

DOCTORAL THESIS

Single particle investigations of aerosol using a dual-beam optical trap

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Statement of Objectives

This thesis aims to conduct single particle investigations of aerosol using a novel dual-beam optical trapping setup. Specifically, we shall investigate the optical properties of these particles by quantifying the complex refractive index, which determines how the particles scatter and absorb light. We also aim to demonstrate the use of the dual-beam optical trap to measure surface tension at the single particle level. Finally, we aim to investigate more closely how the optical trap itself works, by looking at the possible stable trapping positions a particle may occupy.

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Abstract

Faculty of Science Department of Chemistry

Doctor of Philosophy

Single particle investigations of aerosol using a dual-beam optical trap

by Aidan Rafferty

Aerosol particles are ubiquitous in the atmosphere, and currently contribute a large uncertainty to climate models. Part of the endeavour to reduce this uncertainty takes the form of improving our understanding of aerosol at the microphysical level, thus enabling chemical and physical processes to be more accurately represented in larger scale models. In addition to modeling efforts, we are required to develop new instruments and methodologies to interrogate the physicochemical properties of aerosol. This work presents the development and application of a powerful new tool for single particle investigations of aerosol: the dual-beam optical trap. As the name suggests, this utilises two laser beams as opposed to the more widespread single-beam implementation of optical tweezers. This thesis demonstrates several ways that this two-beam configuration can be applied to making measurements on single aerosol particles. We begin by demonstrating a methodology for the retrieval of the complex refractive of weakly absorbing aerosol. By increasing the amount of laser light incident on the particle, we change the amount of energy absorbed by the particle and thus its surface temperature. This in turn causes the particle to change size in order to re-establish equilibrium with the surrounding air. By measuring the size change associated with a given change in laser power, we are able to determine the complex refractive index. We then demonstrate the measurement of surface tension at the single particle level. The incident laser light creates an optical stress on the particle surface, which leads the particle to become deformed until the optical stress is balanced by the particle surface tension. This deformation causes the optical resonances observed in cavity-enhanced Raman spectra to split into a series of peaks. By measuring the splitting of the peaks, we are able to measure nanometre-scale deformations in the particle, and thereby infer the particle surface

tension. Finally, through a combination of modelling and experiments, we investigate the workings of the dual-beam optical trap more intimately. We discover that when the focal points of the two laser beams are displaced from one another, contrary to what is often assumed, the particle may become trapped away from the midpoint between the two focal points. Furthermore, when trapped away from the midpoint, the particle's trapping position may oscillate both parallel and perpendicular to the trapping-beam axis as it changes in size. We investigate how various factors affect these oscillations, and demonstrate that by monitoring the oscillations as the particle changes in size, we can determine the relative positions of the focal points and the particle. Taken together, these studies represent a useful addition to the arsenal of techniques at aerosol researchers' disposal for investigating aerosol at the single particle level.

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Doctorat

Single particle investigations of aerosol using a dual-beam optical trap

par Aidan Rafferty

Les particules d'aérosols sont omniprésentes dans l'atmosphère et contribuent actuellement à une grande incertitude dans les modèles climatiques. Une partie des efforts pour réduire cette incertitude consiste à améliorer notre compréhension des aérosols au niveau microphysique, ce qui permet ainsi aux processus chimiques et physiques d'être représentés plus précisément dans les modèles à plus grande échelle. En plus des efforts de modélisation, nous sommes amenés á développer de nouveaux instruments et méthodologies pour interroger les propriétés physicochimiques des aérosols. Ce travail présente le développement et l'application d'un nouvel outil puissant pour étudier les particules d'aérosols uniques: le piège optique à double faisceau. Comme son nom l'indique, le piège utilise deux faisceaux laser, contrairement à la mise en œuvre plus répandue d'un seul faisceau de pinces optiques. Cette thèse démontre plusieurs façons d'appliquer la configuration à deux faisceaux aux mesures de particules individuelles piégées. Nous commençons par démontrer une méthodologie pour mesurer l'indice de réfraction complexe d'aérosol faiblement absorbant. En augmentant l'intensité de la lumière incidente sur la particule, la particule absorbe plus d'énergie causant une augmentation de sa température de surface. Cela amène à son tour la particule à changer de taille afin de rétablir l'équilibre avec l'air ambiant. En mesurant le changement de taille associé à un changement de la puissance du laser, nous sommes en mesure de déterminer l'indice de réfraction complexe. Ensuite, nous effectuons des expériences de tensiométrie au niveau d'une seule particule. La lumière laser incidente crée une contrainte optique sur la surface de la particule, ce qui conduit la particule à se déformer jusqu'à ce que la contrainte optique soit équilibrée par la tension superficielle de la particule. Cette déformation provoque une scission dans les résonances optiques de la particule observée dans le spectre Raman. En mesurant la

différence des changements de fréquence, nous pouvons mesurer la déformation de la particule à l'échelle nanométrique, et ainsi déduire sa tension superficielle. Enfin, nous étudions plus en détail le fonctionnement du piège optique à double faisceau. Nous découvrons que lorsque les foyers des deux faisceaux laser s'éloignent l'un de l'autre, contrairement à ce qui est souvent supposé, la particule peut se retrouver piégée à l'écart du point médian entre les deux foyers. De plus, lorsqu'elle est piégée loin du point médian, la position de piégeage de la particule peut osciller à la fois parallèlement et perpendiculairement à l'axe du faisceau de piégeage et cela en fonction de sa taille. Nous étudions comment divers facteurs affectent ces oscillations et démontrons qu'en surveillant les oscillations dépendant de la taille, nous pouvons déterminer les positions relatives entre les points focaux et la particule. Prises ensemble, ces études représentent un ajout utile à l'arsenal de techniques disponibles aux chercheurs sur les aérosols au niveau de la particule unique.

Contribution to Original Knowledge

This thesis contains a number of original scholarly contributions. Chapters 2–4 are all published articles and as such are sufficiently original to be published.

Chapter 2 outlines a novel approach to measuring the complex refractive index of aerosol particles at the single particle level. Using a dual-beam optical trap, aerosol particles are heated and the corresponding size change measured in order to infer the imaginary part of the particle's refractive index. Whilst the principle of such measurements has been laid out previously, the approach demonstrated here greatly expands the range over which measurements can be made. Additionally, we present a framework for understanding and predicting the phenomenon of thermal locking.

Chapter 3 describes a unique approach to determining the surface tension of single aerosol particles. This technique uses the optical stress exerted on a trapped aerosol particle to deform it. The splitting of morphology-dependent resonances is then used to measure the deformation of the particle and determine its surface tension. The application of this technique to aerosol particles, the method of measuring the splitting, and the surface tension retrieval are all original work.

Chapter 4 looks at the stable trapping positions available to a particle in a dualbeam optical trap. It was previously discovered that, in defiance of simple intuition, the particle is not always trapped midway between the focal points. Our findings expand on this, demonstrating that the stable trapping position away from the midpoint between the focal points oscillates as a function of particle radius. The effects of several factors on these oscillations are investigated, constituting further original scholarship, and finally a method is outlined by which the relative positions of the focal points can be determined.

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List of Abbreviations

- **O:C O**xygen to Carbon Ratio
- SSA Single Scattering Albedo
- MAC Mass Absorption Coefficient
- CCN Cloud Condensation Nuclei
- IN Ice Nuclei
- **RH R**elative Humidity
- LLPS Liquid-Liquid Phase Separation
- EDB ElectroDynamic Balance
- TM Transverse Magnetic
- TE Transverse Electric
- MDR Morphology-Dependent Resonance
- WGM Whispering Gallery Mode
- CERS Cavity-Enhanced Raman Spectroscopy
- GLMT Generalized Lorenz-Mie Theory
- BSC Beam-Shape Coefficient
- IPCC Intergovernmental Panel on Climate Change
- D-BOT Dual-Beam Optical Trap
- **HWP** Half-Wave Plate
- GTP Glan-Taylor Polarizer
- PBS Polarizing Beam Splitter
- AOT Aerosol Optical Tweezers
- AFM Atomic Force Microscopy

1 Introduction

1.1 Atmospheric Aerosol

An aerosol is defined as a suspension of particles, either solid or liquid, in a gas.^{1,2} Thus, particulate matter suspended in the air constitutes an aerosol. Such particulate matter is ubiquitous throughout the atmosphere, with its concentration, size distribution and composition varying over space and time.^{1,3–5} Atmospheric aerosol has a number of effects on human health^{6–10} and climate,^{1,3,4} which depend on such properties. Exposure to certain aerosol is responsible for millions of deaths each year.^{10–12} With regards to climate, the largest uncertainties in current climate models arise from the direct and indirect effects of aerosol.¹³

Aerosol enters the atmosphere in a variety of ways and as such can have a diverse range of components.^{14–16} A collection of particles entering the atmosphere directly are called primary aerosol, whereas particles which form in the atmosphere are known as secondary aerosol.^{2,14,16,17} The major sources of primary aerosol emission are sea spray, biomass burning, industrial activity and suspension of mineral dust by wind.¹² Secondary aerosol forms through chemical transformation of gases from both anthropogenic and biogenic sources.^{2,12,14,15} This diversity of sources leads to a wide array of compositions.

1.1.1 Composition of Atmospheric Aerosol

It is common to distinguish between the organic and inorganic fractions of atmospheric aerosol, with each fraction then being further subdivided. In the case of the inorganic fraction, the dominant species are sulfates, nitrates, ammonium and ions from sea salt.⁴ Sea spray aerosol, also frequently called sea salt aerosol, is emitted in the form of primary particles from wind and wave action over the oceans.^{18–20} The primary component of sea spray aerosol is NaCl, but sea spray aerosol also contains sulfate, and along with particle emissions from volcanic activity provides a way for sulfate to enter the atmosphere *via* primary aerosol.¹³ Sulfate aerosol can also be produced by the oxidation of SO₂, producing secondary sulfate aerosol.^{2,12,21–24}

2

Similarly, nitrate- and ammonium-containing aerosol also forms from the chemistry and gas-particle partitioning of gases in the atmosphere, namely NO_x and NH_3 .^{2,21,22,24,25}

The organic fraction of aerosol is not so well understood as the inorganic fraction, and is currently the topic of much research. As with the inorganic fraction, organic aerosol enters the atmosphere as both primary and secondary particles. Primary organic aerosol consists largely of soot, produced through the burning of fossil fuels or biomass.^{12,16,26} So-called brown carbon (see Sec. 1.1.2 for an expanded discussion) can also be produced this way.^{27–29} There is also some organic matter which enters the atmosphere directly from sea spray aerosol.^{20,30,31} Secondary organic aerosol forms from a variety of sources. This produces a wide number of compounds which condense onto already-existing atmospheric particles.^{4,15} Indeed, it has been estimated that over 10,000 unique organic compounds may exist in the atmosphere.³² While the formation pathways for each are also unique, there are some commonalities amongst them. Generally, secondary organic aerosol formation begins with the emission of volatile organic compounds from either biogenic (e.g. plants and trees) or anthropogenic (e.g. fossil fuel) sources.^{4,12,15,33} These tend to have a low oxygen to carbon ratio (O:C) and high vapour pressures, leaving them reluctant to deposit onto aerosol particles in either the solid or liquid phase. However, gas-phase reactions with atmospheric oxidants (including O₃, NO_x, HO[•] and NH₃) or photochemical reactions can gradually increase the O:C ratio, yielding lower volatility products which more readily condense onto other particles and form secondary organic aerosol.^{4,14,15,32} The type of precursor and oxidant can have a profound effect on the properties of secondary organic aerosol, for example leading to the formation of light-absorbing compounds.^{27–29,34,35} Condensation of these lower volatility products into the aerosol phase can then facilitate further transformations.^{17,33,36,37}

1.1.2 Atmospheric Effects of Aerosol

The diverse array of aerosol compositions gives aerosol diversity in its properties. Indeed, according to Prather *et al.*, "Field measurements show that nearly every particle differs in size, physical properties and chemical characteristics".¹⁶ Aerosol affects the atmosphere in three main ways: by scattering and absorbing radiation, by altering cloud properties, and through participation in heterogeneous chemical processes.^{1,2,33} Scattering and absorption is referred to as the direct effect of aerosol on climate, whereas the modification of cloud properties is termed the indirect effect.^{3,11,29} Chemical processes alter the aerosol- and gas-phase compositions of the atmosphere, thereby changing both the aerosol direct and indirect effects. Currently,

aerosol is thought to contribute a net negative radiative forcing, meaning it acts to cool the planet.^{3,13} However, because our understanding of both the direct and indirect effects is limited, the error on the value of the radiative forcing attributed to aerosol is comparable to its magnitude.^{13,38,39} Here, we shall examine some of atmospheric aerosol's most important properties and how they contribute to its climatic effects.

Direct Effects

The optical properties of aerosol describe how an ensemble of particles interacts with radiation entering the atmosphere from the Sun. This is primarily controlled by two factors; the size distribution of the particles and their refractive index.^{3,4} Particle shape also plays a role,^{40,41} but to a lesser degree and is not considered in detail here. While the particulars of this interaction at the single particle level will be discussed in detail in Section 1.3, we will now examine the properties of the ensemble of particles in order to better understand the climatic effects of aerosol, or specifically the effect of aerosol on the Earth's energy balance.

Whilst there is no universally adopted definition of the size range for aerosol particles, it is generally considered to begin between 1–10 nm with an upper limit in the 10–100 μ m range.^{2,4,11,12,16,42} The aerosol size distribution is usually further decomposed into several subdivisions, or modes: the nucleation mode (diameter <20 nm), the Aitken mode (20–100 nm), the accumulation mode (0.1–2 μ m), and the coarse mode (2–50 μ m).⁴ The relative concentrations of each affect the scattering of light markedly, as they span a large range of sizes from the Rayleigh regime (particle size much smaller than the wavelength of the scattering light) to the Mie regime (particle size comparable to the wavelength of the scattering light).⁴³ This in turn affects two of the key parameters in determining the radiative forcing from a layer of aerosol. The first is the single scattering albedo (*SSA*):^{3,12,35}

$$SSA = \frac{C_{\rm sca}}{C_{\rm sca} + C_{\rm abs}},\tag{1.1}$$

where C_{sca} and C_{abs} are the scattering and absorption cross sections of a particle, respectively. The second is the upscatter fraction, which is the fraction of light which is scattered back into space away from the Earth.^{4,44,45} Generally, larger particles scatter more light; however, they also tend to scatter more in the forward direction, thus reducing the upscatter fraction.^{43,44} The sum of the scattering and absorption from all the particles then gives the optical depth of the aerosol.³

The key parameter that determines how condensed matter interacts with light is the refractive index.³ This can be written as a complex number, m = n + ik, where *n*

is the real part and *k* the imaginary part. These can loosely be thought of as the scattering part and the absorbing part of the refractive index, respectively. Both parts also vary as a function of the wavelength of light, and in order to fully characterise the interaction between aerosol and solar radiation one must consider scattering and absorption across the full solar spectrum. It is then clear why *m* plays such an important role in determining the optical properties of aerosol. The relative magnitudes of *n* and *k* influence the relative magnitudes of C_{sca} and C_{abs} , in turn determining the *SSA* (Eq. 1.1) across the solar spectrum. A method for the determination of the complex refractive index is demonstrated in Chapter 2.

From the point of view of optical properties, aerosol are commonly categorised as either absorbing or nonabsorbing.^{3,29} This classification implies a false dichotomy, where aerosol particles either do one or the other. In reality, the nonabsorbing fraction will absorb some small amount of light,^{3,46,47} and the absorbing fraction will also scatter light.^{29,45,48–50} It is the balance between the two which determines the climatic effects of aerosol. Aerosol which predominantly scatters leads to a cooling effect, whereas predominantly absorbing aerosol will lead to heating.^{3,22,26,29}

The optical properties of aerosol are closely linked to their composition.^{1,3,24,27,47} The inorganic fraction of aerosol can be approximated as nonabsorbing in the visible wavelength range, ^{46,51} with the exception of mineral dust, which is known to absorb in the visible range due to the presence of hematite.^{3,34,52} The absorbing properties of organic aerosol, on the other hand, can vary widely. While the majority of secondary organic aerosol is transparent, there is a significant fraction which does in fact absorb light in the visible wavelength range.^{29,35} This can be thought of as consists mostly of primary soot particles which absorb strongly and approximately uniformly across all visible wavelengths.^{29,35,52} Brown carbon, on the other hand, has a noticeable wavelength dependence, absorbing strongly in the near-ultraviolet range and less so at longer wavelengths, leading to the brown colour which is its namesake.^{28,29,35,52}

The wavelength dependence of the absorption is commonly characterised by the mass absorption coefficient (MAC):^{29,34,35}

$$MAC = \frac{A(\lambda)\ln(10)}{lc},$$
(1.2)

where $A(\lambda)$ is the absorbance at a given wavelength, λ , l is the path length through which light passes, and c is the mass concentration of the absorbing species. This is often recast into a power law of the form:^{27,29}

$$MAC = K\lambda^{-AAE},\tag{1.3}$$

where *K* is a constant and *AAE* is the absorption Ångström exponent. Whilst ideally *AAE* would be measured over a continuous wavelength range, experiments often only determine *MAC* at 2 to 4 discrete wavelengths and then use Equation 1.3 to interpolate.^{28,29,35,52,53} Larger values of *AAE* indicate a sharper wavelength dependence, and hence more brown carbon-like behaviour, whereas $AAE \approx 1$ indicates black carbon-like behaviour.^{27,29,35} The *MAC* can then be related to the imaginary part of the refractive index by:^{29,52}

$$k = \frac{MAC\rho\lambda}{4\pi},\tag{1.4}$$

where ρ is the density of the solution. This equation only holds for bulk solutions; however, a correction exists to convert *MAC* of a bulk solution to that of aerosol.^{53,54}

The ultimate goal of laboratory measurements and models of aerosol properties is to be able to predict the properties of an aerosol based on its measured composition.^{5,42,47} In the case of optical properties, this means predicting the extent of absorption and scattering across the visible and near-visible wavelength range based on the known constituents. From this perspective there is still much work to be done. For the inorganic fraction, some parameterizations have been constructed which can be used to achieve this goal.^{46,47,55} However, these do not include the absorbing mineral dust which also falls under the inorganic category. With regards to the organic fraction, even less progress has been made (excluding black carbon). For the weakly absorbing fraction, Bain & Preston have proposed the effective oscillator model, which uses three parameters to determine the real and imaginary parts of the refractive index across the visible wavelength range.⁴⁷ Their results suggest that the parameters for substances with similar functionalities, e.g. dicarboxylic acids, show very similar optical properties and thus could be treated with a single set of oscillator parameters. On the brown carbon front, work is not so advanced. While several broad categories of chemical constituents have been identified, links between these and the optical properties of brown carbon are not well resolved.^{27–29,53} However, work to this end has begun.^{50,56}

Indirect Effects

The two primary ways in which the indirect effects of aerosol manifest themselves is through particles acting as either cloud condensation nuclei (CCN) or ice nuclei (IN) in clouds.^{1–4,12,28,29,38,39,57} In the case of CCN, aerosol particles act to form liquid droplets, whereas in the case of IN the product is a solid. Both play important roles in several cloud processes, and act to modify the properties of the cloud as a whole.^{4,38,39,57} For a fixed water content, a cloud with a larger number of smaller

droplets will have a higher albedo, scattering more light back into space.⁵⁸ In certain environments where little aerosol is available, increasing aerosol concentration could lead to more or longer-lived clouds.⁵⁹ The height at which clouds form also impacts climate. The same number of ice nucleating particles are predicted to produce a cooling effect in lower lying clouds, whereas higher in the atmosphere these particles will contribute to a net heating from the cloud.^{38,57,60}

Aerosol particles as cloud condensation nuclei The ability of aerosol particles to act as CCN is well described by the Köhler equation, which describes the equilibrium relative humidity (RH) at the particle surface. In the context of Köhler theory, this is called the saturation ratio, S:^{4,61–64}

$$S = a_{\rm w} \exp\left(\frac{4\sigma M_{\rm w}}{RT\rho_{\rm w}D}\right),\tag{1.5}$$

where a_w is the water activity in the droplet, σ is the surface tension at the waterair interface, M_w is the molecular weight of water, R is the gas constant, T is the droplet surface temperature, ρ_w is the density of water, and D is the particle diameter. This equation captures two effects on S simultaneously: the Kelvin effect, which describes the elevation of the vapour pressure at a curved surface relative to a flat one; and the Raoult effect, which describes the lowering of the saturation vapour pressure at the surface due to the solute dissolved in the solution.^{4,12,61,64,65} This is seen more explicitly when the equation is written in the form:^{4,12,64,66}

$$\ln(S) = \frac{A}{D} - \frac{B}{D^3},\tag{1.6}$$

where:

$$A = \frac{4M_{\rm w}\sigma}{RT\rho_{\rm w}},\tag{1.7}$$

$$B = \frac{6n_{\rm s}M_{\rm w}}{\pi\rho_{\rm w}},\tag{1.8}$$

and n_s is the number of moles of solute in the droplet. It is common to refer to the first term in Equation 1.6 as the Kelvin term and the second as the Raoult term. This gives us some useful insight into the relative importance of each as the droplet size evolves. The Kelvin term depends only on D^{-1} , whereas the Raoult term depends on D^{-3} . Thus, assuming *A* and *B* remain constant — as is commonly done — we expect the Raoult term to dominate at low particle diameters, whereas the Kelvin effect will become the main factor at larger diameters. A useful modification to Köhler theory, known as κ -Köhler theory, was proposed by Petters and Kreidenweis:⁶³



FIGURE 1.1: Sample Köhler curve for a sodium chloride particle with a dry diameter of 50 nm (green), calculated using equation 1.5, with contributions from the Kelvin and Raoult effects shown in black dashed lines. The critical radius and supersaturation are indicated by the vertical and horizontal dotted grey lines, respectively.

$$S = \frac{D^3 - D_d^3}{D^3 - D_d^3 (1 - \kappa)} \exp\left(\frac{4\sigma M_w}{RT\rho_w D}\right),$$
 (1.9)

where D_d is the dry diameter of the particle, i.e. the diameter of a sphere consisting only of the solute, and κ is the hygroscopicity parameter, or simply the hygroscopicity. This can be interpreted as the amount of water taken up by a given amount of solute.^{63,67,68} The usefulness of this approach is twofold. Firstly, the growth of a particle in response to a change in RH can be determined using a single parameter, κ . Secondly, the κ value for a mixture of solutes can be calculated from a simple volume-fraction weighting.^{63,65,69} The latter potentially allows a simple way to predict the hygroscopic properties of complex, real aerosol systems from laboratory results on single solutes. However, there are suggestions that the framework needs to be modified somewhat in order to account for RH-dependent hygroscopicities.^{65,68,70}

The primary importance of Köhler theory is that it predicts the supersaturation threshold for cloud droplet activation to occur. In other words, it predicts the height

of the barrier over which an aerosol particle must pass in order to become a cloud droplet. As shown in Fig. 1.1, there is a peak in the equilibrium vapour pressure as the particle grows, known as the critical supersaturation. The radius at this critical supersaturation is called the critical radius. If this aerosol particle were to enter a cloud where the supersaturation were below this critical supersaturation, cloud droplet activation would not occur, and the particle size would remain below the critical radius. On the other hand, if the supersaturation in the cloud were to exceed this critical supersaturation, then the aerosol would undergo cloud droplet activation and continue to grow beyond the critical radius and — following further cloud processing — potentially even lead to the formation of precipitation. This demonstrates the importance of Köhler theory in predicting cloud properties (linked to the size distribution of particles within the cloud)⁷¹ and precipitation formation (linked to the number of CCN undergoing cloud droplet activation).⁷²

Aerosol particles as ice nuclei By comparison to cloud droplet formation, ice nucleation is more complex and uncertain. Ice formation in the atmosphere can proceed by either homogeneous or heterogeneous mechanisms.^{4,12,73–76} Homogeneous freezing occurs when a liquid droplet freezes, and occurs at or below the homogeneous freezing temperature of water (-38°C) .^{12,31,60,75–81} This mode of freezing is relatively well understood and parameterized.^{80,82,83} The heterogeneous freezing mechanisms allow the formation of ice at higher temperatures and are crucial to the formation of ice in mixed-phase clouds.^{31,60,73,78,84,85} However, a detailed microphysical understanding of these processes which allows representation in cloud and climate models remains elusive.^{1,60,76,86,87}

The two most important parameters for predicting ice nucleation are temperature and saturation ratio with respect to ice.^{74,76,84,86,88} The combination of these two determines which ice nucleation pathway is dominant. Above the homogeneous freezing temperature ice nucleation must proceed heterogeneously, with deposition nucleation (i.e. direct deposition of water vapour onto a nucleus) and immersion freezing (i.e. nucleation by solid inclusions with a droplet) being the most important pathways. Their relative importance depends on the system in question.^{18,74,76,89,90} Homogeneous freezing becomes the most important at high saturation ratios and temperatures at or below the homogeneous freezing temperature.^{60,76,89,91} Ice nucleation may also proceed by contact nucleation (i.e. freezing induced by an ice nucleating particle at the interface of a liquid particle) or condensation freezing (i.e. freezing happening concurrently with liquid water uptake).^{12,74,86,92,93}

Historically, effective IN were thought to share several core characteristics: insolubility, relatively large size, the ability to bind water in a similar arrangement to ice, and the presence of active sites.^{12,76,88,93} The most well-known sources of IN are mineral dust, biological particles and particles emitted by combustion.^{1,78,88,93,94} In particular, the dusts kaolinite, ^{93,95} montmorillonite, ⁹⁵ letovicite, ⁹¹ feldspars, ^{93,96} illite,⁸⁸ and Arizona test dust⁸⁸ have all been observed to be IN active. In terms of biological particles, the specific particles responsible are not always identifiable. However, IN activity has been identified for multiple fungi and bacteria,^{88,93} and marine diatoms.^{31,74} The IN properties of soot and ash emitted from fossil fuel combustion or biomass burning generally show little activity above the homogeneous freezing temperature, but this can vary widely depending on the source and temperature at which the particles were produced and chemical aging.^{76,88,93} Recent results also challenge some previous assumptions about the common characteristics of effective IN mentioned above. For example, common CCN materials such as (NH₄)₂SO₄^{83,88,93} and NaCl¹⁸ have also been shown to nucleate ice. Additionally, dissolved organic matter has also been shown to be able to nucleate ice,^{85,97} as well as nanoparticles.^{31,73}

Microphysical Properties 1.1.3

While the aerosol contribution to cloud and climate models relies on calculating the properties of the ensemble of particles which constitute the aerosol, it is becoming increasingly clear that we must better understand the properties of the individual particles making up the ensemble.^{1,5,11,16,42,98} As noted in Sec. 1.1.1, aerosol particles may contain a wide array of different components. The distribution of those components across the particle ensemble is also important. Individual particles within an aerosol may show considerable diversity in their composition, ^{1,16,99–102} giving each particle different properties, which in turn manifests itself as a different response between particles to the same conditions.^{1,11} This diversity in composition can be captured by the mixing state of the aerosol. For equal amounts of the same compounds distributed across a fixed number of particles, the mixing state may range from internally mixed (all particles contain the same proportions of the same compounds) to externally mixed (all particles contain a single compound, which may or may not be the same as any other particle).^{1,11,99} In the atmosphere, neither extreme occurs.^{100–102} Different distributions of the chemical components may lead to different physical properties, thus changing the behaviour of the particle ensemble.^{1,5,11,99,103,104}

Particle Phase

It is important to identify the phase state of a particle, in the context of aerosol meaning whether the particle is solid or liquid.^{4,10,17,99,103,105,106} There are two distinct phase behaviours which aerosol particles may display. The first is a hysteresis behaviour. Beginning with a completely dry crystal at 0% RH, upon increasing the RH the particle will remain dry until reaching the deliquescence RH (equal to the bulk solubility limit). At this point the particle will undergo a step change in size due to water uptake. Further increasing the RH leads to further growth of the particle. If one were then to decrease the RH back to the deliquescence RH, the particle would not crystallize. Instead, the particle remains in a metastable supersaturated state until reaching the efflorescence RH, at which point the particle will crystallize back to its original dry size. This size remains constant back down to 0% RH.^{4,103,106–109} This is the behaviour seen for almost all inorganic salts (with the exception of MgSO₄ which forms a gel)¹¹⁰ and some organic compounds.^{42,108} The supersaturated solution can be induced to crystallize upon contact with an appropriate seed.¹⁰⁷ Understanding this behaviour is important, as the size and phase of a particle will be controlled not only by the RH, but by the RH history of the particle. This will in turn affect the particle's optical properties, since solids and liquids scatter light differently.

