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

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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-Smith 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

1 accuracy, sensitivity and applicability, but common to each is the use of Mie theory, an exact
2 solution to Maxwell's equations for the scattering of electromagnetic radiation in a sphere (Mie,
3 1908). In an optical tweezers, for example, a droplet is held at the tight focus of a laser passed
4 through a microscope objective. This introduces a large amount of light into the droplet, producing
5 spontaneous Raman emission due to inelastic light scatter and surpassing the intensity threshold
6 to allow stimulated light scattering to occur at wavelength corresponding to the resonance of the
7 optical cavity, producing so-called whispering gallery modes (WGMs). The microscope objective
8 efficiently captures this light and the wavelength positions of the WGMs, as measured with a
9 spectrometer, allows the radius and refractive index (RI) to be determined to very high accuracy,
10 on the order of nanometers for the radius and <0.001 for RI (Preston and Reid, 2013). However,
11 many droplet levitation methods are unable to take advantage of this technique as WGM
12 production is a non-linear optical process, and requires the light intensity to reach above a certain
13 threshold. Alternative spectroscopic methods have been applied to determine the size using elastic
14 light scattering. When a droplet is illuminated by a broadband light source, the wavelength
15 dependence of the RI of the droplet leads to a characteristic series of fringes at a fixed scattering
16 angle when observed as a function of wavelength (Steimer et al., 2015; Zardini et al., 2006). Mie
17 theory may also be applied here to measure the size and RI. In the absence of a spectrometer,
18 angularly resolved elastic light scattering replaces the spectrometer with a CCD camera, recording
19 the fringe pattern as a function of scattering angle with a light source of fixed wavelength (Mason
20 et al., 2014; Taflin et al., 1988). These data may be interpreted in a similar way to the spectrally
21 resolved patterns, providing the angular range is known.

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

1 nm when the RI is known and scattering is collected at $< 60^\circ$ from the propagation direction of the
2 laser. Fourier transform analysis of the scattering pattern has also been used (Min and Gomez,
3 1996; Steiner et al., 1999), resulting in a parameter akin to the number of fringes per degree of
4 scattering, along with information on the position of fringes in the scattering pattern. This improves
5 slightly on the results of geometrical optics, but still suffers from an uncertainty and sensitivity
6 limit of around 1-2%.

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

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

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

14 **Droplet Levitation and Confinement**

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

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

21 **Droplet Sizing Methods and Results**

22 *1. Light Scattering and Droplet Radius*

23 The first step towards quantifying the mass of a droplet using electrostatic analysis is to measure
24 its optical size from its elastic light scattering pattern, as shown in Figure 1B. The light and dark
25 fringes that comprise the pattern are characteristic of the size and RI of the sample. There are two
26 commonly used methods to derive size information from this pattern – the use of Mie theory to
27 simulate scattering patterns to find the closest match to the experimental observation, and the use
28 of geometrical optics to link the spacing of the fringes to the radius. The former is non-trivial, with
29 many potential solutions, especially for larger droplets or when RI is not well known. The latter is
30 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 $\sim 15^\circ$ 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.

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

13 2. *Relative Mass and Density*

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

$$20 \quad mg = \frac{q_1 V_{DC1} C}{z} \quad (1)$$

21 where m the mass of the droplet, g is the acceleration due to gravity, q_1 is the charge on the droplet,
22 z is the distance from the droplet to the electrode and C is a geometrical constant to account for
23 the deviation in the electric field from that of an infinite plate electrode. Typically, q_1 and C are
24 unknown, but are assumed to be fixed for a given droplet at a specific height above the electrode,
25 such that V_{DC1} will vary linearly with the mass of the droplet. Therefore, for a droplet with a fixed
26 density, the DC voltage and radius-cubed should exhibit a linear relationship that tends through
27 the origin. This is indeed the case, as can be seen in Figure 5B. This supports the implicit
28 assumption that the charge does not vary in the droplet. Only when the charge density exceeds a
29 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 ±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:

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

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 :

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

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:

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

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

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.

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

15

16 **Summary and Conclusions**

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

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

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

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

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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

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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

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 **Figure 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 $\pm 0.06 \mu\text{m}$ with sensitivity to changes as small as $0.01 \mu\text{m}$. 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 N₂, providing a size (13.0 μm) and known density (pure glycerol, $\rho = 1.26 \text{ g cm}^{-3}$) 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 $x = y$.