Radius measurements of optically trapped aerosols through Brownian motion

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Abstract. Optical trapping of liquid aerosols from polydisperse samples provides unique problems for measuring their radii. Perhaps the most precise method, cavity-enhanced Raman spectroscopy (CERS), is limited to relatively large aerosols (\textgtrsim2 \mu m in radius). Determining particle perimeters in video microscopy lacks precision and, although simple, can be ambiguous. Here we demonstrate a simple and precise method based on studying the Brownian motion of droplets as they approach a nearby surface. We obtain results with greater precision and reliability than video microscopy, and with no size limitation conclude the technique could compete with CERS in terms of precision and accuracy.

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1. Introduction

Airborne optical manipulation provides precision tools for studying atmospheric chemistry with its ability to localize single [1] and multiple airborne particles [2] for indefinite periods of time [3]. Many fundamental properties of individual droplets are governed by their radius hence the great importance of measuring aerosol size [4]. Using cavity-enhanced Raman spectroscopy (CERS) and fitting to the excited whispering gallery modes is the most precise technique to size trapped aerosols to date and enables very detailed studies [3]. These have mostly concentrated on the coarse mode of atmospheric aerosols (>1 μm in radius) but have not extended into the accumulation or nucleation modes (<1 μm). For studies of these aerosols CERS fails in measuring their radii because the quality factor, Q, diminishes and the modes become too widely spaced to observe more than a single peak in measured spectra [5]. The study of accumulation mode aerosol is very important as it contributes the largest proportion of atmospheric aerosol by surface area to volume ratio and so dominates atmospheric chemistry [4]. As optical trapping moves into this region CERS will become redundant and must be replaced by a new method of radius measurement.

Optical tweezers have been coupled with advanced position detection systems providing incredibly precise measurements of force [6], displacement [7] and, in conjunction with complex numerical simulations, physical properties of microscopic systems [8] in the liquid phase. Position and force measurement relies on calibration of the detection system or measurement of trap stiffness, respectively. Usually the power spectrum method [9] of calibration is used, which is considered the most reliable [10].

Methods to obtain the properties of objects and their surroundings in conventional optical tweezers have relied on trap stiffness or position detector calibration and normally require more than one independent experiment. In the monodisperse colloid area of optical tweezers the particle size is usually known, through use of size-calibrated microspheres, and so techniques are aimed at obtaining those parameters that remain, for example viscosity, trap stiffness, displacement and forces. Recent methods have combined two calibration techniques so these properties can be measured from experimental measurements in a single experiment [11], enabling, for example, the determination of local viscosity [12]. This technique could equally work for determining the radius of spheres if the medium’s viscosity is known.

The size of optically trapped aerosols is not precisely known before the experiment because the nebulized sample is highly polydisperse. We propose to determine their radius by studying their confined Brownian motion and show that being airborne presents us with unique challenges and solutions, specifically the calibration techniques important in water need not be applied due to the significant contribution to the motion from inertia.

2. Theory

A short review of literature shows one could study the low frequency plateau in the power spectrum of force fluctuations, which is proportional to particle size, to give an indirect measure of radius [13, 14] but we would like an absolute measurement. It is possible to measure the absolute size of colloidal particles suspended in a water environment from their position fluctuations in free Brownian motion by using detection instruments with absolute position calibration. Einstein’s diffusion coefficient can be extracted from the position data and the particle radius determined assuming knowledge of viscosity. Through this method Viana et al
[15] determined the radius of spheres by measuring position in a ‘switched’ optical trap using a camera, however, this method of detection has limits on its precision [16]. Furthermore, the distance a given particle can diffuse in a set time is approximately an order of magnitude greater when suspended in air rather than water which means the droplet quickly disappears from the focal plane disabling the possibility of video tracking. Additionally, the laser modulation to take the object in and out of free Brownian motion could cause failure of the airborne optical trap [17]. So, for these reasons the particle must remain localized within the optical tweezers.

To ensure the position information of the trapped droplet is not undersampled and to obtain a representative set of position data, we image its scattered laser light, related to its position, onto a high-speed photodiode via a condenser lens [18]. The signal to position calibration here is a little more complex than for cameras, for example, a fixed sphere can be translated across the beam waist in known increments and the relation with the quadrant photodiode (QPD) signal found. This is not a good replica of experiments and is certainly not in an airborne system. The high-frequency tail in the power spectrum of position fluctuations of the particle can be used to calculate the detector calibration [19, 20] but for suspensions in both water and air media the particle radius is needed a priori.

As alluded to in the introduction Tolić-Nørrelykke et al [11] have shown that using the power spectrum coupled with analysing the response of a trapped particle to a given flow enables the viscous damping, trap stiffness and detector calibration to be determined from experimentally measured parameters alone. In the context of airborne tweezers, it is unknown what affect lateral trap oscillation will have on particle dynamics and also whether sample stage oscillation will indeed induce the required flow in the current chamber environment.

