Chapter 1

Introduction

1.1 Optical Tweezers

Precise manipulation of micro-particles and measurements of microscopic forces has been development in scientific research. It has long been known that the motion of microscopic particles is due to multiple random collisions, measuring the average momentum transferred is often done by generating a potential well constructed using light - more commonly referred to as optical tweezing.

Since the mid 1900's it was known that light can transfer momentum to a medium, being referred to as 'radiation pressure', initially this was applied by transferring both linear and angular momentum to suspended mirrors [58]. This allowed researchers to measure the momentum of light carried by a single photon [58]. It was Ashkin who showed that by constructing a precise wavefront one could confine biological cells as small as a few microns [33]. This was especially useful as the process was non-invasive, preserving the internal organelles while keeping the cell trapped.

The working principle is that a collimated light source - such as a laser - can confine a particle in the plane perpendicular to the beam [33]. The radiation pressure previously observed is due to the momentum transferred to the target, when directed at an isotropic scatterer the light the momentum transfer is minimised when the target particle is centred on the laser beam. Initially, confinement in the direction of the laser was achieved by matching the laser power so that the radiation pressure transferred

would equal the mass of the target [33]. Soon after, Ashkin showed that the by focusing the light source through a lens would confine the target particle in all 3 Cartesian directions regardless of the laser power [34]. The use of lenses to create a focal point allowed for the development of much stronger optical traps that could trap complex particles and biological materials.

Beyond simply observations, optical tweezing allowed for precise measurements of microscopic forces. Later it would be used to probe microscopic properties such as the Brownian forces exerted within a pure vacuum [36, 37]. Due to the predictable behaviour of light, optical tweezers have become essential for measuring and exerting precise forces on the magnitude of pico-newtons. However, these measurements are based on the idea that the trapped particle in question is an isotropic scatterer, meaning that particle is can be approximated as a sphere. This is an apt approximation if we only care about measuring the force exerted due to translational motion. In reality, rotational motion is a significant factor to the trajectory of non-spherical particles, in which case our understanding of how light interacts with particles is incomplete without considering the optical torque exerted by a focused beam.

1.1.1 Optical Torque and rotation

Electromagnetic fields can transfer both linear and angular momentum [58]; more accurately the field is said to have both orbital and spin momentum. Though there is some debate on how to decompose the total momentum into these two components [59, 60], for this project we do not need to calculate the exact quantities and will instead look at the broader effects of both components. Orbital angular momentum arises from the shape of the wavefront of the particular field in question; for simple Gaussian beams the wavefronts are uniform and equally spaced resulting in the typical radiation pressure that Ashkin and co demonstrated [34]. However, higher order modes of a Gaussian beam (for example: Laguerre-Gaussian modes) have non-uniform wave fronts meaning the orbital momentum has both angular and linear components; depending on the relative size of the target particle one can induce rotation, or orbiting [59, 61].

Spin angular momentum (SAM) is attributed to the spin density of the field, early

research has shown that the spin density is non- zero for any beam despite the fact that the total SAM transferred to a medium is 0 [60, 62]. This has sparked debate if SAM is even a physical quantity as it does not aid in the transport of energy directly [62] and so cannot be directly observed in some cases despite being non-zero. This paradox is resolved by representing the wave as an array of spin momentum loops that cancel one-another out when the medium is homogeneous.Spacial inhomogeneities cause these spin loops to no longer be equal, resulting in non-zero spin density, anisotropic mediums (such as birefringent crystal lattices) experience a transfer of spin angular momentum, imparting an optical torque.

Birefringence is a material property often seen in crystalline materials, where the crystal lattice has a different structure dependent on its orientation. Since light is composed of waves that propagate in orthogonally to one another, a birefringent material will refract light differently depending on the light's polarisation. Therefore it can be said that the material has two separate refractive indices. For circularly polarised light this inhomogeneity results in a high degree of SAM being transferred to the target object [63, 64]. The greater the difference between the two refractive indices the greater the angular momentum transfer.

