

Aerosol SANS: A new method to probe the structure of nanodroplets

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Abstract. Small angle neutron scattering (SANS) is proving to be an invaluable tool for probing the structure of nanodroplets. By fitting the SANS scattering spectrum one can derive the key properties of the aerosol, i.e. the number density, the average particle size, and the polydispersity, under conditions where conventional aerosol measurements are not possible. Furthermore, in binary nanodroplets it appears feasible to identify scattering from an enriched surface layer of the droplet, a capability that is relevant for understanding the aerosol formation process as well as the heterogeneous chemistry of the multi-component nanodroplets.

INTRODUCTION

Nanodroplet aerosols form readily in the supersonic expansions that occur, for example, in turbomachinery, jet exhausts and volcanic eruptions. Thus understanding particle formation and growth when cooling rates approach $1\text{K}/\mu\text{s}$ is of broad scientific interest. From a fundamental point of view, particles with radii $<10\text{ nm}$ are important because they lie in the critical transition zone between large molecular clusters and bulk material. Furthermore, in multi-component nanodroplets, there is strong theoretical and indirect experimental evidence that the surface and interior compositions of the droplets can differ significantly. Since surface enrichment affects nucleation, growth and evaporation kinetics, and the heterogeneous chemistry of aerosol droplets, direct evidence for this phenomenon can deepen our fundamental understanding of aerosol formation and growth processes.

SANS is a well established method for examining the properties of microemulsions.¹⁻⁴ The experimental challenges inherent in applying SANS to aerosols are best understood by comparing the characteristics of these two systems. Microemulsions are almost ideal samples: they are stable, the droplet number density N is usually $>10^{16}\text{ cm}^{-3}$ leading to a volume fraction ϕ of the disperse phase in the range 0.01-0.9, and, finally, less than 1 cm^3 of material is required per sample. In contrast, an aerosol is not stable and must be produced continuously in the neutron beam line. Finite nucleation rates and rapid coagulation combine to keep N below $\sim 10^{14}\text{ cm}^{-3}$ and ϕ below $\sim 10^{-5}$. Thus the scattering signals from aerosols are many orders of magnitude smaller than from microemulsions. Fortunately, background scattering in the aerosol SANS experiments is primarily instrument related and is also several orders of magnitude lower than in a typical microemulsion experiment.

EXPERIMENTAL

Aerosols with $N \sim 10^{12} \text{ cm}^{-3}$ and a mean particle radius $\langle r \rangle \sim 10 \text{ nm}$, are produced in a supersonic nozzle by rapidly expanding a dilute vapor mixture of D_2O (or other condensible liquid) and N_2 . As illustrated in Fig. 1, our experiments⁵ clearly prove the feasibility of applying SANS to liquid droplet aerosols in the 5-10 nm size range even though N is many orders of magnitude lower than in a typical microemulsion. Unlike earlier light scattering experiments⁶, the structure in the SANS spectrum let us determine simultaneously for the first time $\langle r \rangle$, N , and the average width of the distribution σ using only the simple assumption that the aerosol has a log-normal or Gaussian distribution. In our first experiments⁵ we found that $\langle r \rangle$ increased with the partial pressure of the condensible vapor p_v but did not depend strongly on the total pressure at the inlet to the nozzle p_0 , while N decreased with p_v thereby confirming our model predictions of droplet nucleation and growth in the supersonic nozzle.

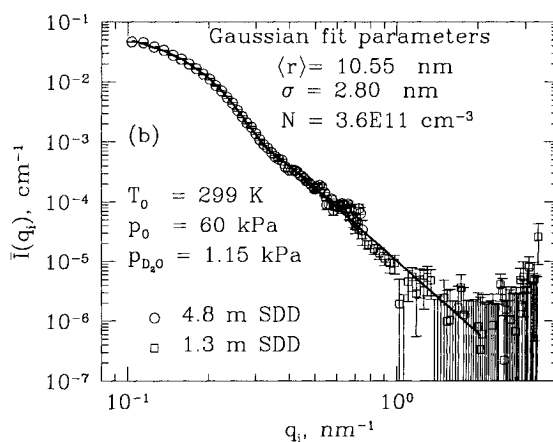


FIGURE 1. The circularly averaged scattered intensity from a pure D_2O aerosol. The solid line shows the fit to the data for the parameters given in the figure.

