can still obtain elemental composition. Specifically, we are interested in detecting sulfur and carbon, which are not vaporized during the process of acquiring an EDS spectrum. We note that although we use

carbon-coated TEM grids, the carbon present in the particles yields additional signal over the relatively constant background levels, and thus we can use the sulfur to carbon ratios to determine if the particles have uniform composition. Figure S2 shows sample EDS spectra for two 60/40 PEG-400/ammonium sulfate particles: one phase-separated and one homogeneous. The homogeneous and phase-separated particles presented in the spectra below are approximately the same size and have an identical EDS spectrum. We note that the copper signal results from the cryo-TEM sample holder and the TEM grid support film, while the silicon signal is primarily from the TEM grid background.





Figure S2. Energy dispersive X-ray spectroscopy (EDS) spectra for (a) a 60/40 PEG-400/ammonium sulfate phase-separated particle and (b) a 60/40 PEG-400/ammonium sulfate homogeneous particle.

We have obtained EDS spectra for the 60/40 PEG-400/ammonium sulfate system and analyzed a total of 62 particles (29 homogeneous and 33 phase-separated) with particle sizes ranging from 105 nm to 426 nm. We note that the sulfur peak becomes difficult to detect for particle diameters less than 100 nm. The peak areas from the EDS spectra were analyzed using DeskTop Spectrum Analyzer II (DTSA-II; National Institute of Standards and Technology, Gaithersburg, MD). The average sulfur to carbon ratios are presented in Fig. S3. In addition to the identical EDS spectra observed for homogeneous vs. phase-separated particles, we have shown that regardless of particle morphology, we obtain similar sulfur to carbon ratios for the particles studied, indicating uniform overall particle composition.



Figure S3. Sulfur to carbon ratios derived from EDS spectra peak areas using DTSA-II for 60/40 PEG-400/ammonium sulfate phase-separated and homogeneous particles. The error bars result from the measurement of sulfur to carbon ratios for multiple particles.

Data for the 60/40 and 45/55 PEG-400/Ammonium Sulfate Systems

The 60/40 and 45/55 PEG-400/ammonium sulfate systems behave similarly to the 80/20 PEG-400/ammonium sulfate mixtures in terms of the size dependent behavior observed. The samples analyzed for the 60/40 PEG-400/ammonium sulfate system consisted of 2968 particles (266 homogeneous and 2702 phase-separated). The smallest phase-separated particles are 80 nm in diameter, and the largest homogeneous particles are 198 nm in diameter (Fig. S4). Particles larger than these size regimes are phase-separated, and those that are smaller are homogeneous.



Figure S4. Histogram showing the size dependent behavior of the morphology of the 60/40 dry mass ratio PEG-400/ammonium sulfate mixture. Large particles are phase-separated (blue), while smaller particles have a homogeneous morphology (red).

The samples analyzed for the 45/55 PEG-400/ammonium sulfate system consisted of 2436 particles (575 homogeneous and 1861 phase-separated). The smallest phase-separated particles are 64 nm in diameter, and the largest homogeneous particles are 214 nm in diameter (Fig. S5). Particles larger than these size regimes are phase-separated, and those that are smaller are homogeneous.



Figure S5. Histogram showing the size dependent behavior of the morphology of the 45/55 dry mass ratio PEG-400/ammonium sulfate mixture. Large particles are phase-separated (blue), while smaller particles have a homogeneous morphology (red).

The results for the 60/40 and 45/55 PEG-400/ammonium sulfate mixtures can be explained by considering the bulk phase diagram and the activation barrier as we approach the critical point. The predicted phase diagram shows that inside the composition space where two liquid phases are stable, the same final compositions of the liquid phases can be reached from different initial single phase compositions located along the same tie-line (i. e. when they are located approximately at the same water activity), including from points with 60/40 or 80/20 overall PEG-400/ammonium sulfate dry mixtures initially. That is, the difference in the initial mixture compositions will lead to different final phase compositions; rather, the different initial compositions will lead to different final volumes of the two liquid phases. If the nucleation barrier is associated directly with the final liquid phase composition, for example, by

nucleating a PEG-rich phase from the initial one-phase system, the nucleation barrier could be similar for both 60/40 and 80/20 mixtures. As a result, if the phase separation mechanism for both 60/40 and 80/20 mixtures is by nucleation-and-growth, it is possible that the histograms for both cases look similar. The difference as seen from the predicted phase diagram, is that one could expect that the 80/20 mixture can only phase separate by nucleation-and-growth, while in the case of the 60/40 mixture, the spinodal limit is crossed during drying, which then would allow for phase separation by spinodal decomposition. The reason that did not occur in many cases for very small particles in the experiments could be related to the time scale for drying of the particles.