The ability to transfer angular momentum has been exploited to rotate microspheres as fast as 1000 Hz while suspended in a bulk medium [64] as well as a means of measuring the local temperature and shear response of said medium [65, 66]. Calculating the optical torque applied to a birefringent material is given via:

$$\begin{aligned}\tau_{opt} = &- \frac{\epsilon}{2\omega_{laser}} E_0^2 sin(kd(\Delta n)) cos2\theta sin2\phi \\ &+ \frac{\epsilon}{2\omega_{laser}} E_0^2 (1 - cos(kd(\Delta n)) sin2\phi)\end{aligned} \tag{1.1}$$

Where Δn is the difference between the two refractive indices, θ is the angle between the particle's long axis and the polarisation vector of the local EM field, and ϕ is the phase shift in the EM field. The first term represents the 'orientational' torque which aligns the long axis of the particle with the electric field, when aligned $\theta = 0$ meaning the entire term is negligible for particle's with a stable orientation. The second term is

due purely to the polarisation of the laser, for circularly polarised light $\phi = \pi/4$ thus maximising the torque transferred to the target particle. Eq. (1.1) is only applicable for particles with a known birefringence, but there are other mechanisms that result in optical torque.

A common example is shape induced birefringence. If a particle has an anisotropic shape, it is more susceptible to being polarised along its longer axis than its shorter axis. Consider, for example, an ellipsoid elongated along one of its primary axis' ($r_z > r_x = r_y$). In a plane polarised beam such a particle will align with the polarisation vector. Therefore, the particle will rotate as angular momentum is transferred along its long axis. One common feature, regardless of shape, is that a particle with shape birefringence will rotate when it lies perpendicular to the direction of propagation. This is seen most evidently with spherical dimers [36, 67] but even for elliptical particles rotational motion is only detected when their long axis is not aligned with the direction of propagation [68, 69].

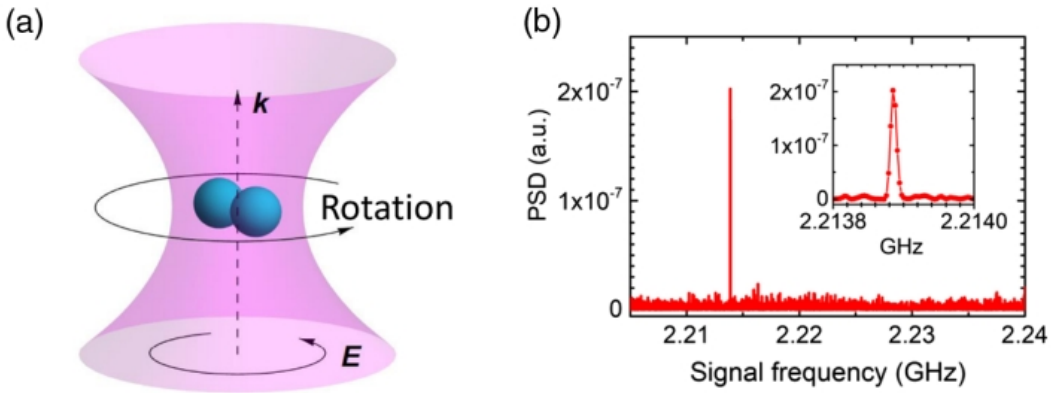

Figure 1.1: Example of nano-dimer undergoing optical rotation in a circularly polarised beam. Due to the dimer's anisotropic susceptibility it is polarised along its long axis, the dimer will therefore align its long axis with the polarization vector. Reproduced with permission from [67].

Often the optical torque experienced is far greater than similar spherical particles that are birefringent [59]. Currently spherical dimers are being rotated in vacuums to measure quantum forces and torques [36, 67]. There are some alternative cases where particles are rotated while not being aligned in the plane of the polarisation. However

in these cases their shape is often specifically engineered to scatter light in such a way that the net momentum change always occurs in one direction regardless of the laser polarisation [70].

Other examples of optical torque is when an anisotropic particle is aligned with the beam's direction of propagation (in which case $\theta = \pi/2$ and the first term disappears). This is analogous to an optically trapped sphere, where alongside a restoring force the particle also experiences a restoring torque. This seemingly random rotational motion is referred to as libation [59],often in typical suspension trapping situations (where the particle is suspended in a fluid) the rotational motion is washed out by the translational motion. As such, many experiments elect to trap in low pressure environments to precisely measure the optical torque being exerted by the optical trap [36]. This has lead experiments to try and achieve '0 kelvin' motion, where by trapping a silica dimer they were able to restrict its motion using 3 optical traps simultaneously. Despite this, they found that the dimer's rotational motion about its long axis could not be controlled leading to the undesired rotational modes [71].

The detection and measurement of optical torque is still a field of intense research, not only does it have potential to understand quantum fluctuations in a particle's motion but also allows for the creation of more effective micro-rotors. The latter being especially pertinent for understanding the behaviour of fluids experiencing localised shearing.

