UC Riverside
UC Riverside Previously Published Works

Title
Mass, charge, and radius of droplets in a linear quadrupole electrodynamic balance

Permalink

Journal

ISSN

Author
Davies, James F

Publication Date
2019-03-04

DOI

Peer reviewed

1   **Mass, Charge and Radius of Droplets in a Linear Quadrupole Electrodynamic Balance**

2   James F. Davies

3   *Department of Chemistry, University of California Riverside, CA USA*

4   **Abstract**

5   Single particle levitation is a key tool in the analysis of the physicochemical properties of aerosol

6   particles. Central to these techniques is the ability to determine the size of the confined particle or

7   droplet, usually achieved via optical methods. While some of these methods are extremely

8   accurate, they are not suitable for all applications and sample types, such as solid or optically

9   absorbing particles. In this work, measurements of the radius, mass and charge of droplets in a

10   linear quadrupole electrodynamic balance (LQ-EDB) are reported. Using the elastic light

11   scattering pattern produced by laser illumination, a method to determine the radius is described,

12   with an accuracy of as good as ±60 nm and a sensitivity to changes on the order of 10 nm. The

13   effect of refractive index on these measurements is explored by application of the technique to

14   simulated data using Mie theory. In addition to radius, the relative and absolute mass and charge

15   of droplets in the trap is measured from the voltage required to stabilize their vertical position.

16   These measurements are facilitated by stacking multiple droplets in the LQ-EDB and solving the

17   force balance equations to yield both parameters. These approaches are demonstrated through

18   measurements of the evaporation of pure ethylene glycol and pure water droplets, the change in

19   density of an aqueous glycerol solution as water evaporates, and the mass and charge of pure

20   glycerol droplets.

21

1   Introduction

2   Understanding the physical and chemical characteristics of aerosol is important for a broad range
3   of applications, from particles and clouds in the atmosphere, haze and fog, pollution in urban
4   environments, industrial processes such as spray drying, and pharmaceuticals for the inhalation of
5   medicines (Bzdek and Reid, 2017; Pöschl and Shiraiwa, 2015). To facilitate research in these
6   areas, techniques have been developed over many years using focused laser beams, resonant
7   acoustic cavities and electric fields to confine and levitate single droplets in the absence of any
8   supporting surfaces (Davis, 1997; Krieger et al., 2012). These techniques have a wide application
9   in aerosol physics and chemistry and allow a broad scope of measurements. For example, surface
10   tension and viscosity may be measured by observing the resonant shape distortion frequency of
11   coalescing droplets (Bzdek et al., 2016; Power et al., 2013), diffusion coefficients may be
12   measured by observing the timescales for isotope exchange or evaporation (Bastelberger et al.,
13   2017; Davies and Wilson, 2016), activity coefficients in high ionic strength solutions may be
14   determined from evaporation rates or equilibrium size changes (Chan et al., 2005; Davies et al.,
15   2013; Lee et al., 2008; Rovelli et al., 2016; Yeung et al., 2010), and both heterogeneous and
16   homogeneous chemical reactions may be explored (Dennis-Smither et al., 2014; Gorkowski et al.,
17   2016; Jacobs et al., 2017; Pope et al., 2010; Steimer et al., 2014). Recently, measurements of pH
18   on the single droplet level have been reported (Craig et al., 2017; Wei et al., 2018) and the
19   formation of complex phase morphologies due to liquid-liquid phase separation or slow mass
20   transport have been explored (Gorkowski et al., 2017; Stewart et al., 2015). Electrodynamic
21   balance techniques have now also been coupled to mass spectrometry for chemical analysis
22   (Birdsall et al., 2018; Jacobs et al., 2017). While individual techniques have been developed to
23   independently measure specific properties, there remains no method that allows a complete
24   physical and chemical characterization of a sample, a key aim for developing our understanding
25   of the connection between physical properties and evolving composition.

26   A fundamental aspect of any particle levitation instrument is the ability to gauge the size of the
27   sample with sufficient accuracy and sensitivity. For spherical and non-absorbing particles, size is
28   typically determined using one of several optical techniques based on the elastic scattering of light
29   from a laser, a white light illumination source, or the inelastic light produced due to the absorption
30   and reemission of radiation (Raman scattering). These techniques vary significantly in their

accuracy, sensitivity and applicability, but common to each is the use of Mie theory, an exact solution to Maxwell's equations for the scattering of electromagnetic radiation in a sphere (Mie, 1908). In an optical tweezers, for example, a droplet is held at the tight focus of a laser passed through a microscope objective. This introduces a large amount of light into the droplet, producing spontaneous Raman emission due to inelastic light scatter and surpassing the intensity threshold to allow stimulated light scattering to occur at wavelength corresponding to the resonance of the optical cavity, producing so-called whispering gallery modes (WGMs). The microscope objective efficiently captures this light and the wavelength positions of the WGMs, as measured with a spectrometer, allows the radius and refractive index (RI) to be determined to very high accuracy, on the order of nanometers for the radius and <0.001 for RI (Preston and Reid, 2013). However, many droplet levitation methods are unable to take advantage of this technique as WGM production is a non-linear optical process, and requires the light intensity to reach above a certain threshold. Alternative spectroscopic methods have been applied to determine the size using elastic light scattering. When a droplet is illuminated by a broadband light source, the wavelength dependence of the RI of the droplet leads to a characteristic series of fringes at a fixed scattering angle when observed as a function of wavelength (Steimer et al., 2015; Zardini et al., 2006). Mie theory may also be applied here to measure the size and RI. In the absence of a spectrometer, angularly resolved elastic light scattering replaces the spectrometer with a CCD camera, recording the fringe pattern as a function of scattering angle with a light source of fixed wavelength (Mason et al., 2014; Taflin et al., 1988). These data may be interpreted in a similar way to the spectrally resolved patterns, providing the angular range is known.