The second phase behaviour which may be displayed by an aerosol particle is a continuous variation in size in response to RH.^{10,17,87,111–114} This size change brings with it a marked change in viscosity, meaning the phase state can be broken down into three regimes: liquid (viscosity $<10^2$ Pa·s), semisolid (10^2-10^{12} Pa·s) and glassy ($>10^{12}$ Pa·s).^{17,37,105,113,115} Such states are predicted to be widespread in the atmosphere.¹⁰ Many aerosol processes are assumed in models to occur instantaneously (or at least on a short timescale relative to others).^{105,113} This will only hold in many cases if mass transport within the aerosol particles is fast. While this is generally true for inorganics, the presence of organics which form a semisolid or glassy state will challenge that assumption.^{17,105,111,113,115} This challenge is supported by a number of studies. For example, water uptake and gas-particle partitioning and heterogeneous chemistry has been shown to be delayed by viscous organic materials.^{17,105,111,113} Viscous organics have also been shown to suppress the efflorescence of inorganic salts^{42,116} and play a role in determining ice nucleation pathways.^{87,89}

Particle Morphology

The morphology of aerosol particles, that is their shape and the distribution of components within the particle, is another key property of aerosol particles.^{42,117–119} In terms of shape, it is known that soot and mineral dust particles are both irregularly shaped and not well approximated by spheres.^{1,120} For liquid particles, the shape is always spherical and the particle may adopt one of three structures: homogeneous, core-shell or partially engulfed.^{42,50,109,121–125} When homogeneous, all constituents of the particle are distributed evenly throughout the particle. In the core-shell or partially engulfed morphologies, there is a separation between two or more phases within a single particle. As the name suggests, core-shell means that one phase forms a shell around the other, whereas in the partially engulfed case one phase covers only a part of the other's surface. It is common to assume for the purposes of cloud and climate models that particles are homogeneous. However, there is a growing body of evidence to suggest that phase separation, in particular linead linead another of the particles are homogeneous.

ticular liquid-liquid phase separation (LLPS), is somewhat common in the atmosphere.^{37,109} LLPS has been observed in particles containing both inorganic and organic material,^{42,117–119,121,124,126} solely organic material,^{65,127,128} and even three liquid phases have been observed in laboratory studies.¹²⁹ One may also observe solidliquid phase separation if the inorganic core undergoes efflorescence.^{42,105,117,125,129} Phase separation has also been found to depend on particle size, with smaller particles remaining homogeneous under conditions where larger particles phase separate.^{130,131}

The implications of phase-separated morphologies for aerosol particles are numerous. However, the aspect which has arguably inspired the most interest is the effect of phase separation on the CCN activity of aerosol particles. LLPS in atmospheric aerosol tends to lead to the formation of an organic-rich shell around a liquid core, accompanied by a reduction in particle surface tension.^{61,65,118,124,132,133} As seen in Eq. 1.5, the equilibrium supersaturation at the particle surface depends on the particle surface tension. Thus, alteration of the surface tension through LLPS will lead to changes in the growth of the particle as the RH evolves and, perhaps most importantly, modify the cloud droplet activation barrier. 61,65,119,128,132–135 Cloud models typically assume that the surface tension is equal to that of pure water (72 mN/m), but recent results suggest that discrepancies between observed and calculated CCN numbers could be resolved by accounting for surface tension depression.^{71,72,133} Thus, the modelling of LLPS and consequent surface tension reduction has seen both experimental and modeling interest. 61,65,71,119,132,134,136-139 Indeed, Chapter 3 of this thesis represents another experimental contribution to the investigation of surface tension in aerosol particles. Aside from surface tension depression, LLPS has also been investigated with regards to water uptake, 140,141 heterogeneous chemistry,¹²¹, gas-particle partitioning,^{37,105} optical properties,^{50,124} and ice nucleation.^{84,142}

With the complexity of the atmospheric aerosol problem established, we now turn to methods of addressing the gaps in our existing knowledge, with special attention paid to optical trapping, the method of choice for this thesis. As outlined by Marsh et al.,⁵ one may take one of two broad approaches to filling in the gaps in our current knowledge of aerosol and its climatic effects. The "top-down" approach involves making field measurements and comparing this data with predictions from large-scale models. This necessarily captures the full complexity of aerosol in the atmosphere, and provides a useful benchmark against which models can be tested and improved. However, this approach offers little in the way of fundamental insight into the processes affecting aerosol particles. This is where the "bottom-up" approach becomes important. Through consideration of simpler model systems, one may interrogate the microphysical processes affecting aerosol particles. Such studies in turn provide physical insight which may guide the development of more accurate models to bridge the gap between current models and field measurements. A more fundamental understanding of aerosol microphysics can also help evaluate the best way to approximate such processes for use in larger scale models, wherein a full treatment of all processes occurring for each particle within the ensemble is currently intractable. A particularly effective way of interrogating aerosol particles is through the use of single particle techniques.^{5,11,42} Single particle techniques overcome the effects of ensemble averaging to allow the determination of particle properties with a high degree of accuracy. This in turn allows the effects of different processes to be quantified accurately. Given the number of remaining mysteries surrounding aerosol and its properties, there is a need not only to make more single particle measurements, but also to develop new single particle techniques. As previously outlined, doing so using optical trapping is the primary focus of this thesis. With this in mind, we now examine the basic principles of optical trapping and its various advantages and disadvantages relative to other techniques.

1.2 Optical Trapping

Optical trapping involves the use of light to stably suspend a particle at a given location in space. While the idea of radiation pressure had been proposed and demonstrated in the 19th and 20th centuries, it was thought to have no potential applications as it was a very weak effect.^{143–146} However, with the invention of the laser giving rise to a much more intense source of light, it was realised that radiation pressure could be used to manipulate small objects.^{145,147–149} Optical trapping was first achieved by Arthur Ashkin, who demonstrated the acceleration of polymer spheres by a single laser beam and then the trapping of said spheres by

the addition of a second counterpropagating beam.¹⁴⁷ Ashkin was subsequently awarded the Nobel Prize in Physics in 2018 for later work which developed this idea. Since its initial demonstration, the applications of optical trapping have grown in number substantially. Optical trapping is now widely used in subfields of physics and biology, manipulating objects from single atoms and molecules to biological cells.^{143–145,148,150–152} With regards to aerosol, Ashkin & Dziedzic demonstrated the first optical levitation of a particle in air,¹⁵³ and some further studies of particles in air were performed in the 80s and 90s, although these remained primarily concerned with topics in physics (note references do not represent an exhaustive list, merely some examples).^{154–162}

The application of optical trapping to problems of atmospheric aerosol science really only began in the last two decades. This was aided greatly by Ashkin et al.'s development of the single-beam gradient force optical trap, which later came to be known as optical tweezers.¹⁶³ Whereas previous implementations of optical trapping had used a loosely focused laser beam and relied on the balance between gravity and the optical forces (often referred to as optical levitation), optical tweezers use a tightly focused beam which allows trapping of the particle with negligible influence from the gravitational force.¹⁴⁸ This affords more stable trapping than optical levitation. However, due to additional challenges inherent to trapping particles in air rather than a liquid medium,¹⁶⁴ the first demonstration of optical tweezers in air did not occur until just over a decade later, and even then for glass spheres rather than liquid aerosol particles.¹⁶⁵ Since then the use of optical trapping in aerosol science has expanded and been used to interrogate many of the properties mentioned in Section 1.1, including hygroscopicity,^{68,166} efflorescence/deliquescence,^{107,116,167,168} viscosity,^{110,114,169} phase separation, ^{118,123,124,170} surface tension, ^{137,138,171} and optical properties. ^{46,47,55,172–174} Recent years have also seen the development of additional trapping geometries aimed at specific applications within aerosol science. Examples include: hollow beam traps used to trap absorbing and irregularly shaped particles, ^{48,175,176} Bessel beam traps to extend the lower size limit on particles which can be characterised, 173,177-181 mixedbeam traps to study droplet collisions, ^{107,116,168} holographic traps to study multiple particles, 137, 138, 182, 183 and dual-beam traps (strictly speaking dual Gaussian beam traps, however, the Gaussian nature of the beams should be assumed herein unless otherwise stated).^{166,167,184–186}

Optical trapping is achieved by manipulating the optical forces on a particle in order to create a position in which the particle will remain stably. This can be understood fairly simply using ray optics. Optical forces arise from momentum transfer to the particle from incident photons, which carry momentum, *p*, according to the

de Broglie relation, $p = h/\lambda$, where *h* is Planck's constant and λ is the wavelength of light.^{145,149} For the purposes of the ray optics description, however, it is more convenient to consider the momentum carried by a ray, p = (nP)/c,^{143,187,188} where *n* is the real part of the refractive index of the medium in which the ray is propagating, *P* is the power of the ray, and *c* is the speed of light. When incident upon the boundary between a particle and the surrounding medium, some of the light will reflect from the surface and some will undergo refraction and enter the particle. Each process results in a force, *F*, on the particle, F = QnP/c, where *Q* is the efficiency with which momentum is transferred to the particle.^{144,149,188,189} If the incident light can be described by a collection of rays, then the total force on the particle is the sum of the forces from each individual ray.

In order to more intuitively understand the optical forces on a particle comparable to or larger than the wavelength of the trapping light (the Mie regime), it is useful to borrow some terminology from the forces on a particle much smaller than the wavelength of light (the Rayleigh regime). In the Rayleigh regime the force on a particle can be neatly decomposed into two components: the scattering force, which acts in the direction in which the beam is propagating and is proportional to the intensity of the light at a given point; and the gradient force, which acts in the direction of the highest field intensity and is proportional to the gradient of the electric field at that point.^{143,149,164} Thus, if a Rayleigh particle were placed in a Gaussian beam (the standard laser beam profile), the scattering force would push the particle in the direction the beam was propagating, and the gradient force acts to push the particle towards the centre of the beam (Fig. 1.2a).

When discussing larger particles outside of the Rayleigh regime this distinction no longer applies; however, to borrow the words of Čižmár *et al.*, "this terminology explains the problem more lucidly without severe incorrectness".¹⁹⁰ The analogy between Rayleigh and larger particles can be illustrated using two rays, as shown in Fig. 1.2b). Both rays are propagating parallel to one another and are incident on the particle equidistant from the axis through the particle centre. Both impart forces onto the particle parallel and perpendicular to this axis. However, as the right hand ray is more intense than the left, its contribution to both components is greater. While in the forward direction this only affects the magnitude, in the perpendicular direction this causes a net force on the particle towards the more intense ray. Thus, by analogy to the Rayleigh case, we call the force acting in the direction in which the rays are propagating force, and the force acting perpendicular to this the gradient force.

In the case of a tightly focused Gaussian beam, things become a little more complex. Now there is a gradient in intensity both parallel and perpendicular to the



FIGURE 1.2: a) Direction of forces acting on a Rayleigh particle. b) Forces acting on a large particle from two rays. c) Forces acting on a particle in optical tweezers. d) Forces acting on a particle in a dualbeam optical trap. F_s and F_g denote scattering and gradient forces, respectively. Black arrows show the direction of the corresponding force. Green arrows show the direction in which the beam or ray is propagating. The opacity of the rays indicates their intensity, with a more opaque line indicating greater intensity. B1 and B2 denote the rightward and leftward propagating beams in d), respectively.

beam propagation axis, since the intensity is maximal at the focal point of the beam. Thus, the gradient force acts both to pull the particle into the centre of the beam, and to negate the scattering force acting in the direction of beam propagation, as shown in Fig. 1.2c).

The basic workings of the dual-beam optical trap used in this thesis can also be explained using scattering and gradient forces. Both beams propagate parallel to the optical table and thus perpendicular to the direction in which gravity acts, and are sufficiently loosely focused that an individual beam does not form a gradient force optical trap. In this geometry, the scattering force from each beam acts to cancel the other, and the gradient forces from each draw the particle to the shared axis along which the beams propagate. This is shown schematically in Fig. 1.2d), where the components of the gradient force acting parallel to the beam axis are omitted for clarity. A more thorough investigation of the forces and trapping positions in dual-beam optical traps is given in Chapter 4.

Whilst useful for developing an intuition for optical forces, ray optics is an approximation to the full electromagnetic theory. The primary deficiency of ray optics is that it does not capture interference and resonance phenomena, such as the excitation of morphology-dependent resonances (discussed further in Sec. 1.3).^{187,191,192} Calculations of the optical forces on a particle require the full calculation of the electromagnetic fields due to both the incident light and the light scattered from the particle.^{187,192–197} The basics of this calculation are covered in more detail in Section 1.3. However, at the core of the full optical force calculation is the evaluation of the Maxwell stress tensor:^{192,193,198–200}

$$T = E \otimes D + B \otimes H - \frac{1}{2}I(E \cdot D + B \cdot H)$$
(1.10)

where, respectively, *E* and *H* are the electric and magnetic fields, *D* and *B* are the auxiliary fields, given by $D = \epsilon E$ and $B = \mu H$, and ϵ and μ denote the dielectric permittivity and magnetic permeability of the medium. *I* is the identity tensor. The time-average of the radial component of *T* gives the optical stress, also known as the radiation pressure or force density,^{187,192,200} and the integral of this over the surface of the particle gives the total force on the particle.^{193,198} Both the optical stress and the optical force are pertinent to this thesis. The optical stress leads particles to become deformed, best exemplified by the optical stretcher developed to measure the mechanical properties of biological cells.^{192,201–204} We utilise a conceptually similar approach in Chapter 3 to realise surface tension measurements on aerosol particles. The calculation of the net optical force is key to understanding where particles reach a stable equilibrium position, the primary concern of Chapter 4.
1.2.1 Comparison with other single particle techniques

Broadly speaking, one can distinguish two types of single particle experiment on aerosol: substrate-based experiments and particle levitation experiments. Substratebased experiments involve the deposition of particles onto a substrate of some kind, e.g. a microscope slide, before being interrogated experimentally. This allows particles to be investigated by a number of different microscopy methods, an exhaustive list of which is beyond the scope of this introduction and has been reviewed elsewhere.^{11,16,99} Common approaches include the use of optical microscopy, Raman microscopy, electron microscopy and X-ray microscopy. Arguably the primary advantage of these approaches is that they offer easy access to analysis of the spatial distribution of components in aerosol particles. It is easier to identify phase separation by optical microscopy than by spectroscopic methods, and when coupled with techniques allowing chemical characterisation, e.g. Raman^{205–207} or fluorescence, ^{129,208,209} the spatial distribution of the aerosol components can be determined.^{11,99} Electron microscopy and X-ray microscopy offer this same capability, with additional access to the most important size range for aerosol in the atmosphere (10–1000 nm). Furthermore, they offer higher resolution of chemical constituents across that size range (~ 1 nm for electron microscopy and 10s of nm for X-ray microscopy).⁹⁹ The main issue shared by all of these is that particles must be deposited on some kind of substrate, which may influence measurements of aerosol properties.⁴² In particular, it was shown that the substrate can influence the morphology of phase-separated particles.²⁰⁵ It has also been suggested that substrates may affect certain approaches to viscosity measurements.¹⁷ Additionally, electron microscopy requires experiments to be done under vacuum, removing its ability to simulate the response of aerosol to humidity changes.⁹⁹

Particle levitation removes the need for potentially problematic substrates. Particles are suspended in a contact-free environment and can be interrogated without contacting any surface. This better simulates the atmosphere, and thus could offer superior results to substrate-based methods. There are three established methods for achieving particle levitation: acoustic levitation, optical trapping and use of an electrodynamic balance (EDB). Acoustic levitation excites a standing wave in an acoustic cavity in order to levitate particles. This has seen some application to atmospheric aerosol problems.^{210,211} However, acoustic levitation is limited to large particles (in this context meaning > 100 μ m) than the other two techniques and is thus less suitable for atmospheric aerosol research.⁴²

The EDB imparts a charge onto the particle, then uses an electric field to exert a force on the particle in order to achieve trapping. As such, EDBs are suitable for trapping solid or liquid particles of any shape, and without limitations on the degree to which the particle absorbs light.⁴² In principle, the EDB can trap particles as small as several hundred nanometres in size, but in practice levitated particles are typically several microns in radius or larger,¹⁸¹ with an upper size limit of around 100 μ m.⁴² However, the need to charge the particle in order to suspend it can potentially affect experimental results, e.g. reaction rates.^{209,212} Additionally, in order to extract any information about the levitated particle, further instrumentation is required, e.g. a laser or light-emitting diode to monitor light scattering.

Optical trapping, at least in the standard optical tweezers implementation, offers only a modest reduction in the lower limit of particle size which can be trapped and observed to around 1 μ m in radius, giving it a slight advantage over the EDB in this regard. The upper limit on particle size is much lower than that of the EDB ($\sim 10 \ \mu$ m), but from the perspective of atmospheric aerosol research where we are primarily concerned with particles of $\leq 10 \ \mu$ m, this is of little consequence. Perhaps the main limitation of optical tweezers is in terms of the types of particle which it can interrogate. Optical tweezers require the particle to have a high degree of symmetry to achieve trapping, limiting it to liquid or highly symmetric solid particles. Additionally, particles must be weakly absorbing to ensure the scattering force does not overcome the gradient force. Neither of these limitations affects the other single particle methods discussed here. A practical advantage offered by optical tweezers is that it already involves illuminating the particle using light. This light can then be used to interrogate the particle properties *via* light scattering, e.g. cavity-enhanced Raman spectroscopy.^{213,214}

Since several different approaches to optical trapping can be taken, this makes the technique adaptable, giving researchers room to overcome the limitations inherent to the standard optical tweezers setup. In particular, the number or profile of the trapping beams may be changed in order to facilitate different experiments. Use of two laser beams rather than one is known to provide more stable trapping along the beam-propagation axis. This has been applied to attempts to trap ice crystals, with moderate success.¹⁸⁵ Dual-beam traps also provide the opportunity to manipulate the particle trapping position, which was applied in the development of the optical balance.¹⁸⁶ Chapters 2 and 3 demonstrate further uses of the dual-beam approach. Zero-order Bessel beams consist of a central maximum surrounded by a series of concentric rings. These are produced by the interference of light, and as such offer the capability to more tightly confine light around the central maximum, giving rise to stronger gradient forces. This can be applied to extend the lower limit on particle size which can be trapped into the submicron range.^{173,177–181} Hollow beams consist

of a central intensity void surrounded by an intensity maximum. This type of optical trap has been used to overcome two main limitations of optical tweezers. Traps using hollow beams are capable of trapping both irregularly shaped particles and particles which strongly absorb light.^{48,175,176}

Mass spectrometry has also proven to be a powerful technique for investigating aerosol at the single particle level, both in lab and field measurements.^{16,99,215,216} Mass spectrometry provides a high level of detail on the composition of aerosol particles of sizes as low as tens of nanometres.^{215,216} However, resolving the spatial distribution of those components is not possible.^{11,99} Mass spectrometry can also be used to monitor the progress of chemical reactions in aerosol particles.^{98,212,217} Recent work has sought to combine insights into aerosol physical properties available from particle levitation with chemical insights from mass spectrometry, leading to the development of EDB-mass spectrometry instruments.^{217–219}

With our chosen method for isolating single particles now described, we reach the final piece of the puzzle in terms of making single particle measurements. Once isolated, we require some method by which to measure the properties of our isolated aerosol particle. As alluded to above, a particularly good way to do this is to use the light scattered from the particle. Thus, we will now discuss some basic concepts to understand the interaction between particles of the size we typically trap in our experiments and the light we use to trap them.

1.3 Light Scattering

Light scattering is a topic which has been studied now for several centuries. At a fundamental level, scattering of light is caused by the interaction between electromagnetic waves and electric charges, such as electrons. When charges are placed in an electromagnetic field, they will oscillate, leading to the reradiation of further electromagnetic waves, not necessarily in the same direction as the initial wave.⁴³ This is the process of scattering. Optical trapping typically uses visible light to trap particles with several-micron radius, placing us in the Mie regime. Thus, the appropriate theory to use to analyse the light scattered from a particle is Mie theory, and variations thereof.

1.3.1 Mie Theory

Mie theory is the exact solution to Maxwell's equations for the interaction of a plane wave with a homogeneous spherical particle.^{43,194,220,221} A full and detailed derivation can be found in the textbook of Bohren and Huffman.⁴³ Here, we shall only provide an overview of the basic principles and important results for this thesis. In Mie theory, Maxwell's equations are solved in spherical polar coordinates by expanding the incident, internal and scattered electromagnetic fields as a series of vector spherical wave functions. These vector spherical wave functions can be denoted as being either transverse magnetic (TM, meaning no magnetic field component in the radial direction) or transverse electric (TE, meaning no electric field component in the radial direction).^{43,222–224} Each wave function is weighted by its corresponding expansion coefficient. For the purposes of this work, we are only concerned with the scattering coefficients for the external electric field. These are given by:⁴³

$$a_{n} = \frac{\mu_{m}m^{2}j_{n}(mx)[xj_{n}(x)]' - \mu_{p}j_{n}(x)[mxj_{n}(mx)]'}{\mu_{m}m^{2}j_{n}(mx)[xh_{n}^{(1)}(x)]' - \mu_{p}h_{n}^{(1)}(x)[mxj_{n}(mx)]'}$$
(1.11)

and:

$$b_{n} = \frac{\mu_{p} j_{n}(mx) [x j_{n}(x)]' - \mu_{m} j_{n}(x) [mx j_{n}(mx)]'}{\mu_{p} j_{n}(mx) [x h_{n}^{(1)}(x)]' - \mu_{m} h_{n}^{(1)}(x) [mx j_{n}(mx)]'}$$
(1.12)

for the nth TM and TE mode, respectively. Here, $\mu_{p/m}$ denotes the magnetic permeability of the particle/medium, *m* is the relative refractive index (i.e. the ratio of the refractive index of the particle to that of the medium) and *x* is the size parameter of the particle, given by $x = (2\pi n_m a)/\lambda$, where n_m is the refractive index of the medium, *a* is the particle radius and λ is the wavelength of the incident light. j_n and $h_n^{(1)}$ denote the spherical Bessel function and spherical Hankel function of the first kind, respectively, and a prime indicates differentiation with respect to the argument of the function inside the square brackets (i.e. *x* for the first term in the numerator of Eq. 1.11 and *mx* for the second).

At this point we know enough to understand the workings of one common method for extracting particle parameters from light scattering. This technique is known as angular light scattering and relies on the observation of the scattered light over some angular range. Each of the vector spherical wave functions has associated with it some angular distribution of scattered light, in addition to the amplitude as given by the scattering coefficients.⁴³ When imaged in the plane of the particle, this takes the form of two bright spots, whereas when observed in the far field, the scattering pattern takes the form of a series of bright and dark fringes.²²⁶ This fringe pattern is often called the phase function and an example is shown in Fig. 1.3. The



FIGURE 1.3: a) Raw angular scattering gathered in an experiment. b)
 Calculated phase function for particle parameters. c) Calculated Fresnel diffraction pattern for objective parameters. d) Measured diffraction pattern with Fresnel diffraction removed. Reproduced with permission from Elsevier.²²⁵

spacing and intensity of these fringes depends on both the particle size and its refractive index at the wavelength of the incident light, thus the observed phase function can be fit using a grid search to determine these two properties.²²⁵ The phase function is often observed through an objective lens, and the observed image (example shown in Fig. 1.3a) consists of two components: the angular scattering pattern and a series of concentric rings due to Fresnel diffraction from the back aperture of the objective lens (calculations shown in Figs. 1.3b) and c), respectively).²²⁵ The retrieved image an be smoothed or filtered to retrieve only the angular light scattering (Fig. 1.3d). While the whole 2D image may be used for analysis, it is more common to take a horizontal slice through the centre of the image, or average the intensity in each column, to reduce to a single dimension. It has been reported that analysis of the 2D image gives more accurate results, but comes at increased computational cost.²²⁵ Angular light scattering is frequently coupled with particle levitation and has allowed for a number of novel experiments, particularly those observing phase transitions and submicrometre particles.^{42,107,111,116,141,168,180,181,217,227,228}



FIGURE 1.4: Extinction efficiency as a function of size parameter for a fixed refractive index of 1.38.