1.1.2 Characterisation of rotational motion

Rotational motion about a single axis is easiest to account for. When the power spectra of elliptical polystyrene particles was fitted by Yogesh *et al* [72], they assumed that the rotational motion was purely in the transverse plane. As such they did not have to account for any variance in the trapping strength due to orientation nor did they need to consider non-periodic rotational behaviour. In the case where rotational motion is stochastic the problem is more complex. For example, when an optical fibre trap characterisation technique was implemented by Saffron *et al* [73, 74], they were able to use dynamic light scattering to characterise both the axial and lateral trap stiffness

acting on microspheres.

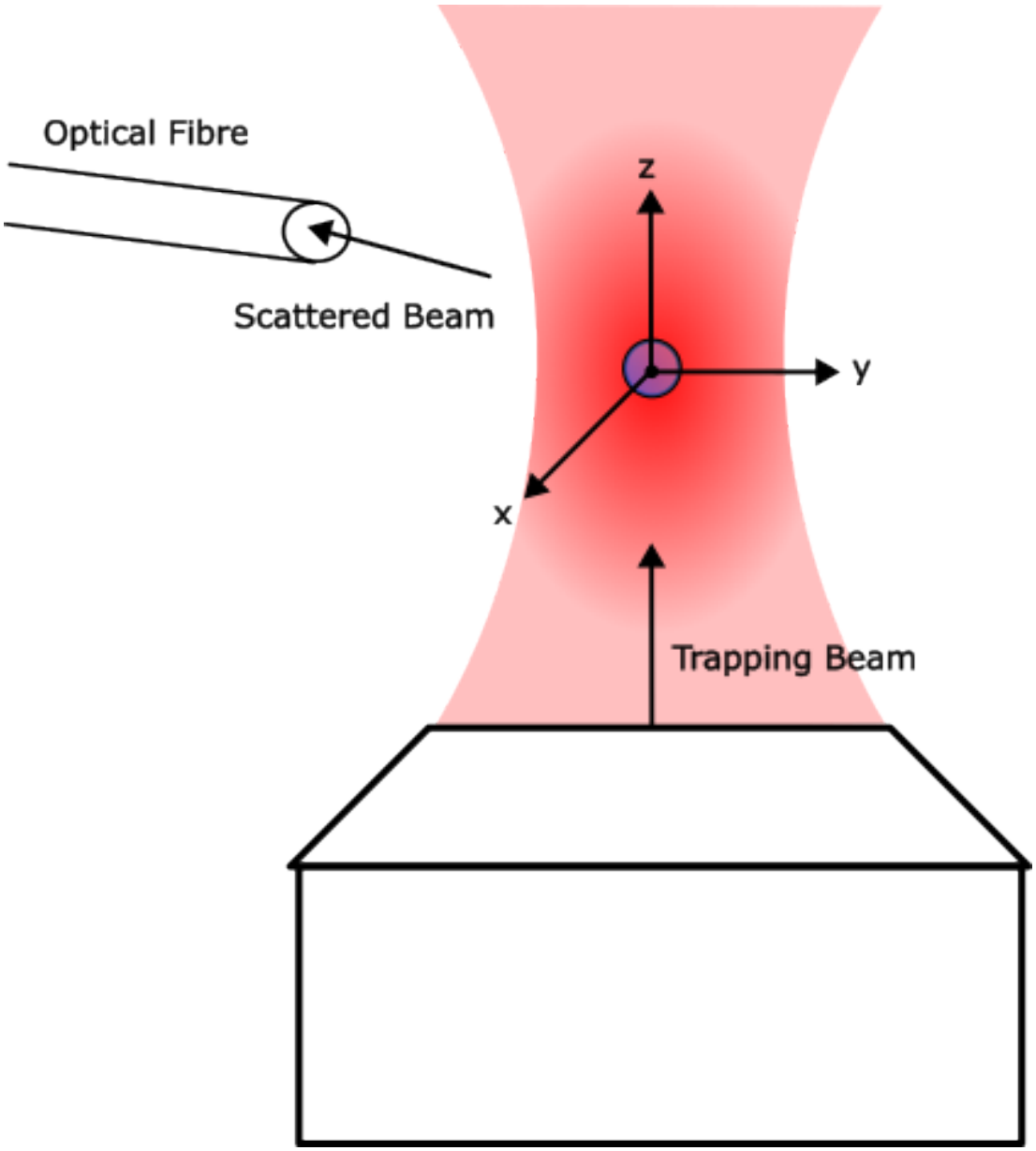

Figure 1.2: Diagram depicting the setup used by [73], a microsphere is trapped by a focused beam. The scattered beam is collected by an optical fibre situated close to the trapped sphere. Using DLS they are able to relate the autocorrelation function of the collated signal to characterise the trap stiffness of the optical trap.