While these methods provide accurate measurements of the size and, in some cases, RI, they are limited in their application due to the cost and complexity of their implementation, their ability to resolve rapid changes, and/or the time associated with analysis. For these reasons, simplified theories have been used to relate characteristics of the scattering pattern to the droplet size. Davis et al. simply used the number of fringes observed within a given range (Davis et al., 2015), and many groups use a geometrical optics approximation to Mie theory, providing a simple relationship between the angular spacing of fringes in the scattering pattern to the size of the droplet (Davies et al., 2012a; Glantschnig and Chen, 1981). These methods are faster and more economical, but do not yield highly accurate results and lack sensitivity to resolve small changes in size. In the geometrical optics framework, both accuracy and sensitivity are on the order of 250

nm when the RI is known and scattering is collected at $< 60°$ from the propagation direction of the laser. Fourier transform analysis of the scattering pattern has also been used (Min and Gomez, 1996; Steiner et al., 1999), resulting in a parameter akin to the number of fringes per degree of scattering, along with information on the position of fringes in the scattering pattern. This improves slightly on the results of geometrical optics, but still suffers from an uncertainty and sensitivity limit of around 1-2%.

Mass measurements of levitated droplets are less common and are specific to electrostatic methods, resolving either relative or absolute mass. They are not limited by the requirement that particles be spherical and non-absorbing, allowing the size of solid particles and absorbing species to be determined (Jakubczyk et al., 2013). The most common approach is the characterization of an electrostatic balancing force to counter the weight of a particle, allowing the relative mass of the sample to be deduced from the required voltage. The change in absolute mass can be established from the variation in voltage if the diameter and droplet density can be established at a fixed point from optical measurements, or if particle charge is known and the electric fields are well-characterized. For example, in measurements similar to Millikan's oil droplet experiments, the absolute charge on a droplet may be deduced from changes in charge brought about by UV illumination, thus allowing the mass to be determined (Philip et al., 1983). In the extensive work of E. J. Davis, the mass of a droplet was estimated from its oscillation in an electric field, allowing the balancing voltage to be directly related to the mass (Davis, 1980). The ability to measure both mass and volume in a single technique allows density to be determined, an important physical property, and one that may vary over the course of a measurement due to changes in composition (e.g. chemical processing, water uptake/loss). Establishing the absolute mass independently of other measurements is challenging, however, and there has been little development of such techniques, even as electrodynamic trapping methods have progressed.

In this work, the development of optical and electrostatic sizing methods in a linear quadrupole electrodynamic balance (LQ-EDB) are reported. The LQ-EDB is able to confine multiple particles of any shape in a linear array, increasing the scope of possible measurements far beyond a pure single droplet instrument. Single droplets or populations of droplets may be chemically sampled by mass spectrometry to determine composition, and droplets may be coalesced, potentially allowing access to rheological and surface properties (Jacobs et al., 2017). A simplification to

4

previously reported sizing methods is described here, using the angular position of the peaks in the scattering pattern rather than the scattering pattern in full. This decreases computation time relative to a full comparison to Mie theory, and significantly improves the sensitivity compared to the geometrical optics approach. The size may be determined in real-time (experiments reported here at 50 Hz) and applied to even rapidly evaporating water droplets. Alongside measurements of the optical size, the electrostatics required to maintain droplet position are used as a sensitive measure of the mass of both liquid and solid particles. The size evolution during the evaporation of pure water and pure ethylene glycol droplets will be reported, the evolving density of water-glycerol droplets will be measured, and the absolute mass of pure glycerol droplets will be determined and compared to the optically derived values. The LQ-EDB is a highly versatile instrument (Hart et al., 2015; Jacobs et al., 2017; Lane et al., 2018; Sivaprakasam et al., 2017; Woźniak et al., 2015), and these sizing techniques combine to effectively complement its capabilities across a broad spectrum of physical and chemical characterization.

Droplet Levitation and Confinement

A linear quadrupole electrodynamic balance (LQ-EDB), in a newly designed chamber constructed in-house, was used to levitate droplets of ethylene glycol, glycerol, and pure water. The principles of this technique have been reported elsewhere and the associated methodology will be presented only briefly here (Hart et al., 2015; Jacobs et al., 2017; Woźniak et al., 2015). The LQ-EDB consists of four stainless steel rods with a diameter of 6 mm and length of 15 cm, positioned with a diagonal separation of 12 mm. The rods are mounted on machined PEEK end caps and enclosed within an aluminum chamber with 1" windows through the walls to observe the droplet and an opening at the lowest point of the chamber to allow laser light in and gas flow to exit. A single droplet is introduced into the LQ-EDB using a piezoelectric microdroplet dispenser (Microfab MJ-ABP-01) mounted on the edge of the chamber and supplied with a voltage pulse from an in-house constructed pulse amplifier. For a given pulse shape (amplitude and width) the size reproducibility of the droplet is usually < 1% (Davies et al., 2012b). As the liquid jet forms at the tip of the dispenser, a voltage of between 150 and 500 V applied to an electrode placed ~1 mm from the tip induces charge separation, producing a net charge in the resulting droplet. The droplet travels horizontally over ~25 mm into the central axis of the linear quadrupole rods. The droplet falls under gravity along the axis of the rods, guided by the electric field established by the 600 – 1200

V / 400 – 800 Hz voltage applied to the rods in a quadrupole arrangement (Figure 1A), until its weight becomes balanced by the repulsive electrostatic force produce by a disc electrode with an applied DC voltage. The lowest droplet position is maintained by programmatically adjusting the DC voltage, as necessary, using an analog output signal produced by a DAQ card controlled by LabVIEW software. Assuming the droplet charge remains constant and the only force acting on the droplet is gravity, the balancing voltage is directly proportional to the mass of the droplet when a single droplet is present. Multiple droplets may be stacked along the axis of the quadrupole rods, held apart by electrostatic repulsion, and the voltage required becomes a function of mass and droplet separation. This observation is a key facet of the absolute mass and charge measurements discussed later, and the arrangement is summarized in Figure 1A. Confined droplets are illuminated by unfocussed collimated light from a 532nm Gem laser (Laser Quantum) with a beam width of ~1 mm and a power of ~150 mW, as shown in Figure 1B. The elastic light scattering pattern of the lowest droplet in the stack is recorded at 90˚ to the laser illumination, parallel to the polarization of the beam, over an angular range of up to 22˚. The light was collected using a 1" diameter 50 mm focal length plano-convex lens and reduced in size by a factor of 4× to be imaged on the CMOS sensor of a DCC1545 camera (Thorlabs), operated within LabVIEW software at a frame rate of 30 – 100 Hz. In the measurements reported here, the temperature was a constant ambient value of 18 ˚C and the relative humidity was controlled using either dry or humidified nitrogen, introduced from the top of the chamber at flow rates up to 50 sccm, low enough to ensure that the aerodynamic force on the droplet was minimal and did not affect droplet position.