The extinction efficiency (ratio of extinction cross section to geometric cross section) as a function of size parameter is shown in Fig. 1.4. This shows two main features: relatively broad, periodic oscillations, and the appearance of irregularly spaced, sharp peaks at certain size parameters. The periodic oscillations are known as the interference structure, so called because they arise from interference between the incident and scattered light.^{43,229} Whilst of some interest, the more useful feature of the scattering pattern is the sharp peaks appearing in the spectrum. These correspond to the excitation of morphology-dependent resonances (MDRs), also known as Mie resonances or whispering gallery modes (WGMs).^{222–225,230–233} While the phrases MDR and WGM are frequently used interchangeably, WGMs actually represent a subset of MDRs, with WGMs characterised by their particularly high quality factors and near-surface electric field distribution.²³¹

MDRs can be intuitively understood as follows. Consider light which enters a particle and then undergoes total internal reflection repeatedly around the circumference of the particle. If the optical path length that the light takes is commensurate with an integer number of wavelengths, the light will constructively interfere after one cycle.^{162,194,224,230,231,233,234} This leads to an increase in the electric field intensity close to the surface and thus an increase in both the scattering and absorption cross sections at specific wavelengths, producing the sharp peaks seen in

Fig. 1.4. 162,194,230,233

The resonance condition for excitation of a WGM can be obtained by setting the denominator of either Eq. 1.11 or Eq. 1.12 to zero and solving for the size parameter. The resonance condition can be compactly written (assuming $\mu_p = \mu_m$) as:^{235,236}

$$mp\frac{j'_{n}(mz)}{j_{n}(mz)} = \frac{h_{n}^{(1)'}(z)}{h_{n}^{(1)}(z)} + \frac{1-p}{z}$$
(1.13)

where p = 1 for TE modes and $p = 1/m^2$ for TM modes and z is the complex size parameter, z = x + iy, where x is the real size parameter in Eqs. 1.11 and 1.12. MDRs can be uniquely assigned using three indices, in the form P_n^l , where P indicates the polarization of the mode (either TE or TM), n is the mode number (i.e. number of wavelengths required to make a round trip of the particle circumference), and l is the mode order (specifying the number of radial nodes in the electric field distribution). The calculation of these resonance positions can be somewhat complex, as it is not a trivial task to determine which mode order corresponds to the resonance calculated by Eq. 1.13.^{235,236} Thus an approximate expression was developed by Lam *et al.* which explicitly calculates the resonance position for different mode orders.²³² These approximate resonance positions can then be used as initial guesses and refined by applying a root-finding algorithm to Eq. 1.13, for example the Newton-Raphson method.^{235,236}

1.3.2 Inelastic Light Scattering

In Sec. 1.3.1 we were assuming that light scattering was an elastic process, that is the energy of the incident and scattered light was the same. However, molecules in a particle may also undergo inelastic scattering processes, such as fluorescence or Raman scattering.^{156,160–162,234,237–240} We shall focus on the phenomenon of Raman scattering, as this is used in Chapters 2–4. Briefly, when light is incident on a molecule, the light may excite the molecule into a higher electronic state through absorption of a photon. In the case of scattering, the molecule is excited into a virtual state and decays through emission of a photon.^{237,241,242} Elastic scattering occurs when the decay returns the molecule to the same vibrational state as it was initially, giving the emitted photon the same energy as the incident photon. Inelastic scattering occurs when the molecule returns to a different vibrational state, thus the emitted photon differs in energy to the incident photon. If the emitted photon energy is less than that of the incident photon we observe Stokes Raman scattering, with the former being



FIGURE 1.5: Cavity-enhanced Raman spectrum with mode assignments for each mode. Reproduced with permission from Elsevier.²²⁵

the more prominent of the two effects at room temperature.²⁴¹ Both, however, are significantly weaker than the elastic scattering process.^{237,241}

In particles, Raman scattered light is capable of exciting MDRs, enabling the possibility of cavity-enhanced Raman spectroscopy (CERS).^{233,234} When molecules near the surface of a particle emit Raman scattered light, it will undergo total internal reflection at the particle surface and can achieve the same standing-wave behaviour as described above for the incident light.^{162,234} Thus, the incident light may excite multiple MDRs at multiple wavelengths through the process of Raman scattering. It is the excitation of multiple MDRs simultaneously which enables CERS.^{213,233–236} Fortunately for atmospheric scientists, the OH stretching Raman band of water is relatively broad, helping in the endeavour to excite multiple MDRs at the same time. An example CERS spectrum is shown in Fig. 1.5. There are two main features; a broad band due to the spontaneous Raman scattering from water, and five sharp peaks atop this corresponding to different MDRs. The positions of the MDRs are very sensitive to the size and refractive index of the particle, meaning the positions of the MDRs may be used to determine the radius and refractive index of a particle to accuracies of 1 nm and 10^{-4} , respectively.^{236,243} Such accuracy can only be achieved if the refractive index dispersion, i.e. its wavelength dependence, is taken into account.^{235,236,240} Thus, when fitting one must assume some functional form of the refractive index. The most common choices are either a linear form, $n = n_0 + n_1/\lambda$, or the Cauchy form, $n = n_0 + n_1/\lambda^2$. This means the fit of the MDRs requires three variables. Given the number of parameters and lack of an analytical solution linking the three to the collection of mode positions, the natural choice for solving the problem is a grid search, in which mode positions are calculated for each combination of variables and then the error between observed and calculated

mode positions is minimised.^{174,240} The primary disadvantage of this is the computational expense. It was later shown that this 3D grid search could be reduced to a quasi-2D grid search by excluding n_1 as a variable to get rough values for radius and n_0 , then subsequently including it over a reduced range.²³⁵ Preston & Reid then demonstrated that knowledge of the mode assignment of each MDR can be used to construct a matrix equation which can then be solved to obtain the best-fit particle parameters.²³⁶ This approach allows a particularly fast retrieval.

Since many processes lead to changes in the physical properties of a particle, CERS has been applied to a number of different problems. For example, droplet heating has been studied using CERS,^{243,244} as well as phase separation^{118,123,124} and mass transfer.^{110,112,214,245} Some studies also make use of the fact that CERS, in addition to allowing precise determination of the droplet's physical characteristics, also provides chemical information about the particle. This has allowed studies of particle composition,^{161,234,246,247} photochemistry,¹⁸⁴ and acidity.^{248,249} Chapters 2 and 3 will illustrate further uses of CERS.

As noted above, MDRs may also be excited by light external to the particle. While lasers have a very narrow bandwidth, and are generally only capable of exciting a single MDR, broadband sources such as light-emitting diodes may excite many simultaneously, thus providing an alternative method by which to measure particle properties. This method is also widely used in conjunction with optical trapping and EDBs.^{49,50,121,167,178,186,218} Since broadband scattering may excite MDRs over a broader wavelength range, a single broadband scattering spectrum will contain more MDRs than a typical CERS spectrum. This has the advantage of decreasing uncertainties in the retrieved parameters (up to a certain number of modes)²¹³ and allowing the characterisation of smaller particles than would be possible through CERS.¹⁷⁸ However, the broadband spectrum contains no chemical information about the particle, meaning other techniques must be used to infer things about the particle composition and changes thereof.

1.3.3 Generalized Lorenz-Mie Theory

As stated above, Mie theory is the solution to the interaction of a plane wave with a homogeneous sphere. In optical trapping experiments, however, we illuminate the particle with a laser beam, often focused to a comparable or even smaller size than the particle itself. The realisation that this may alter the light-particle interaction led to the development of generalized Lorenz-Mie theory (GLMT), so called because the framework may be applied to a beam of arbitrary shape.¹⁹⁴ Computationally, the calculation of the incident field is the most difficult task for any of the variants of

GLMT.²⁵⁰ This has led to the development of several approximations for describing the incident beam (which for the purposes of this section will be a Gaussian beam).

One of the earliest which is still widely used is the Davis-Barton approach.^{251,252} The incident field here is expanded as a Taylor series in terms of the beam confinement parameter, $s = 1/(kw_0)$, where k is the wavenumber of the incident light and w_0 is the beam waist of the Gaussian beam. The number of terms used in the expansion increases the accuracy of this representation, however, terms only up to the order of s^5 are known.²⁵³ Another approach uses the localized approximation to derive beam-shape coefficients (BSCs) for the incident beam.^{250,253–258} The localized approximation associates a given BSC with effects in a narrow region of space.²⁵⁰ The localized approximation allows for a particularly fast computation of the BSCs.^{250,258} Other approaches include an explicit description of the incident beam in terms of the vector spherical wavefunctions, ^{259–261} and expression as an angular spectrum of plane waves.^{258,262–264} Whilst efficient, the latter requires further calculations in order to be compatible with subsequent scattering or force calculations using vector spherical wavefunctions.^{258,262,263} We shall see a specific example in Chapter 2 of the importance of using GLMT as opposed to Mie theory, but it should be stressed that this is of vital importance throughout the thesis. All calculations relating to optical forces and particle optical properties require the use of GLMT in order to be accurate.

1.3.4 Spheroidal Particles

Another way in which we may deviate from Mie theory is to consider the interaction of light with nonspherical particles. It is instructive to return to our simple model of MDRs where we consider light undergoing constructive interference after repeated total internal reflections around the particle circumference. In a sphere, the circumference of any slice through the particle is the same, thus the wavelength of light which will excite an MDR is the same in all cases. If, however, the particle is deformed from this spherical shape into a spheroid, then the circumference of a slice depends now on its orientation. Some slices will have a larger circumference than the undeformed sphere, and some shorter. This leads an MDR to split into a series of peaks in a spheroid, compared to a single peak in the spectrum of a perfect sphere. Each of this series of peaks can be specified by considering a further MDR index, *m*, the azimuthal mode number, which specifies the orientation of the plane in which the MDR precesses according to $m = n \cos(\theta)$, where *n* is the MDR mode number and θ is the angle between the normal to the precession plane and the polar axis of the spheroid.^{160,265,266} A MDR of mode order *n* has an azimuthal degeneracy of 2n + 1, with *m* taking values m = -n, -n + 1, ..., 0, ..., n - 1, n. Expressions for the MDR positions as a function of azimuthal mode number were also developed assuming the particle adopts an ellipsoidal shape:^{266,267}

$$\frac{1}{\lambda_n^m} = \frac{1}{\lambda_n^{\text{Mie}}} \left[1 - \frac{e}{6} \left(1 - \frac{3m^2}{n(n+1)} \right) \right]$$
(1.14)

where λ_n^m is the resonant wavelength of the m^{th} azimuthal mode, λ_n^{Mie} is the MDR position in the undeformed sphere, and $e = (r_p - r_e)/r_s$ is the amplitude of deformation, with r_p , r_e and r_s being the polar, equatorial and spherical-equivalent radii, respectively. This shows that a single MDR will split into n + 1 peaks upon ellipsoidal deformation, since the shift is proportional to m^2 . This is because m values of the same magnitude represent precession in the same plane but in opposite directions. The full solution to the problem of light scattering by a nonspherical particle is given by the T-matrix method.²⁶⁸ Such calculations have produced interesting results, including the result that deformations from sphericity as small as 1% may be sufficient to suppress the scattering enhancement due to an MDR.⁴¹ More general expressions for the positions of MDRs in particles with arbitrary deformed shape have been developed, ^{238,267} and recent work has also combined both GLMT and T-matrix calculations.^{238,269–271}

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Chapter 2 Rationale

As discussed in section 1.1.2, determining the optical properties of aerosol is crucially important to understanding its impact on climate. We saw that a key property is the complex refractive index, consisting of a real part which determines the scattering properties of the aerosol and an imaginary part which quantifies its absorption. Both must be known in order to fully characterise the interaction between aerosol and solar radiation. Since most aerosol is only weakly absorbing, this task entails measuring very small absorbances. This is a challenge in itself, without even trying to do so on single aerosol particles. Normally, this would be overcome by utilising long path length devices so that the total absorbance could be amplified. With a particle only a few microns in radius, the path length cannot be changed much. Previous work had figured out how to measure the weak absorbance of single aerosol particles in principle. Use the trapping laser to heat the particle, and measure the associated size change in order to determine the imaginary part of the refractive index. However, the implementation of this technique was limited to a narrow range of relative humidity. Aerosol particles in the atmosphere experience a wide range of humidities, and thus their properties must be characterised across that full range. Since the balance of the optical forces in the dual-beam optical trap is different than for the optical tweezers used in the previous implementation, we reasoned this may be useful in extending that method across the entire range of relative humidity. This led to the work carried out in the following chapter.

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2 Measuring the size and complex refractive index of an aqueous aerosol particle using electromagnetic heating and cavity-enhanced Raman scattering

Abstract

A quantitative understanding of light scattering by small homogeneous particles requires accurate knowledge of the particle's geometry and complex refractive index, m = n + ik. In weakly absorbing particles, k can be on the order of 10⁻⁹, which is well below the detection limit of almost all light scattering based instruments. Here, we describe a dual-beam optical trap that can simultaneously determine n, k, and the radius, s, for weakly absorbing aerosol particles. We utilize cavity-enhanced Raman scattering to determine *n* and *s* and electromagnetic heating from the trapping laser itself to determine k. The relationship between particle size, the trapping cell conditions, the parameters of the trapping laser, and electromagnetic heating is thoroughly discussed and it is shown that the proper choice of a light scattering model is necessary to retrieve accurate values of k when fitting measurements. The phenomenon of optical multistability and its connection to thermal locking and thermal jumping is investigated through both modeling and measurements as understanding this behavior is essential when interpreting results from electromagnetic heating experiments. Measurements are made on three different atmospheric aerosol model systems and *k* as low as 5.91×10^{-9} are found.

2.1 Introduction

Modeling the scattering and absorption of light by atmospheric aerosol particles is a challenging task as many aspects of the interaction are poorly quantified. Indeed, the latest report from the Intergovernmental Panel on Climate Change (IPCC) contains the oft-quoted statement that "clouds and aerosols continue to contribute the largest uncertainty to estimates and interpretations of the Earth's changing energy budget."¹ In addition to the larger scale effects of aerosols, such as their interactions with clouds, it important to understand the microphysical behaviour of aerosols and characterise their properties. One such property of aerosols which has proven difficult to investigate is the complex refractive index, m = n + ik, consisting of the real part, n, and the imaginary part, k, both of which vary with wavelength (the phenomenon of dispersion).^{2,3} For aqueous particles, k can reach rather high values in the near-infrared region (e.g. $k = 2.57 \times 10^{-4}$ at 1500 nm)⁴ but will typically be much lower in the optical region (e.g. 6.2×10^{-9} at 532 nm).⁵ The weak absorption at optical wavelengths, combined with the small size of aerosol particles, means that any experiment aimed at determining k must be highly sensitive.⁶

A particularly accurate way of determining aerosol properties is through measurements on single particles. Single particle measurements isolate an individual particle from within an ensemble and allow measurements to be made in the absence of any averaging effects caused by distributions in particle shape, size, and composition that are present in the larger aerosol sample. One such method of acquiring single particle measurements is through the use of optical trapping.^{7,8} Aerosol particles with radii of a few micrometres can be isolated this way, and a number of single particle optical trapping techniques have been developed.^{7,9,10} A particularly sensitive way of monitoring the size and real part of the refractive index of an aerosol particle is through cavity-enhanced Raman scattering (CERS).^{5,11} This technique monitors the positions of whispering gallery mode (WGM) resonances in order to extract the size and real part of the refractive index of a particle with an accuracy of up to 1 nm and 10^{-4} , respectively.^{12,13} The absorption of light leads to particle heating and, for particles containing volatile species, this will be accompanied by a change in the evaporation rate that will affect the time-dependent particle size.^{14,15} By heating the particle using light, for example through laser irradiation, one can use the associated size change in order to infer *k* at the wavelength of light used.4,5

Early work on electromagnetic heating of aerosols was only able to access relatively high k; achieved either through the use of infrared light¹⁶ or through doping with small amounts of dye.¹⁷ When examining the interaction of atmospherically relevant aerosols with light, however, we are often concerned with interactions in the visible range in the absence of dyes. Aerosol particles with k around 10^{-7} were later measured by studying the evaporation of organic droplets in an electrodynamic balance.¹⁵ More recent work has led to more sensitive measurements in the visible range, with k as low as 6.2×10^{-9} at $\lambda = 532$ nm being measured by Miles *et al.*⁵ However, this approach was limited to conditions close to 100% relative humidity (RH) and cannot be used at lower RH.⁴ This limitation arises because the size changes which can be induced in trapped droplets are too small to be resolved, limited by the maximum laser power which can be used for trapping (below 100 mW). This is because the optical scattering force is proportional to the incident laser power, causing the trap to become unstable at higher laser powers. If, however, there were some other force to oppose this scattering force, trapping could be achieved at higher powers.

The dual-beam optical trap (D-BOT) uses two laser beams to trap a particle rather than the much more common single beam trap.⁷ As long as the two incident beams are of the same power, their scattering forces will cancel each other out. Despite being more challenging to construct,⁹ the D-BOT allows access to much higher laser powers than the single beam implementation and could potentially allow for the measurement of lower values of *k* in the visible region. The use of higher laser powers should lead to larger, and therefore resolvable, changes in the droplet radius upon heating. Additionally, the complexity of analyzing the results should also be reduced. Since changing the laser power causes the position of a particle in a single beam optical trap to change,⁷ this leads to a change in the beam radius at the particle's position which must be accounted for in calculations.^{5,14,16} In contrast, with the D-BOT, the position at which the particle is trapped should be independent of laser power, meaning such corrections for beam radius changes need not be carried out.

An important phenomenon for aerosol particles which can be monitored in this way is condensational growth and evaporation.^{5,6} The growth and evaporation of aerosol particles in the atmosphere is important for a number of reasons, as aerosol particle size alters the interaction of aerosols with light, changing their effect on the Earth's radiation budget both directly and indirectly.¹ The growth and evaporation of aerosols is commonly modeled using the steady-state equation.¹⁸ However, this equation is only applicable for single component droplets, i.e., droplets consisting of only one substance. In addition to this, more general models of droplet heating have been derived, which account for potential non-uniformities in the droplet temperature profile.¹⁵ However, the composition of atmospheric aerosol is known to vary widely,¹⁹ and Köhler theory tells us that the composition of aerosols has a strong effect on the equilibrium size of aerosols.^{18,20,21} Thus, use of the steady-state growth equation to describe anything other than single component droplets is incorrect. In spite of this, work on more realistic systems is sparse.^{18,22}

In this paper, we outline an experimental set-up which employs a D-BOT to trap an aerosol particle and collect CERS spectra at a series of laser powers. We



FIGURE 2.1: Schematic of the set-up used to perform experiments.

then derive an equation for the condensational growth and evaporation of a binary aerosol droplet, which coupled with equations for the heating of the droplet can be used to extract the imaginary refractive index of an aerosol droplet from a series of size measurements at different laser powers. Experimental measurements on three aqueous systems are presented and k of best-fit for each is found using the heated binary-droplet model developed here. We also investigate the phenomena of thermal jumping and locking using both experiments and theory. Results concerning these are compared to the theory. Finally, the potential limits of this new set-up are assessed.

2.2 Experimental

The experiments utilised a dual-beam optical trap (D-BOT) shown in Fig. 2.1. Our set-up uses light from the second harmonic of an Nd:YAG laser with $\lambda = 532$ nm (Ventus 532, Laser Quantum). The light is passed through a 1.2× beam expander so that the beam diameter is just smaller than the back aperture of the trapping objective lenses. The beam power has to be split evenly between the two arms leading to each objective lens. This is achieved using a half-wave plate (HWP) and a Glan-Taylor polarizer (GTP), where the former rotates and the latter remains fixed. The

GTP is fixed at an angle such that the light passing through it is polarized at 45° relative to the plane of incidence with the polarizing beam splitter (PBS), so that when it is incident on the PBS its intensity is split evenly, as required. The HWP is rotated using a stepper motor with Kinesis software (K10CR1, Thorlabs). The relative angle between the transmission axis of the GTP and the polarization of the incident light controls the proportion of light which is transmitted through the GTP, dictated by Malus' Law.²³ Thus, by rotating the HWP, the incident power on the trapped particle can be controlled and rapidly changed. Each arm is guided to a $50 \times$ objective lens (SLMPLN50X, Olympus). The two objective lenses are aligned so that their focal points overlap.

Aerosol created by a vibrating orifice nebuliser (Micro-Air, Omron) is drawn into the trapping cell, and a single particle may be trapped at the point where the focal points of the two objectives overlap. Here, the solutions nebulised were either aqueous sodium chloride (ACP Chemicals), lithium chloride (MP Biomedical) or citric acid (Fisher). Each solution was prepared to a concentration of 1 M by dissolving the appropriate solute in deionised water.

The trapping cell consists of four windows on each wall of a cuboidal block, with holes cut behind the windows. At the top and bottom of the cell are 'shower-head' type inlets, which ensure that turbulent flow into the cell is minimized. The top shower-head also has an extra inlet to allow aerosol to be drawn into the cell. The light from the two objectives passes through windows on opposite sides of the cell to achieve overlap of the focal points. A third, $20 \times$ objective lens (PSM-PLAPO20X, Motic) is placed at one of the windows perpendicular to the beam path in order to gather the elastically scattered light from the particle, also known as the phase function.² This light is imaged on a CMOS camera (DCC1545M, Thorlabs) and is used to ensure that a particle is trapped and stable. The forward- and back-scattered Raman light from the particle is gathered through one of the $50 \times$ trapping objectives and passed through a laser line mirror, and further to the CCD camera of a spectrograph (Isoplane SCT-320, Princeton Instruments).

A representative CERS spectrum for an optically trapped, aqueous LiCl particle is shown in Fig. 2.2. This spontaneous Raman spectrum shows the OH stretch band of water with sharp WGM resonances sitting on top of it. The WGM peak positions were extracted using MATLAB, and the radius, *s*, and the real part of the refractive index, *n*, were determined by fitting these peak positions using the MRFIT program.^{12,24} The methodology behind the fitting of WGM peaks for homogeneous spherical particles in order to retrieve *s* and *n* has been thoroughly discussed in Ref. 12. In all cases analyzed here, the model for the wavelength-dependent real part of the refractive index was $n(\lambda) = n_0 + n_1/\lambda^2$ (a two-term Cauchy equation). Along



FIGURE 2.2: Representative CERS spectrum for an aqueous droplet (in this example LiCl and water held in equilibrium at an RH of 78.5 \pm 1.8%). The peaks have been labeled with their WGM assignments, e.g. TE²₅₉ is a second order transverse electric (TE) wave with a mode number of 59. The other polarization label corresponds to transverse magnetic (TM) waves.

with *s*, both n_0 and n_1 can readily be found using MRFIT.

Once an aerosol particle has been trapped, the RH of the cell is controlled using two mass flow controllers (MF-1, MKS Instruments); one of which controls the flow of dry nitrogen and the other humidified nitrogen. Mixing of these produces 'air' of the desired RH, which is then flowed into the cell. The RH is monitored by two sensors (SHT75x, Sensirion); one placed before the cell and the other inserted through the fourth face of the cell, in place of the fourth window. Once the particle is observed to have reached equilibrium with its surroundings in the cell, the laser power was set to the desired output, with this output then adjusted to the incident power desired for experiments using the HWP/GTP system.

Two kinds of experiment were performed here. To demonstrate thermal locking and jumping, the power was ramped up from 100–300 mW and then back down to 100 mW. This was achieved by turning the rotating HWP at a constant rate until the final power was achieved, then turning in reverse to the original position at the same rate. This was done so that the rate of change of power was approximately 1 mW/s. For experiments measuring *k*, particles were held at 100 mW for 100 s, and then the incident power was changed at this point to the desired final incident power, where it was then held for 200 s. Final powers used here ranged from 150–500 mW. The beam waist, w_0 , was measured to be 4.3 μ m using the knife edge method.²⁵ CERS spectra were taken at a rate of 1 fps. According to Fig. 2.3, we then expect changes in radius to appear instantaneous. This means that frames taken during the

period in which the HWP rotates to its final position (approximately 1–3 s) cannot be reliably fitted, since the peaks are broadened significantly by the changing size of the particle. These frames are omitted from data analysis.

2.3 Theory

2.3.1 Growth or evaporation of a binary droplet

Here we examine the growth or evaporation of a binary droplet within the continuum regime. We consider a spherical droplet with a radius s(t) composed of two species A and B, where A is volatile and B is non-volatile. The droplet is surrounded by a medium consisting of vapour of the volatile species A and a gas. In this gaseous medium, the convection-diffusion equation for species A will be

$$\frac{\partial \rho_{\rm A}^{\rm v}}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_{\rm A}^{\rm v} v_r^{\rm v}) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho D \frac{\partial w_{\rm A}^{\rm v}}{\partial r} \right), \qquad (2.1)$$

where *D* is the binary mutual diffusion coefficient, w_A^v is the mass fraction of A in the gas phase, ρ_A^v is the mass concentration of the volatile species in the gas phase, $\rho = \rho_A^v + \rho_g$ is the total density of the gas phase (where ρ_g is the mass concentration of the surrounding gas without any of the volatile species), and v_r^v is the radial component of the mass average velocity in the gas phase.

When the system reaches a steady state, $\partial \rho_A^v / \partial t = 0$ and the mass flux of air will be zero yielding

$$v_r^{\rm v} = \frac{D}{w_{\rm A}^{\rm v} - 1} \frac{\partial w_{\rm A}^{\rm v}}{\partial r}.$$
(2.2)

Applying these results to Eq. 2.1 gives

$$\frac{\partial}{\partial r} \left(\frac{r^2 \rho D}{w_{\rm A}^{\rm v} - 1} \frac{\partial w_{\rm A}^{\rm v}}{\partial r} \right) = 0, \qquad (2.3)$$

which is the steady-state equation for mass transport in the gas phase. If ρ and D are treated as constants and the time-dependent gas-phase weight fraction of A at r = s(t) is $w_{A,s}^{v}(t)$ and the weight fraction of A at $r = \infty$ is $w_{A,\infty}^{v}$ then the solution to Eq. 2.3 is

$$w_{\rm A}^{\rm v} = 1 + (w_{\rm A,\infty}^{\rm v} - 1) \left(\frac{w_{\rm A,s}^{\rm v} - 1}{w_{\rm A,\infty}^{\rm v} - 1}\right)^{s/r}.$$
(2.4)

In the condensed phase, species A and B will have mass concentrations ρ_A^c and ρ_B^c , mass fractions w_A^c and w_B^c , and the mass density of solution will be $\rho_c = \rho_A^c + \rho_B^c$.

Conservation of species *A* at the droplet surface gives

$$(\rho_{\rm A}^{\rm v} - \rho_{\rm A}^{\rm c})\frac{ds}{dt} = D_{\rm c}\rho_{\rm c}\frac{\partial w_{\rm A}^{\rm c}}{\partial r} - D\rho\frac{\partial w_{\rm A}^{\rm v}}{\partial r} - v_{r}^{\rm c}\rho_{\rm A}^{\rm c} + v_{r}^{\rm v}\rho_{\rm A}^{\rm v}, \tag{2.5}$$

where D_c is the diffusivity in the condensed phase, and v_r^v is the radial component of the mass average velocity in the condensed phase.

To simplify Eq. 2.5, we first recognize that the condensed-phase mass concentration of A at the surface of the droplet, $\rho_{A,s}^c$, is much greater than the gas-phase mass concentration of A at the surface. Second, in the steady state, the concentration profile inside the droplet is always uniform and no diffusive or convective mass transport will occur in the condensed phase $(\partial w_A^c / \partial r = 0 \text{ and } v_r^c = 0)$. Applying these conditions to Eq. 2.5 and combining the result with Eq. 2.4 yields

$$\frac{ds}{dt} = \frac{\rho D}{s\rho_{A,s}^{c}} \ln\left(\frac{w_{A,s}^{v} - 1}{w_{A,\infty}^{v} - 1}\right).$$
(2.6)

In the gas phase, the relationship between *a*, the activity of species A, and w_A^v is

$$a = \frac{w_{\rm A}^{\rm v} \rho RT}{p^{\circ} M_{\rm A}},\tag{2.7}$$

where M_A is the molar mass of A, p° is the saturation vapour pressure of A, *T* is the temperature, and *R* is the gas constant. Eq. 2.7 allows Eq. 2.6 to be written as a function of activity, saturation vapour pressure, and temperature:

$$\frac{ds}{dt} = \frac{\rho D}{s\rho_{A,s}^{c}} \ln\left[\left(\frac{a_{s}p_{s}^{\circ}M_{A}}{\rho RT_{s}} - 1\right) \middle/ \left(\frac{a_{\infty}p_{\infty}^{\circ}M_{A}}{\rho RT_{\infty}} - 1\right)\right],$$
(2.8)

where a_{∞} , p_{∞}° , and T_{∞} are the activity of A, saturation vapour pressure of A, and temperature at $r = \infty$, respectively, and a_s , p_s° , and T_s are the activity of A, the saturation vapour pressure of A, and temperature at r = s(t), respectively. We have ignored the effect of surface curvature.

Eq. 2.8 is the governing equation for the steady-state growth or evaporation for a binary droplet with one non-volatile component. Using some manipulation and a first-order Taylor series expansion, it can be approximated as

$$\frac{ds}{dt} = \frac{DM_A}{s\rho_{A,s}^c R} \left(\frac{a_\infty p_\infty^\circ}{T_\infty} - \frac{a_s p_s^\circ}{T_s} \right).$$
(2.9)

Eq. 2.9 describes the growth or evaporation when convection is neglected and mass transport is only governed by diffusion. This statement can be verified by repeating



FIGURE 2.3: Calculated steady-state evaporation of an aqueous LiCl droplet at 78.5% RH. The initial radius of the droplet is 5.0 μ m. The temperature of the droplet, T_s , is 300 K and the temperature at $r = \infty$, T_{∞} , is 296 K. The curve labeled 'Numerical' was calculated using the numerical solution to Eq. 2.9. The curve labeled 'Analytical' was calculated using an analytical solution to Eq. 2.9 that was found by assuming that $\rho_{A,s}^c$ and a_s were constant and remained fixed at their t = 0 values. The equilibrium radius, s_{eq} , is indicated by a dotted line and was calculated using Eq. 2.11. The density of aqueous LiCl was calculated using tabulated data²⁶ and the activity was calculated using AIOMFAC.²⁷ Here, and in all subsequent calculations in this work, the temperature-dependent saturation vapour pressure of water was calculated using Eq. 1.10 from Ref. 28.

the solution presented above for the case where $v_r^v = 0$ (i.e. convection is neglected). With this method, when the conservation of mass at r = s(t) is combined with the gas-phase concentration profile of A, the result will be Eq. 2.9 instead of Eq. 2.8. For an aqueous droplet, species A will be water and, for a very dilute droplet, Eq. 2.9 and Eq. 13-21 from Ref. 18 will be approximately the same.