The only drawback admitted to in their work was that the technique was constrained to isotropic scatters as their theoretical model for describing the auto-correlation func-

tion was predicated on the fact that any variations in the signal are due to the particles translational motion within the confines of a cylindrical trap [73]. Where the upper limit of the cylindrical trap is given by the Rayleigh range ($z_R = n\omega_0/NA$). This is discussed further in chapter 3 in the discussion of dimer dynamics, the axial traps of spherical aggregates is often situated far beyond the Rayleigh range (for a 1.2 NA laser this is $\pm 5.985\mu m$).

1.2 Laser induced nucleation

From as early as 1996 it has been known that laser irradiation using a Gaussian beam is a viable method of inducing nucleation within a supersaturated solution [38]. The first reported case was notable as it used a 1.064 μm laser, the glycine solutions would appear transparent to such a laser which would suggest there was no photo-chemical reaction. Later studies into this phenomena found that the laser polarisation can influence the polymorph produced. With circularly polarised light producing α-glycine and linearly polarised light forming γ-glycine [39]. Future research has found nucleation can be induced by 1 of 3 routes.

1.2.0.1 Non-Photochemical Laser Induced Nucleation

Non-photochemical laser induced nucleation (NPLIN) involves irradiating a solution with a pulsed laser [38, 39, 40]. The laser itself does not have to be heavily focused, instead irradiating a large region of the solution all at once. The choice of laser is of particular importance; with nucleation probability changing depending on the wavelength. A study of KCl solutions found that for lower intensities it was found that nucleation was favoured for lower wavelengths but above a peak intensity of $5MW/cm^2$ the wavelength independence disappeared [41]. Measurements of the intensity prior and after irradiation confirmed this wavelength dependence was not due to any photo-chemical interactions [41].

Additionally, the choice of solute will effect the setup, not only because some solute's are unaffected, but also because there is a minimum laser threshold before nucleation is

observed [39]. Several papers have debated the exact mechanism that induces NPLIN [39, 42]. A suggested theory to this is an optical Kerr effect: For anisotropically charged solute molecules the electric field can reorient them to match the propagation direction [39]. If enough molecules are co-aligned the free energy barrier is reduced to allow for ambient nucleation [42]. An alternative theory is the dielectric polarisation effect, in conditions that are unfavourable to cluster formation the polarising effect can stabilise the clusters [43]. As the cluster concentration rises so does the likelihood of nucleation [14].

Both theories are similar to one another but where the optical Kerr theory is limited to anisotropic solute molecules, the direct polarisation theory is more flexible. Regardless both theories struggle to explain why the phenomena is not observed in all nucleation systems [44], such as acetamide which is similar to urea which does nucleate when irradiated [45]. One of the benefits of NPLIN is that since the pulses are relatively low in their intensity they can be fired off quickly in succession, allowing for continuos crystallisation set ups. Overall, the NPLIN phenomena needs further research to properly describe its effects. The mean pulse intensity needs to be kept relatively low (on the order of $0.1 - 0.01 GW/cm^2$), as high intensity pulses lead to a completely different nucleation mechanism.

1.2.0.2 High Intensity Laser Induced Nucleation

High intensity laser induced nucleation (HILIN), where the pulse intensity is on the order of several PW/cm^2 is far simpler a mechanism to explain in comparison to NPLIN. The production of nuclei can be wholly associated to a cavitation process within the target solution, where the laser focus results in thermo- cavitation and the subsequent pressure wave leads to a nucleation event around the focus of the laser [46, 47, 48].

What remains in question is both how the physical properties (size, polymorph, etc) are influenced by the cavitation process, and how the pressure change triggers nucleation. The former has already been investigated; by adjusting the focal position Ikeda *et al* could control the polymorph of indomethacin [49], this is not a universal method however, as it has also been shown that laser power can influence the crystal

polymorph [50]. The latter is a tricky task to address due to the fact that these cavitation bubbles form and collapse in less than 100 μs. Using fluorescence dyed proteins, researchers were able to observe a sudden spike in fluorescence just as the cavitation bubble began to collapse, they suggested that due to the collapse of the cavitation bubble the protein clusters are brought together at the lasers focal point. However, while the fluorescence imaging indicates a local concentration increase it is difficult to quantify this change depending on the size of the bubble [44]. It has been suggested that in theory any solution can undergo HILIN [44], but proving such a theory requires a clear understanding of the phenomena both before and after cavitation occurs. Current research aims to combine experimental research with computer simulations to develop a universal theory, with the hope that this could also be related to NPLIN.