Droplet Sizing Methods and Results

1. Light Scattering and Droplet Radius

The first step towards quantifying the mass of a droplet using electrostatic analysis is to measure its optical size from its elastic light scattering pattern, as shown in Figure 1B. The light and dark fringes that comprise the pattern are characteristic of the size and RI of the sample. There are two commonly used methods to derive size information from this pattern – the use of Mie theory to simulate scattering patterns to find the closest match to the experimental observation, and the use of geometrical optics to link the spacing of the fringes to the radius. The former is non-trivial, with many potential solutions, especially for larger droplets or when RI is not well known. The latter is limited to scattering angles of < 60˚ and does not have good sensitivity to changes in size as fringe

1 spacing only varies monotonously with size over a large size range. Thus, changes in size less than

2 250 nm are not reliably measured. However, the position of the peaks in the scattering pattern

3 varies monotonously with droplet radius over a much smaller size range, as shown in Figure 2.

4 The method described here compares the positions of each measured peak in an experimental

5 scattering pattern with those from Mie theory, allowing the size to be determined with a greater

6 accuracy than the geometrical optics approach and with very high sensitivity to small changes.

7 This method does not require as much computation time, as only a few points are compared to a

8 theoretical prediction rather than the full scattering pattern. Furthermore, it exhibits a decreased

9 sensitivity to uncertainty in the RI as the variation in the intensity of the scatter over the angular

10 range is omitted, thus providing an attractive alternative to established methods with only a

11 minimal cost to the accuracy.

12 The peak positions and intensities measured experimentally over an angular range of ~15° were

13 individually compared to a library of peak positions generated using Mie theory as a function of

14 size at a fixed RI. For each measured peak, the closest simulated peak was found in each simulated

15 pattern. The sum of the squared-difference of all the individual measured peaks from the closest

16 simulated peaks was found as a function of size, shown in Figure 3A. The lowest error size is

17 attributed to the best radius that describes the particular experimental frame. Using a peak library

18 with a range from 5 to 25 µm and a precision of 5 nm, this fitting process occurs in real time during

19 an experiment with a camera framerate of 50 Hz.

20 In a typical experiment with a droplet, small fluctuations in position and random noise on the CCD

21 lead to deformation of the peak shapes and can modify the angular position of the peak. This can

22 cause the lower error to jump between nearby values (black points in Figure 3B), and it is not

23 always clear which is the correct absolute size in a given single frame. When the RI is known and

24 the angular range is correct, a single track is usually clearly identified across a wide change in

25 radius (blue line in Figure 3B), allowing very precise measurements of how the radius evolves

26 over time, down to a precision of around 10-20 nm. In order to gauge a reliable value for the

27 absolute size in a single frame, given several low error solutions, an average of the low error sizes

28 is found. For the data presented here, 15 of the lowest error size points were averaged, resulting in

29 a value that broadly corresponds to the minimum of the envelope of low-error sizes shown in

30 Figure 3A (gray points in Figure 3B). For clarity throughout this manuscript, this will be referred

1 to as the averaged radius. It is shown later that even though the uncertainty in a single frame is still

2 rather large, when averaging over a small range of sizes or time, the result is much more

3 constrained (red circles in Figure 3B).

4 There are two main factors that limit the accuracy of this method – the angular range and the

5 refractive index. To a first approximation, the angular range may be determined geometrically by

6 comparing the width of the image to the collection angle defined by the optical path. To refine the

7 solution, the data from an evaporating pure component droplet (i.e. water) may be used, as this

8 spans a broad range of sizes with a known refractive index. Across the full dataset, the best angular

9 range is found by minimizing the fluctuations in the best fit size. This is shown in Figure 3C for

10 angular ranges of 19.5, 20 and 20.5°. This method allows the angular range to be determined to

11 within 0.5°, or 2.5%. Although this imprecision increases the absolute error corresponding to the

12 best fit solution, it does not compromise the absolute accuracy as the same size is still found to be

13 the best fit (Figure 3C). For larger errors in angular range, other sizes may be found to have the

14 lowest error, thus leading to a larger inaccuracy in size.

15 In order to determine how the accuracy and sensitivity of these sizing methods depend on

16 knowledge of refractive index, simulated data was produced using Mie theory with known size

17 and RI. The lowest error size (not shown) tracks the correct answer perfectly when using the

18 correct refractive index, as expected given the ideal data. The averaged size using the correct RI,

19 taken from the average of the low error sizes (gray points in Figure 4A), results in close agreement

20 to a one-to-one relationship. However, the result does oscillate over ±200 nm, with a 'period' of

21 oscillation of around 60 nm. For this reason, if the radius changes by 60 nm, the averaged radius

22 over this period can be determined to within a range of ±30 nm by further averaging the data over

23 this change (black crosses in Figure 4A). If the RI is known to within ±0.02, typically within the

24 error range of estimation methods (Cai et al., 2017), the averaged radius is determined with an

25 accuracy within 100 nm of the correct size (blue and red points in Figure 4A). While typically RI

26 changes are associated with changes in radius, it is important to note that a RI change alone can

27 look like a change in size when tracking a single low error size (black crosses in Figure 4B). The

28 averaged size, however, still reports a value that is within 3%, even when assuming a fixed RI that

29 differs by up to 0.07 from the actual value (red points in Figure 4B). This is similar to the

30 geometrical optics dependence on RI.

Overall, the accuracy reported here is as good, if not better, than the geometrical optics approach and absolute measurements of the radius depend only on the uncertainty in angular position of the peaks (Davies et al., 2012b). Where this method performs much better, however, is in its ability to detect small changes in size. Regardless of whether the absolute radius is known accurately, by tracking a single low error peak, small changes are resolved to a high degree of precision. Figure 5A and 6A show the evaporation of droplets of pure ethylene glycol and pure water, respectively, in the LQ-EDB. With known RI values corresponding to the pure components, the change in radius is resolved with a sensitivity of as low as 0.1%, or 10 nm. Based on estimates from applying the sizing method to simulated data, the absolute size is known to within around 60 nm. This demonstrates a significant improvement over geometrical optics, which is only capable of resolving changes as small as ~250 nm. A summary of the optimum accuracy and sensitivity of these methods is given in Table 1.