In air, it is possible to analyse the power spectrum of the particle’s position fluctuations to extract the radius without calibrating the detection system a priori or using the method of Tolić-Nørrelykke et al in situ, as we shall now discuss. We also note the same data and extracted parameters then allows detector system and trap stiffness calibration a posteriori [19, 20].

We treat the optically trapped aerosol as a damped harmonic oscillator, experiencing a Hookean restoring force when displaced from equilibrium. Due to air’s low dynamic viscosity and high experimental time resolution we cannot ignore inertial effects, therefore the Langevin equation describing the motion of an aerosol of radius $R$, mass $m$, trapped with stiffness $\kappa$, in a fluid of temperature $T$, and dynamic viscosity $\eta$ is [21]

$$ \ddot{x}(t) + \Gamma \dot{x}(t) + \Omega^2 x(t) = \Lambda \eta(t), $$

(1)

where $\Omega = \sqrt{(\kappa/m)}$, the droplet’s natural angular frequency, $\Gamma = (6\pi\eta R)/(mC_c)$ is the viscous damping of the medium, and $\Lambda = (2k_B T \Gamma/m)^{1/2}$ [22], the Brownian stochastic force where $k_B$ is the Boltzmann constant. We correct for the finite Knudsen number of the system by including the empirical slip correction factor, $C_c$, [23]. Fourier transforming (1) we obtain the power spectrum of position fluctuations, with angular frequency $\omega$, to be

$$ S^\text{inertia}_x(\omega) = \frac{2k_B T}{\kappa} \frac{\Omega^2 \Gamma}{(\omega^2 - \Omega^2)^2 + \omega^2 \Gamma^2} $$

(2)

and measured voltage power spectra

$$ S^\text{inertia}_v(\omega) = \frac{\Lambda^2}{(\omega^2 - \Omega^2)^2 + \omega^2 \Gamma^2} $$

(3)
Figure 1. A Gaussian beam is expanded with lenses L1 and L2 and steered by mirrors M and DM to slightly overfill the back aperture of a Nikon objective (TOBJ). The LWD objective collects the droplet’s scattered light and its back aperture is imaged onto the QPD via a 4f lens system. Power is controlled using a polarizing beam cube (PBC) and half wave plate (WP). The Nikon objective with appropriate tube lens (TL) images the sample through a dichroic mirror (DM) and filter (F) onto the firewire camera (CMOS). The QPD, COBJ and TOBJ are each mounted on three axis translation stages with the TOBJ axial axis controlled by a digital micrometer.

Fitting equation (3), for $\Omega$, $\Gamma$ and $\Lambda*$, to voltage power spectra of optically trapped aerosols gives the damping coefficient $\Gamma$, the full-width at half-maximum of the resonance peak in the power spectrum, hence giving $R$, with knowledge of the dynamic viscosity.

However, high NA optical tweezers trap objects close to coverslip surfaces and Faxén showed Stokes’ law is the ‘in bulk’ limiting case of a more complex viscous damping dependent on surface proximity. Here we only consider the correction in the lateral direction although both axial and rotational equivalents exist [24, 25]. Faxén’s law shows the lateral viscous drag on a sphere increases as it approaches a plane surface according to [26]

$$\Gamma_{Faxen} = \frac{\Gamma}{1 - \left( \frac{9R}{16L} \right) + \frac{1}{8} \left( \frac{R}{L} \right)^3 - \frac{45}{256} \left( \frac{R}{L} \right)^4 - \frac{1}{16} \left( \frac{R}{L} \right)^5}, \quad (4)$$

where $L$ is distance from the surface to the centre of the sphere. In this investigation, we demonstrate that fitting equation (4), with the free parameter $L$ and knowledge of $\eta$ ($= 1.84 \times 10^{-5} \text{ Pa s}$) and $C_c$, to a plot of viscous damping versus distance from the coverslip enables measurement of droplet radius.

So, measuring $\Gamma$, which has units of Hz, allows determination of the aerosol droplet radius with no precalibration or measure of trap stiffness necessary. However, these can be calculated from the data and fitting parameters as a result of the radius determination. Therefore, in air, the system for radius determination is fairly simple with cheap diodes, electronics and a method of altering the droplet to surface height being the only addition to normal optical tweezers.
3. Experimental

The custom built optical trapping system is illustrated in figure 1. A 532 nm Gaussian beam from a Laser Quantum Finesse 4W cw laser is expanded to slightly overfill the back aperture of a Nikon Plan 100× (NA = 1.25) oil immersion microscope objective lens. The beam is focused through and just above a type one coverslip. Having passed through the trapping region scattered light is collected by a long working distance (LWD) Mitutoyo 100× (NA = 0.55) microscope objective lens, whose back aperture is conjugate to a QPD (Hamamatsu S5980). The sample is illuminated with the Mitutoyo lens via Köhler illumination (not shown) from a halogen fibre illuminator (ThorLabs). The Nikon objective images the sample via an appropriate tube lens onto a Basler A602f CMOS firewire camera.