1.2.0.3 Trapping Induced Nucleation

Lastly, there is trapping induced nucleation, this is where optical tweezers come into play (see below). Due to the radiation pressure created by the focused beam, it is possible to manipulate the solute, this was demonstrated with amino acids such as glycine [51]. Whether or not a crystal forms is due to the location of the laser focus. When focusing on the cover slip, supersaturated solutions of glycine and D_2O were shown to create a dense liquid droplet of glycine and water [52, 53]. The dipole moment of the glycine molecules is too small to be influenced by the optical trap, as such it would suggest that larger aggregates are being manipulated. Applying dynamic light scattering analysis to the dense liquid region showed that it was populated by clusters that would consolidate together upon being focused by the optical trap [54]. Molecular simulations of glycine solutions showed that these clusters are unstable when using pure glycine below the saturation point suggesting that the clusters are formed due to glycine reaction products [55]. When the optical trap is moved from the cover slip to the air-solution interface, nucleation would occur before a dense liquid region could form [52]. Repeated experiments where the laser is focused on the air-solution interface have lead to a variety of different nucleation events. In some instances the nucleation occurs spontaneously after a short period of time [52]. Whereas allowing a solution to

age results in the formation of amorphous precursors that when irradiated will nucleate immediately [22]. The precursors are only seen when the solution is irradiated by an optical tweezer and the growth rate can be controlled somewhat by varying the laser power [22]. The reason why nucleation is only seen at the air-solution interface is due to the limited molecular mobility close to the interface. Often tweezing experiments will use a hydrophilic coating to minimise the height of the solution droplet and further limit the molecular mobility [53, 54].

Walton and Wynne discussed a plausible model for how the tweezer focus could result in a nucleation event. Put simply, when the laser is focused at the solution the radiation pressure draws in solute material, creating a concentrated region of solute. This also creates a depleted region around the focus and raises the local temperature. When the laser is turned off the depleted region around the focus quickly cools back to the ambient temperature. This sudden cooling allows for nucleation to occur just outside the focus.

Laser induced nucleation has the potential to be a viable method for *in-situ* studying of nucleation events. Using high numerical aperture lens one can localise the nucleation event to a specific region of the solution. The current issue is that the mechanism behind laser induced nucleation is not fully understood, as such it is rather difficult to modify the laser for different solution parameters. Instead it may be more effective to manipulate the solution using trapped particles. One way would to generate an optical torque on a trapped particle and therefore shear the surrounding fluid, a method that is already in common use for micro-rheological studies [56, 57].

1.3 Shear induced Nucleation

It has long been known that fluid shear rate plays a role in influencing nucleation; however, the exact relationship between shear rate and nucleation rate has only been recently understood for specific solutions. Theoretical research into shear induced nucleation suggests that there should be a slight increase in the nucleation rate at low shear rates, reaching a maximum increase in nucleation rate, and then at higher shear

rates the nucleation rate begins to drop off.

This has been shown theoretically for both simple colloidal [75, 76, 77] and ice crystal formation [78]; however, no experimental work into these systems has been conducted to confirm these theories. There is some experimental evidence for this phenomena in simple salt and protein solutions - though the authors emphasise that mechanical agitation cannot be ruled out - there has not been a exhaustive study into the shearing effects apart from in glycine solutions. In [76] it was found that a shear rate of around 3000 s^{-1} was the maximum shear rate that would yield the highest nucleation rate. Using the theoretical model established in [75, 79] which modifies the CNT to account for the effects of a nucleus undergoing shearing, accounting for the fact that a nucleus' growth is undergoing competition between flow-mediated molecular transport and the strain applied by the flow field which inhibits the growth of the nucleus. There central conclusion (from both the theoretical and experimental results) is that there is an optimal shear rate in which the nucleation rate is maximised.

However, a question that arises from this result, if there is a optimal shear rate in which molecular transport is maximised and strain is minimised, then surely there should also be a shear rate in which the molecular transport and strain are equal - allowing one to suspend a nucleus at a constant radius. In this scenario, the molecular transport would prevent the nucleus from dissolving, but the strain would prevent the nucleus from growing. This however would require one to be able to apply a continuous shear rate to a targeted nucleus with high precision, there is also no model for an individual nucleus in a continuous fluid field.