2. Relative Mass and Density

Having now established a method for measuring the optical size, these data can contribute to the development of a method to measure the mass and density. The full dataset showing the radius and balancing voltage evolution during the evaporation of an ethylene glycol droplet is shown in Figure 5. The voltage required to maintain a fixed vertical position decreases by a factor of around 100× over the measurement. At a given height in the chamber and in the absence of any external forces, the voltage (V_{DC1}) is proportional to the mass. For a single droplet, the force balance equation is:

$$mg = \frac{q_1 V_{DC1} C}{z} \qquad (1)$$

where m the mass of the droplet, g is the acceleration due to gravity, q_1 is the charge on the droplet, z is the distance from the droplet to the electrode and C is a geometrical constant to account for the deviation in the electric field from that of an infinite plate electrode. Typically, q_1 and C are unknown, but are assumed to be fixed for a given droplet at a specific height above the electrode, such that V_{DC1} will vary linearly with the mass of the droplet. Therefore, for a droplet with a fixed density, the DC voltage and radius-cubed should exhibit a linear relationship that tends through the origin. This is indeed the case, as can be seen in Figure 5B. This supports the implicit assumption that the charge does not vary in the droplet. Only when the charge density exceeds a certain threshold, termed the Rayleigh limit, will charge loss occur via droplet fission.(Duft et al.,

1   2002; Li et al., 2005) A similar set of data was collected for pure water droplets. These exhibit

2   more rapid evaporation due to the larger vapor pressure of water. These measurements were

3   performed in a humidified chamber (approximately 80% RH) in order to slow the evaporation

4   event down to ~10 s. Figure 6 shows the radius and voltage data for the evaporation of a water

5   droplet and the correlation between radius-cubed and voltage remains, with a linear relationship

6   passing through the origin shown in Figure 6B.

7   These measurements effectively demonstrate the capabilities of the combined optical and

8   electrostatic approach to droplet size measurements, with changes in radius on the order of 0.1%

9   and changes in relative mass on the order of 0.5% clearly detected. Given these sensitivities, it is

10   possible to estimate changes in density, shown in Figure 7 for an aqueous droplet of glycerol

11   evaporating into dry conditions. As the droplet loses water by evaporation, the density tends from

12   the initial value corresponding to the dilute solute, to its final value characterized by the density of

13   pure glycerol (1.26 g cm^{-3}). Using the averaged low-error radius to determine the volume and

14   binning the data in 500 nm intervals, the change in density is clearly observable with a sensitivity

15   of around $\pm 2\%$. Here, the dry size of the droplet was used to determine the mass fraction and

16   provide a known data point for which the relative change in mass could be converted to absolute

17   density.

18   *3. Absolute Mass and Charge*

19   As shown in the previous section, one advantage of using a linear quadrupole EDB is the ability

20   to use the electrostatic force induced by the DC voltage, V_{DC1}, as a precise indicator of the (relative)

21   mass, m, of the droplet. There are challenges with establishing an absolute mass using this

22   technique, however, as there are several unknowns in the governing equations. With only one

23   droplet, there are three unknowns, m, C and q_1. The following describes a calibration procedure to

24   determine the constant C for a particular geometry of electrodes and droplet position. A separate

25   calibration, following the same steps, is required should any facet of the design or layout change.

26   We start by introducing a second droplet into the trap with charge q_2, and we can compile a series

27   of equations that describe the force balance of the system. By considering the force balance of the

28   first droplet in the lower position (Figure 1A), we can write:

29   $$mg + \frac{k_e q_1 q_2}{r^2} = \frac{q_1 V_{DC2} C}{z} \qquad (2)$$

1   where V_{DC2} is the voltage to balance two droplets, r is the separation of the droplets, and k_e is the

2   Coulomb constant. The second term on the left hand side is the additional downward force due to

3   the repulsion from droplet 2. Thus, the balancing voltage required is increased by a small amount

4   ($V_{DC2} > V_{DC1}$). The upper droplet still experiences an electrostatic force from the electrode, but

5   reduced in magnitude due to the greater distance from the electrode. The second droplet is

6   supported by the repulsive force acting upwards from the lower droplet and the repulsive force

7   from the electrode itself.

8   We must then measure radius from the light scattering here to assign a value to one of our

9   unknowns – the mass. This is possible if the density is known, and for the purposes of calibrating

10   the system to find the geometrical constant, a well-characterized droplet can be used. We must

11   ensure that the charge is the same, such that $q_1 = q_2 = q$. This is done experimentally by ensuring

12   that the radius of the droplets are within 100 nm and the balancing voltages for each individual

13   droplet are within 1 % (the second droplet is measured after the first is ejected to ensure equality).

14   In the ideal case, two droplets with the same radius would be balanced individually by the same

15   voltage, indicating the mass and charge are identical. For the pairs of droplets analyzed here,

16   around 25% conformed to this requirement. Equation 1 can be rearranged to yield an expression

17   for q and substituted into Equation 2. Some further rearranging gives an expression for C:

18   $$C = \left[\frac{k_e mg}{V_{DC1}(r/z)^2(V_{DC2}-V_{DC1})}\right]^{1/2} \qquad (3)$$

19   Experimentally, the voltages and the ratio of the separation of two droplets to the height of the

20   lower droplet above the electrode are required. A camera image of the laser light scattering from

21   the plane of the droplets was used to find ratio of the separation (in pixels) to the height (in pixels)

22   of the droplet above the electrode that was positioned at the end of the image. It is more convenient

23   to find a ratio than measure absolute lengths as a well-defined scale bar is not required. For a

24   droplet of known radius and density, the mass may be easily determined. Table 1 shows the

25   measured data contributing to the calculation of the geometrical constant C, using droplets of

26   glycerol, with a density of 1.26 g cm^{-3}. The average value was 0.149±0.004, where the uncertainty

27   comes from the standard deviation of the measurements and the error in the radius. The geometrical

28   constant is specific to the geometry of the trap and the electrode configuration. Here, the electrode

1 is a flat copper disk with a 2.5 mm diameter hole punched through the center, and the droplet

2 balance point lies 5 mm above.