We also clearly observe a Doppler shift in the momentum of the scattered neutrons that arises from the directed motion of the high velocity (400-450 m/s) particles and the geometry of our experiment. The presence of a Doppler shift is unique to our SANS experiments. Because the size distribution parameters derived from the experimental data depend critically on correctly interpreting the 2-d scattering patterns, in our second set of experiments⁷ we designed a sequence of runs to carefully explore the phenomenon. Figure 2 illustrates the 2-d scattering patterns measured for constant inlet conditions and three different neutron wavelengths. As the neutron wavelength changes from 0.5 to 1.5 nm, corresponding to a change in the neutron velocity from 800 to 267 m/s, we see a clear change from a nearly circular to a highly elliptical scattering pattern. Two-body scattering theory⁸ quantitatively predicts the changes that occur as the relative velocity of the neutrons and particles is varied. The contour lines superimposed on the experimental data are the predicted scattering

intensities based on the parameters of the aerosol size distribution derived from fitting the data at $\lambda = 1$ nm. As a potentially interesting application we can use the Doppler shift as a simultaneous flow diagnostic to directly measure the velocity of the particles^{7,8}. For a test case, the average velocity derived from the Doppler shift was within 2% of the mean flow velocity, 440 m/s, expected in the viewing volume from the pressure trace data under these conditions.

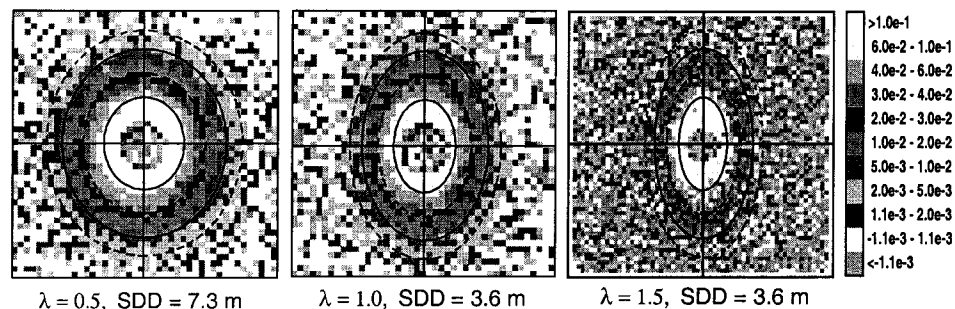


FIGURE 2. The observed 2-d scattering patterns as a function of neutron wavelength and sample-to-detector distance (SDD). The solid contour closest to the center of the detector corresponds to an absolute scattering intensity of 0.08 cm^{-1} . The remaining contours correspond to absolute intensities of 0.03 , 0.008 and 0.003 cm^{-1} respectively.

Finally, our binary aerosol experiments have included aerosols formed from H_2O , D_2O , and n-butanol or its fully deuterated analogue d-butanol. Our preliminary results for D_2O - H_2O aerosols are presented elsewhere in these proceedings. In contrast to the complete miscibility found in D_2O - H_2O mixtures, bulk samples of H_2O and n-butanol have a wide miscibility gap near room temperature. No one has measured a lower critical solution temperature for the system. Thus, our working assumption is that binary nanodroplets containing H_2O (or D_2O) and d-butanol (or n-butanol) will exhibit a water-rich core and an alcohol-rich shell. Since the scattering length of H is negative and about half the magnitude of that of D, scattering signals are usually dominated by the scattering intensity from the deuterated compound. In experiments with D_2O -n-butanol droplets (not shown here) the signal intensity decreases as q^{-4} in the high q region, which is consistent with the picture that a D_2O -rich core contributes to most of the signal. In contrast, Fig. 3 illustrates that the scattering from the H_2O -d-butanol aerosol is much weaker and, although quite noisy, the signal appears to fall off as q^{-2} in the high q region, which is consistent with the picture of shell-scattering.

In summary, aerosol SANS provides us with a powerful new way to study the properties of nanometer sized liquid droplets in the environment in which they form. Combined with pressure trace measurements and modeling, SANS provides additional information critical to our understanding of droplet formation and droplet growth in the nanometer size regime.

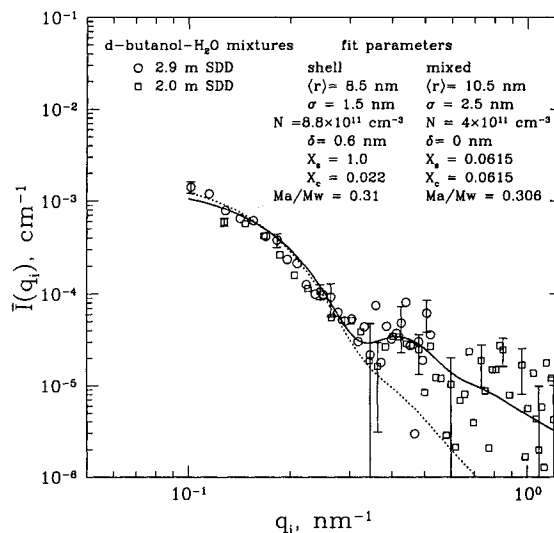


FIGURE 3. The observed SANS spectra is compared to a diffuse shell and a well mixed droplet model. The parameters of the fit are given in the legend. The data are more consistent with the shell model than with the well-mixed droplet model. For clarity only every 5th error bar is displayed.

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