In the limiting case of a single-component droplet, analytical solutions to the growth or evaporation of a droplet are possible and are well known.¹⁸ However, for a binary droplet, both $\rho_{A,s}^c$ and a_s will have a strong dependence on *s* and analytical solutions to either Eq. 2.8 or Eq. 2.9 are likely not possible. Therefore, these equations will need to be solved numerically. This can be done by expressing both *s* and a_s as functions of $\rho_{A,s}^c$. The resulting nonlinear ordinary differential equation can then be solved numerically using off-the-shelf software (e.g. both Mathematica and MATLAB were used here).

Fig. 2.3 shows the calculated evaporation of an aqueous LiCl droplet. The droplet is held at a constant relative humidity (RH) of 78.5%, the radius at t = 0 is 5 μ m, $T_s = 300$ K and $T_{\infty} = 296$ K. The relationship between s(t) and $\rho_{A,s}^c$ can always be found by recognizing that the total mass of species B in the droplet is

constant over time. For t > 0, conservation of mass then yields

$$s(t)^{3} = \frac{\rho_{c_{0}} - \rho_{A_{0}}^{c}}{\rho_{c}(t) - \rho_{A}^{c}(t)} s_{0}^{3},$$
(2.10)

where ρ_{c_0} is the initial mass density of the droplet, $\rho_{A_0}^c$ is the initial mass concentration of A in the droplet, $\rho_c(t)$ is the mass density of the droplet for t > 0, and $\rho_A^c(t)$ is mass concentration of A in the droplet for t > 0. In a binary droplet, $\rho_c(t)$ can be parameterized as a function of $\rho_A^c(t)$ so the only time-dependent function on the right-hand side of Eq. 2.10 will be $\rho_A^c(t)$.

The conditions in Fig. 2.3 are typical of those that will be discussed in experiments below. It can be be seen that the characteristic time for the numerical curve is several milliseconds. In the experiment, however, the time between our measurements will be approximately one second. Therefore, we can assume that for measurements taken after t = 0 the radius of the binary droplet will always be at $s(t \to \infty)$. We will refer to the radius in the $t \to \infty$ limit as the equilibrium radius, s_{eq} . At equilibrium, ds/dt = 0 and, based on Eq. 2.9, the droplet activity, a_s , will satisfy

$$\frac{a_s p_s^\circ}{T_s} = \frac{a_\infty p_\infty^\circ}{T_\infty}.$$
(2.11)

Therefore, s_{eq} can be calculated directly by using Eq. 2.10 and the mass concentration of A that yields a_s in Eq. 2.11. The equilibrium condition in Eq. 2.11 will be identical regardless of whether Eq. 2.8 or Eq. 2.9 is used (the inclusion of convection in the steady-state model only affects the transient behaviour of the radius and has no effect on s_{eq}). Fig. 2.3 also shows that s_{eq} calculated using Eq. 2.11 matches that found using the numerical solution to Eq. 2.9.

2.3.2 Electromagnetic heating of an aerosol droplet

Absorption cross-section of a spherical droplet located in a Gaussian beam

As described in Section 2.2, we will heat a droplet using two focused, counterpropagating Gaussian beams that can hold a single droplet at their shared focal point. In order to understand the relationship between the beam parameters, droplet temperature, size, and composition, we will assume that at any given laser power, the heat source in the droplet is uniform. For weakly absorbing spherical droplets in the size regime of interest here, this uniform heat source approximation has been shown to be satisfactory.¹⁵ For a Gaussian beam with a total power *P* that is focused



FIGURE 2.4: Absorption cross-sections, $C_{\rm abs}$, calculated using GLMT for a Gaussian beam focused to various beam waists, w_0 . The refractive index of the sphere is $1.4 + i10^{-8}$ and $\lambda = 532$ nm. The sphere is centred on the focal point of the Gaussian beam.

to a beam waist w_0 , the heat source, Q, is

$$Q = \frac{3C_{\rm abs}I_0}{4\pi s^3},$$
 (2.12)

where C_{abs} is the absorption cross-section of the droplet and I_0 is the peak intensity of the beam and is defined as (Ref. 29, p. 676)

$$I_0 = \frac{2P}{\pi w_0^2}.$$
 (2.13)

Using Mie theory² to calculate C_{abs} will not yield accurate results as a focused beam is not well described as a plane wave. Therefore, we will calculate C_{abs} with general-ized Lorenz-Mie theory (GLMT)^{30–32} using the beam-shape coefficients for a Gaussian beam.³³

Fig. 2.4 shows examples of C_{abs} calculated using GLMT for a Gaussian beam with various w_0 . As w_0 becomes smaller than the droplet, the sharp peaks associated with the excitation of WGMs are greatly diminished. For the smallest beam waist shown here, $w_0 = 1.5 \mu m$, the peaks are no longer visible. This phenomenon has been well studied for Gaussian beams^{34–37} and can be explained using van de Hulst's localization principle:³⁸ light rays interact with WGMs in spherical particles through the evanescent field of the WGM. Therefore, WGMs are optimally excited when incident rays pass through a region just outside the surface of the sphere. If a sphere is located at the focal point of a beam and the beam becomes more tightly focused there will be less rays passing through the evanescent region of the WGM. Consequently, the excitation efficiency of the WGM decreases and the corresponding peak in the spectrum will be diminished.

The second important result from Fig. 2.4 is the demonstration that standard Mie theory can only give accurate C_{abs} when the beam waist is much larger than the radius of the sphere. Even when $w_0 = 6 \ \mu m$, C_{abs} is still much smaller than $w_0 = \infty$ (the plane-wave/standard Mie theory result). Therefore, unless the beam is very loosely focused, GLMT should always be used when calculating C_{abs} .

Droplet temperature in the steady-state

The steady-state heat equations for the condensed and gas phases will be

$$\frac{\kappa_{\rm c}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_{\rm c}}{\partial r} \right) = -Q \tag{2.14}$$

and

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial T_g}{\partial r} \right) = 0, \tag{2.15}$$

respectively, where κ_c is the thermal conductivity of the condensed phase, T_c is the radial temperature distribution in the condensed phase, and T_g is the radial temperature distribution in the gas phase. These equations are readily solved to yield

$$T_{\rm c} = T_s + \frac{Q}{6\kappa_{\rm c}}(s^2 - r^2)$$
 (2.16)

and

$$T_{\rm g} = T_{\infty} + \frac{s}{r}(T_s - T_{\infty}).$$
 (2.17)

When the binary droplet reaches equilibrium, ds/dt = 0 and conservation of energy at r = s will give the boundary condition

$$\kappa_{\rm c} \frac{\partial T_{\rm c}}{\partial r} = \kappa_{\rm g} \frac{\partial T_{\rm g}}{\partial r},\tag{2.18}$$

where κ_g is the thermal conductivity of the gas phase. Inserting the temperature distributions from Eqs. 2.16 and 2.17 into Eq. 2.18 and applying Eqs. 2.12 and 2.13 yields

$$\Delta T = \frac{C_{\rm abs}P}{2\pi^2 w_0^2 s \kappa_{\rm g}},\tag{2.19}$$

where $\Delta T = T_s - T_{\infty}$, is the change in temperature due to the absorption of the focused laser beam. In all calculations performed here, the value of κ_g was set to 0.026 W/(m·K), which is the value for nitrogen at T = 300 K.²⁶



FIGURE 2.5: Calculated equilibrium radius, s_{eq} , as a function of laser power, *P*, for an aqueous NaCl droplet in a Gaussian beam focused to various beam waists, w_0 , with a surrounding RH of (a) 95%, (b) 80%, and (c) 65%. The temperature at $r = \infty$ is $T_{\infty} = 296$ K. The real part of the wavelength- and temperature-dependent refractive index was calculated using the parameterizations in Ref. 39. The imaginary part of the refractive index was fixed at 1.9×10^{-9} .⁵ The density of aqueous NaCl was calculated using tabulated data²⁶ and the activity was calculated using AIOMFAC.²⁷

2.4 **Results and Discussion**

2.4.1 The equilibrium size of an aqueous droplet during laser heating

Fig. 2.5 shows the calculated equilibrium radius of a binary droplet, s_{eq} , as a function of laser power, *P*, for the system of water and NaCl. The curves were calculated as follows: First, Eq. 2.10 (conservation of mass) is used to determine the ρ_A^c and ρ_B^c for every s_{eq} of interest. In Fig. 2.5, species A is water and species B is NaCl. Second, with these mass concentrations, the mole fraction of A in the condensed phase can be found and Eq. 2.11 can then be solved for T_s , which will be the only unknown. Once T_s is found for each s_{eq} , Eq. 2.19 can be used to determine the corresponding *P*.

The existence of multiple s_{eq} at each value of *P* is known as optical bistability or multistability.^{17,40,41} This phenomenon can readily be seen in many of the curves shown in Fig. 2.5. It is the result of the excitation of WGM resonances and, as expected based on Fig. 2.4, the effect becomes less pronounced as w_0 decreases. In fact, for all of the $w_0 = 1.5 \ \mu m$ curves in Fig. 2.5, s_{eq} can accurately be described as a straight line when plotted as a function of *P* as WGMs are not excited by this small beam waist. It is only for the larger incident beam waists ($w_0 = 3 \ \mu m$ and $6 \ \mu m$) that WGMs are excited and multiple s_{eq} can be observed for the same *P*. In Fig. 2.5a if we consider a vertical line drawn at P = 0.3 W, we see that the number of s_{eq} that such a line would intersect is different for all three beam waists. The line would intersect the $w_0 = 6 \ \mu m$ (red) curve 11 times, the $w_0 = 3 \ \mu m$ (blue) curve 7 times and the $w_0 = 1.5 \ \mu m$ (green) curve only once. Therefore, in this system, optical multistability only occurs when WGMs are excited.

Fig. 2.5 also demonstrates that GLMT must be used when calculating C_{abs} as all three beam waists produce very different curves. Even if the WGM resonances are ignored, the rate of change of s_{eq} with respect to *P* differs between the curves which means that, when fitting size change data, using an inaccurate value of w_0 (or ignoring it completely and relying only on Mie theory) will yield an inaccurate best-fit for *k*. The beam waist for our set-up was measured by the knife-edge method²⁵ to be 4.3 μ m.

Fig. 2.6a and 2.6b show the measured WGM peak positions of an aqueous LiCl droplet as the laser power is increased (Fig. 2.6a) from 100 to 300 mW and then decreased (Fig. 2.6b) back to 100 mW. During this measurement, the laser power is changed at a rate of approximately 1 mW/s. Fig. 2.6c shows the resulting radii of best-fit for these measured peaks, along with a calculated s_{eq} curve produced using



FIGURE 2.6: Upper and middle graphs show the WGM positions for an aqueous LiCl particle as power is changed from a)100 to 300 mW and b)300 to 100 mW at a constant rate. The lower graph shows the fitted radii for each, in the same colours, and a theoretical curve calculated by the method outlined in Sec. 2.4.1.

the method outlined above.

In Fig. 2.6, the radius and WGMs can be seen to depend heavily on whether the power is being increased (Fig. 2.6a and red points in 2.6c) or decreased (Fig. 2.6b and blue points in 2.6c). This can be understood as being due to thermal effects caused by the excitation of WGMs. Whilst the laser power is increasing, we see a gradual change in radius interspersed with several small, sudden drops in radii that occur at powers of approximately 170, 205, 255 and 285 mW. Due to the uncertainty in the radii of best-fit, these sudden changes are more apparent in the WGM trajectories (Fig. 2.6a). The origin of these changes are the 'temperature jumps' described in Ref. 14, and may be understood by considering Fig. 2.5. Following, for example, the red curve in Fig. 2.5b from low to high power, we see a point at around 450 mW where the equilibrium power curve begins to double back on itself. The result of increasing *P* beyond this point will be a drop in s_{eq} to a lower point on the equilibrium curve. This is consistent with the small, sudden changes observed in Fig. 2.6a and 2.6c.

After the laser power is increased to 300 mW and the power begins to decrease, there are large regions where both the WGMs (Fig. 2.6b) and radii (blue points in Fig. 2.6c) remain nearly constant. This is the phenomenon of thermal locking,^{13,42} and can also be understood by examining our theoretical curves. Considering the behaviour of the red curve of Fig. 2.5a upon moving from high to low *P*, we see that s_{eq} will generally increase gradually until it reaches a WGM resonance; where the change in s_{eq} with respect to *P* tends to zero. This is again due to extra heating of the particle caused by excitation of a WGM, caused by a sharp increase in C_{abs} . The particle radius will be maintained approximately constant so long as C_{abs} is sufficiently large to sustain the particle at a constant temperature. When this is no longer the case, the particle will rapidly increase in radius until reaching equilibrium again according to Fig. 2.3. This is the cause of the sudden increases in radii seen at powers around 260 and 102 mW in Fig. 2.6c.

Comparing the observed and calculated radii in Fig. 2.6c, we see mostly good agreement with some exceptions. For instance, most of the points during the increasing power correspond very well to the calculated curve. Additionally, as the power is decreased, there is a close match between the calculated and observed radius where the main region of thermal locking (lowering the power from 235 to 102 mW). However, the small radius drop at around 170 mW during the power increase, appears to fall between two WGM resonances. We attribute this to the fact that the positions of resonances are highly sensitive to *n* (the real part of the refractive index) whereas the overall slope of the *s*_{eq} curve without resonances is dependent on *k*. As such, small inaccuracies in the parameterization of *n* can significantly shift WGM resonance positions but will have little impact on the fitted value of *k*.



FIGURE 2.7: Radius as a function of time for an aqueous LiCl droplet held at an RH of $78.5 \pm 1.8\%$ for a series of power changes as described in Section 2.2. The vertical gray line indicates the time at which the power was increased from the initial power (100 mW) to the final power (between 150 and 500 mW).

Therefore, we attribute the differences between the calculations and observations in Fig. 2.6c to the high sensitivity of WGM resonance positions to *n*.

2.4.2 Determining the imaginary component of the refractive index

Fig. 2.7 shows the measured radii from a series of experiments on an aqueous LiCl droplet, as described in Section 2.2. The power is rapidly increased at t = 100 s from 100 mW to final powers from 150 to 500 mW. Before beginning each experiment, *P* was decreased to below 100 mW and then elevated in order to ensure that the particle did not begin from a thermally locked state. It can be seen from Fig. 2.7 that as the power after the change is increased, the final radius decreases, consistent with both the predictions made in Fig. 2.5 and the intuitive expectation that increasing *P* will lead to more heating and a decrease in s_{eq} . We also see that the radius remains approximately constant both before and after the power change, consistent with the equilibration time seen in Fig.2.3.

To obtain the *k* of best-fit for electromagnetic heating measurements, such as the one shown in Fig. 2.7, a data set containing the measured s_{eq} at various *P* is constructed. Then, a one-dimensional grid search is used in order to find the value of *k* that minimizes the sum square error between between calculated and measured s_{eq} . When calculating s_{eq} in this minimization, the only unknown will be *k* as all other quantities are either (i) experimental variables (beam power, cell RH, etc.), (ii) readily calculated from tabulated data (density and activity), or (iii) determined from fitting peaks in CERS spectra using MRFIT (*n* and *s*).



FIGURE 2.8: Comparison between the predicted change in radius (red curve) and the observed changes in radius (black points) after increases in trapping laser power for aqueous (a) NaCl, (b) citric acid, and (c) LiCl droplets held at an RH of $78.5 \pm 1.8\%$. The value of *k* used to generate each predicted curve is given in the top right of each plot. This is the value which generates the curve which best fits the data based on the method outlined in Sec. 2.4.2. Curves were calculated using the average relative humidity and surrounding temperature from each series of measurements. Densities and activities of aqueous inorganic salts were calculated from tabulated data²⁶ and AIOMFAC²⁷ respectively. The density and activity of citric acid was calculated using Ref. 43. The real part of the refractive index was determined from a linear fit of the fitted refractive index at each radius.

Fig. 2.8 lists the *k* of best-fit found for each of the three solutions used in this experiment and shows a comparison between the observed radius changes for each power and a theoretical curve calculated using the *k* of best-fit. We see a different value of *k* is calculated for each, specifically 5.91×10^{-9} for aqueous NaCl, 9.98×10^{-9} for aqueous citric acid and 2.03×10^{-8} for aqueous LiCl. At $\lambda = 532$ nm, the value of *k* for pure water is known to be 1.5×10^{-9} .⁴⁴ All of the values of *k* found here are greater than this value indicating that the solute increases the absorption in these particles. Therefore, while *k* is still small, it is larger than that of pure water. One can see that assuming that all of these weakly absorbing particles have the same *k* as pure water can lead to large errors in subsequent calculations as *k* can readily be an order of magnitude larger than that value.

We can also use uncertainty associated with these measurements to predict the RH range over which our set-up will be useful for determining such low absorbances. All experiments presented here were performed at 78.5 \pm 1.8% RH, already exceeding the lower limit on previous methods.⁴ The average standard deviation of the radii measured in the experiments shown in Fig. 2.7 was found to be 3.2 nm. With the D-BOT, we have been able to trap particles using laser powers of up to 2 W. This means that if a laser power of 2 W can induce a size change of at least 3.2 nm, then the imaginary part of the refractive index should be able to be measured using this set-up. Fig. 2.9 shows the predicted equilibrium power for a 4 μ m aqueous citric acid droplet across a range of RH values from 10 to 90%. The black line indicates a size change required to allow *k* to be calculated. We see that all of the curves drawn cross this line before a power of 2 W is reached, indicating that our set-up could be used to measure *k* at very low RH in weakly absorbing aerosol particles.

2.5 Conclusions

We have presented the theory underlying the electromagnetic heating of binary aerosol droplets, as well as an experimental set-up capable of measuring the size and complex refractive index of weakly absorbing aerosol particles. Very small values of the imaginary part of the complex refractive index were measured here (k on the order of 10^{-8} and 10^{-9}). The theory outlines the governing equations for the growth or evaporation of binary aerosol droplets subject to heating by electromagnetic radiation. These equations provide an expression more relevant for assessing droplet size changes than the commonly used steady-state equation for single component droplets. Their use provides a method by which the laser power required to sustain a particle at a given radius and composition can be determined.



FIGURE 2.9: Graph showing the predicted size evolution of aqueous citric acid particles at a series of RH values, with a hatched region indicating the cut-off final radius above which *k* cannot be determined. Density and activity were calculated using Ref. 43 and refractive index by fitting tabulated data.²⁶ The value of *k* used was 9.98×10^{-9} .

These calculations can then be used in conjunction with our experimental set-up to determine k for weakly absorbing particles. Additionally, information from CERS spectra allow us to determine both n and s meaning that both the size and complex refractive index of spherical particles can be determined with high accuracy and precision. The D-BOT described here (Fig. 2.1) allows particles to be trapped at higher powers than traditional single-beam optical tweezers. This in turn allows the particles to be heated to higher temperatures, resulting in larger size changes and overcoming a key limitation of a previous optical tweezers-based technique for the determination of k (a limitation which meant that experiments had to be carried out at relative humidities near 100%). Analysis of experiments is also simplified and more accurate because, unlike a single-beam trap, the position of the particle is no longer dependent on beam power as the net scattering force acting on the particle is always zero. This means that particle position will not change with beam power and a single value of the beam waist can be used in all calculations.

Curves generated by the outlined theoretical method predict both thermal jumping and thermal locking. These two phenomena were both observed in experiments where laser power was changed continuously from low to high power and back again (Fig. 2.6). Experiments involving discrete power changes allowed the retrieval of *k* for three different aqueous droplets held at an RH of $78.5 \pm 1.8\%$ (aqueous NaCl, LiCl, and citric acid). The measurement of $k = 5.91 \times 10^{-9}$ at the single particle level, to our knowledge, is on par with the most sensitive measurements made so far. Calculations exploring the potential limits of the set-up described here showed that it should be possible to use it to measure values of *k* for aqueous, weakly absorbing aerosol particles at RHs above 10%. This represents a significant improvement on previously described methods, which required RH close to 100%. Given the enhanced abilities of the D-BOT compared to previous experimental set-ups, it should be possible to use it to measure even smaller imaginary refractive indices than those measured here, although this would likely necessitate measurements at higher relative humidities.

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Chapter 3 Rationale

Section 1.1.3 emphasises the potentially important role of surface tension in the process of cloud droplet activation, especially for particles which have undergone liquid-liquid phase separation. Measuring the surface tension of single aerosol particles is especially challenging, with only a few methods available to date. The methodology developed here uses the fact that an optically trapped aerosol particle will be deformed to some extent by the trapping laser beams. The balance of the scattering and gradient forces means optical tweezers are limited to operate at fairly low laser powers, thus the deformation of the particle is small enough to be neglected. The dual-beam optical trap, on the other hand, is not limited in this way, meaning the deformation can be increased to measurable levels. However, the deformation is still small (a few nanometres on a several micron particle) and requires a very sensitive technique to probe. We use the sensitivity of MDRs to the particle shape, as discussed in Section 1.3.4, in order to measure the particle deformation, and thereby infer the particle surface tension. This work also makes use of an effect which we discuss at length in Chapter 2, namely thermal locking, in order to amplify the scattering from the particle and enable the measurement. This represents an interesting application of what was previously an intriguing, but fairly esoteric effect, as demonstrated in the next chapter.

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3 Optical deformation of single aerosol particles

Abstract

Advancements in designing complex models for atmospheric aerosol science and aerosol-cloud interactions rely vitally on accurately measuring the physicochemical properties of microscopic particles. Optical tweezers are a laboratory-based platform that can provide access to such measurements, as they are able to isolate individual particles from an ensemble. The surprising ability of a focused beam of light to trap and hold a single particle can be conceptually understood in the ray optics regime using momentum transfer and Newton's second law. The same radiation pressure that results in stable trapping will also exert a deforming optical stress on the surface of the particle. For micron-sized aqueous droplets held in the air, the deformation will be on the order of a few nanometers or less; clearly not observable through optical microscopy. In this study, we utilize cavity-enhanced Raman scattering and a phenomenon known as thermal locking to measure small deformations in optically trapped droplets. With the aid of light-scattering calculations and a model that balances the hydrostatic pressure, surface tension and optical pressure across the air-droplet interface, we can accurately determine surface tension from our measurements. Our approach is applied to two systems of atmospheric interest: aqueous organic and inorganic aerosol.

3.1 Introduction

Aerosol optical tweezers (AOT) allow for contactless confinement of pico- and femtoliter sample volumes across phase states and timescales which are inaccessible through bulk measurements. Coupled with high-precision light-scattering techniques^{1,2}, AOT have enabled researchers to interrogate the important microphysical properties of hygroscopicity³, surface tension^{4,5}, metastable states^{6,7}, viscosity^{4,8}, liquid–liquid equilibrium^{9–11}, and atmospheric multiphase chemistry^{12,13}. The stable trapping provided by the optical gradient force from a focused laser is foundational to this area of research¹⁴. However, the tightly focused beam will do more than hold a single particle at a fixed position.

Two of the most commonly asked questions about AOT are: "Does the trapping laser heat the droplet?" and "Does the trapping laser deform the droplet?". The answer to both questions is "Yes", but for most atmospheric aerosol studies the magnitude of either effect will be minimal. Consider an aqueous sodium chloride particle with a radius of 5 μ m which is held using typical AOT¹⁵ and is in equilibrium with water vapor at 80% relative humidity (RH). The calculated surface temperature increase of the trapped droplet is 23 mK, and the maximum deformation from a spherical shape is 0.5 nm. From this example, we see that the heating and deformation impacts are both small; therefore, it is reasonable to neglect them in hygroscopic growth and evaporation studies of aqueous aerosol particles. However, at higher laser powers, both heating and deformation will become more pronounced, and their effect on a single droplet will allow for the investigation of the complex refractive index (through heating) and surface tension (through deformation).

Studying optical deformation with a single-beam trap is challenging as the equilibrium position of the droplet will change with laser power due to the optical scattering force¹⁶. Eventually, at a high enough laser power, the scattering force pushes the droplet out of the trap. In the experiments performed here, droplets are held and deformed using two focused, counterpropagating beams of equal power; thus, the two opposing scattering forces will cancel each other out¹⁷. Of course, the idea of using light to deform micron-sized objects is not new¹⁸. There are many examples of so-called optical stretchers (essentially two counterpropagating beams) that have been used to study cell membranes^{19–21}. Large deformations of the referenced biological systems can readily be observed using optical imaging, but due to the much higher surface tension of aerosol particles this type of characterization may fail. For instance, the surface tension of pure water at 25° C is \sim 72 mN/m²² which is nearly $17,000 \times$ larger than the effective interfacial tension of a typical phospholipid vesicle in aqueous solution²¹. Even for large laser powers, the deformation of airborne micron-sized aqueous droplets will be at most a few nanometers (see Fig. 3.1). Such small deformations will not be observable with optical microscopy, but could be observed by monitoring changes in optical resonances.

When a droplet is optically trapped, whispering gallery modes (WGMs) can be

excited through cavity-enhanced Raman scattering (CERS)^{23–25}. The spherical microdroplet acts as a weakly absorbing, high-quality factor optical cavity which supports whispering gallery modes (WGMs)^{26–29}. These optical modes are very sensitive to particle size, composition, and shape. For a particle that is well described as a homogeneous sphere, the observed WGM resonances can be fitted using Mie theory, which retrieves the radius and refractive index with precision on the order of 1 nm and 10^{-4} , respectively^{1,15}. When the optical cavity is deformed from that of a perfect sphere, the azimuthal degeneracy of the WGMs is lost and frequency splitting of the multiplet occurs^{30,31}. This splitting allows for the detection of nanometer-sized deformations on micron-sized particles and enables measurement of the surface tension of single microdroplets.

Surface tension (and its change during aerosol particle growth) has emerged in recent years as a potentially important factor in the formation of cloud droplets, and thereby indirectly precipitation, due to its influence over the process of cloud droplet activation. It was long thought to be unimportant and was typically treated as constant; however, it has now been shown that it can be a dominant factor during cloud droplet activation^{34–36}. This has led to a renewed interest in the development of methods for measuring surface tension in aerosol particles. Conventional tensiometry cannot access compositions beyond the bulk solubility limit, where aerosol particles often exist³⁷, meaning techniques which can investigate this regime are essential. This represents a weakness in one approach which has been employed to measure aerosol surface tension; falling droplet chain measurements. Due to the short times over which measurements are taken, droplet compositions remain below the solubility limit^{5,38}. Another method used to determine aerosol surface tension is atomic force microscopy (AFM)^{39–41}. This approach is able to access sizes below those that are feasible with optical trapping. However, because particles sit on a substrate and are directly interrogated by an AFM probe, such measurements are not contact-free like optical trapping-based approaches. In this work, we experimentally and theoretically investigate the optical deformation of single aerosol droplets. We describe and validate a novel method of measuring surface tension on two model atmospheric aerosol systems: aqueous NaCl and aqueous citric acid.