It is also important to note that the activation barrier for phase separation decreases near the critical point.^{1,15} Our results suggest that a 60/40 mixture is likely not close enough to the critical point to have a significant effect on the activation barrier. This may also explain why as we move to the 45/55 mixture (which is slightly closer to the critical point than the 60/40 mixture), we are nearing the threshold where the activation barrier decreases and phase separated particles are observed at slightly smaller diameters compared to the 60/40 case.

Distinguishing between Homogeneous and Phase-Separated Particles

In our cryo-TEM experiments, we use image contrast and electron beam damaging behavior to characterize the morphology of the aerosol particles studied. For phase-separated particles with a resulting core-shell morphology, we are able to see an organic-rich shell that surrounds the inorganic-rich core down to particle diameters on the order of 20 nm. We note that in these experiments we study particles only down to ~20 nm. Particles smaller than this size regime become difficult to distinguish from the background at higher magnifications in addition to undergoing immediate electron beam damage.

The homogeneous particles appear spherical and are uniform in morphology. We can further distinguish the two observed morphologies (i.e. core-shell and homogeneous) using the electron beam damaging behavior. Although we image our particles at approximately 93 K to minimize electron beam damage, longer exposure times will eventually damage the particles. Figure S6 shows the damaging behavior of a phase-separated and a homogeneous PEG-400/ammonium sulfate particle. As the phase-separated particles damage, voids begin to form in the particle core and around the perimeter of the core. The voids slowly move towards the outer diameter of the particle but do not fully form throughout the entire particle. As seen in Fig. S6a, there is an organic shell that is still clearly visible even after the particle has undergone electron beam damage. From the electron beam damaging behavior of the phase-separated particle, it appears that the particle is divided into three sections: the inorganic-rich core, the voids around the core, which may consist of both the organic and inorganic phase, and the pure organic shell surrounding the voids and the core. We note that despite the three regions that are observed upon electron beam damage, the phase-separated particle is still a two-phase system. Since PEG-400 is a surfactant and is surface active in aqueous solution droplets, the organic-rich phase has a PEG-400 rich exterior and a salt-containing area near the core. Raman microscopy of dry particles containing an organic/inorganic component has shown that surface active organics have a higher concentration near the particle edge while the inorganic component decreases in concentration at the air/particle interface.^{13,14} The homogeneous particles, on the other hand, damage uniformly through the formation of voids. As seen in Fig. S6b, the homogeneous particle forms voids throughout the entire particle. Thus, in addition to the clearly visible core and shell for the phase-separated particles (and a lack of these morphology features in homogeneous particles), we are also able to use electron beam damage to distinguish between phase-separated and homogeneous particles.



PEG-400/Ammonium Sulfate

Figure S6. Cryo-TEM images of electron beam damage to (a) a phase-separated PEG-400/ammonium sulfate particle, and (b) a homogeneous PEG-400/ammonium sulfate particle. The time of exposure under the electron beam and particle damage increases from left to right.

In addition to using phase contrast and electron beam damaging behavior to distinguish between phase-separated and homogeneous particles, we also use scanning TEM high angle annular dark field (STEM HAADF) imaging. STEM HAADF imaging is sensitive to the mass of the element being detected. A higher atomic (Z) number leads to a greater loss of energy as electrons interact with the sample. Thus, regions with high Z atoms appear bright as they scatter more strongly. As seen in Fig. S7, we can distinguish between a homogeneous and core-shell morphology based on mass contrast. The core-shell particle (Fig. S7a) has a bright core and a shell that becomes darker near the outer regions of the particle, indicating that PEG-400 is surface active. The homogeneous particle shown in Fig. S7b appears uniform throughout and does not show any phase separation.



Figure S7. Scanning TEM high angle annular dark field (STEM HAADF) image of (a) an 80/20 dry mass ratio PEG-400/ammonium sulfate phase-separated particle and (b) an 80/20 mass ratio PEG-400/ammonium sulfate homogeneous particle.

Resolution of Cryo-TEM below 100 nm

As shown in the histogram plots for the PEG-400/ammonium sulfate systems in the main text, cryo-TEM allows us to characterize the morphology of particles studied at diameters well below 100 nm. Through the use of the cryo-TEM technique, we observe both phase-separated and homogeneous morphologies at particle diameters on the order of 50 nm and less. As seen in Fig. S8, a core and shell is visible in the case of a phase-separated particle (Fig. S8a) and a lack of phase separation is evident in the homogeneous particle (Fig. S8b).

PEG-400/Ammonium Sulfate



Figure S8. Cryo-TEM images of (a) a phase-separated PEG-400/ammonium sulfate particle, and (b) a homogeneous PEG-400/ammonium sulfate particle showing the resolution of cryo-TEM at diameters on the order of 50 nm.

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