3 Using the geometrical constant and optical size, a charge may be assigned to each measurement,

4 also shown in Table 1. For a fixed configuration of the droplet dispenser, the charge varied in a

5 linear fashion with the induction electrode voltage (between 50 fC and 200 fC over the range 200

6 to 600 V). Previous work has measured the charge accumulation on a plate housed in a Faraday

7 cage, with droplets produced in the same manner as described in this work (Haddrell et al., 2012).

8 The magnitude of the charge on single droplets here agrees well with the estimated single droplet

9 charge reported by Haddrell et al.

10 Having established the value of C for this electrode configuration, we can formulate and apply

11 expressions to calculate m and q for any droplets:

12 $$q = \frac{Cr(r/z)}{k_e}[V_{DC1} - V_{DC2}] \qquad (4)$$

13 $$m = \frac{V_{DC1}C^2(r/z)^2}{k_e g}\left[\frac{V_{DC2}}{V_{DC1}} - 1\right] \qquad (5)$$

14 These expressions require voltage data when both one and two droplets of approximately equal

15 charge and mass are present in the trap and allow the absolute mass and charge of the sample

16 droplet to be determined. Again using glycerol, but over a broader range of droplet sizes, the

17 measured mass compared to the mass determined from the radius is shown in Figure 8.

18 Measurements of charge can also be performed, however the absolute separation (in m) of the

19 droplets is required (see Equation 4). This is established from the pixel separation of the droplets

20 and the measured distance between the electrode and the droplet, and has an estimated uncertainty

21 of approximately 5%. The mass measured here typically fell within 5% of the value derived from

22 the radius. Given that this is on the order of the uncertainty in the mass derived from the optical

23 size, measurements of mass may actually provide a more accurate indicator of the size, especially

24 as the size tends towards the micron level and there is insufficient light scattering to characterize

25 the radius from the fringes. For solid particles where the light scattering cannot be used to

26 determine size, the mass data is an effective alternative, allowing mass transfer kinetics in non-

27 spherical particles to be measured.

These measurements of mass and density have some limitations and they are not well suited to measuring changes in absolute density over the course of a chemical or physical change (such as oxidation or change in humidity). This is because the separation of two droplets and the balancing voltage of a single droplet are required, so multiple measurements on the same evolving droplet are not possible. However, under those conditions, the absolute density at the start of the measurement can be established using this procedure, allowing the change in V_{DC1} to indicate the change in mass, even when the density varies. This assumes, of course, that the charge remains constant. While true for physical changes such as evaporation, at least until such time as charge ejection occurs at the Rayleigh instability, the changes in charge during chemical transformations may be less well characterized (Thomson and Iribarne, 1978). Although the measurements described here were performed manually, the procedure could be fully automated, allowing the process to be completed in under a second. While still not appropriate for rapidly evaporating droplets that change significantly over this time, it would allow the mass of lower volatility droplets to be determined.

Summary and Conclusions

In this work, a linear quadrupole electrodynamic balance has been used to demonstrate a new approach to measurements of droplet size. The optical size is found by fitting the angular location of peaks in their elastic scattering pattern. This method is capable of running in real-time during a typical experiment, has an accuracy equal to or better than the geometrical optics approximation for radius, and can reveal changes in size as small as 10 nm, significantly improving on the sensitivity when compared to geometrical optics. It is shown that the accuracy has only a weak dependence on the RI, making this a robust tool for the analysis of samples of unknown composition in a wide range of single particle levitation devices. While this method cannot replace the more detailed spectroscopic approaches discussed in the introduction in terms of accuracy, it is much more economical and efficient, and produces data that rivals more sophisticated methods in terms of sensitivity. The mass is found using the voltage applied to a disc electrode in the LQ-EDB, which produces a balancing force against the droplet's gravity, as a precise indicator of the changing mass of the droplet. With a known reference point and optical measurements of the size, the mass and therefore density may be inferred, as exemplified by the change in density of an

13

evaporating glycerol/water solution. Absolute measurements of mass were facilitated by stacking an additional droplet on top of the confined sample. A calibration with droplets of known density and size established the geometrical constant of the trap, describing the deviation of the electric field from that of an infinite plate electrode. Assuming the charge is the same, the separation of these droplets is indicative of their charge and a force balance equation is solved to yield both the charge and the mass of the droplet.

Overall, these measurements provide accurate and highly useful data allowing changes in size, mass and density to be determined with minimal computation or analytical tools. Within the LQ-EDB, droplets may be exposed to a variety of conditions, and the methods discussed here will be applied to exploring the response of samples to changes in humidity and to reactive transformations. Further technique development, as mentioned in Jacobs et al. (Jacobs et al., 2017), who reported the coalescence of droplets, may yield measurements of viscosity and surface tension, as well as chemical reaction kinetics, uptake coefficients, vapor pressures and diffusion coefficients. These require knowledge of the size and/or mass and thus the methods described here will facilitate detailed explorations in future experiments. As alluded to in the introduction, the LQ-EDB has the potential to act as an all-in-one platform for a complete characterization of physical properties and their connection to chemical transformations and a robust sizing framework is critical to its success.

1 **References**

2 Bastelberger, S., Krieger, U. K., Luo, B. and Peter, T.: Diffusivity measurements of volatile

3 organics in levitated viscous aerosol particles, Atmos. Chem. Phys., 17(13), 8453–8471,

4 doi:10.5194/acp-17-8453-2017, 2017.

5 Birdsall, A. W., Krieger, U. K. and Keutsch, F. N.: Electrodynamic balance–mass spectrometry

6 of single particles as a new platform for atmospheric chemistry research, , 115194, 33–47,

7 doi:10.5194/amt-11-33-2018, 2018.

8 Bzdek, B. R. and Reid, J. P.: Perspective: Aerosol microphysics: From molecules to the chemical

9 physics of aerosols, J. Chem. Phys., 147(22), 220901, doi:10.1063/1.5002641, 2017.

10 Bzdek, B. R., Power, R. M., Simpson, S. H., Reid, J. P. and Royall, C. P.: Precise, contactless

11 measurements of the surface tension of picolitre aerosol droplets, Chem. Sci., 7, 274–285,

12 doi:10.1039/C5SC03184B, 2016.