FIGURE 3.1: Calculated (a) optical stress, (b) deformation, and (c) extinction cross-section, Cext, for a spherical aqueous NaCl particle with a radius of 5 μ m in equilibrium with 80% relative humidity. In (a) the total beam power is 1 W, and the optical stress on the surface of the sphere is shown for two azimuthal angles, ϕ , as a function of the polar angle, θ . The two azimuthal angles are the angles at which the incident beams are polarized relative to the plane of the page. In (b) the total beam powers are indicated next to their respective curves. In (b) droplet deformation from a sphere is plotted for 0 W to 1 W total beam power and the surface tension is set to 72 mN/m (the value for pure water at $25^{\circ}C^{22}$). In (a) and (b) the counterpropagating beams each have half the total beam power (e.g. for 1 W total power, each beam has 0.5 W). Both beams are linearly polarized, with these polarizations being mutually orthogonal. In (c), T-Matrix ellipsoid calculations^{32,33} are used to simulate extinction spectra and are compared to Eq. 3.1. The plot on the left is a simulation for a transverse electric (TE) resonance, and the right is a transverse magnetic (TM) resonance. Curves in (c) are offset vertically for clarity.

3.2 Results

3.2.1 Modeling optical deformation

We use generalized Lorenz-Mie theory (GLMT) to calculate the optical stress on the surface of the trapped droplet. GLMT fully accounts for the incident laser profile and interference effects, such as the excitation of WGMs, on the stress⁴². The induced surface stress from the laser is used in the stress-balance equation to determine the resulting shape (see SI Appendix). Fig. 3.1a shows the optical stress for a 1 W trapping laser that has been split into two counterpropagating 0.5 W beams with orthogonal polarizations. Fig. 3.1b shows the resulting deformation for an aqueous NaCl droplet. Even at 1 W, the maximum deformation of this 5 μ m radius droplet is only 4 nm. A cross-section of the deformed spheroid is almost a perfect ellipse (only slightly subelliptical). Unlike simplified models²¹, the GLMT model has no *a priori* deformation shape; however, in this case approximating the cross-section as an ellipse is valid.

3.2.2 Whispering gallery modes in a deformed droplet

Conventional optical imaging methods cannot detect nanometer deformations of micron-sized droplets, but measurable shifts in WGM resonance positions will occur due to perturbation of the resonating cavity. For small elliptical deformations, the resonant wavelengths, λ_n^m , of a prolate spheroid can be accurately calculated with³⁰

$$\frac{1}{\lambda_n^m} = \frac{1}{\lambda_n^{\text{Mie}}} \left[1 - \frac{e}{6} \left(1 - \frac{3m^2}{n(n+1)} \right) \right],\tag{3.1}$$

where *n* is the mode number, *m* is the azimuthal mode number, and λ_n^{Mie} are the resonant wavelengths of the volume-equivalent sphere of radius r_s . The amplitude of deformation is defined as $e = (r_p - r_e)/r_s$, where r_p is the polar radius and r_e is the equatorial radius.

Fig. 3.1c shows simulated extinction spectra for the deformed droplets shown in Fig. 3.1b (prolate spheroids of equivalent volume). For each laser power, two simulated spectra are shown; one observed from the polar axis and one observed along the equatorial axis. Along the polar axis, a single peak corresponding to the m = 0 mode is observed. Along the equatorial axis, peaks associated with all of the non-degenerate azimuthal WGMs can be observed. Resonances from Eq. 3.1 are superimposed on the spectra. For these small deformations, Eq. 3.1 is very accurate, demonstrating its suitability when analyzing WGMs from deformed droplets. The small discrepancies originate from the treatment of the refractive index: in Eq. 3.1 the refractive index is fixed at the value used to calculate λ_n^{Mie} , whereas the simulated extinction spectra are calculated using the full wavelength-dependent refractive index.

3.2.3 Droplet heating

With the deformation effect on the WGMs understood, the electromagnetic heating of the droplet is the last major complication. Consider again a 5 μ m aqueous NaCl droplet trapped in a cell with an RH of 80% and a temperature of 295 K. When the trapping power is at 0.25 W, as it is for one of the examples given in Fig. 3.1, the increase in the surface temperature of the droplet will be 195 mK. This small temperature increase will lead to a predicted decrease in droplet radius of 57 nm due to the evaporative loss of water¹⁷. The blueshift in the WGM peak position of the TE¹₆₀ mode due to this size change is 7.290 nm (calculated using Mie theory²). In Fig. 3.1c, the maximum blueshift relative to the Mie resonance due to optical deformation is 0.055 nm ($m = \pm 60$), and the maximum redshift is 0.028 nm (m = 0). This example illustrates that the spectral shifts due to heating-induced size changes will dominate the much smaller shifts due to deformation (see also SI Appendix, Fig. S1).

A potential solution to overcoming the large shifts that are caused by heating is to examine the relative positions of azimuthal mode peaks in spectra rather than their absolute positions. This is not straightforward, as small deformations do not resolve the non-degenerate azimuthal modes if light scattering is collected along a single axis⁴³. However, as shown in Fig. 3.2a, the angular range over which light scattering occurs for a WGM will depend on its azimuthal number. We simultaneously collect spectra parallel (0° spectrum) and perpendicular (90° spectrum) to the trapping-beam axis using two orthogonal objectives. This collection method is the key part of our optical set-up illustrated in Fig. 3.2b (the full set-up is shown in SI Appendix, Fig. S2). The WGMs that are confined close to the equatorial plane of the spheroid will only be collected by the objective that is orthogonal to the two counterpropagating beams (Fig. 3.2a). The resonant wavelengths of these WGMs will correspond to the case where $|m| \sim n$ in Eq. 3.1. Conversely, CERS along the axis that is collinear with the two trapping objectives will only contain resonant peaks associated with WGMs where $|m| \ll n$. In Fig. 3.2c a typical pair of spectra collected at 0° and 90° are shown. While the individual non-degenerate modes cannot be seen, splitting clearly occurs. This splitting between the peaks provides information on the resulting shape of the deformed droplet. The 0° spectrum provides


FIGURE 3.2: (a) The calculated radial component of the electric field on the surface of a sphere for select azimuthal numbers, *m*. In all cases, the mode number is n = 60. The angular range over which scattering from different *m* can occur is indicated for a single plane by the violet shaded region. Electric fields were calculated using the Debye potential method in the spherical coordinate system²⁸. (b) Depiction of the experimental collection geometry employed using two opposing objectives of which one collects the 0° scattered light. The orthogonal objective collects the 90° scattered light. (c) Representative spectra showing the observed 0° scattered light in red and 90° scattered light in blue. The spectra are centered on the broad O-H Raman band, and the WGMs are identified and labeled.

information on the polar radius of the ellipse, whereas the 90° spectrum contains information on the equatorial radius.

3.2.4 Thermal locking

Using a dual-beam optical trap, we hold an aqueous droplet in equilibrium with the cell RH and collect CERS spectra as a function of laser power. The measured radius of an aqueous NaCl solution droplet is shown in Fig. 3.3a, where the laser power is first increased and then decreased. The measured radii are found by fitting the peak positions of WGM resonances located atop the O-H stretching band of water (e.g. Fig. 3.2c). With increasing laser power, the radius decreases in a roughly linear fashion as the surface temperature of the droplet increases. In contrast, when the laser power is subsequently lowered, there are large regions where the radius shows little to no change and appears independent of laser power. This effect is the thermal locking phenomenon^{17,44,45}. When the laser power incident on a droplet is reduced, the droplet will generally cool and its size will increase as it equilibrates with the surrounding RH. However, when the droplet approaches a size which is resonant with the trapping laser wavelength, its absorption cross-section increases. This resonance, along with the high intensity of the trapping laser light, leads to heating which counteracts the cooling effect of reducing the laser power. A temperature profile is shown in SI Appendix, Fig. S3.

Thermal locking is accurately predicted by the equilibrium radius calculation, which is superimposed on the measurements shown in Fig. 3.3a. While decreasing laser power, the droplet becomes locked on two different resonances. First, it becomes locked when the trapping laser excites a resonance near a droplet radius of 4.6307 μ m (TM²₆₃). After the laser power is lowered to 0.15 W, a jump in droplet size occurs and the droplet radius subsequently becomes locked near 4.6560 μ m (TM¹₆₉). In the experiment shown in Fig. 3.3a, the droplet is thermally locked for nearly the entire time that the laser power is decreased.

Preparing a droplet in a thermally locked state is experimentally useful as the size changes that occur with varying laser power are greatly reduced. Additionally, large amplitudes of deformation can be achieved at relatively low laser powers. For instance, in Fig. 3.3b, at 0.2 W the calculated *e* is 1.94×10^{-4} when the laser power is increasing but 5.19×10^{-4} when the droplet is thermally locked during the laser power decrease. However, the major benefit of thermal locking is that the CERS intensity will greatly increase when the wavelength of the trapping laser is commensurate with a WGM within the droplet. This double-resonance Raman scattering^{25,45-47} is key to our surface tension measurements and was always observed



FIGURE 3.3: (a) The measured volume-equivalent radius for an optically trapped aqueous NaCl droplet where the laser power is first increased and then decreased. The droplet was held at $77\pm2\%$ RH. The calculated equilibrium radius for the laser power range is superimposed on the measurements. (b) The calculated amplitude of deformation for the laser power range in (a). In (c) and (d) the peak positions for TE¹₅₆ and TM¹₅₆, respectively, measured using the 0° scattered light (red circles) and 90° scattered light (blue circles). The measurements in (c) and (d) were taken while the laser power was being decreased and the droplet was thermally locked.

during thermal locking.

From the trapping geometry, we expect the focused laser beam to excite the $|m| \ll n$ WGMs during thermal locking. The Raman scattering from these excited WGMs will not lead to a uniform enhancement of CERS across all azimuthal mode numbers. In the plane of the |m| = n mode (the upper left panel of Fig. 3.2a), the resulting Raman scattering from the $|m| \ll n$ modes, which are excited by the trapping laser, primarily couples into TM modes rather than the TE modes. The reason for this is that polarization of the two focused beams will be almost entirely in the plane of |m| = n. Thus, very little Raman scattering will excite TE modes with |m| = n, as the polarization of this TE mode is perpendicular to the plane of |m| = n. However, the polarization of TM modes lies mostly in the same plane as that of the trapping beams. Therefore, the observed splitting between the CERS peaks measured using the two orthogonal objectives will then be less for TE modes than TM modes. Fig. 3.3c and d show an example of such a measurement across a range of trapping powers for a thermally locked droplet. As anticipated, splitting of the peaks associated with TM_{56}^1 mode is larger than the splitting of the peaks associated with the TE_{56}^1 mode.

3.2.5 Surface tension measurements

Our experimental results focus on optically deforming aqueous inorganic and organic aerosol droplets. The two aqueous systems in Fig. 3.4 were chosen as they are often used as surrogates for aqueous atmospheric organic and inorganic aerosol. For example, aqueous citric acid has been used as a model system for high-viscosity, glass-forming aerosol particles^{48–53}. These two systems are also representative examples of surface tensions relevant to aqueous atmospheric aerosol. The surface tension of the aqueous inorganic droplet is greater than that of pure water while the surface tension of the aqueous organic droplet is less than that of pure water.

Our calculated surface tensions using the splittings and laser powers in Fig. 3.4a and b are shown in Fig. 3.4c and d, respectively. The single aerosol droplets were thermally locked during all experiments shown here. The positions of the WGMs are plotted relative to their corresponding WGMs in an undeformed, volume-equivalent sphere (see SI Appendix). As surface tension is independent of laser power, measurements can be averaged across multiple laser powers. The experimental analysis yields accurate surface tension values that compare well to theoretical calculations for these mixtures^{54,55}.

3.3 Discussion

Surface tension measurements of atmospheric aerosol are becoming increasingly important as aerosol models improve and attempt to simulate physicochemical processes more realistically. Measurements on single particles offer particular advantages to characterize this accurately. Earlier, we remarked that the idea of using optical deformation to study surface tension was by no means new. However, a practical implementation of this concept for aerosol particles was not obvious due to their high surface tension. Here we have shown that it is possible to optically trap single aerosol droplets and to deform them in a controllable manner in a dualbeam optical trap. While this deformation is indeed very small (a few nanometers on a $\sim 5 \ \mu$ m radius droplet), we have demonstrated that it can be observed and quantified through small shifts in the WGMs observed in CERS spectra collected orthogonally to each other.

The dual-beam optical trap system overcomes difficulties related to the scattering force which would arise when using a more conventional, single-beam optical tweezers set-up. This trap controllably deforms a single aerosol droplet by changing the trapping laser power. The magnitude of the deformation induced by the laser light is quantified by measuring shifts between WGMs in two CERS spectra measured parallel and perpendicular to the trapping-beam axis. By thermally locking a droplet, we were able to largely eliminate spectral shifts due to electromagnetic heating while simultaneously gaining access to large deformations at low laser powers. During thermal locking double-resonance Raman scattering occurs, resulting in



FIGURE 3.4: Measured WGM positions from CERS spectra collected at 0° and 90° for (a) an aqueous NaCl droplet held at an RH of $62\pm2\%$ and (b) an aqueous citric acid droplet held at an RH of $86\pm2\%$ as a function of decreasing laser power. The WGM positions of each optically deformed droplet are shown relative to their corresponding WGMs in a spherical droplet (see SI Appendix). The standard deviation of the WGM peak positions is shown as a shaded region. Droplets were thermally locked during the entirety of the measurement. The surface tension calculated using each pair of points in (a) and (b) is shown as blue circles in (c) and (d), respectively. The mean value of these surface tension measurements is shown as a solid blue line and the standard deviation is shown as a shaded region. The predicted surface tension 54,55 for the water activity at which these measurements were taken is plotted as dotted black lines.

greater coupling of light into modes with $|m| \sim n$ and an observed increase in WGM splitting. Understanding and exploiting these effects enabled accurate surface tension measurements of both single aqueous organic and inorganic aerosol particles serving as model systems. The results are in excellent agreement with existing surface tension models^{54,55}.

Going forward, additional surface tension measurements on complex atmospheric systems will be probed. One class of systems particularly interesting to the atmospheric community are those in metastable, supersaturated states^{37,56}. Surface tension measurements on such systems are vital, as they are inaccessible to bulk measurements due to solubility limits, but a lack of experimental methodology means this remains largely unexplored. We have, in fact, demonstrated the ability of our set-up to interrogate such states. The mole fraction-based water activity of the aqueous NaCl droplet characterized in Fig. 3.4 was 0.60; well below the water activity of 0.75 corresponding to the bulk solubility limit of NaCl in water at 298.15 K⁵⁷.

Other systems of atmospheric interest include high-viscosity, semi-solid and solid particles^{58–61} and particles which undergo liquid–liquid phase separation^{9–11}. We anticipate that our set-up will be useful in the interrogation of both, although the rheological model used to describe the deformation of the droplet will need to be changed from an incompressible Newtonian fluid to a viscoelastic fluid and, eventually, to an elastic solid with increasing viscosity. One of the limitations of previous optical trapping-based methods for surface tension measurement was that viscous damping restricted the range over which surface tension could be measured to the order of 10^{-2} Pa·s or less^{4,5}. Since our methodology measures a static deformation as opposed to droplet oscillations, the range of viscosity over which we can measure surface tension has, in principle, no lower or upper limits. However, practical measurement durations with the AOT are unlikely to be longer than a few hours for which comparable particle relaxation times⁶² give a maximum viscosity on the order of 10^7 Pa·s (for the principal mode of a 5 μ m particle with a surface tension of 72 mN/m). Measurements on particles exhibiting liquid–liquid equilibrium should also be possible, although the formalism used for analysis will again require adjustment for the core-shell morphology.

As the methodology set out here applies to any particle that supports WGMs, it can readily find applications outside the field of aerosol science. For instance, it is realistic to speculate that measurements on the micron-sized droplets in oil-in-water emulsions would be feasible with a modified trapping cell as their interfacial tensions are typically ten times smaller than the systems studied here⁶³. A related

example comes from the field of droplet-based microfluidics⁶⁴ where interfacial tension plays a key role and there are already many existing demonstrations of optical manipulation⁶⁵. Dynamic tensiometry is also achievable through the sinusoidal modulation of the trapping beam power. Analogous to dynamic drop tensiometry experiments that have been performed using millimeter-sized droplets⁶⁶, this would allow for investigations into the viscoelastic properties of a wide range of interfaces (e.g. adsorbed protein layers, surfactants). Our methodology only fails if the WGM splitting caused by the deformation is below the detection limit, in our case 0.02 nm. This limit is a function of several parameters, both material and experimental. For example, higher surface tension leads to a reduction in splitting, but this could obviously be countered by using higher laser power. This should provide researchers with a degree of flexibility to adapt our method to their chosen application. Illustrative examples of experimental limits are included in the SI Appendix.

3.4 Materials and Methods

Optical deformation was calculated using a stress-balance equation at the air-droplet interface⁶⁷. The effect of electromagnetic heating on particle radius was calculated using a previously derived equilibrium condition¹⁷. Aerosol particle measurements were performed using a dual-beam optical trap, the schematic of which is shown in SI Appendix, Fig. S3. Detailed materials and methods are described in the SI Appendix.

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Chapter 4 Rationale

Accurate calculations using generalized Lorenz-Mie theory (see Section 1.3.3) require knowledge of the position of the particle centre relative to the laser beam waist. When using dual-beam optical traps, it is common to assume that the focal points of each beam overlap and the particle becomes trapped at this location, or if the focal points are not overlapped that the particle will become trapped midway between them. It was discovered as far back as the 70s that this was not always the case, and the particle may become trapped elsewhere along the beam propagation axis. Despite this, awareness of this result within the optical trapping community is not universal. We resolved to investigate this further, both theoretically and experimentally, leading to the work shown in the following chapter.

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4 Trapping positions in a dual-beam optical trap

Abstract

Optical trapping has become an important tool in a wide range of fields. While these traps are most commonly realized using optical tweezers, dual-beam optical traps offer specific advantages for certain experiments. It is commonly assumed that a particle will become trapped midway between the focal points of the two beams. However, this is not always the case. We perform a theoretical and experimental investigation of trapping positions of weakly absorbing, spherical particles in a dual-beam optical trap. We evaluate the effect of offsetting the beams in the direction of propagation and identify four regimes with distinct trapping behaviour. The effect of an offset perpendicular to the propagation direction and an imbalance in power between the two beams is also considered. Experiments utilize an aqueous aerosol particle whose size can be readily controlled and monitored over hundreds of nanometers. As such, it serves as an excellent probe of the optical trap. We demonstrate that it is possible to fit the evolution of the particle trapping position in order to determine the position of the particle relative to the focal point of each beam. The results presented here provide key insights into the workings of dual-beam optical traps, elucidating more complex behaviours than previously known.

4.1 Introduction

Since its first demonstration in 1970,¹ optical trapping has become widely used in a variety of fields, including biology, physics and aerosol science.^{2–8} Optical trapping uses the forces exerted on a particle, typically a few microns in size or less, by the reflection and refraction of light at the particle surface to immobilise it at a particular location in space. This is achieved by manipulating the laser light incident on the particle in order to balance the optical forces. While the first implementation of optical trapping used two laser beams to achieve this balance,¹ the most widespread



FIGURE 4.1: Scattering force, F_z , as a function of particle *z*-position for a particle of radius 3.55 μ m and refractive index $1.38 + i10^{-8}$ in a medium of refractive index 1 illuminated by a focused Gaussian beam with wavelength 0.532 μ m, power 150 mW and beam waist (a) 4 μ m, (b) 0.55 μ m.

method currently uses a single, tightly focused laser beam, originally referred to as a gradient force optical trap⁹ but now more commonly known as optical tweezers. However, in recent years, the utilisation of dual-beam optical traps has increased due to their superior suitability for applications such as trapping of high refractive index particles,¹⁰ trapping of large cells,¹¹ optical deformation,^{7,12} and trapping of multiple particles.^{13,14}

It is conceptually useful in optical trapping to split the optical force on the particle into two components:^{5,15,16} The scattering force, which acts in the direction that the incident light is propagating, and the gradient force, which acts towards the region of highest light intensity. The interplay between these forces and the gravitational force on the particle leads to trapping. In the dual-beam optical trap, two laser beams are aligned so that they propagate in opposite directions to one another and their focal points overlap. As such, the scattering forces from the two beams cancel each other out at the shared focal point. The gradient force then balances the gravitational force.

A simple and intuitive model for understanding where a particle becomes stably trapped along the shared propagation axis is the following: One would anticipate that the scattering force acting along the propagation axis is proportional to the laser light intensity, leading to a maximum at the focal point of the beam that diminishes as the particle moves in any direction away from this. There is also some asymmetry as the beam converges before and diverges after the focal point, producing a profile similar to Fig. 4.1(a). Therefore, if the focal points are perfectly overlapped, the particle will become trapped at this point, and if the focal points of the beams are offset from each other, the particle will become trapped midway between the two focal points. However, this simple approach neglects more complex effects which arise due to the interference of light and the size of the laser beam waist relative to the particle. These effects may lead to the scattering force taking an "M-shaped" profile, as first shown by Roosen using geometric optics¹⁷ and more rigorously by Barton and Schaub using the full electromagnetic theory.¹⁸ Such a profile is plotted in Fig. 4.1(b). This means that moving towards (away) from the focal point may in fact result in a decrease (increase) in the scattering force, potentially leading to more complex behaviour than the simple, intuitive model detailed above would suggest. For example, this "M-shaped" profile is responsible for the bistability in trapping position observed by Knox *et al.* using optical tweezers.¹⁹

The problem of where a particle becomes trapped in a dual-beam optical trap was first approached by Roosen.¹⁷ Using a fairly simple geometrical optics approach, Roosen demonstrated both theoretically and experimentally that the midway point between the focal points does not always form a stable trap. Instead, two traps that are symmetric around the midway point can be created. Since then, it has been shown that three stable trapping positions are also possible,^{20,21} and related investigations have examined multiple particles,¹⁴ spheroids,²² different beam shapes²³ and anisotropic particles²⁴ in similar setups. It seems, however, that the potential importance of these results is somewhat underappreciated. For example, Lindballe *et al.* reported the observation that particles in their experiments became trapped away from the midway point between their focal points without explanation or reference to any of the above studies.¹³ Additionally, several studies have assumed or stated as fact that particles become trapped between the focal points.^{25–28}

The manipulation of the trapping position of a particle in dual-beam traps has also received some attention in the literature. This is primarily achieved by controlling the relative powers of each beam. For instance, the effective trap stiffness in the axial direction can be improved through use of a feedback loop to adjust the powers of the counterpropagating beams.²⁶ Power imbalances between beams can also be used to hold the particle in the imaging plane of an objective used to focus one of the beams.^{27,29} Recently, oscillations in the power ratio of the two beams led to the development of an optical balance.³⁰

In this paper, we provide an experimental and theoretical investigation of the trapping positions of weakly absorbing, spherical particles in a dual-beam optical trap, paying particular attention to the variation with particle radius. We begin by investigating the force on a particle from a single Gaussian beam, examining in detail the relationship between the relative size of the particle and the beam waist of



FIGURE 4.2: Schematic of the setup used to make measurements.

the Gaussian beam. We then look at the predicted trapping positions and how they change as the two beams are offset along the *z* axis (parallel to the beam-propagation axis). The additional effects of having offsets in the *x*-direction (perpendicular to the beam-propagation axis), and of a power imbalance between the two beams are also investigated theoretically. Experimentally, we perform a series of measurements where the focal points of the two beams forming a dual-beam optical trap are offset by different amounts. At each offset, we track the position of an aqueous NaCl particle as it shrinks in size. Aqueous aerosol particles are a powerful tool for these measurements as their size can be measured with high precision (± 1 nm) and controlled by changing the relative humidity of the surrounding air.³¹ We also demonstrate that particle trajectories can be fit in order to determine the offsets of the Gaussian beam focal points in the *x*- and *z*-dimensions, as well as the power imbalance between the two beams.

4.2 Experimental

Our experiments utilise a dual-beam optical trap, a schematic of which is shown in Fig. 4.2, similar to the setup described in Ref. 32. Briefly, a $\lambda = 0.532 \,\mu$ m laser beam (Opus 532, Laser Quantum) is passed through a $1.2 \times$ beam expander. A polarizer then ensures the polarization of the beam is such that the light is split evenly into two arms when incident on a polarizing beamsplitter. Each arm is then focused

through a 50× objective (SLMPLN50X, Olympus) into a custom-built trapping cell to a beam waist of $w_0 = 0.55 \ \mu$ m as measured by the knife-edge method. Aqueous NaCl aerosol was introduced into the cell using a medical nebulizer (TurboBOY SX, PARI), where a single particle became trapped. The relative humidity (RH) in the cell was controlled by mixing dry and humidified nitrogen, the flow rates of which were controlled by mass-flow controllers (MF-1, MKS Instruments). In our experiments, the RH was initially set to 90 %, then lowered in 2 % increments every 100 s to 60 %. This was repeated multiple times, with one of the objectives having been translated in the *z*-direction by 10 μ m each time.

Once trapped, the particle was illuminated through a window perpendicular to the trapping-beam axis with a blue LED (M455L3, Thorlabs). This allowed the particle to be imaged using a $10 \times$ objective (ELWD PLAN APO 10X, Motic) and a CMOS camera (DCC1545M, Thorlabs). Concurrently, cavity-enhanced Raman spectra were measured using a Raman spectrograph (IsoPlane SCT 320, Princeton Instruments) connected to a CCD (PIXIS:100b eXcelon, Princeton Instruments).

4.3 Theory

Optical forces were calculated using generalized Lorenz–Mie theory (GLMT)^{33–35} using the mathematical expressions for the radiation pressure forces from Ref. 36. Computational time constraints required the use of analytic expressions for the GLMT beam-shape coefficients (BSCs). Gaussian BSCs were calculated using previously derived expressions.³⁷ As the beam used in our experiments was tightly focused, i.e. $s = 1/(w_0\lambda) = 0.154$, the accuracy of these analytic BSCs was verified across a range of representative cases using BSCs that were calculated numerically using the fields of a fifth-order corrected Gaussian beam.³⁸ While calculated forces for the numerical and analytic results did not always show good agreement, the results of interest to the current work are equilibrium positions and those always matched extremely well between the two sets of calculations. Therefore, the analytic BSC expressions were determined to be suitable for the model of our dual-beam optical trap.

To calculate the forces from two beams, we take the axis along which the Gaussian beams propagate to be the *z*-direction, with the net force in this direction denoted as F_z . While F_z also contains a contribution from the gradient force, we refer to it as the scattering force throughout for simplicity.³⁹ Since we are considering a geometry in which we have two counterpropagating beams, one propagates in the +*z*-direction (+*z*-beam), and the other in the -*z*-direction (-*z*-beam). The focal point of the -*z*-beam is taken to be z = 0, with the beam offset, Δz , denoting the



FIGURE 4.3: Scattering force, F_z , on a particle as a function of radius and *z*-position from a single Gaussian beam of beam waist (a) 0.55 μ m, (b) 2 μ m, (c) 4 μ m, and (d) 10 μ m. In all cases, the beam wavelength is 0.532 μ m and has a power of 150 mW. The refractive indices of the particle and medium are $1.38 + i10^{-8}$ and 1, respectively.

position of the +*z*-beam focal point relative to this chosen 0. Thus, for any particle position along the *z* axis, we can find the position of the particle relative to each focal point and use a single-beam calculation to find the scattering force from each beam. For convenience, we denote the midway point between the two focal points as z_{mid} . F_z at a given point along the *z* axis is $F_z = F_z^{+z} - F_z^{-z}$, where F_z^{+z} and F_z^{-z} are the scattering forces on the particle from the +*z*- and -*z*-beams, respectively. The particle's (*x*, *y*)-coordinates are fixed at (0,0) as this is where the gradient force will draw the particle to irrespective of the particle's *z*-coordinate (except for calculations in which the beams are also offset along *x* axis). We use two criteria to assess whether a *z*-position represents a stable trapping position or not: (i) F_z must be equal to 0, and (ii) there must be a restoring force to return the particle to this position were it to deviate, i.e. $\partial F_z/\partial z < 0$.

