Manipulation of arrays of aerosol droplets and studies of aerosol coagulation dynamics

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Introduction

The coagulation of aerosol particles is a fundamental process that influences the size distribution of aerosols and the mixing state of different aerosol components. Both the physical and chemical properties of aerosols are dependent on particle size and composition. Thus, fundamental studies of interparticle interactions and coagulation will provide important insights into the mechanisms of aerosol transformation in scientific disciplines as diverse as atmospheric chemistry and physics, combustion science, plasma physics, toxicology and epidemiology, and nanotechnology.

Recently we have demonstrated that optical tweezers (a single-beam gradient force optical trap) can be used to trap and control single aerosol droplets 2-15 µm in diameter.[1] Further, we showed that the coagulation of two aerosol droplets could be directly studied by forming two traps. By coupling the optical tweezing instrument with a spectrograph and CCD, we demonstrated that the Raman spectrum of a trapped droplet could be acquired with high temporal and spectral resolution. It was shown that the spectroscopic signature contains information not only on the composition of the droplet, but allows the accurate determination of droplet size with nanometre precision. Stimulated Raman scattering surpasses threshold only at discrete wavelengths commensurate with whispering gallery modes (WGMs), leading to a strong enhancement of the Raman scattering at these wavelengths.[2] By comparison of the wavelengths of the WGMs with Mie calculations, the size of the droplet can be determined.

This breakthrough in aerosol control and characterisation now permits the direct in situ characterisation of aerosol dynamics to a detail that had not been previously realisable.[3] In the work reported here, we have extended these measurements to studies of mixing state and the coagulation of two different chemical components that are immiscible in the bulk phase. Specifically, we have compared the coagulation of decane and water droplets and compared this with the coagulation of an ethanol droplet with a water droplet, two miscible components. Further, we have examined the relative importance of optical forces and interparticle forces in governing the coagulation dynamics by varying the optical trapping strength of the two traps. Finally, we have explored the possibility of forming arrays of trapped aerosol particles, and have simultaneously trapped 4 aerosol droplets by using an acousto-optic modulator (AOM) to achieve rapid beam steering and trap sharing.

Experimental Description

The experimental design of the instrument has been described in detail previously and will only be briefly reviewed here.[1,3] The optical trap is formed from a tightly focussed beam of laser light at 514.5 nm, using a commercial Leica DM IRB microscope to both form the optical trap and acquire a conventional brightfield image of the trapped particle. A wavelength in the visible region is chosen as this minimises heating of the aerosol sample. Aerosol is generated with a commercial medical nebuliser and aerosol particles are trapped directly from the aerosol flow which passes through a custom-designed cell. Backscattered Raman light is imaged into a spectrograph (focal length 0.5 m) and the Raman scatter is dispersed by a 1200 g/mm grating, allowing an entire Raman spectrum to be recorded with sub-second time-resolution. Multiple traps were either formed using a simple beam splitter arrangement, or through rapid beam steering and time sharing of the laser beam between multiple trapping sites with the AOM.

The Coagulation of Oil and Water Droplets

To explore the advantages of the optical tweezing approach for characterising aerosol dynamics, we have investigated the coagulation of an aqueous droplet with miscible and immiscible organic droplets, ethanol and decane, respectively.[4] As illustrated in Figure 1, a water droplet was trapped in one optical trap. A droplet of decane was then trapped in the second optical trap. By direct manipulation of the trapped droplets through beam steering, the coagulation of the two droplets could be controlled.

Figure 1. Example of the control achieved over coagulation.

The Raman spectra of the trapped droplets were acquired before and after coagulation, as illustrated in Figure 2. The spectrum of the water droplet prior to coagulation shows both the spontaneous Raman scattering arising from the OH stretching vibrations of water and the stimulated Raman scattering occurring at resonant wavelengths from which the size of the droplet can be accurately determined. In this example, the water droplet has a size of 4.352 ± 0.002 µm. The Raman spectrum of the coagulated droplet consists of both a spontaneous Raman signature from the water component and a signature of the decane component at Raman shifts corresponding to excitation of the CH stretching vibrations. Noticeably, the stimulated Raman scattering at discrete wavelengths has disappeared. Inhomogeneities in refractive index in a biphase droplet