We nebulize a salt solution (20–80 g L$^{-1}$) with an Omron MicroAir NE-U22 nebulizer to produce polydisperse liquid droplets (MMAD = 4.9 µm). The trapped droplet size was imprecisely controlled in two ways. Firstly, varying the salt solution concentration changes the droplet’s vapour pressure, causing them to equilibrate with their surroundings at different sizes and, secondly, with, on average, a positive linear dependence of captured droplet size on laser power [2].

The sample chamber is a plastic enclosure ~9 mm high and ~35 mm in diameter with a type zero coverslip at the top to allow transmission of scattered light. This chamber is placed on top of the type one coverslip and both are held down with a heavy ring of metal, preventing flex in the coverslip with sample stage movement. At the top of the chamber we place tissue paper saturated in distilled water to assist in creating a humid environment. The lower coverslip was treated with ‘Decon 90’ to increase hydrophilicity so any settling aerosol produces a thin uniform water layer beneath the trapping region.

Currents produced by the QPD were amplified using a standard method [19] and acquired at a sampling frequency of 50 kHz for 4 s via a National Instruments PCI-6014E DAQ card. The voltage versus time data was Fourier transformed using LabVIEW and any remaining data analysis was performed offline at a later time to maximize experiment speed, hence minimize any parameter variation over the time span of the process. An image of the trapped droplet was also taken with each power spectrum.

To control the droplet to water surface height the sample is placed on a three axis translation stage that moves around the fixed Nikon objective. The axial axis is controlled by a digital micrometer (Newport NSA12). We first focus the beam ~15 µm above the coverslip for ease of trapping; once an aerosol is caught the sample stage is lowered, hence the droplet is moved away from the water surface. The micrometer has a large amount of hysteresis so the droplet is first moved to approximately twice the distance from where the first measurement is made. The sample stage is now raised in 1 µm increments until the position desired for the first measurement is reached, by which time any hysteresis has been removed and motion is as expected. The height was recorded and a power spectrum taken before moving the sample stage up, hence droplet down, by the desired increment where the next spectrum is taken. Here, we begin the increments at 1 µm and decrease this to 0.5 µm as the surface is approached due to the high gradient of Faxén’s correction in this region. Measurement stops when the droplet falls from the trap, probably due to coagulation with the underlying water layer.

The trapping beam is focused through two interfaces with mismatched refractive indices (glass:water and water:air), which shifts the focal position of the optical trap. A rigorous

4 Datasheet accompanying Omron MicroAir NE-U22 nebulizer.
Figure 2. Example of a power spectrum of position fluctuations for an aerosol droplet trapped 13 µm above a coverslip and water surface with a power of 70.8 ± 1.2 mW. The droplet has a radius of 4.8 ± 0.2 µm measured using video microscopy and 5.4 ± 0.3 µm determined using its Brownian motion. The errorbars are the standard error of the mean and arise due to the binning of the original power spectrum into blocks of 50 data points. The fit is found through a nonlinear least squares algorithm by minimizing $\chi^2$ weighted with the associated standard deviation. Inset is a linear–linear plot of the peak region.

description of this is complex [27] and not discussed, instead a simple paraxial approximation calculates the focus height, hence trapping position, inside the sample chamber from the objective displacement. Clearly the fit to Faxén’s correction is critical upon knowing the distance to the surface and as such we include an offset, $h$, so that $L \rightarrow L + h$, in equation (4) to compensate for any errors in the trap position-paraxial focus assumption or measurements on the relative positions of the interfaces [15, 28].

4. Results and discussion

To extract the damping coefficient, $\Gamma$, from the experimental data the following procedure was followed for each power spectrum taken at each height. The power spectrum of position fluctuations output from the LabVIEW software has one data point every 0.25 Hz due the measurement time of 4 s. The data are binned for each 50 data points resulting in a mean power and associated uncertainty for a mean frequency. The data analysis package OriginPro was used to fit equation (3) to the experimental data to obtain the best fitting parameters. The software was used to implement a nonlinear least squares fit using a Levenberg–Marquardt algorithm to minimize $\chi^2$ weighted with the uncertainty in each bin; their standard deviation. The fit was performed over the frequency range of 100 Hz–5 kHz.
Figure 3. Experimental data divided by the value from the theoretical fit for figure 2. The blue dashed lines indicate ±1 standard deviation expected theoretically from the data measured centred around a residual value of unity. These residuals support that our data are explained and fit well by the model with approximately 2/3 of the data within the blue dashed lines and 1/3 outside [29].

