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Supplemental Information

Effect of Crystallization Kinetics on the Properties of Spray Dried Microparticles

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EXPERIMENTAL DETAILS

Chemicals

The solubility of NaNO₃ in water at the droplet temperature, *i.e.*, the wet bulb temperature, is needed for the theoretical model. Wet bulb temperatures depend on the temperatures of the external environment and the evaporation rate (Vehring et al. 2007). Assuming a constant wet bulb temperature through the process, at the temperatures of 10, 20, 25, 30, 35 and 40°C, the solubilities are 870, 930, 970, 1020 and 1070 mg/ml, respectively (Holden and Morrison 1982). However, vapor pressures are influenced by the percentage of solute contained in the evaporating droplet. Since the weight percentage of NaNO₃ increases due to the evaporation of water, the evaporation rate decreases and the wet bulb temperature increases during the particle formation process (Sadafi et al. 2015). As a consequence, the solubility increases according to the weight percentage of NaNO₃ in DI H₂O.

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Solution preparation began by weighing out NaNO_3 on an analytical balance (ME204E, Mettler Toledo, Mississauga, Ontario, Canada) and adding it to the solvent within a volumetric flask. The solution was closed with a paraffin film (PM992, Pechiney Plastic Packaging, Chicago, IL, U.S.) and agitated for 15 minutes using a wrist action shaker (Model 75, Burrell Scientific, Pittsburg, Pennsylvania, U.S.).

Experimental setup

Determination of viscosity

The composite particle underwent relaxation to a single spherical droplet, governed by the balance of surface and bulk viscous forces. A detailed description of the aerosol optical tweezers technique and its use in studying particle coalescence has been presented previously (Power et al. 2012; Power et al. 2013). Frequency doubled light from a Nd:YVO₄ laser at 532 nm was incident on a liquid-crystal-on-silicon spatial light modulator (LC-R 2500, Holoeye Photonics AG, Berlin-Adlershof, Germany), conjugated to the back focal plane of an inverted microscope objective (ACH oil, 100 x, NA 1.25, Olympus Niko, Chiyoda Tokyo, Japan) to form a tightly focused optical trap within a custom built aerosol trapping cell. The spatial light modulator imparted a phase-only modulation on the profile of the Gaussian beam, allowing the creation of two gradient-force optical traps within the trapping chamber. The axial and lateral trap positions were determined by the modulation pattern applied to the spatial light modulator by user-controlled software, allowing spatial manipulation of the optical traps to initiate particle coalescence.

Two particles, 3 to 6 μm in radius, were trapped from a plume of aqueous sodium nitrate aerosol introduced into the trapping cell using a medical nebulizer (NE U22, Omron, Kyoto, Japan), with particles passing through the focal point of each optical trap caught and confined in three dimensions by the strong gradient force. Particles were trapped within a relative humidity (RH) controlled environment, maintained by a constant gas flow (< 0.2 l/min), and generated by mixing different proportions of dry and humidified nitrogen. The gas flow RH was measured after the trapping cell using a calibrated capacitance probe (Honeywell 500, Honeywell, Morristown, New Jersey, USA). By varying the gas phase RH, different sodium nitrate solute mass fractions, and thus viscosities, could be accessed in the trapped particles.

Inelastically back-scattered light from each particle was collected by the same objective and dispersed using a spectrograph onto a Peltier-cooled CCD camera (SpectraPro SP550i, Pixis 256,

Acton, Princeton Instruments, Buckinghamshire, UK). Raman active species within the trapped particles were excited by the 532nm laser light, leading to spontaneous Raman emission at Stokes shifted wavelengths characteristic of the molecular species present. At wavelengths commensurate with whispering gallery modes, the trapped particles acted as optical cavities, enhancing Raman scattering at discrete wavelengths and leading to a superposition of narrow stimulated Raman peaks on the broad spontaneous Raman bands. Measurement of the whispering gallery mode wavelengths through cavity enhanced Raman spectroscopy (CERS) and subsequent comparison with Mie theory calculations allows the radius and refractive index of a particle to be determined with accuracy ± 2 nm and ± 0.0006 , respectively. Trapped particles were imaged using brightfield microscopy, with a maximum camera frame rate of 1000 frames per second. Elastically back-scattered light from one of the particles was isolated and collected by a silicon photodetector (Thorlabs DET110, Thorlabs, Ely, UK).