13 Cai, C., Marsh, A., Zhang, Y. H. and Reid, J. P.: Group Contribution Approach to Predict the

14 Refractive Index of Pure Organic Components in Ambient Organic Aerosol, Environ. Sci.

15 Technol., 51(17), 9683–9690, doi:10.1021/acs.est.7b01756, 2017.

16 Chan, M. N., Choi, M. Y., Ng, N. L. and Chan, C. K.: Hygroscopicity of Water-Soluble Organic

17 Compounds in Atmospheric Aerosols: Amino Acids and Biomass Burning Derived Organic

18 Species, J. Env. Sci. Technol., 39(6), 1555–1562, 2005.

19 Craig, R. L., Nandy, L., Axson, J. L., Dutcher, C. S. and Ault, A. P.: Spectroscopic

20 Determination of Aerosol pH from Acid-Base Equilibria in Inorganic, Organic, and Mixed

21 Systems, J. Phys. Chem. A, 121, acs.jpca.7b05261, doi:10.1021/acs.jpca.7b05261, 2017.

22 Davies, J. F. and Wilson, K. R.: Raman Spectroscopy of Isotopic Water Diffusion in Ultra-

23 Viscous, Glassy and Gel States in Aerosol Using Optical Tweezers, Anal. Chem., 88, 2361–

24 2366, doi:10.1021/acs.analchem.5b04315, 2016.

25 Davies, J. F., Haddrell, A. E., Miles, R. E. H., Bull, C. R. and Reid, J. P.: Bulk, Surface and Gas-

26 Phase Limited Water Transport in Aerosol, J. Phys. Chem. A, 116(45), 10987–10998, 2012a.

27 Davies, J. F., Haddrell, A. E. and Reid, J. P.: Time-resolved measurements of the evaporation of

volatile components from single aerosol droplets, Aerosol Sci. Technol., 46(6), 666–677, 2012b.

Davies, J. F., Haddrell, A. E., Rickards, A. M. J. and Reid, J. P.: Simultaneous Analysis of the Equilibrium Hygroscopicity and Water Transport Kinetics of Liquid Aerosol, Anal. Chem., 85(12), 5819–5826, 2013.

Davis, E. J.: Single Aerosol Particle Size and Mass Measurements Using an Electrodynamic Balance, J. Colloid Interface Sci., 75(2), 566–576, 1980.

Davis, E. J.: A History of Single Aerosol Particle Levitation, Aerosol Sci. Technol., 26(3), 212–254, 1997.

Davis, R. D., Lance, S., Gordon, J. A. and Tolbert, M. A.: Long Working-Distance Optical Trap for in Situ Analysis of Contact-Induced Phase Transformations, Anal. Chem., 87(12), 6186–6194, doi:10.1021/acs.analchem.5b00809, 2015.

Dennis-Smither, B. J., Marshall, F. H., Miles, R. E. H., Preston, T. C. and Reid, J. P.: Volatility and oxidative aging of aqueous maleic acid aerosol droplets and the dependence on relative humidity, J. Phys. Chem. A, 118(30), 5680–5691, doi:10.1021/jp504823j, 2014.

Duft, D., Achtzehn, T., Müller, R., Huber, B. A. and Leisner, T.: Rayleigh jets from levitated microdroplets, Phys. Rev. Lett, 89(JANUARY), 0845031–0845034, 2002.

Glantschnig, W. J. and Chen, S.-H.: Light scattering from water droplets in the geometrical optics approximation, Appl. Opt., 20(14), 2499–2509, 1981.

Gorkowski, K., Beydoun, H., Aboff, M., Walker, J. S., Reid, J. P. and Sullivan, R. C.: Advanced aerosol optical tweezers chamber design to facilitate phase-separation and equilibration timescale experiments on complex droplets, Aerosol Sci. Technol., 50(12), 1327–1341, doi:10.1080/02786826.2016.1224317, 2016.

Gorkowski, K., Donahue, N. M. and Sullivan, R. C.: Emulsified and Liquid-Liquid Phase-Separated States of α-Pinene Secondary Organic Aerosol Determined Using Aerosol Optical Tweezers, Environ. Sci. Technol., 51(21), 12154–12163, doi:10.1021/acs.est.7b03250, 2017.

Haddrell, A. E., Davies, J. F., Yabushita, A. and Reid, J. P.: Accounting for changes in particle charge, dry mass and composition occurring during studies of single levitated particles, J. Phys.

Chem. A, 116(40), 9941–9953, 2012.

Hart, M. B., Sivaprakasam, V., Eversole, J. D., Johnson, L. J. and Czege, J.: Optical measurements from single levitated particles using a linear electrodynamic quadrupole trap, Appl. Opt., 54(31), 174–181, 2015.

Jacobs, M. I., Davies, J. F., Lee, L., Davis, R. D., Houle, F. and Wilson, K. R.: Exploring Chemistry in Microcompartments Using Guided Droplet Collisions in a Branched Quadrupole Trap Coupled to a Single Droplet, Paper Spray Mass Spectrometer, Anal. Chem., 89(22), 12511–12519, doi:10.1021/acs.analchem.7b03704, 2017.

Jakubczyk, D., Derkachov, G., Kolwas, M. and Kolwas, K.: Combining weighting and scatterometry: Application to a levitated droplet of suspension, J. Quant. Spectrosc. Radiat. Transf., 126, 99–104, doi:10.1016/j.jqsrt.2012.11.010, 2013.

Krieger, U. K., Marcolli, C. and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques., Chem. Soc. Rev., 41(19), 6631–6662, 2012.

Lane, P. A., Hart, M. B., Jain, V., Tucker, J. E. and Eversole, J. D.: Characterization of single particle aerosols by elastic light scattering at multiple wavelengths, J. Quant. Spectrosc. Radiat. Transf., 208, 188–195, doi:10.1016/j.jqsrt.2017.12.017, 2018.

Lee, A. K. Y., Ling, T. Y. and Chan, C. K.: Understanding hygroscopic growth and phase transformation of aerosols using single particle Raman spectroscopy in an electrodynamic balance, Faraday Discuss., 137(852), 245–263, doi:10.1039/B704580H, 2008.