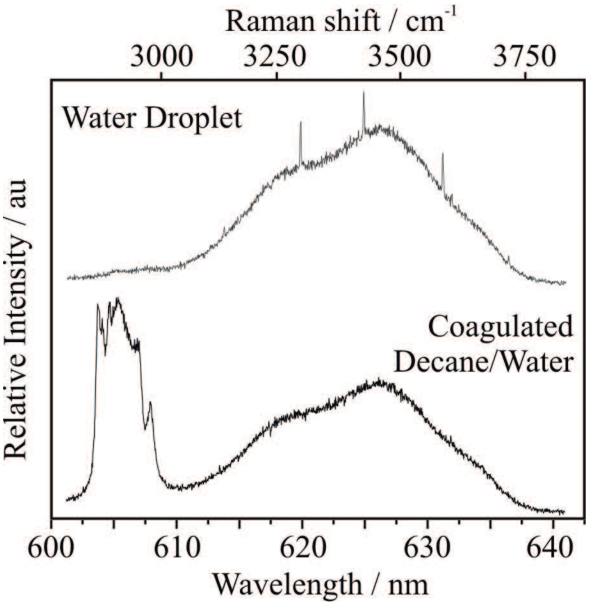

Figure 2. Raman spectrum of water droplet prior to coagulation and decane/water droplet after coagulation.

and loss of spherical symmetry are considered to quench the non-linear scatter by disrupting the optical cavity otherwise formed by a spherical droplet of uniform refractive index.

The presence of oil inclusions within a host water droplet, or water inclusions within a host oil droplet, can be observed from the brightfield microscopy. As illustrated in Figure 3, complex arrangements of decane and water leading to phase partitioning have been observed. The formation of these inhomogeneous droplets without spherical symmetry leads to the quenching of the stimulated Raman scattering signal, as illustrated in Figure 2. This also confirms that the decane and water components phase segregate within the coagulated droplet, analogous to the phase separation that occurs in the bulk phase.

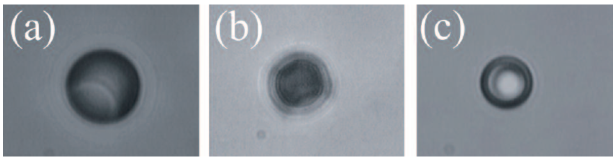

Figure 3. Typical images of coagulated decane/water droplets illustrating the phase separation that occurs.

The shape of the OH stretching band further confirms that the oil and water components are phase segregated. The shape of the OH stretching band is sensitive to the hydrogen bonding environment experienced by water molecules within the sample.[3,5] The consistent shape of the OH band in the biphase droplet with that in a pure water droplet indicates that the hydrogen bonding environment of the aqueous component is not perturbed by the presence of the oil component, indicating that the two components are not mixed.

Further investigations have examined the coagulation of a water droplet with an ethanol droplet. The bulk phase miscibility of these two components is reflected in their mixing state in the coagulated aerosol droplet. The images of the coagulated droplets indicate that the two components are well mixed. This conclusion is supported by the appearance of progressions of WGMs in the stimulated Raman scattering that extend over both the OH and CH stretching bands, implying that the droplet retains its spherical form and that the two components are mixed.

Investigating the Interplay of Optical and Interparticle Forces at Coagulation

The restoring force of an aerosol particle trapped with a gradient force trap is dependent on the trapping laser power. During the coagulation of two aerosol droplets, if one optical trap is formed with a slightly higher power than the other then the optical forces can be expected to drive the coagulation event by forcing trap hopping prior to coagulation (Figure 4(a)). Even if the droplets encounter each other at longer range than the extent of the optical forces, the identity of the final trapping site is expected to be determined by the trapping site with the largest trapping restoring force. We have rigorously investigated this hypothesis by varying the relative trapping strengths of the two optical traps (Figure 4(b)) and have confirmed that the outcome of the coagulation event can be controlled optically.[6] Further, by examining the interparticle separation at which coagulation occurs and comparing the distance to the sum of the droplet radii, we have clearly shown that for droplets with a combined radius larger than 7 µm, the droplets encounter each prior to the occurrence of trap hopping and capillary forces drive the coagulation event. For these coagulation events, the separation at which coagulation occurs is correlated to the distance of closest approach (the sum of the radii) as anticipated. This investigation has provided a crucial benchmark test for assessing the limiting conditions under which the optical forces or interparticle forces govern the coagulation event.