4.4 **Results and Discussion**

4.4.1 Force from a single beam

Fig. 4.3 shows the scattering force on a particle as a function of its z-position and radius from a single Gaussian beam with different beam waists: (a) 0.55 μ m, (b) 2 μ m, (c) 4 μ m and (d) 10 μ m. The refractive indices of the particle and its surrounding medium are $1.38 + i10^{-8}$ and 1, respectively, chosen to represent a weakly absorbing aqueous aerosol particle suspended in air. In the most tightly focused case (Fig. 4.3(a)), we see that across all radii there are two maxima, one on either side of z = 0. Additionally, there is a third peak which appears periodically as a function of radius at $z \approx 0$. In Fig. 4.3(b) the beam waist increases to 2 μ m. Similar to Fig. 4.3(a), the beam waist is smaller than the particle radius in all cases and we retain the two peaks either side of z = 0. However, there is no longer the periodic appearance of the third peak at $z \approx 0$. Instead there is a periodic oscillation in the central minimum of the "M-shaped" profile. In Fig. 4.3(c), where the beam waist is 4 μ m, we see a transition in behaviour. When the particle radius is less than the beam waist the force profile takes the form of a single, asymmetric peak. However, as the radius becomes comparable to and then exceeds the beam waist, we see that this peak splits into two separate peaks which diverge with growing radius, similar to the behaviour observed in Fig. 4.3(b). Finally, in Fig. 4.3(d) the beam waist is larger than any of the radii considered. In this case, the force profile consists of a single asymmetric peak across all radii. Any slice at a fixed radius is qualitatively similar to the curve shown in Fig. 4.1(a).

Single-peak profiles are explained as follows: So long as the particle is smaller than the beam width (i.e. the radius of the Gaussian beam) at a given point on the z axis, then the smaller the beam width the more light is incident on the particle, thus leading to an increased scattering force. This would result in a symmetric peak centred around the beam waist. However, because the beam is converging for z < 0and diverging for z > 0, the forces on either side of the beam waist are different, leading to an asymmetric peak reaching a maximum before the beam waist.

Two-peak profiles can be rationalised using a similar logic. When the particle is larger than the beam width, there is relatively little diffraction compared to when the width is similar to the particle radius. Hence, the scattering force increases on either side of z = 0 until the beam width approximately matches the particle radius. Thereafter, the scattering force falls as the beam width increases, as there is a decrease in the amount of light interacting with the particle. Again, the difference between the converging and diverging parts of the beam introduces asymmetry into the force profile, both in the magnitude of the peaks and their positions relative to



FIGURE 4.4: Scattering force, F_z , from a single Gaussian beam at z = 0 as a function of radius for several beam waists, with force profiles from an optical slab and a plane wave added for comparison. The Gaussian beam has a wavelength of 0.532 μ m and a power of 150 mW in all cases, and the refractive indices of the particle and its surrounding medium are $1.38 + i10^{-8}$ and 1, respectively. The results for the optical slab used a refractive index of 1.38 for the slab.

z = 0. As is clear in Figs. 4.3(a–c), the peak in the converging region of the beam is greater in magnitude than the peak in the diverging region. Furthermore, the peak in the converging part of the beam appears closer to z = 0 than the peak in the diverging region, although this becomes less pronounced as the beam waist increases.

We also observe a third peak appearing periodically near z = 0 in Fig. 4.3(a). Specifically, when considered as a function of the particle diameter, adjacent peaks in the $F_z(z = 0)$ slice are separated by $\lambda/2n$, where λ is the wavelength of the incident light in the surrounding medium and n is the real part of the particle's refractive index. This can be explained by considering the effect of light which is incident on the particle directly along the z axis. In this case, we can approximate the light as propagating through an optical slab equal in thickness to the diameter of the particle. This simple model is presented in the Appendix and yields that the radiation pressure on the slab varies as a function of $\cos(2nD/\lambda)$, where D is the slab thickness (equivalent to particle diameter), thus matching the periodicity observed for the central peak in Fig. 4.3(a).

Fig. 4.4 shows $F_z(z = 0)$ as a function of radius for several beam waists, as well as the results for an optical slab (bottom) and a plane wave (top). Beginning from the bottom curve, the results for the optical slab show the aforementioned sinusoldal oscillation. This oscillation remains the dominant feature of the $F_z(z = 0)$ curves for beam waists up to 1.5 μ m, with the peaks undergoing a slight shift as the beam waist increases. For beam waists of 2–3 μ m, the amplitude of the sinusoidal oscillations decreases markedly. Finally, upon further increase of the beam waist we observe the appearance of sharp peaks, corresponding to the excitation of morphology-dependent resonances (MDRs). This trend is explained as follows: By virtue of the Gaussian profile of the beam, the light intensity is greatest at its centre (i.e. exactly along the *z* axis). Furthermore, the smaller the beam waist, the greater the intensity of the light propagating along this axis. Thus, for small beam waists a large fraction of the light incident on the particle interacts with the particle as if it were an optical slab, producing the sinusoidal oscillations we observe. Here we note that Burnham and McGloin have previously observed sinusoidal oscillations in particle height above a cover slip using optical tweezers.⁴⁰ Given the tight focusing achieved by the oil-immersion objective used in that study, we suggest that this oscillating peak around z = 0 may explain the behaviour observed in that experiment. As we increase the beam waist, we simultaneously decrease the contribution of "slab effects" and increase the contribution of refraction to the total scattering force on the particle. This leads to the diminishing amplitude of the oscillations and the transition to an almost linear profile, with small oscillations as a function of particle size. Finally, as the beam waist becomes comparable to the particle size, we begin to excite MDRs,⁴¹ where light experiences constructive interference as it propagates via total internal reflection inside the surface of the particle. This increasingly becomes the dominant effect in our force profiles, eventually nearly matching the case of the plane wave, which represents the limiting case of purely refractive effects on F_z .

4.4.2 Effect of beam offset in *z*-direction

We now consider the optical forces exerted on a particle by two counterpropagating beams. Fig. 4.5 shows the net scattering force on the particle as a function of radius and *z*-position for various offsets between the two focal points. Note that in order to fulfill the requirements given in Section 4.3, stable trapping positions on these plots appear white, with red on the left and blue on the right. Going from (a) to (f), the +z-beam is moved in the +z-direction while the -z-beam is fixed, and in doing so several different behaviours emerge. Beginning with (a), we see that across all radii,

 z_{mid} is a stable trapping position. Furthermore, for some radii, there are additional stable trapping positions near either focal point. In (b), we have undergone a transition. Now z_{mid} is not stable for any particle. Instead, the only stable traps are located near either of the two focal points. Furthermore, we see that these stable trapping positions oscillate as a function of radius. Moving the focal points even closer together in (c), we see that neither z_{mid} nor the focal points are stable across all particle radii. Instead, the midway point forms a stable trap over small ranges of radii. Outside of these ranges there are two possible trapping positions, again which oscillate with radius. These two behaviours (stable at the midway point and bistable away from the midpoint) alternate as the particle grows/shrinks. When the focal points are perfectly overlapped (not shown), particles of all radii only become trapped at the shared focal point. As the offset becomes positive in (d), we return to similar behaviour to that observed in (c), with z_{mid} forming a stable trap only for some radii. Upon further increasing Δz , we obtain the situation shown in (e), where the only stable trapping position is at z_{mid} . Finally, in (f), we observe that, once again, z_{mid} is no longer a stable trapping position and stable trapping positions are only formed for certain radii near either focal point. This set of results seemingly contradicts the work of Kraikivski et al.,²⁷ who claim that when the particle is smaller than the beam waist stable trapping only occurs for $\Delta z > 0$ (note that the sign convention for Δz in their paper is the opposite from that which we have chosen). The beam waist is smaller than all radii shown in Fig. 4.5, yet we predict that trapping will occur for particles of all radii over a range of Δz spanning from negative to positive values (and we demonstrate this experimentally in Section 4.4.5), although we note that there is a lower degree of symmetry in the work of Kraikivski et al. than exists in the calculations shown here.

We can gain insight into the cause of these different behaviours and over what ranges of offset we can expect to observe them by examining Fig. 4.6. This figure shows sample force profiles for the +*z*-beam at different offsets for a particle with three peaks in its force profile (radius 4 μ m, shown in green) and a particle with two peaks in its force profile (radius 3.94 μ m, shown in blue). The magnitude of the force from the corresponding –*z*-beam is shown in black for both. The different behaviours can be characterised by the offset between the two focal points and the positions of the maxima in the force profile. Considering a two-peak force profile, such as the one shown in Fig. 4.1(b), we denote the maximum occurring at *z* < 0 as z_{max}^{-} , and the maximum occurring at *z* > 0 as z_{max}^{+} . To identify stable trapping positions in these plots, we require the +*z*- and –*z*-beam profiles to intersect (giving $F_z = 0$), and for the force from the -z-beam to be larger at values of *z* slightly greater than this intersection (giving $\partial F_z/\partial z < 0$).



FIGURE 4.5: Sample calculations of scattering force, F_z , as a function of radius and particle *z*-position for two counterpropagating Gaussian beams, with focal point offsets of (a) $-45 \ \mu$ m, (b) $-20 \ \mu$ m, (c) $-5 \ \mu$ m, (d) $5 \ \mu$ m, (e) $20 \ \mu$ m and (f) $45 \ \mu$ m. Each beam has wavelength 0.532 $\ \mu$ m, beam waist 0.55 $\ \mu$ m and power 150 mW. The refractive indices of the particle and medium are $1.38 + i10^{-8}$ and 1, respectively.



FIGURE 4.6: Magnitude of the force acting in the +z-direction, $|F_z^{+z}|$, as a function of z for particles of radius 4 μ m (green) and 3.94 μ m (blue) with the +z-beam focused at (a) -45 μ m, (b) -20 μ m, (c) -5 μ m, (d) 5 μ m, (e) 20 μ m and (f) 45 μ m. The magnitude of the force acting in the -z-direction, $|F_z^{-z}|$, is shown in black in all cases, with the midway point between the two focal points indicated by the black dashed line. Each beam is a Gaussian beam of wavelength 0.532 μ m, beam waist 0.55 μ m and power 150 mW. The particle and its surroundings have refractive indices of $1.38 + i10^{-8}$ and 1, respectively.

The different regimes of trapping behaviour depend on the relative positions of the peaks in the force profiles of the +z- and -z-beams. In Fig. 4.6(a), the beams are aligned such that $\Delta z + z_{max}^+ < -z_{max}^+$ (i.e. z_{max}^+ of the +z-beam occurs before z_{max}^+ of the -z-beam). We see that both the two- and three-peak profiles form stable optical traps at the midway point between the focal points (black dashed line). Furthermore, the two-peak profile produces an additional two stable traps. It is clear how this results in the behaviour seen in Fig. 4.5(a), where the midway point is always stable, and additional traps form intermittently as a function of radius. Moving to Fig. 4.6(b), the beams are now aligned such that $-z_{max}^+ < \Delta z + z_{max}^+ < -z_{max}^-$ (i.e. z_{max}^+ of the +z-beam is located between the peaks in the -z-beam force profile). We see that both examples display the same general behaviour: The midway point does not form a stable optical trap, with traps forming on either side of the midway point, as seen across all radii in Fig. 4.5(b). Fig. 4.6(c) displays another case of $-z_{max}^+ < \Delta z + z_{max}^+ < -z_{max}^-$. Whilst the behaviour of the two-peak profile has not changed from (b), the three-peak profile has. Now, a stable optical trap only forms at z_{mid} . Thus, the intermittent appearance of the peak at $z \approx 0$ as a function of radius, as shown in Fig. 4.3(a), leads to the alternating behaviour seen in Fig. 4.5(c), where z_{mid} is stable for some radii but not others. As Δz becomes positive, its magnitude in combination with z_{max}^{-} becomes important, beginning with the case where $-z_{max}^+ < \Delta z + z_{max}^- < -z_{max}^-$ (i.e. z_{max}^- of the +z-beam profile lies between the peaks of the -z-beam profile). While the behaviours seen in Fig. 4.5(c) and (d) appear similar, with z_{mid} being stable only over certain ranges of radius, we can discern a subtle distinction between the two cases by considering Fig. 4.6(c) and (d). Whereas in (c) the midway point is stable for radii showing three peaks in their force profile, and unstable for radii with only two, the opposite is true in (d). The three-peak profile now forms one stable trap on either side of the midway point, and the two-peak profile produces a single stable trapping position at z_{mid} . In Fig. 4.6(e), we remain in the regime $-z_{max}^+ < \Delta z + z_{max}^- < -z_{max}^-$, but the central peak in the three-peak profile no longer plays a role. A single, stable optical trap forms at z_{mid} for all radii, giving us the behaviour observed in Fig. 4.5(e). Finally, in Fig. 4.6(f) we consider the behaviour of beams aligned such that $\Delta z + z_{max}^- > -z_{max}^-$ (i.e. z_{max}^- of the +z-beam is located after z_{max}^- of the -z-beam). In this case, we see that for the three-peak example, no stable traps are formed at all. However, in the two-peak example, there are two possible trapping positions, one on either side of z_{mid} . This produces the results seen in Fig. 4.5(f), where z_{mid} never forms a stable optical trap, but traps can be seen over limited ranges of radii.

To summarise, there are four broad regimes of focal point offsets which lead to transitions in the trapping behaviour of a particle in a dual-beam optical trap: $\Delta z + z_{max}^+ < -z_{max}^+, -z_{max}^+ < \Delta z + z_{max}^+ < -z_{max}^-, -z_{max}^+ < \Delta z + z_{max}^- < -z_{max}^-$ and $\Delta z + z_{max}^- > -z_{max}^-$. In these regimes, a particle of a given radius may have between 0 and 3 stable trapping positions as shown in Figs. 4.5(a,b,e,f). Additionally, if the beams are sufficiently tightly focused such that the force profile at a given radius may display three peaks as opposed to two, then the middle two regimes may be further divided, displaying the behaviour as a function of radius seen in Fig. 4.5(c,d). It is important to emphasise that, based on the results of Sections 4.4.1 and 4.4.2, these four regimes will exist whenever the particles being trapped are larger than the beam waist of the beams used to form the dual-beam optical trap. Researchers designing and using dual-beam optical traps should be aware of this, and account for it when interpreting results that depend on where the particle is trapped.

4.4.3 Combined effect of offsets in *x* and *z*

We now examine the potential effects of the focal points being simultaneously offset in both the *z*-direction (parallel to the direction of light propagation) and in the *x*direction (perpendicular to the direction of light propagation). This complicates the calculation of trapping positions because now we must scan the *xz*-plane for points which form both a stable optical trap in the *x*-dimension ($F_x = 0$ and $\partial F_x / \partial x < 0$) and in the *z*-dimension ($F_z = 0$ and $\partial F_z / \partial z < 0$).

Calculations examining this are shown in Fig. 4.7 for various *x*-offsets and combinations of beam polarization, with the *z*-offset such that a particle is always trapped at z_{mid} . We see that when the beams are polarized in the same plane (a–c), offsetting the focal points in the *x*-dimension does not affect the trapping position in the *z*-dimension. The particle will remain trapped midway between the focal points irrespective of its radius. In contrast, when the beams are cross-polarized (d–f), an *x*-offset between the focal points gives rise to a change in the particle's trapping behaviour in the *z*-dimension. As shown in Fig. 4.7(d), in the absence of an offset in *x*, the particle is trapped midway between the focal points independent of its radius. However, as the beams are offset by 1 μ m and 2 μ m (Fig. 4.7(e) and (f), respectively), we see that the stable trapping position begins to oscillate with size, and also its mean position shifts away from the midway point in the *z*-dimension. Also notable is that the amplitude of the oscillations with radius is markedly smaller than those observed when the beams are coaxial in *x* but offset in *z* such that particles are trapped away from z_{mid} , e.g. Fig. 4.5(b).

Further calculations examining the effect of *x*-offsets are shown in Fig. 4.8, now with Δz chosen such that particles are trapped away from z_{mid} . This time we see that the particle trajectory as a function of radius changes irrespective of the relative



FIGURE 4.7: Scattering force, F_z , on a particle as a function of radius and *z*-position from two counterpropagating Gaussian beams, with stable trapping positions indicated by the black line. In all cases, the particle refractive index is $1.38 + i10^{-8}$ and the refractive index of the surrounding medium is 1. Each beam has wavelength 0.532 μ m, beam waist 0.55 μ m and power 150 mW. The focal points of the beams are offset by $\Delta z = 10 \ \mu$ m in the *z*-direction. Offsets in the *x*-direction are 0 μ m (a,d), 1 μ m (b,e) and 2 μ m (c,f). In the left column (a–c), the beams are polarized perpendicular to one another.



FIGURE 4.8: Scattering force, F_z , on a particle as a function of radius and *z*-position from two counterpropagating Gaussian beams. In all cases, the particle refractive index is $1.38 + i10^{-8}$ and the refractive index of the medium is 1. Each beam has wavelength 0.532 μ m, beam waist 0.55 μ m and power 150 mW. The focal points are offset by $\Delta z = -20 \,\mu$ m in the *z*-direction. Offsets in the *x*-direction are 0 μ m (a,d), 1 μ m (b,e) and 2 μ m (c,f). In the left column (a–c) the beams are polarized in the same plane, and in the right column (d–f) the beams are polarized perpendicular to one another.

polarization of the beams. Thus, parallel polarization of the beams only suppresses the effect of an offset in x when the particle is trapped at z_{mid} . Additionally, the effect of the x-offset on the z trapping position for perpendicular beam polarization is less noticeable when the particle is not trapped at z_{mid} than when it is (compare Fig. 4.7(d–f) and Fig. 4.8(d–f)). In the latter case, the oscillations in trapping position are dominated by the effects of the z-offset, whereas when the particle is trapped at or close to z_{mid} any oscillations are caused solely by the x-offset.

We make similar observations when considering the trapping position of the particle in the *x*-dimension. Fig. 4.9 shows the trapping position of particles in the *x*-dimension with $\Delta z = 10 \,\mu$ m and Δx set to $0 \,\mu$ m (a,d), $1 \,\mu$ m (b,e) and $2 \,\mu$ m (c,f). The beams are polarized in the same plane in the left column (a–c), and perpendicular to one another in the right column (d–f). As expected when $\Delta x = 0$, the particle is trapped at x = 0 independent of its radius, with no difference between the two combinations of polarization. Upon offsetting the beams in the *x*-dimension, the difference between the two combinations of polarization is clear. Whereas particles of any radius are always trapped midway between the two focal points in *x* when the beams are polarized in the same plane (panels (b) and (c)), this is not the case when the beams are polarized in perpendicular planes. Not only are particles not trapped at the midway point in *x* when the beams are polarized perpendicular to one another, but the *x* trapping position also oscillates as the particle radius changes.

As with the *z* trapping position, the effects of polarization on the *x* trapping position are less pronounced when the particle is trapped away from z_{mid} , as shown in Fig. 4.10. The beams are polarized in the same plane in the left column (a–c) and perpendicular to one another in the right column (d–f). As with Fig. 4.8, the relative polarization of the beams makes only a small difference. Regardless of the relative polarizations, we see that, as in Fig. 4.9, particles are trapped at x = 0 independent of their radius when there is no *x*-offset (panels (a) and (d)). However, in contrast to Fig. 4.9, displacing the beams in the *x*-dimension leads to small oscillations in the stable *x* trapping position irrespective of the relative polarization of the beams. Furthermore, rather than becoming trapped close to, or exactly, midway between the focal points in the *x*-dimension, the oscillations instead occur close to one of the focal points, with small differences in the proximity to the focal point dependent on the relative polarization of the beams. Thus, similar to the observations for the *z* trapping position in Fig. 4.8, the relative polarization of the beams has little effect on the trapping positions.

In summary, introducing an offset between the focal points in the *x*-dimension affects the trapping behaviour of particles as a function of radius both in the *x*- and



FIGURE 4.9: Gradient force, F_x , acting on a particle as a function of radius and *x*-position from two counterpropagating Gaussian beams. In all cases, the particle refractive index is $1.38 + i10^{-8}$ and the refractive index of the medium is 1. Each beam has wavelength 0.532 μ m, beam waist 0.55 μ m and power 150 mW. Beams are polarized in the same plane in the left column (a–c), and mutually perpendicular in the right column (d–f).The focal points are offset by $\Delta z = 10 \ \mu$ m in the *z*-direction. Offsets in the *x*-direction are 0 μ m (a,d), 1 μ m (b,e), and 2 μ m (c,f). Stable trapping positions are shown in black.



FIGURE 4.10: Gradient force, F_x , acting on a particle as a function of radius and *x*-position from two counterpropagating Gaussian beams. In all cases, the particle refractive index is $1.38 + i10^{-8}$ and the refractive index of the medium is 1. Each beam has wavelength 0.532 μ m, beam waist 0.55 μ m and power 150 mW. Beams are polarized in the same plane in the left column (a–c), and mutually perpendicular in the right column (d–f).The focal points are offset by $\Delta z = -20 \ \mu$ m in the *z*-direction. Offsets in the *x*-direction are 0 μ m (a,d), 1 μ m (b,e), and 2 μ m (c,f). Stable trapping positions are shown in black.

z-dimensions. These effects differ based on the relative polarization of the two counterpropagating beams, and whether the particle is trapped at or away from z_{mid} in the *z*-dimension. When trapped at z_{mid} , the effect of relative polarization is most obvious. If the beams are polarized in the same plane, then the particle's *xz* trapping position does not vary with the particle size. Particles of all radii are trapped midway between the focal points in both the *x*- and *z*-dimensions. On the other hand, if the beams are polarized in perpendicular planes then offsetting the focal points in the *x*-dimensions. When particles are trapped away from z_{mid} , then the effects of relative polarization are less pronounced. Irrespective of relative polarization, an offset in the *x*-dimension. With respect to the *x*-dimension, both combinations of polarization also produce small oscillations in the *x* trapping position. Furthermore, the *x* trapping positions are located close to the focal points, rather than close to midway between them.

4.4.4 Effect of imbalance in beam powers

So far, we have assumed that the power in each of the counterpropagating beams is perfectly matched. Now, we consider the implications of the beams having slightly different powers. Computationally, this is easy to do since the scattering force scales linearly with beam power. Therefore, rather than having to recalculate the force for each beam power we wish to consider, we need only a single calculation for the perfectly balanced case, which is then multiplied by some factor. If the total power of both beams is P_t , then the power in a single beam is $P_b = P_t/2$. Denoting the powers of the +*z*- and -*z*-beams as P^{+z} and P^{-z} respectively, we define the power imbalance as $\Delta P = (P^{+z} - P^{-z})/P_t$. We can then calculate the power in each beam for a given value of ΔP using

$$P^{\pm z} = P_b \pm \frac{\Delta P}{2} P_b, \tag{4.1}$$

and the total scattering force for a given power imbalance is:

$$F_z = \frac{P^{+z}}{P_b} F_z^{+z} - \frac{P^{-z}}{P_b} F_z^{-z}.$$
(4.2)

Fig. 4.11 shows the effect of a power imbalance between the beams for two *z*-offsets: $\Delta z = -20 \ \mu m$ (a–c) and $\Delta z = 0 \ \mu m$ (d–f). We see that when the particle is trapped at z_{mid} in the absence of a power imbalance, e.g. Fig. 4.11(e), then a power imbalance between the beams gives rise to small oscillations in the trapping


FIGURE 4.11: Scattering force, F_z , on particles as a function of radius and *z*-position from two counterpropagating Gaussian beams offset in the *z*-direction by $-20 \ \mu\text{m}$ (a–c) and perfectly overlapped (d–f). The difference in power between the beams, ΔP , is -10% (a,d), 0% (b,e) and +10% (c,f). Each beam has wavelength 0.532 μ m and beam waist 0.55 μ m, and the total power in both beams is 300 mW in all cases. The particle and surrounding medium refractive indices are $1.38 + i10^{-8}$ and 1, respectively.

position as a function of radius (shown in Fig. 4.11(d,f)). On the other hand, when the particle is trapped away from z_{mid} , e.g. Fig. 4.11(b), then a power imbalance between the beams does little to alter the trapping position as a function of radius, as seen by the similarity between (a–c).

4.4.5 Experimental observations

Some of the predictions made in Section 4.4 were tested experimentally. To do so, we used an aqueous NaCl particle suspended in moist air. This is a particularly suitable tool for testing our predictions, as the size of the particle can be controlled easily by changing the relative humidity of the surrounding air, and the radius and refractive index can be retrieved with high accuracy (1 nm and 10^{-4} respectively).⁴² In our experiments, the particle was trapped at high relative humidity, which was then gradually lowered in order to make the aqueous NaCl particle shrink. While this happened, the particle position was monitored using a microscope and images were analysed using a MATLAB script. Cavity-enhanced Raman spectra were collected simultaneously and analysed using the MRFIT code to determine the particle radius and refractive index.⁴² Combining these allows us to track the particle position as a function of radius. This experiment was repeated multiple times, with one objective being translated along the *z* axis in between repetitions.

The relative positions of the focal points of the two objectives in the *xz*-plane, Δx and Δz , and the power imbalance between the beams, ΔP , are obtained by fitting the measured particle trajectory from the microscope using a grid search. First, we calculate the force from a single beam on particles over the radius range obtained through the fitting of cavity-enhanced Raman spectra as a function of x and z. Then, the total force on a particle is found by summing the forces from each beam for a given combination of Δx , Δz and ΔP . This provides a map of the forces on the particle in the *xz*-plane. Stable trapping positions for a given combination of offsets are then determined by scanning this force map for points meeting the conditions outlined in Section 4.4.3. In cases where there are two stable trapping positions for each radius, these are separated into two distinct trajectories. The last task is to project the particle positions obtained in the microscope images onto the z axis of the calculations. This is done by finding the position of the particle in each frame of the microscope images relative to the mean position for the experiment. Then, based on the trajectories for a given combination of offsets, we choose a range of z-values to be the mean position. For each of these chosen means, we calculate the sum square error, with the minimum of these taken to be the error for a given

Panel	Δz_{exp} (μ m)	Δz_{fit} (μ m)	Δx_{fit} (μ m)	ΔP_{fit} (%)
(a)	-40	-19.5	4.00	
(b)	-30	-11.5	3.50	—
(c)	-20	-6.5	0.50	-8.0
(d)	-10	2.5	0.75	-5.5
(e)	0	10.0	0.50	-6.5

TABLE 4.1: Best-fit results for the series of experiments shown in Fig. 4.13.

combination of offsets and power imbalance. The best-fit combination of offsets and power imbalance is then the combination which has the overall minimum error.