In figure 2, we plot the spectrum of the position fluctuations of a single optically trapped aerosol with under-damped motion as an example of the experimental data obtained. One can observe the characteristic $\omega^{-4}$ high-frequency tail and the appearance of a resonance peak because the system is underdamped. Also illustrated is the fit to the data using equation (3).

In figure 3, we show a ‘residual’ plot (as in figures 5 and 6 of [9]) to indicate how well our experimental data are fit by the theoretical power spectrum.

Repeating the procedure used to obtain figure 2 at many heights for a single droplet, we can extract the viscous damping the droplet experiences as a function of its distance from the water layer surface. An example is shown in figure 4.

Repeating the measurements made for figure 4 for different droplets, we obtain figure 5, a comparison between radii measurements through video microscopy and from viscous damping.

Figure 5 demonstrates droplets of varying radius, even those for which CERS is unsuitable ($< 2 \mu m$ radius), can be sized with high precision in comparison to video microscopy by studying the damping the droplet experiences only. There is a significant shift from the radius measured by microscopy which we believe highlights the ambiguity in sizing aerosols from microscope images. Figure 6 shows four images of the same droplet taken at various stages of a sizing experiment, exemplifying the difficulty in video imaging. We believe this difficulty is caused through several reasons; the trapping objective is not designed to image through air, the condenser lens is optimized for collection of scattered light not illumination, and there is a high-refractive index mismatch between the object and the medium. These contribute to increased diffraction and decreased resolution and so the ambiguity in determining the perimeter of the droplet images.

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Figure 4. Variation of viscous damping experienced by a droplet, trapped with 6.2 ± 0.1 mW, as a function of surface-droplet height. The droplet radius is measured from video microscopy to be 2.80 ± 0.16 and 3.17 ± 0.02 µm from the fit to experimental damping data. For this case $h = -2.88 ± 0.17$ µm.

Figure 5. Comparison of radius measurements made by video microscopy and fitting to variations in viscous damping. $x$ and $y$ errorbars are standard errors.
Figure 6. Images taken during the sizing process showing the variation in droplet appearance and indicating the ambiguous nature of determining the perimeter. By studying the damping experienced during Brownian motion this ambiguity is removed. This droplet is measured to be $4.77 \pm 0.21 \mu m$ from video microscopy and $5.25 \pm 0.07 \mu m$ from fitting to Faxén’s correction. Scale bar $= 5 \mu m$.

The method described here removes any subjectivity or ambiguity and as such these results are considered to be more accurate and reliable than those from video microscopy. Without the necessary equipment to obtain CERS measurements it is difficult to obtain or state an absolute accuracy for the experiment but this is an appealing experiment and will hopefully be performed in future.

5. Conclusions

The precision to which aerosols can be sized is currently limited by the apparatus iteration. With the outstanding precision possible in more refined experiments [24], it is believed this method can compete with CERS and will become important when studying aerosols $< 2 \mu m$ in radius where CERS does not work [5].

Several problems exist, firstly, the water layer on the surface of the cover slip creates a relative humidity gradient and as the droplet approaches this layer its size can increase [3]. Secondly, mathematical modelling (data not shown [30]) shows airborne droplets are trapped significantly, $\sim R$, below the paraxial focus of the beam and hence our simple paraxial approximation for the droplet position will be slightly offset. This potential error can be absorbed into the offset $h$, mentioned above, but with further work we believe much could be inferred about both the relative humidity gradient and the axial position offset while providing a more accurate technique. It is also proposed that through the incredible precision of optical tweezers and by using solid particles of known radius, a verification or perhaps improvement of the empirical slip correction factor, $C_c$, may be achieved.

Another problem is the axial stability of the droplets; low frequency axial oscillations can occur which in a misaligned system causes the droplet to, or appear to, displace laterally. Furthermore the oscillations mean the particle position is sampled at many heights rather than a single one. It is believed removing the central core of the trapping beam, by using Laguerre–Gaussian beams for example, would improve the stability and hence accuracy.

In this study, we have neglected the appearance of an effective mass due to entrained fluid [31] and the frequency dependent Stokes’ friction [32] but have taken into account the induction of flow within the fluid sphere [26]. These effects and subsequent corrections to the parameters describing droplet motion can be significant so to increase precision and accuracy must be considered in future.
In conclusion, we have proposed and confirmed the principle of sizing optically trapped liquid aerosols through studying their Brownian motion. The apparatus allows sizing to a greater precision than through video microscopy, works at smaller size regimes than CERS can, should work for arbitrarily small particles as long as they can be trapped, but it is difficult to quote an absolute accuracy. The low dynamic viscosity of air, the inclusion of inertial terms in the Langevin, and measuring the viscous damping in frequency space negate the need for a priori system calibration making the process simple. We have not perfected the technique so there is potential for incredible increases in precision from more advanced techniques and apparatus.

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