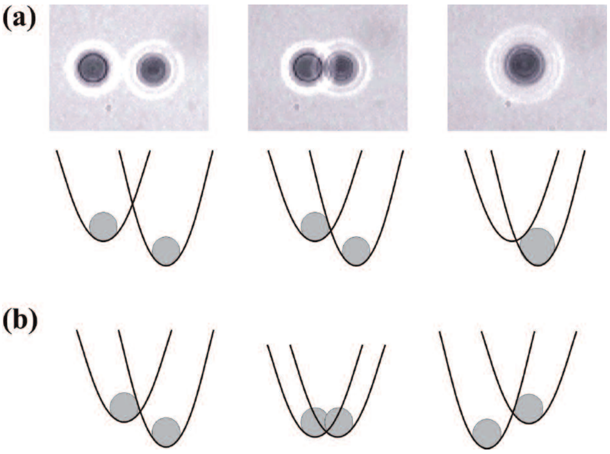

Figure 4. (a) Translation of the traps towards each other can allow the relative range of the optical forces to be probed. (b) Varying the relative trap strengths can allow control over the final trapping location of the trapped droplet.

Arrays of Optically Trapped Aerosol Droplets

The direct control over and analysis of samples of picolitre volumes is an important objective of lab-on-a-chip devices and digital microfluidics.[7,8] Rather than controlling single coagulation events between two aerosol droplets, the ability to parallelise coagulation of many droplets could provide a new strategy for performing digital microfluidic operations. We have investigated this possibility by trapping arrays of aerosol droplets. In this preliminary work, the AOM was used to rapidly steer the trapping laser beam between 2, 4 and 8 trapping sites. While trapping arrays of 4 droplets was achieved, increasing the number of trapping sites further did not allow the stable formation of larger arrays. Sedimentation of the trapped droplets was found to compete with the restoration of the trap. Once more than 4 sites were established, sedimentation of the trapped droplets to the coverslip occurred more rapidly than the sharing of the beam between the trapping sites. However, the simultaneous trapping of 4 droplets illustrated that parallelising the manipulation of aerosol droplets is possible. The control available from a spatial light modulator creating a constant holographic pattern of traps is now being investigated as providing a more robust approach.

Summary

We have demonstrated that optical tweezing can be used to investigate the coagulation and mixing state of different aerosol components, specifically comparing the coagulation of two miscible or immiscible chemical components. We have also investigated the range of the optical forces and their influence on the coagulation event, determining the conditions under which interparticle forces govern the coagulation event. Finally, we have demonstrated in preliminary measurements that arrays of aerosol particles can be manipulated.

References

1. R. J. Hopkins, L. Mitchem, A. D. Ward and J. P. Reid, *Phys. Chem. Chem. Phys.* **6** 4924 (2004)
2. R. Symes, R. M. Sayer and J. P. Reid, *Phys. Chem. Chem. Phys.* **6** 474 (2004)
3. L. Mitchem, J. Buajarern, R. J. Hopkins, A. D. Ward, R. J. J. Gilham, R. L. Johnston and J. P. Reid, *J. Phys. Chem. A,* **110** 8116 (2006)
4. L. Mitchem, J. Buajarern, A. D. Ward and J. P. Reid, *J. Phys. Chem. B,* in press
5. G. E. Walrafen, *Raman and Infrared Spectral Investigations of Water Structure, in Water: A Comprehensive Treatise;* Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, p. 151
6. J. Buajarern, L. Mitchem, A. D. Ward, N. H. Nahler, D. McGloin and J. P. Reid, *J. Chem. Phys.,* submitted
7. D. Erickson and D. Q. Li, *Analytica Chimica Acta* **507** 11 (2004)
8. J. A. Schwartz, J. V. Vykoukal and P. R. C. Gascoyne, *Lab on a Chip* **4** 11 (2004)