Following capture, the two particles were left to equilibrate with the humidity in the gas phase until no further change in either particle's size was observed over a period of 30 minutes. Once equilibrated, the two droplets were positioned such that the separation between the surfaces of the two particles was lower than 1 μm before removing one of the optical traps. The optical field of the remaining trap extended over sufficient range to draw the free particle in to the remaining trap, initiating particle coalescence. Depending on particle viscosity, the timescale for coalescence could be monitored using elastic light scattering, brightfield imaging or Raman spectroscopy. The viscosity range accessible by each technique depended on their maximum rate of data acquisition: higher than 100 MHz for elastic light scattering, 1 kHz for brightfield imaging and 1 Hz for Raman spectroscopy. In the work presented here, the relaxation in particle shape following coalescence was monitored using elastic light scattering as all relaxation times were shorter than 10 ms with viscosities lower than 10 Pa s (Power et al. 2013; Power and Reid 2014).

The intensity of elastically back-scattered light from a particle is a function of its scattering cross-section, dependent on the particle size and shape, and its position within the optical trap. As the second optical trap is removed and the coalescence of the particles begins within the optical field of the remaining trap, an increase in the elastically scattered light intensity recorded by the photodetector is observed due to the increase in size of the composite scattering body within the sampling volume. The back-scattered light intensity then decreases to a constant final

value as the coalesced particle relaxes to a spherical shape driven by capillary forces. Motion of the composite particle due to trapping forces is negligible over the time scales studied, likewise the optical forces are many orders of magnitude weaker than the restoring capillary forces and play no part in determining the dynamics. For particles with a viscosity below the critical damping threshold (~ 20 mPa s for the particle sizes considered here), the relaxation is accompanied by shape oscillations and corresponding oscillations in backscattering intensity, which takes the form of a damped harmonic oscillator. The oscillation frequency and the damping time can be used to estimate the surface tension and viscosity of the droplet, respectively. For particles of higher viscosity, the time dependence can be fit to a single exponential decay whose characteristic relaxation time can be determined. This is equivalent to the time taken for the elastically back-scattered light intensity to fall to $1/e$ (37%) of its initial value, and can be used to determine the particle viscosity. Correspondence between the elastic light scattering signature and the change in particle shape has been discussed in detail in our previous work, including a detailed comparison of light scattering calculations for an oscillating sphere with the measured signal, and we refer the reader to this earlier work for more information (Bzdek et al. 2015; Power et al. 2013).

To estimate the particle viscosity from the relaxation time, it is necessary to know the radius and true density of the coalesced particle. The radius of the coalesced particle is calculated from fitting the CERS spectra, and the true density is determined from the Extended Aerosol Inorganics Model using the RH as measured by the capacitance probe to determine the particle water activity (Clegg 2014; Clegg et al. 1998).

Seventeen sodium nitrate particle coalescence events were observed at RHs in the range 86.5% to 24.2%. The uncertainty associated with the capacitance probe RH measurement increases with increasing humidity, reaching values higher than 3% at humidities approaching 90% RH. To mitigate this uncertainty, the sodium nitrate mass fraction of solute in all coalesced particles equilibrated above 50% RH was calculated from the refractive index determined from the Raman spectra rather than from the RH measurement, employing the parameterization shown in previous literature (Tang and Munkelwitz 1991). The dispersion in refractive index (i.e., variation in refractive index with wavelength) retrieved from fitting the Raman spectra was used to compensate for the differences in refractive index measured using CERS (at a wavelength of 650 nm) and the model treatment (at a wavelength of 632.8 nm) (Tang and Munkelwitz 1991).

For coalescence measurements performed on particles equilibrated below 50% RH, the uncertainty in the water activity was observed to be less than the variation between successive measurements and thus the probe RH was used directly to calculate the mass fraction of sodium nitrate in the coalesced particles using a second parameterization (Tang and Munkelwitz 1994). Measured data points were binned in to water activity ranges, with viscosities reported as an average and standard deviation.

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