Li, K.-Y., Tu, H. and Ray, A. K.: Charge limits on droplets during evaporation., Langmuir, 21(9), 3786–3794, doi:10.1021/la047973n, 2005.

Mason, B., Walker, J., Reid, J. P. and Orr-Ewing, A. J.: Deviations from Plane-Wave Mie Scattering and Precise Retrieval of Refractive Index for a Single Spherical Particle in an Optical Cavity, J. Phys. Chem. A, 118(11), 2083–2088 [online] Available from: http://pubs.acs.org/doi/pdf/10.1021/jp5014863 (Accessed 10 July 2014), 2014.

Mie, G.: Contributions to the Optics of Turbid Media, Especially Colloidal Metal Solutions, Ann. Phys., 25, 377–445, 1908.

17

1 Min, S. L. and Gomez, a: High-resolution size measurement of single spherical particles with a

2 fast Fourier transform of the angular scattering intensity., Appl. Opt., 35(24), 4919–26,

3 doi:10.1364/AO.35.004919, 1996.

4 Philip, M. A., Gelbard, F. and Arnold, S.: An absolute method for aerosol particle mass and

5 charge measurement, J. Colloid Interface Sci., 91(2), 507–515, doi:10.1016/0021-

6 9797(83)90365-X, 1983.

7 Pope, F. D., Gallimore, P. J., Fuller, S. J., Cox, R. A. and Kalberer, M.: Ozonolysis of Maleic

8 Acid Aerosols: Effect upon Aerosol Hygroscopicity, Phase and Mass, J. Env. Sci. Technol., 44,

9 6656–6660, 2010.

10 Pöschl, U. and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere-Biosphere Interface

11 Influencing Climate and Public Health in the Anthropocene, Chem. Rev., 115(10), 4440–4475,

12 doi:10.1021/cr500487s, 2015.

13 Power, R., Simpson, S., Reid, J. and Hudson, A.: The transition from liquid to solid-like

14 behaviour in ultrahigh viscosity aerosol particles, Chem. Sci., 4, 2597–2604,

15 doi:10.1039/c3sc50682g, 2013.

16 Preston, T. C. and Reid, J. P.: Accurate and efficient determination of the radius, refractive

17 index, and dispersion of weakly absorbing spherical particle using whispering gallery modes, J.

18 Opt. Soc. Am. A, 30(8), 2113–2122, doi:10.1364/JOSAB.30.002113, 2013.

19 Rovelli, G., Miles, R. E. H., Reid, J. P. and Clegg, S. L.: Accurate Measurements of Aerosol

20 Hygroscopic Growth over a Wide Range in Relative Humidity, J. Phys. Chem. A, 120(25),

21 4376–4388, doi:10.1021/acs.jpca.6b04194, 2016.

22 Sivaprakasam, V., Hart, M. B. and Eversole, J. D.: Surface Enhanced Raman Spectroscopy of

23 Individual Suspended Aerosol Particles, J. Phys. Chem. C, 121(40), 22326–22334,

24 doi:10.1021/acs.jpcc.7b05310, 2017.

25 Steimer, S. S., Lampimäki, M., Coz, E., Grzinic, G. and Ammann, M.: The influence of physical

26 state on shikimic acid ozonolysis: a case for in situ microspectroscopy, Atmos. Chem. Phys.,

27 14(19), 10761–10772, doi:10.5194/acp-14-10761-2014, 2014.

28 Steimer, S. S., Krieger, U. K., Te, Y.-F., Lienhard, D. M., Huisman, A. J., Luo, B. P., Ammann,

M. and Peter, T.: Electrodynamic balance measurements of thermodynamic, kinetic, and optical aerosol properties inaccessible to bulk methods, Atmos. Meas. Tech., 8(6), 2397–2408, doi:10.5194/amt-8-2397-2015, 2015.

Steiner, B., Berge, B., Gausmann, R., Rohmann, J. and Rühl, E.: Fast in situ sizing technique for single levitated liquid aerosols., Appl. Opt., 38(9), 1523–1529, doi:10.1364/AO.38.001523, 1999.

Stewart, D., Cai, C., Nayler, J., Preston, T. C., Reid, J. P., Krieger, U., Marcolli, C. and Zhang, Y.-H.: Liquid-Liquid Phase Separation in Mixed Organic/Inorganic Single Aqueous Aerosol Droplets, J. Phys. Chem. A, 119, 4177–4190, doi:10.1021/acs.jpca.5b01658, 2015.

Taflin, D. C., S. H. Zhang, T. Allen and Davis, E. J.: Measurement of Droplet Interfacial Phenomena by Light-Scattering Techniques, Am. Inst. Chem. Eng., 34(8), 1310–1320, 1988.

Thomson, B. A. and Iribarne, J. V: The fate of electrical charges in evaporating cloud droplets, Rev. Geophys., 16(3), 431–434, doi:10.1029/RG016i003p00431, 1978.

Wei, H., Vejerano, E. P., Leng, W., Huang, Q., Willner, M. R., Marr, L. C. and Vikesland, P. J.: Aerosol microdroplets exhibit a stable pH gradient, Proc. Natl. Acad. Sci., 201720488, doi:10.1073/pnas.1720488115, 2018.

Woźniak, M., Derkachov, G., Kolwas, K., Archer, J., Wojciechowski, T., Jakubczyk, D. and Kolwas, M.: Formation of Highly Ordered Spherical Aggregates from Drying Microdroplets of Colloidal Suspension, Langmuir, 31, 7860–7868, doi:10.1021/acs.langmuir.5b01621, 2015.

Yeung, M. C., Ling, T. Y. and Chan, C. K.: Effects of the polymorphic transformation of glutaric acid particles on their deliquescence and hygroscopic properties, J. Phys. Chem. A, 114(2), 898–903, doi:10.1021/jp908250v, 2010.

Zardini, A. A., Krieger, U. K. and Marcolli, C.: White light Mie resonance spectroscopy used to measure very low vapor pressures of substances in aqueous solution aerosol particles., Opt. Express, 14(15), 6951–6962, doi:10.1364/OE.14.006951, 2006.

Table 1: The sensitivity is determined by the deviation of the measured radius from a best fit line through the data, and is indicative of the minimum magnitude of change in radius that may be observed. The accuracy is established from applying the sizing method to simulated data and indicates a fundamental limitation of the method.