Fig. 4.12 compares the quality of fits searching only for Δz (a,d), for both Δz and Δx (b,e) and for Δz , Δx and ΔP (c,f). Whilst in (a) we capture the experimental trajectory quite well using only Δz as a fitting parameter, we do not capture any of the oscillations present in the second experiment shown in (d). Furthermore, because several values of Δz produce a straight trajectory, we do not retrieve a unique value of Δz . Expanding the search to include Δx improves the fits of both. Comparing (b) to (a), we see that the amplitudes of the predicted oscillations now match the observed oscillations much more closely, as well as the general shape. Comparing (e) to (d), we now see that our best-fit trajectory contains oscillations, leading to a much better comparison with the experimental trajectory. However, the predicted amplitudes of the oscillations are slightly smaller than the measurements. Lastly, the inclusion of ΔP as a fitting variable has mixed success. In the case of the first experimental trace, there is no obvious improvement to the fit as we compare (c) to (b), albeit we do see a small decrease in the sum square error. On the other hand, comparison of (f) to (e) reveals a strong improvement in the fit, both visually and in terms of reduction in the sum square error. Whilst the fit in (e) is certainly good, the fit shown in (f) is excellent, with the amplitudes of the oscillations in the predicted trace now matching those of the observed trace almost exactly. This reflects the above observation that a power imbalance between the beams plays a significant role when the particle is trapped at z_{mid} , but only a minor role when the z-offset is such that large oscillations in trapping position are induced. As such, when fitting particle trajectories we only use ΔP as a fitting parameter when the particle is trapped close to z_{mid} .

Best fits of a series of measurements are shown in Fig. 4.13, with the corresponding best-fit parameters shown in Table 4.1. We see that in all cases accurate fits are obtained, utilising only Δz and Δx in Fig. 4.13(a,b), with fits for panels (c–e) also fitting for ΔP . As stated in Section 4.2, the objective transmitting the +*z*-beam was translated by 10 μ m in the +*z*-direction between experiments, meaning we expect



FIGURE 4.12: Sample fits of two experiments fitting only for Δz (a,d), fitting for Δz and Δx (b,e), and fitting for Δz , Δx and ΔP (c,f). The calculated scattering force is indicated by the colorscale, the experimental datapoints by green circles, and the best-fit trajectory by a black line. Best-fit parameters are: (a) $\Delta z = -21.5 \ \mu$ m; (b) $\Delta z = -19.5 \ \mu$ m, $\Delta x = 4 \ \mu$ m; (c) $\Delta z = -18.5 \ \mu$ m, $\Delta x = 4 \ \mu$ m, $\Delta P = 10 \ \%$; (d) $\Delta z = 9 \ \mu$ m; (e) $\Delta z = 6 \ \mu$ m, $\Delta x = 1 \ \mu$ m; and (f) $\Delta z = 10 \ \mu$ m, $\Delta x = 0.5 \ \mu$ m, $\Delta P = -6.5 \ \%$. Each beam is a Gaussian of wavelength 0.532 $\ \mu$ m and beam waist 0.55 $\ \mu$ m, with a combined power of 300 mW in all cases.

Particle radii and refractive indices were retrieved using MRFIT.



FIGURE 4.13: Best fits of particle trajectories for a series of measurements. The colorscale indicates the calculated scattering force, F_z , the measured particle trajectory is shown in green circles, and best-fit trajectories are shown in black. For calculations, each beam is a Gaussian beam of wavelength 0.532 μ m and beam waist 0.55 μ m, with a total power in both beams of 300 mW. Particle radii and refractive indices were retrieved using MRFIT.

that the retrieved values of the offset, Δz_{fit} , should also be spaced by 10 μ m. Examination of Table 4.1 reveals that our fits did not return such steps, instead giving smaller changes in Δz between each experiment. However, the trend is correct as Δz increases between all measurements. Furthermore, the quality of the fits we obtained to the experimental data indicates that the values of Δz we retrieve by fitting are accurate. We suggest the reason for the discrepancy between expected and retrieved changes in Δz is due to a decline in the accuracy of the translation stage over time. Translation stages are also the likely origin of the offset in the *x*-direction. Although the beams are aligned in the x-direction prior to trapping a particle, as the objective is translated in the z-direction, despite our best efforts, small shifts in the objective's x-position cannot be eliminated. The origin of the power difference between the beams is likely due to a combination of factors. Prior to trapping a particle, the powers of the two beams are balanced using power meters placed before each of the trapping objectives using the polarizer placed before the beamsplitter. During the experiment, mechanical vibrations could alter the position of the polarizer, leading to an imbalance in the beam powers. Additionally, the power meters may have slightly different sensitivities, and the objectives may have slightly different transmissions. Therefore, the cause of the power imbalance is likely a combination of these three factors.

Whatever the origins of these deviations from the ideal case of the beams being coaxial in *x* and having equal power, the ability to fit particle trajectories and determine offsets and power imbalances is important for the interpretation of several experiments. Calculations which use GLMT require knowledge of the relative position of the particle and the focal point of the beam, and these relative positions affect not only the optical forces on the particle but also light scattering. While one may make assumptions about the relative positions of the focal points and the particle, erroneous assumptions may lead to misinterpreted results. Being able to measure the relative positions removes the need for making assumptions, allowing more accurate calculations and reducing the possibility of misinterpreting results.

4.5 Conclusions

We have presented a theoretical and experimental investigation of particle trapping positions in a dual-beam optical trap as a function of particle radius. We began by examining the scattering force from a single Gaussian beam on a particle, confirming previous studies demonstrating that the profile of the scattering force as a function of z consists of a single, asymmetric peak when the particle is smaller in radius than the beam waist, and two peaks when the particle is larger than the beam

waist. We also observed that for particularly tightly focused beams, a third peak in the force profile appears periodically as a function of radius. This third peak can be explained by considering the interference of light incident on the particle along the beam axis. We then examined the trapping position(s) of a particle illuminated by two counterpropagating beams whose focal points are offset by some amount in the z axis. We identified four regimes of offset with distinct trapping behaviours, with some additional nuances dependent on whether the particle's force profile displayed two or three peaks. Importantly, we observed that while the trapping position is constant as a function of radius if the particle is trapped at z_{mid} , trapping positions away from that point oscillate as a function of radius. The effects of allowing an additional offset in the x-direction are polarization-dependent. If the beams are polarized in the same plane, then an additional offset in x only affects trapping positions away from z_{mid} . On the other hand, when the beams are polarized perpendicular to one another, this leads to changes in trapping positions irrespective of the *z*-offset. In particular, the trapping position at z_{mid} , when stable, also begins to oscillate as a function of radius. Lastly, our calculations touched on the effect of having an imbalance between the powers of the two beams. We found that altering the beam powers had little effect on trapping positions away from z_{mid} . However, the power imbalance did affect the trapping positions at z_{mid} , inducing small oscillations around z_{mid} . Taken together, these calculations can potentially be used by experimentalists when designing dual-beam optical traps, for example in order to plan how tightly to focus their beams for the particle size range they intend to investigate, or how to arrange the focal points of beams to induce/suppress oscillations in trapping position.

We also performed experiments to observe the behaviours that were predicted. Using a microscope, the particle position was monitored as an aqueous particle shrank in response to lowering of the relative humidity. This was repeated several times, with one objective being moved in between experiments. Fitting the particle trajectories using a grid search, we were able to retrieve best-fit values of Δx and Δz , and in certain cases also ΔP . The ability to fit particle trajectories in order to retrieve these parameters may be important, as knowledge of the particle position relative to the laser focal point removes the possibility of making incorrect assumptions and misinterpreting results. Furthermore, the calculations and experiments taken together demonstrate that particles held in dual-beam optical traps display more complex behaviour than previously thought, potentially facilitating further novel experiments and applications.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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5 Discussion

Having demonstrated the use of the dual-beam optical trap to novel ends, we now examine the work of this thesis and its potential for further uses in a broader context. In Section 1.1, several key areas for aerosol research were highlighted. The development of these new approaches lays the groundwork for further research which can advance our fundamental understanding of aerosol at the single particle level, and be used to build models for use in larger scale simulations. We shall first examine how the work presented on aerosol optical properties and surface tension may help towards the broader goal of understanding aerosol properties and their atmospheric effects. We will then discuss how the results of Chapter 4 may be incorporated into further research. Additionally, we evaluate some prospects for the dual-beam optical trap to be used in meeting other challenges described in Section 1.1.

As emphasised in Chapters 1 and 2, the complex refractive index is arguably the most important parameter in determining the direct effect of aerosol on the atmosphere. While methods for determining either the real or imaginary part of the refractive index in bulk samples are well established, the simultaneous retrieval of both is more challenging, and to do so at the single particle level introduces further complexity. It is, however, necessary to make measurements on single particles in order to access the supersaturated states which aerosol particles frequently enter in the atmosphere. Extrapolation from measurements in the bulk are not always reliable. Chapter 2 demonstrates that our methodology can retrieve accurate values for the real part of the refractive index across the entire wavelength range, and the complex part of the refractive index at the laser wavelength. Furthermore, it is demonstrated that this should be applicable across a very broad range of relative humidity (RH). The results, however, are only for simple model systems, which do not rise to the complexity of real, atmospheric systems. Also, the imaginary part of the refractive index is determined only at a single wavelength, rather than across the entire wavelength range. These two challenges — applicability to real systems and retrieval of the wavelength-dependent imaginary part of the refractive index need to be addressed by future work.

In fact, some of this work has already taken place. Bain *et al.* used this method in conjunction with their proposed effective oscillator model in order to determine the

complex refractive index across the visible spectrum for a number of model atmospheric systems as a function of RH.¹ This was achieved by treating the refractive index in the visible spectrum as resulting from the tail of an absorption band in the far-ultraviolet range. The real and imaginary parts of the refractive index can then be related using the Kramers-Kronig relations, giving both parts across the entire visible wavelength range. This approach overcomes the limitation of the methodology described here, in that it can describe the complex refractive index over the entire wavelength range, even though the imaginary part is measured only at a single wavelength. Furthermore, the effective oscillator model lends itself to describing more complex systems. Since the refractive index of a mixture is described as a sum of effective oscillators, the complex refractive index of a mixture can be determined straightforwardly from a mass fraction-weighted addition. This then lends itself to the description of real systems, so long as the composition in terms of components with known oscillator parameters can be determined.

Typically, the composition of aerosol measured in the field is not known in terms of various salts. The most common way to determine the chemical composition of aerosol in the field is mass spectrometry.^{2,3} In the case of the inorganic aerosol fraction, this means the composition is determined in terms of ion concentrations, rather than the concentration of various salts. Bain & Preston therefore determined the oscillator parameters for individual ions rather than salts in subsequent work.⁴ They also derived oscillator parameters for a suite of model organic compounds. However, this was only done for the real part of the refractive index, and used optical tweezers rather than the dual-beam trap set out in Chapter 2. A logical extension of this work is then to use the methodology of Chapter 2 to also determine the imaginary part of the refractive index. It is worth noting, however, that from the point of view of larger scale regional and global climate models there is currently little interest in determining such small values of the imaginary part of the refractive index. As mentioned in Section 1.1.2, aerosol is often characterised as either absorbing or nonabsorbing. Since all of the systems measured in references 1 and 4 fall into the nonabsorbing category, the imaginary part in larger scale models is simply set to zero.⁵ However, whilst small, incorporation of the imaginary part of the refractive index would increase the accuracy of simulations.

As the title of Chapter 2 specifies, our methodology applies to weakly absorbing particles. It bears asking if this could be extended to more strongly absorbing aerosol, and if so, how? Certainly in principle, the idea of heating a particle and measuring the associated size change could be applied to any kind of particle. However, the setup and analysis framework would need to be modified. Firstly, the dual-beam optical trap described here is not suitable for trapping strongly absorbing particles.⁶ Thus, a different, more suitable type of beam profile must be used, for example a hollow beam.⁶ This would alter the analysis framework set out in Chapter 2 in two ways, both relating to the model for heating by the laser beam. Firstly, the GLMT model would need to be modified to account for the different beam profile. The model presented applies only for a Gaussian beam. Secondly, we make use of the uniform source approximation in our calculations on weakly absorbing particles. Physically, this means assuming that the energy absorbed by the particle is distributed evenly throughout the particle. This has been shown to be valid for weakly absorbing particles,⁷ however, it is not valid for strongly absorbing particles. Indeed, the photophoretic force which enables optical trapping of absorbing particles arises due to nonuniform heating of the particle.⁸ Thus, the modelling of heating in the particle would become much more computationally intensive, requiring generalized Lorenz-Mie theory calculations to determine the source function as opposed to the analytical formula of equation 2.12. This means some assumptions made in the derivations in Chapter 2 would no longer hold, specifically those which rely on symmetry in the polar and azimuthal coordinates. Additionally, other particle levitation-based techniques have already been established for determining the optical properties of strongly absorbing particles.^{9–12}

Chapter 3 represents a proof-of-concept demonstration for our approach to making single particle surface tension measurements. We shall now examine in detail how this compares with other available techniques for surface tension determination at the single particle level, and prospects for future experiments. There are three common approaches to measuring the surface tension of single aerosol particles: utilising atomic force microscopy (AFM),^{13–15} using droplet collisions brought about by optical trapping,^{16–18} and analysis of the oscillations of droplets falling from a droplet dispenser.¹⁹ We shall consider each in turn.

AFM uses a nanoscale cantilever tip to indent the surface of particles and measures the surface tension from the force the particle exerts upon it when retracting the tip. Its relative merits and drawbacks are similar to those discussed for other substrate-based methods in Section 1.2.1. AFM can access a size range which no other single particle surface tension measurement can, namely the important submicron range. However, measurements are limited to somewhat high RH due to viscous effects on the AFM tip.¹⁴ Additionally, AFM measurements are more invasive than most substrate-based methods as they also involve penetration of the particle by the tip.

The droplet collision technique relies on the use of holographic optical tweezers to trap two particles and then bring them together. Upon coalescence, the droplets oscillate for a brief period of time, with the frequency of the oscillations determined by, among other things, the surface tension. The oscillations are tracked by monitoring the amplitude of the backscattered light from the trapping laser. Utilising optical tweezers means this method retains all the advantages of particle levitation discussed in Section 1.2.1. This technique has two main limitations. Firstly, oscillations are damped more quickly as viscosity increases, placing a restrictive upper limit on the possible viscosity at which surface tension measurements can be made.¹⁶ Secondly, oscillations are also more quickly terminated by smaller particle sizes. Thus, this approach is limited to fairly large particle sizes.

Falling droplet experiments also rely on particle oscillations to extract the surface tension. However, unlike the holographic tweezers method, the falling droplets can be analysed very shortly after they are produced, allowing access to nonequilibrium dynamics. However, the timescales over which they can be observed are short, meaning aging over atmospherically relevant timescales cannot be probed. Furthermore, unlike most contact-free measurements, this technique cannot access metastable, supersaturated states. The droplets are formed from bulk solution and do not have time to equilibrate with the RH outside the droplet dispenser, thus limiting them to measurements above the deliquescence point.

The key limitations of the optical deformation technique described in Chapter 3 relative to these are as follows. Firstly, the optical deformation technique cannot be used in the submicron regime like AFM can. While trapping of particles in this size regime is possible, they are too small to support the morphology-dependent resonances (MDRs) which are necessary to measure the particle deformation. Additionally, optical deformation cannot access the early time dynamics available to falling droplet experiments. We gather spectra at a rate of 1 fps. While this could potentially be reduced somewhat, the time resolution will never be able to rival that achievable through falling droplet experiments. From a practical standpoint, our setup is also more complex than the others. AFM instruments and droplet dispensers are commercially available, and while holographic optical tweezers are a little more complex, they are no more so than the dual-beam optical trap. Furthermore, the simultaneous collection of two cavity-enhanced Raman (CERS) spectra requires more complex optics than the collection of backscattered light.

Of course, the use of optical deformation has some advantages too. Perhaps the primary one is that there is in principle no limit to the viscosity range which can be interrogated by this method. This is important because it is known that the viscosity of atmospheric aerosol particles varies over a very wide range $(10^{-3}-10^{12} \text{ Pa}\cdot\text{s})$, as discussed in Section 1.1.3. All of the above techniques are limited to a relatively small part of that range. While viscosity acts to dampen the oscillations necessary

for falling droplet and droplet collision experiments, and interferes with the tip in AFM, the main effect of viscosity on our experiments is that it delays the mechanical response of the droplet to the illuminating light. For example, nondegenerate azimuthal MDRs have been observed during the coalescence of heated polystyrene spheres, with an estimated viscosity of 8×10^6 Pa·s.²⁰ While this experiment was observing the reverse process, i.e. relaxation of a deformed sphere to a sphere, the implication is that our technique would be able to achieve a surface tension measurement for such a viscous system. The approximate viscosity given for polystyrene is orders of magnitude above that achievable by any of the other methods described above. The upper limit in terms of viscosity will be a practical one, namely how long it is feasible to observe the particle as it deforms towards its final shape.

Compared to the other optical methods, optical deformation also allows us access to a smaller size range. While not entering the submicron size range like AFM can, our optical deformation method can be used on particles closer to this size range than either droplet coalescence or falling droplets (2–3 μ m radius for deformation *vs* 7 μ m for coalescence and $\geq 10 \ \mu$ m for falling droplets). In the case of droplet coalescence, this is because the oscillations are damped more quickly in smaller particles than in larger ones. In the case of the falling droplet experiments, particle size limits arise from what the droplet dispenser can produce. Additionally, since the surface tension is measured by optical microscopy, retrieved values become increasingly uncertain the smaller the particle.

The deformation-based method may also allow for novel experiments. Of the three alternative techniques described here, the droplet coalescence method is the most versatile, allowing access to supersaturated states which the other two cannot interrogate. However, one weakness of this approach is that the dependence of surface tension on RH, which is of great interest, must be measured in a fairly time-consuming way. For each RH, two droplets must be trapped, and then after collision the droplet must be ejected and two further droplets trapped in order to continue building up the RH curve. The optical deformation technique allows this to be done in a simpler fashion, and with only one droplet. While we have used changes in laser power to induce thermal locking in Chapters 2 and 3, the same result can be achieved by increasing the RH. Thus, one can imagine measuring the RH dependence of a system simply by gradually increasing the RH over the range of interest, with each period of thermal locking (equivalent to one droplet collision) providing a data point on the surface tension vs RH curve. A potential downside of this is that during thermal locking the temperature would increase; however, given the weak dependence of surface tension on temperature this is unlikely to be a major issue. Additionally, the framework set out in Chapter 2 would allow the heating



FIGURE 5.1: (a) Observed (red) and modeled (blue) cavity-enhanced Raman scattering from a morphology-dependent resonance. (b) Predicted cavity-enhanced Raman scattering from a morphology-dependent resonance filtered by polarization. Red and blue represent orthogonal polarizations. Panel a) used with permission from Optica.²¹

to be calculated and corrected for.

There is room for further development of the optical deformation technique. For example, as noted above, the simultaneous collection of two CERS spectra is relatively complex. Recent work has demonstrated that splitting of an MDR can be observed in only one CERS spectrum, specifically that gathered perpendicular to the trapping-beam axis (Fig. 5.1a).²¹ This offers the possibility to simplify our experimental setup, since the collection of one spectrum is easier than the collection of two. Further calculations suggest that if the cavity-enhanced Raman scattering is filtered by polarization, then the extremes of the azimuthal spectrum can be selectively suppressed (Fig. 5.1b). That is to say, a spectrum of one polarization will be dominated by the m = 0 azimuthal mode, and the orthogonal polarization would be dominated by the $m = \pm n$ azimuthal mode. While this would mean we are once again observing two CERS spectra, the subsequent splitting of a single spectrum into two by polarization requires a less complicated optical setup than the simultaneous collection of spectra from two separate objectives. Furthermore, since splitting the scattering based on polarization allows separation of the scattering from the m = 0 and $m = \pm n$ azimuthal modes, this would allow us to overcome two limitations of the approach as described in Chapter 3.

As stated in Section 3.2.4, our previous methodology requires use of only transverse magnetic modes during periods of thermal locking in order to give accurate results. These requirements arise largely because the scattering from both polarizations perpendicular to the trapping-beam axis is dominated by m = 0 under

nonresonant conditions, and remains so for transverse electric modes under resonant conditions. Splitting the scattering by polarization would overcome this problem and should facilitate accurate surface tension measurements using both transverse magnetic and transverse electric MDRs under resonant and nonresonant conditions. Thus, collecting cavity-enhanced Raman scattering only perpendicular to the trapping-beam axis, then splitting this based on polarization would allow us both to simplify our experimental setup and overcome previous limitations. This could then facilitate measurements of the real-time evolution of surface tension in response to RH changes, as the particle no longer needs to be thermally locked in order to gather data. The RH can simply be decreased slowly from high to low, and the changes in splitting used to determine the surface tension frame by frame. Such an experiment would further lend itself to monitoring, for example, how surface tension changes as a chemical reaction proceeds or gas-particle partitioning occurs. In this case, the RH would be held constant, and some other component would be introduced into the gas flowing into the trapping cell, either partitioning into the particle phase or reacting with a component already in the droplet. The reaction or composition could be monitored by the Raman spectrum, while the surface tension evolution would be monitored by changes in MDR splitting.

While the proof-of-concept experiments set out in Chapter 3 are important, the measurement of the surface tension of homogeneous systems is of little interest to the atmospheric science community. When approaching the critical supersaturation in clouds, such systems are fairly dilute and approximating the surface tension as that of pure water is unlikely to lead to major inaccuracy in models. The primary interest of the atmospheric science community is in the surface tension of systems which have undergone liquid-liquid phase separation (LLPS), as this is when surface tension depression becomes significant (see Section 1.1.3). Thus, the ultimate goal is to make measurements on phase-separated systems. The setup itself as described in Chapter 3 would require no modification in order to achieve this, although the simplification of CERS collection suggested above may be helpful. The main barrier to making measurements on core-shell systems is the need to modify the analysis framework to account for shifts in the MDRs due to the core-shell morphology.

It is known that adding a shell to a homogeneous particle leads to shifts in MDR wavelengths.²² This presents a fitting challenge, as unlike the homogeneous case, one must have *a priori* knowledge of the mode assignment in order to use a fitting program such as MRSFIT.²² Thus, experiments on core-shell particles likely need to be performed on systems which are homogeneous over some RH range. The mode assignments can be obtained when the particle is homogeneous. The mode positions

can then be tracked upon undergoing LLPS, meaning the mode assignment in the core-shell system will be known from the homogeneous mode assignments, either in whole or partially.

The next obstacle is then to interpret the splitting that will be observed. The deformation of core-shell particles and consequent shifts in MDRs has been the subject of recent theoretical interest.^{23,24} This has led to some interesting, and potentially helpful, predictions. As noted in Section 1.1.3, LLPS in atmospheric aerosol usually leads to the formation of an organic-rich shell at the surface of an aqueous inorganic core. In this case, we would expect the refractive index of said shell to be greater than that of the core. Vennes & Preston have predicted that in this case, similar to the homogeneous case, the shell will be stretched along the trapping-beam axis, giving a prolate spheroid. The optical stress on the core, however, will lead to compression along this axis, giving an oblate spheroid.²³ Thus, the shell will be nonuniform in thickness, affecting the splitting. In this case, it is predicted that such deformation will lead to an increase in the splitting of MDRs.²⁴ This is likely to aid in surface tension retrievals for such systems. The main source of uncertainty in our surface tension measurements arises from noise in the measured MDR positions and thus the splitting between them. However, the larger the splitting the less significant this uncertainty becomes. Therefore, for the same surface tension, the splitting in the core-shell system vs a homogeneous system will be greater and reduce the uncertainty in our retrieved values.

As mentioned in Section 1.1.3, there has been interest from the theoretical side in the phenomenon of LLPS. Due to a sparsity of data, the ability to discriminate between bulk-surface partitioning models is currently difficult. Measurements using the optical deformation setup could potentially help to remedy this problem. While the atmospheric science community is largely concerned with surface tension near cloud droplet activation, or current trapping cell is unable to reach such RH conditions. However, at lower RHs different models predict that the surface tension will evolve differently due to differences in surface coverage/concentration.^{25,26} It is in this range where our setup may be of use. An outline of how surface tension may be measured as a function of RH is given above. Such measurements could begin to discriminate between which models provide the most accurate description of surface tension evolution, and perhaps guide further modelling efforts.

Different models for LLPS also predict different thicknesses and compositions of the core and shell phases. Greater propensity for surface partitioning will lead to thicker shells. In some cases, the shell is assumed to have no water, and in others water partitions between the inorganic core and organic shell. The setup described in Chapter 3 can also be used to investigate these. Fitting of MDRs to retrieve the core and shell radii could allow for discrimination between different models based on the retrieved shell thickness. It is currently unclear how thick the shell must be in order to be detectable by light scattering. Additionally, this fitting also determines the refractive indices of the core and shell. By comparison with the refractive indices of the pure components, one could determine how purely organic the shell is. Admittedly, however, this approach is not limited to our setup. The fitting of MDRs to retrieve these parameters is indifferent to the particle levitation method used. Thus, this could be achieved by optical tweezers, electrodynamic balance, or any of the other more exotic trapping geometries discussed in Section 1.2 and 1.2.1. An advantage of the dual-beam trap, however, would be the ability to link the phase composition to the particle surface tension.

Two other important areas of research for atmospheric aerosol were outlined in Chapter 1 which were not interrogated in this thesis: ice nucleation and particle phase state (Sections 1.1.2 and 1.1.3, respectively). We shall now briefly examine the prospects for the dual-beam optical trap to be used to investigate these areas.

With regards to ice nucleation, optical trapping is unlikely to be the best approach to this problem. Optical trapping relies on there being a high degree of symmetry in the trapped particle (excluding traps designed specifically to deal with irregularly shaped particles) as asymmetry gives rise to a destabilising torque on the particle. The freezing process will give rise to such asymmetry, likely causing ejection of the particle from the trap. However, the dual-beam geometry has been the primary approach taken in attempts to interrogate ice nucleation by optical trapping.^{27,28} Recently, supercooled particles have been interrogated using a setup very similar to that described in Chapter 3.²⁹ The likely reason for the use of dual-beam traps to try to interrogate particles undergoing freezing is that, if well enough aligned, the torques exerted by each beam may cancel out. The study set out in Chapter 4 may be of some use in helping to ensure this. If particles are trapped away from the midpoint between the two focal points, the torques from each beam are unlikely to cancel. Thus the beams should be aligned such that the particle will be trapped midway between the focal points. Additionally, it may be advantageous to use beams of either the same polarization, or circularly polarized light. This too will increase the chances of the torque from each beam cancelling out. A more rigorous study of this, taking into account the particle trapping position, would be helpful in trying to facilitate ice nucleation experiments using similar trapping geometries to that described here. However, it is likely that the best approach to studying ice nucleation *via* particle levitation will be the electrodynamic balance, due to its lack of constraints regarding particle shape.

With regards to determining particle phase state, the dual-beam optical trap

has mixed prospects. With regards to identifying efflorescence/deliquescence behaviour, the same problems apply to this as to the study of ice nucleation. Upon efflorescence, trapped particles will most likely be ejected from the trap. However, studying the gradual transformation from liquid to glass in aerosol particles may be feasible. By now there are several methods available to determine the viscosity of single aerosol particles. Some infer viscosity from changes in diffusivity within the particle, e.g. via isotope exchange³⁰ or water diffusion,³¹ and others measure viscosity directly through relaxation after some mechanical perturbation, e.g. droplet coalescence^{16,32} or poking with a needle.^{33,34} An exhaustive list and examination of the relative merits of each is beyond the scope of this discussion and can be found elsewhere.^{35,36} Since the diffusivity-based methods are agnostic with respect to the method of particle levitation used, the dual-beam optical trap could easily be used to facilitate these approaches. This warrants no discussion. However, we shall now discuss a novel optical deformation-based experiment which would fall into the mechanical perturbation category.

Sharp changes in optical stress could be used to perturb the particle shape. We have at hand two mechanisms to achieve this: changes in laser power or changes in RH. Initially it seems like laser power would be the obvious choice. One would trap a particle, let it come to equilibrium at a given RH, then perform a step change in laser power and monitor the deformation of the particle as it approaches and eventually reaches its new deformed shape. However, as demonstrated in Chapter 2, this will also be accompanied by changes in size as the particle temperature also changes. This will also be limited by particle viscosity/diffusion, and distentangling both effects would be a complex task. However, we may once again utilise thermal locking to aid us in our experimental endeavours. When thermally locked, we may use either laser power or RH to control how close the particle is to a resonant radius. Changes in particle size upon approach are very small, to the point of being negligible with respect to the change in deformation that may be expected. Thus, inducing the change in optical stress on a thermally locked particle would allow the effects of water uptake/loss to be minimised and the change in particle shape to dominate. If we were to attempt to induce a perturbation using a change in laser power, the change in laser power would roughly cancel the change in optical stress and lead to minimal perturbation to the deformation (see Fig. 3.3b). A small change in RH, on the other hand, would either increase or decrease the optical stress, leading to a change in the deformation. Thus, our viscosity experiment would look approximately as follows: use the RH control to induce thermal locking in a particle, then once it reaches its equilibrium shape, change the RH by a small amount in a stepwise fashion and observe the MDR splitting as the particle relaxes

to its new equilibrium shape. This approach would likely be of little use for low viscosities as the relaxation time would be within the frame rate at which CERS spectra are gathered. However, it is likely to be particularly suitable for high viscosities, which are of increasing atmospheric interest.

A limiting factor in experiments on high viscosity particles is often a practical one; the relaxation times are so long that running an experiment for the necessary length of time is infeasible. However, since the deformation of our particles is particularly small, this reduces the necessary observation time. For example, Trevitt *et al.* reported that the last phase of the coalescence of their polystyrene microspheres, which would be roughly equivalent to observing the relaxation of a few nanometres deformation, took place on the order of minutes for a viscosity of 8×10^6 Pa·s.²⁰ This would certainly be observable using the proposed method, and implies that deformations at higher viscosities would also be experimentally feasible. However, it is likely that the RH control in our experiments will need to be improved in order to facilitate such sensitive adjustments.

While the work presented in Chapter 4 is fairly complete in and of itself, there are some further avenues for exploration. An obvious one would be an exploration of the variation of trapping position with refractive index. However, this would be of little practical use, in the sense that it is very difficult to imagine an experiment in which particle size remains constant and the refractive index varies. With respect to the work presented here, the only influence of the refractive index is to modify the oscillations somewhat.

A large fraction of the literature on optical trapping concerns itself with the calculation, experimental quantification, or optimization of the trap stiffness. This quantity, as the name suggests, is a measure of how stable an optical trap is, and may be thought of analogously to the spring constant, k, in Hooke's law (F = -kx). This was not explored in Chapter 4 because our generalized Lorenz-Mie theory calculations utilised beam-shape coefficients for a first-order Davis-Barton type beam and would likely not be adequate to accurately calculate the theoretical trap stiffness accurately (see also Section 4.3). However, with the ability to manipulate the trapping position by changing the relative positions of the focal points, it would be worthwhile to see if any correlation between trap stiffness and trapping position could be identified. If so, this would add an extra degree of freedom for researchers seeking to optimise their setups.

An interesting follow-up experiment which could be performed looks at how the scattering cross section of a particle varies with position. When the focal points are aligned such that the particle is trapped away from the midpoint of the two focal points, we have demonstrated that it will oscillate. Closer examination of these



FIGURE 5.2: a) Scattering cross section as a function of particle *z*-position and radius (given by colourscale). The predicted particle trapping position is shown in black. b) Predicted scattering cross section as a function of radius.

curves also indicates that, when we excite an input resonance, the trapping position profile sees a sharp spike (see Fig. 4.13b). This is because the beam width of one beam at the particle, in this case the -z-beam, is larger than the other. This means the input resonance is excited more efficiently by the -z-beam than the +z-beam, thus the force from the -z-beam increases more rapidly than that from the +z-beam, leading to the spike in trapping position. Mie theory tells us that the scattering cross section at an input resonance increases markedly. However, the scattering cross section is also position dependent, and there may be a trade off between the two.

Fig. 5.2 shows some predictions regarding this phenomenon. Fig. 5.2a) shows a colourmap indicating the scattering cross section as a function of radius and *z*-position, with the stable trapping position of the particle superimposed in black. The scattering cross section along the black profile is shown in Fig 5.2b). Panel b) shows that, contrary to what might be expected from Mie theory, the scattering cross section actually decreases sharply at certain radii, while experiencing increases at others. Examination of panel a) reveals that this is a result of changes in the trapping position caused by the excitation of input resonances. The decreasing spikes in scattering cross section are because the decrease associated with the change in trapping position overcomes the increase associated with with the excitation of an input resonance. On the other hand, the increasing spikes are in fact exacerbated by changes in trapping position. A more full investigation of this effect, along with experimental verification, would be of interest to the broader optical trapping community.

We finish with a note on the incorporation of the results from Chapter 3 into experiments. Retrievals of focal point offsets will be most reliable when the particle radius varies continuously through a decrease in RH, rather than in discrete steps as the particle jumps between input resonances, as would be the case if the RH were to be increased. However, this Discussion has proposed several experiments which rely on the excitation of input resonances. Therefore, it is recommended that after alignment of the dual-beam trap, an experiment is performed in which the relative humidity is slowly decreased and thus the particle slowly changes in size. From this, the focal point offsets can be determined using the fitting procedure described in Chapter 4, and then used in calculations for subsequent experiments involving increases in RH, for which the focal point offsets cannot be as reliably determined. This is important for ensuring accurate results in any analysis which involves generalized Lorenz-Mie theory calculations.

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6 Conclusions & Summary

This thesis demonstrates the use of a dual-beam optical trap to perform novel experiments on single aerosol particles levitated in air. The role of aerosol in our atmosphere remains uncertain, and the development of new measurement techniques is crucial to reducing that uncertainty. There are several different challenges which must be met in order to fully understand the role of aerosol in the atmosphere, from gaining a more detailed microphysical understanding of aerosol to improvements to their representation in climate simulations. It is demonstrated that the dual-beam optical trap may be used to make measurements of aerosol properties at the single particle level. In particular, we demonstrate methodologies for measuring the complex refractive index of weakly absorbing particles, pertinent to the cooling effect of aerosol in the atmosphere, and for measuring aerosol particle surface tension, which has been implicated in cloud droplet activation. We also demonstrated new insights into the physics of optical trapping itself, with a detailed study of the variation in trapping position in a dual-beam optical trap. Taken together, this thesis establishes the dual-beam optical trap as a potentially useful tool in the ongoing quest to better understand and characterise aerosol particles.

Chapter 1 establishes the primary challenges and the breadth of the problem to be met by researchers in the atmospheric aerosol science field. Key areas in which understanding must be improved and the challenges in doing so are discussed. Additionally, the basic principles of optical trapping and light scattering are established. Furthermore, the suitability of combining optical trapping and light scattering to make measurements on atmospheric aerosol is shown, with examples of previous studies doing this given.

Chapter 2 outlines a methodology for carrying out highly sensitive absorption measurements on single aerosol particles, and demonstrates how this may be used to determine the complex refractive index of the particle. The convection-diffusion equation is used to find the equilibrium condition for a binary aerosol droplet heated relative to its surroundings, and an equation for the magnitude of electromagnetic heating due to the laser beams is also derived. Together, these can be used to predict the change in particle size in response to a change in laser power. Experimentally, we use a dual-beam optical trap to heat particles using different laser powers, and analyse the associated size change in order to retrieve the imaginary part of the refractive index using a grid search. This was performed for three atmospherically relevant model systems. Additionally, we investigate the somewhat peculiar phenomenon of thermal locking. When a particle is such a size that the trapping laser light may excite a morphology-dependent resonance, the absorption cross section increases markedly, as does the electromagnetic heating from the laser beam. When the laser power is being increased, this leads the particle to undergo certain jumps in size. When decreasing the laser power, however, the additional heating acts to balance the cooling achieved by decreasing the laser power, causing the particle to remain almost constant in size over a range of laser power. This phenomenon is known as thermal locking. Our framework for predicting the equilibrium size of particles as a function of laser power also allows us to accurately predict the occurrence of thermal locking.

Chapter 3 investigates the use of the dual-beam optical trap to controllably deform aerosol particles and measure their surface tension. Light incident on a trapped particle will undergo reflection and refraction, giving rise to an optical stress on the particle surface. This stress causes the particle surface to deform, until the optical stress is balanced by the surface tension of the particle. Once deformed, the morphology-dependent resonances in the cavity-enhanced Raman spectrum lose their azimuthal degeneracy and split into a series of peaks. By measuring two cavity-enhanced Raman spectra at perpendicular angles, we are able to observe the extremes of the azimuthal splitting and use this, in conjunction with an analytical formula for the azimuthal mode positions of an ellipsoid, to determine the surface tension. Due to the way in which light couples into the different azimuthal modes, use of this equation is only valid for the splitting of transverse magnetic modes under conditions of thermal locking. Surface tension measurements were successfully achieved for two model systems.

Chapter 4 looks more closely at the workings of dual-beam optical traps. In particular, we consider the effect of various factors on the potential trapping positions of particles. Contrary to intuition, when the focal points of each beam are displaced along their shared propagation axis, a particle will not always be stably trapped midway between the focal points. Instead, over different ranges of focal point offset, the particle may become trapped behind one focal point or the other. While this result is not new, it was not previously know that when trapped away from the midpoint, the trapping position will oscillate as a function of particle radius. Proceeding from this discovery, we then demonstrate that there will be a minimum of four, and potentially up to six, different ranges of focal point offset with distinct behaviours. The effects of an additional offset along one axis perpendicular to the trapping-beam axis, and the effects of a power imbalance between the beams, are also investigated. Finally, it is demonstrated that the oscillations of a trapped particle during an experiment may be fitted to retrieve the focal point offsets, and in some cases the power imbalance too.

Chapter 5 then examines the thesis as a whole with respect to the challenges in atmospheric aerosol science identified in Chapter 1. Subsequent work using the dual-beam optical trap to build refractive index models is discussed, as well as the prospects for other applications to finding the optical properties of aerosol particles. The surface tension methodology developed in Chapter 3 is compared and contrasted to others which are currently in use. Future work using the surface tension methodology and potential improvements to the optical setup are also laid out. The ability of the dual-beam optical trap setup used throughout this thesis to meet other challenges within atmospheric aerosol science, such as ice nucleation and viscosity measurements is examined. Finally, some further experiments with regards to the effects of particle trapping positions on factors such as trap stiffness and scattering properties are proposed.

Taken together, this thesis describes the use of a novel optical trapping setup to make measurements on single aerosol particles. The use of this setup is demonstrated with application to determining the complex refractive index and surface tension, two key parameters which require further study within the aerosol community. We also examine more fundamental aspects of the setup, specifically the positions at which a particle may become trapped. This result could help future researchers in interpreting their experiments more accurately. With some further uses of this work already demonstrated, it seems that the dual-beam optical trap may find wider application within aerosol science in the years to come, with the work presented in this thesis being important to such endeavours.

A Detailed Materials and Methods for Chapter 3

A.1 Theoretical description of optical deformation

We will consider an aerosol droplet that is optically trapped and deformed by a focused continuous-wave laser. The droplet will quickly reach its equilibrium shape and the stress-balance equation at the static fluid interface will be¹

$$\gamma \nabla \cdot \hat{n} = p_{\rm in} - p_{\rm ext} + \sigma, \tag{A.1}$$

where γ is the surface tension, \hat{n} is an outward unit vector normal to the surface, σ is the radiation pressure (the time-averaged radial component of the Maxwell stress tensor), p_{in} is the interior pressure of the droplet, and p_{ext} is the exterior pressure. In the absence of optical stress ($\sigma = 0$), the droplet will be spherical with a radius r_s and the pressure difference across the interface will be $p_{in}^\circ - p_{ext}^\circ = 2\gamma/r_s$. When optical stress is applied ($\sigma > 0$), the internal pressure increases by an amount Δp so that $p_{in} = p_{in}^\circ + \Delta p$ while the external pressure does not change ($p_{ext} = p_{ext}^\circ$). Therefore, Eq. A.1 can be rewritten as

$$\gamma \nabla \cdot \hat{n} = \frac{2\gamma}{r_s} + \Delta p + \sigma.$$
 (A.2)

We define the deformation at the droplet surface as $h(\theta, \phi)$ and the radial position of the deformed surface as $R(\theta, \phi) = r_s + h(\theta, \phi)$. The deformation can be represented as an expansion in terms of spherical harmonics

$$h(\theta,\phi) = \sum_{n=2}^{\infty} \sum_{m=-n}^{n} h_{nm} Y_n^m(\theta,\phi), \qquad (A.3)$$

where the n = 0 term is zero due to the assumption of incompressibility of the fluid (conservation of volume) and the n = 1 term is omitted as it corresponds to uniform droplet motion². The spherical harmonic function is Y_n^m .

For small deformations, the relation $h \ll r_s$ holds and it is well-known that^{3,4}

$$\gamma \nabla \cdot \hat{n} = \frac{2\gamma}{r_s} + \frac{\gamma}{r_s^2} \sum_{n=2}^{\infty} \sum_{m=-n}^{n} (n-1)(n+2)h_{nm} \Upsilon_n^m(\theta, \phi).$$
(A.4)

The radiation pressure on the surface of a spherical particle can be expanded as

$$\sigma(\theta,\phi) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \sigma_{nm} Y_n^m(\theta,\phi).$$
(A.5)

The last term to consider in Eq. A.2 is Δp . For a droplet with a stationary surface, the Navier-Stokes equation will give $\nabla p_{in} = 0$. Therefore, Δp is a constant and has no angular dependence.

Inserting Eq. A.4 and A.5 into Eq. A.2 and using the orthogonality of the spherical harmonics yields the following relationship between σ_{nm} and h_{nm} :

$$h_{nm} = \frac{r_s^2}{\gamma} \frac{\sigma_{nm}}{(n-1)(n+2)},$$
 (A.6)

For a linearly polarized electromagnetic Gaussian beam whose focal point is at the center of the droplet, GLMT can be used to calculate the components of the scattered electric field at the surface of the droplet⁵. If we denote the sum of the incident and scattered fields at the surface with $\vec{E} = (E_r, E_\theta, E_\phi)$ then the radiation pressure at the surface will be⁶

$$\sigma(\theta,\phi) = \frac{\varepsilon_0}{4} \operatorname{Re}\left[\varepsilon_m - |n_m/n_d|^4 \varepsilon_d E_r E_r^* + (\varepsilon_d - \varepsilon_m) (E_\theta E_\theta^* + E_\phi E_\phi^*)\right], \quad (A.7)$$

where n_d is the refractive index of the droplet, n_m is the refractive index of the medium, ε_d is the relative permittivity of the droplet, ε_m is the relative permittivity of the medium, and ε_0 is the vacuum permittivity. Once Eq. A.7 is inserted into Eq. A.5 the only unknown will be σ_{nm} . These coefficients can be solved for numerically. With this result, the surface deformation can then be calculated using Eqs. A.3 and A.6.

A.2 Electromagnetic heating

The change in particle radius due to electromagnetic heating can be calculated by utilizing the law of conservation of mass and the equilibrium condition⁷

$$\frac{a_s p_s^\circ}{T_s} = \frac{a_\infty p_\infty^\circ}{T_\infty},\tag{A.8}$$

where a_s , p_s° , and T_s are the water activity, saturation vapor pressure, and temperature, respectively, at the surface of the particle and a_{∞} , p_{∞}° , and T_{∞} are the same quantities but in the trapping cell, far from the particle surface.

To calculate the incident laser power, P, at which a droplet of a given radius reaches equilibrium with its surroundings, we proceed as follows: since a_{∞} and T_{∞} are measured, the problem revolves around finding a_s and T_s . After calculating the absorption cross-section, C_{abs} , for each radius using GLMT, one can determine the mass of solute in the droplet. Assuming the solute is non-volatile, as is the case for both NaCl and citric acid in water, the mass fraction and water activity, a_s , can be calculated for all radii using the AIOMFAC model and tabulated data^{8–11}. Eq. A.8 can then be used to determine T_s of the droplet required for equilibrium to be achieved. The temperature elevation relative to the surroundings, ΔT , is obtained by subtracting T_{∞} , and P can then be found by using⁷

$$\Delta T = \frac{C_{\rm abs} P}{2\pi^2 w_0^2 r_s \kappa_{\rm g}},\tag{A.9}$$

where w_0 is the beam waist, measured to be 4.3 μ m for our optical trap, and κ_g is the thermal conductivity of the surroundings, taken to be 0.026 W/(m·K) (the value of nitrogen at 300 K⁹).

A.3 Experimental

In order to create the two beams required for the dual-beam optical trap, the light from a continuous-wave laser (Opus 532, Laser Quantum) operating at $\lambda = 532$ nm is split into two arms using a polarizing beamsplitter. Each beam is ultimately focused through a $50 \times$ objective lens (SLMPLN50X, Olympus). The two objective lenses are aligned such that their focal points overlap and, upon drawing aerosol into the cell, a single droplet will be trapped at this common focal point. The intensity of light incident on the particle is controlled using a combination of a half-wave plate (HWP) and a Glan-Taylor polarizer. The polarizer is fixed at such an angle that the light which passes through it is evenly split between the two arms, in order to ensure that the scattering forces from each beam cancel. The HWP is then rotated using software (Kinesis, Thorlabs) in order to control the beam power passing through the polarizer and ultimately incident on the particle. CERS spectra are collected parallel and perpendicular to the axis of the trapping beams. These two spectra are simultaneously collected on the same CCD (PIXIS:100B_eXcelon, Princeton Instruments) of a spectrograph (IsoPlane SCT-320, Princeton Instruments). A schematic of the set-up is shown in Fig. S3.

In the experiments presented here, the HWP is adjusted so the total laser power incident on the particle initially is 100 mW. The HWP is then rotated at a constant rate until the power reaches a maximum of around 500 mW, before decreasing back to 100 mW. The RH in the cell is held constant by flowing a mixture of nitrogen saturated with water vapor and dry nitrogen into the cell, with the mixing ratio adjusted to attain a desired RH. A combined flow rate of 100 sccm was used in all experiments. The temperature and RH in the cell are monitored with a sensor (SHT75, Sensirion) that was placed about 1 cm away from the trapped droplet. Aerosol particles are produced by nebulizing a solution of either aqueous NaCl or aqueous citric acid using a medical nebulizer (Micro-Air, Omron). Particles are drawn into the cell using a vacuum to pull air through it. A particle becomes trapped at the common focal point of the two laser beams, and the rest leave the cell with the air flow.

A.4 Surface tension retrieval

As individual *m* cannot be resolved in CERS spectra for the small deformations measured here, we rely on m = 0 and |m| = n being the dominant modes in the 0° and 90° spectra, respectively. This allows for the combined fitting of the polar axis and equatorial axis WGMs to a coupled homogeneous Mie model with one refractive index parameterization but two different radii. The retrieved radii represent the polar and equatorial axes of the deformed droplet, which can be used to calculate the radius of the volume-equivalent sphere. The WGMs that are measured as a function of laser power can be used in the GLMT deformation model to iteratively converge to a best-fit surface tension by minimizing the square error between the measured and GLMT-predicted deformation. We then adjust the obtained surface tension using only TM modes, since their splitting more accurately reflects the deformed shape of the particle. To do so, we first calculate the average WGM shift from the homogeneous WGMs for the TM modes. We then use the volume-equivalent radius, the isolated TM WGM shift and Eq. 1 to recalculate r_p and r_e . These recalculated r_p and r_e values are then used in the aforementioned iterative solver for the surface tension of the droplet. By isolating the TM WGMs we account for the different coupling into the TM and TE modes.

A.5 Experimental limits

As was mentioned in the Discussion section, the range over which our experimental methodology may be applicable depends on several parameters, and there is flexibility to adjust the experimental conditions to suit the intended use. Here, we
include some examples to demonstrate the range over which our technique may be applied. The following calculations use 1 W total laser power focused to a beam waist of 4.3 μ m to deform the particle, with a measurement deemed feasible if the WGM splitting induced by this is >0.02 nm (the limit using our spectrograph). For a 5 μ m radius particle with a refractive index of 1.4, the necessary WGM splitting can be achieved for surface tensions up to a few thousand mN/m. For calculations regarding refractive index and radius, we use a relatively high surface tension of 100 mN/m to illustrate the lower limits on the utility of our technique. The range of particle refractive index for which our method is effective depends also on the refractive index of the surrounding medium. Generally, the deformation of the particle increases with increasing refractive index contrast. Again choosing a 5 μ m radius particle, the required refractive index contrast relative to the surrounding medium is around 5%. Finally, in terms of radius, for particles with a refractive index of 1.4, measurable WGM splitting occurs for particles of radius as small as 0.8 μ m.



FIGURE A.1: a) Measured WGM positions for the spectra measured for 0° (red) and 90° (blue) spectra for an aqueous NaCl droplet held at 82 ± 2 % RH during a power increase from 0.1 to 0.5 W. b) Measured WGM positions for 0° (red) and 90° (blue) spectra for the same particle as power is decreased from 0.5 to 0.1 W.



FIGURE A.2: Calculated droplet temperature for the theoretical curve shown in Fig. 3a of the main text. For this calculation, the temperature far from the particle surface, T_{∞} , was set to the measured value of 297 K.



CCD Image

FIGURE A.3: Schematic of the setup used to make the measurements of optical deformation. The laser beam is expanded to slightly underfill the back aperture of the objective lenses. The combination of the rotating half-wave plate and the fixed polarizer allows control over the intensity of light incident on the particle. The polarizing beam splitter creates two beams, which are then focused through $50 \times$ objectives, aligned so that their focal points overlap. Particles are trapped at this common focal point, with the RH in the trapping cell controlled by flowing moist nitrogen. CERS spectra are collected parallel and perpendicular to the trapping beam axis, and passed to the CCD of the spectrograph. The spectra are viewed on the CCD as shown in the lower left.

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B Radiation pressure on an optical slab

In order to model the optical forces on a slab, we follow the approach of Griffiths for transmission and reflection from a single interface,¹ and extend this to two interfaces. In this case, we have a slab of optical material of width D and refractive index n_2 surrounded on either side by a medium of refractive index n_1 . An incident wave, I, propagating in the +z-direction is incident on the first interface of the optical slab, located at z = 0. Some of the light is reflected, creating a wave R_1 propagating in the -z-direction, and some of the light is transmitted, creating a wave T_1 inside the optical slab. Similarly, when wave T_1 is incident on the back surface of the slab, we get reflected and transmitted waves R_2 and T_2 , respectively. Further reflections of R_2 are not considered. The electric, E, and magnetic, B, fields of each wave are given by

$$E^W(z) = E_0^W e^{\pm ik_j z} \tag{B.1}$$

and

$$B^{W}(z) = \pm \frac{1}{v_{j}} E_{0}^{W} e^{\pm ik_{j}z}, \tag{B.2}$$

where E_0^W is the amplitude of the electric field of wave W, k_j is the wavenumber in medium j, and v_j is the wave velocity in medium j. Waves propagating in the +z-direction ($W = I, T_1, T_2$) adopt the positive sign, and those propagating in the -z-direction ($W = R_1, R_2$) adopt the negative sign. The time dependence is $e^{-i\omega t}$, where ω is the angular frequency of the wave, and is omitted from the following equations. Boundary conditions at the front and back surfaces require that

$$E^{I}(0) + E^{R_{1}}(0) = E^{T_{1}}(0) + E^{R_{2}}(0),$$
 (B.3)

$$B^{I}(0) + B^{R_{1}}(0) = \frac{\mu_{1}}{\mu_{2}} \left[B^{T_{1}}(0) + B^{R_{2}}(0) \right],$$
(B.4)

$$E^{T_1}(D) + E^{R_2}(D) = E^{T_1}(D),$$
 (B.5)

$$B^{T_2}(D) = \frac{\mu_1}{\mu_2} \left[B^{T_1}(D) + B^{R_2}(D) \right],$$
(B.6)

where μ_j is the magnetic permeability of medium *j*. Equations B.3–B.6 can be solved to yield the amplitudes of each wave in terms of E_0^I ,

$$E_0^{T_1} = \frac{2E_0^I}{(1+\beta)\left(1-\alpha e^{2ik_2 D}\right)},$$
(B.7)

$$E_0^{T_2} = \frac{2i\beta e^{-ik_1 D} E_0^I}{2i\beta \cos(k_2 D) + (1 + \beta^2) \sin(k_2 D)},$$
(B.8)

$$E_0^{R_1} = \frac{(1-\beta^2) E_0^I \sin(k_2 D)}{2i\beta \cos(k_2 D) + (1+\beta^2) \sin(k_2 D)},$$
(B.9)

$$E_0^{R_2} = -\frac{2(1-\beta)e^{2ik_2D}E_0^I}{(1+\beta^2)(1-\alpha e^{2ik_2D})},$$
(B.10)

where

$$\alpha = \left(\frac{1-\beta}{1+\beta}\right)^2,\tag{B.11}$$

and

$$\beta = \frac{\mu_1 v_1}{\mu_2 v_2}.\tag{B.12}$$

The optical forces exerted on the slab can be understood through considering the radiation pressure carried by each wave, p^W . In general, the radiation pressure carried by a wave is given by

$$p^{W} = \frac{1}{2} n_{j}^{2} \epsilon_{0} |E_{0}^{W}|^{2}, \tag{B.13}$$

where ϵ_0 is the permittivity of free space, $8.845 \times 10^{-12} Fm^{-1}$. Thus, the radiation pressure carried by each wave is

$$p^{T_1} = \frac{\epsilon_0 [(1+\beta)n_2 E_0^I]^2}{(1-\beta^2)^2 [\gamma - \cos(2k_2 D)]'}$$
(B.14)

$$p^{T_2} = \frac{4\epsilon_0 (\beta n_1 E_0^I)^2}{(1 - \beta^2)^2 [\gamma - \cos(2k_2 D)]},$$
(B.15)

$$p^{R_1} = \frac{\epsilon_0 [1 - \cos(2k_2 D)] (n_1 E_0^I)^2}{2[\gamma - \cos(2k_2 D)]},$$
(B.16)

$$p^{R_2} = \frac{\epsilon_0 (n_2 E_0^I)^2}{\gamma - \cos(2k_2 D)},$$
(B.17)

where

$$\gamma = \frac{1 + 6\beta^2 + \beta^4}{(1 - \beta^2)^2}.$$
(B.18)

The net optical force on the slab can then be calculated by summing the net radiation pressure on the front and back surfaces of the slab. The change in radiation pressure at the front is $p^{T_1} + p^{R_2} - (p^I + p^{R_1})$, and at the rear is $p^{T_2} - (p^{T_1} + p^{R_2})$. The net change in radiation pressure is then $\Delta p = p^{T_2} - p^{R_1} - p^I$, which we note is independent of the waves internal to the slab (T_1 and R_2). Physically, this is a consequence of the fact that the pressure carried by each of these internal waves to the front and back surfaces is "equal but opposite". Thus, the radiation pressure on the slab can be calculated using only the waves external to the slab (I, T_2 and R_1). This gives the expression for the change in radiation pressure carried by the light

$$\Delta p = -\frac{\epsilon_0 [1 + \cos(2k_2 D)] (n_1 E_0^1)^2}{\gamma - \cos(2k_2 D)}.$$
(B.19)

By Newton's third law, the radiation pressure exerted on the slab is simply the negative of Equation B.19.

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