RI	Best accuracy / nm	Best sensitivity / nm
Known and fixed	±60	10
Unknown (within ±0.02) and fixed	±100	10
Unknown (within ±0.02) and varying	±100	50

1 **Table 2:** The radius of glycerol droplets as measured from the elastic light scattering and the
2 voltage required to balance that droplet (V_{DC1}). With a second droplet, the voltage required to
3 balance the stack (V_{DC2}) and the ratio of the separation of droplets in the stack to the height of the
4 lower droplet (r/z) were measured. The charge was calculated using Equation 4 and the geometrical
5 constant (C) was measured using Equation 3.

Radius / µm	V_{DC1}	V_{DC2}	r/z	q / fC	C
14.4	56.4	76.2	0.226	83	0.156
14.4	56.8	79.1	0.226	83	0.147
14.4	58.7	81.5	0.224	80	0.144
14.4	58.6	81.0	0.224	80	0.146
14.3	59.3	78.4	0.224	78	0.155
14.5	58.0	81.6	0.224	83	0.144
14.5	58.8	81.0	0.224	82	0.147
14.4	58.3	80.8	0.224	81	0.146
14.4	114.8	134.8	0.166	41	0.149
14.4	96.6	120.8	0.166	49	0.147
14.3	90.0	116.0	0.161	51	0.150
14.3	93.3	119.0	0.161	49	0.148
14.1	30.4	49.0	0.303	145	0.159
14.3	38.5	55.0	0.308	120	0.151
14.5	38.3	57.0	0.308	125	0.145
9.9	26.0	39.5	0.239	59	0.150
10.3	15.5	27.8	0.340	111	0.152
11.5	21.9	34.5	0.340	109	0.149
11.6	22.2	35.3	0.340	111	0.147
11.5	22.8	34.6	0.340	105	0.151
15.6	143.0	165.9	0.149	42	0.156
16.8	38.5	62.4	0.330	194	0.149
16.9	43.0	66.0	0.324	177	0.147
15.7	38.0	60.0	0.320	161	0.145
16.2	44.0	67.4	0.314	152	0.140
15.8	42.5	65.0	0.304	146	0.144
16.3	31.0	52.0	0.373	220	0.149
16.4	33.0	54.0	0.366	209	0.148
16.0	33.0	53.0	0.361	196	0.149
16.0	31.5	51.0	0.375	205	0.149
16.3	33.0	54.0	0.360	207	0.150
16.1	33.5	55.0	0.349	196	0.149
16.0	34.0	55.0	0.352	190	0.147
				mean =	0.149
				stdev =	0.004

6

1   **TOC Figure:** Schematic of the linear quadrupole with two droplets, showing the electrostatic

2   force balance and laser light scattering pattern.

3   **Figure 1:** (A) A section of the linear quadrupole EDB, showing the rods and the DC disc electrode.

4   The voltage arrangement applied to the rods is shown, and the force balance on a stack of two

5   droplets is indicated. (B) The droplets are illuminated by a 532 nm laser beam and the elastic

6   scattering pattern is recorded. Each droplet can be imaged individually by elevating or lowering

7   the stack to bring the droplets into focus onto the camera sensor.

8   **Figure 2:** An example of the measured peak positions (black) and the simulated positions (red)

9   obtained during the sizing procedure for an ethylene glycol droplet.

10   F**igure 3:** (A) Typical error plot for a scattering pattern compared to a library of peak positions

11   generated by Mie theory. The low error average is taken from the mean of the low error radii in

12   the plot. (B) The averaged low error size is shown with gray circles, and the average of this data

13   over 1 s (approximately 100 nm) is shown with red circles. The tracks corresponding to the lowest

14   error are shown with black points, and the single track that best captures the trend over the full

15   dataset is shown with a blue line. (C) Effect of angular range on size result for a water droplet

16   evaporating under humid conditions. Black points indicate best angular width (with 0.040 degrees

17   per pixel), while grey circles and points indicate 0.039 degrees per pixel and 0.041 degrees per

18   pixel, respectively.

19   **Figure 4:** (A) Assessing the effect of choice of RI on the size determined from the average of the

20   low errors sizes for simulated data (at $n = 1.44$) (gray circles), and the average across 100 nm bins.

21   When the RI to size the data matches the actual refractive, the uncertainty is around ~60 nm (black

22   crosses). Using a RI of $n = 1.42$ (blue) and 1.46 (red), the uncertainty is around 100 nm. (B) The

23   absolute size was estimated using a fixed RI of 1.42 from simulated data at a radius of 10 µm

24   across a range of RI.

25   **Figure 5:** (A) Evaporation of a droplet of ethylene glycol, sized using a fixed RI of $n = 1.42$. The

26   accuracy is estimated to be ± 0.06 µm with sensitivity to changes as small as 0.01 µm. The DC

27   voltage required to balance the droplet, indicative of mass, is shown in dark gray on second axis.

28   (B) Volume and relative mass exhibit a linear correlation through the origin.

1   **Figure 6:** The evaporation of a droplet of water in humid conditions. (A) The radius (black) and

2   DC voltage (gray) required to balance the droplet, indicative of mass. (B) Volume and relative

3   mass exhibit a linear correlation through the origin.

4   **Figure 7:** Change in density of a glycerol droplet as water evaporates into low humidity conditions

5   (<50%). Following initial evaporation, the dry droplet size was found by purging the chamber with

6   dry N_2, providing a size (13.0 µm) and known density (pure glycerol, $\rho = 1.26$ g cm^{-3}) to which

7   the other data were scaled. The points show the experimental data in 500 nm bins and the reported

8   density is the scaled average of the balancing voltage divided by droplet volume for each bin. The

9   y-error bars reflect the standard deviation of the size, while the x-error bars reflect the uncertainty

10   in the radius due to use of a fixed refractive index. The solid line is the expected trend in density

11   with a dry diameter of 13 µm and assuming volume additivity in the determination of the mixture

12   density.

13   **Figure 8:** The mass of glycerol droplets in low humidity conditions were measured from the DC

14   balancing voltage, as described in the text, and compared to the mass expected based on a density

15   of 1.26 g cm^{-3} using the radius measured from the elastic scattering pattern. The solid line shows

16   the relationship x = y.