1.4 Significance of Thesis

As I have hoped to make clear in the above introduction, the current state of nucleation theory is rather cumbersome at a micro-level. Models such as CNT and multi-step nucleation are not sufficient for describing the myriad of potential pathways nucleation can go down. As suggested by some review articles, the best way to address this is by developing *in-situ* methods that can study the pre nucleation phase in greater detail

[5]. Furthermore, the ability to localise nucleation allows for better characterisation of the kinetics of crystal growth. Laser induced nucleation stands to be an ideal method to study the nucleation of organic compounds, as the laser output can be concentrated to a small area [44] while not altering the organic compound - as is the case with TEM. However, laser induced nucleation in itself is also poorly understood, meaning trying to study the nucleation kinetics is difficult if the effect of the laser. With this in mind we suggest that we instead utilise another application of optical tweezers, manipulation of micro-scale particles to induce nucleation around a small localised area. The most common method for manipulating a fluid is by localised fluid shearing, which has been shown to directly influence nucleation rates [76]. One challenge lies in the fact that its clear that the local fluid properties have a direct influence on the likelihood of laser induced nucleation from occurring [44, 45, 53, 22].

A way around this would be to try and induce the local fluid without directly relying on the electromagnetic field. Optical tweezers can reliably do so already by applying an optical torque to a trapped particle in order to induce fluid flow [56, 57]. It's already well documented that shearing will enhance nucleation events at a macro-level [76]. Micro-rheological studies using optical tweezing have been more interested in probing the local viscosity rather than try and use it as a means of shearing the fluid to induce crystal growth.

1.5 Overview

Overall the aim of the PhD is to study viability of using micro-rotors to generate localised fluid flow around the beam focus. The results are reported in chapter 3, this is then followed by experimental work where we use a galvano- mirror to move the beam and hence generate shear flow. While overall unsuccessful the addition of a moving beam focus showed that the growth of a nucleus can be localised around the trap focus. This presents a new insights for controlling and studying the growth of a newly formed nucleus by precise movement of the trapping focus.

The latter chapters cover computer simulations into the behaviour of microscopic

spherical dimers in an optical trap. Prior research into dimers using back focal plane interferometry has mostly considered their trapping behaviour to be similar to a single sphere but with a difference in trapping strength. Computer simulations reveal a host of new behaviours dependent on the dimer's size, orientation, proximity to the trapping focus, and even the polarisation of the trapping beam. The latter in particular suggests that multi-spherical particles can act as sophisticated micro-rotors.

However, this raises a its own host of experimental challenges, namely how do we characterise the behaviour of an arbitrary particle. Relying on current characterisation techniques is not possible as they are predicated on the trapping object to behave like an isolated sphere. Two novel methods of measuring rotational motion are discussed in chapter 5; firstly via a novel detection fibre method that allows for instantaneous measurements of the orientational behaviour of optically trapped ellipsoids/dimers; and secondly we create a simulative quadrant photo diode that replicates laboratory results, utilising linear regression techniques we measure the change in orientation in order to measure the optical torque applied to a non-birefringent particle.

Bibliography

[1] Herbert M. Schoen, C. S. Grove, and Joseph A. Palermo. "The early history of crystallization". In: *Journal of Chemical Education* 33.8 (Aug. 1956), p. 373. ISSN: 1938-1328. DOI: 10.1021/ed033p373.

[2] Zhenguo Gao, Sohrab Rohani, Junbo Gong, et al. "Recent Developments in the Crystallization Process: Toward the Pharmaceutical Industry". In: *Engineering* 3.3 (June 2017), pp. 343–353. ISSN: 2095-8099. DOI: 10.1016/j.eng.2017.03.022.

[3] Richard W. Hartel. "Crystallization in foods". In: *Handbook of Industrial Crystallization*. Elsevier, 2002, pp. 287–304. ISBN: 9780750670128. DOI: 10.1016/b978-075067012-8/50015-x.

[4] Allan S. Myerson and Rajiv Ginde. "Crystals, crystal growth, and nucleation". In: *Handbook of Industrial Crystallization*. Elsevier, 2002, pp. 33–65. ISBN: 9780750670128. DOI: 10.1016/b978-075067012-8/50004-5.

[5] Haoyang Fu, Xing Gao, Xin Zhang, et al. "Recent Advances in Nonclassical Crystallization: Fundamentals, Applications, and Challenges". In: *Crystal Growth &; Design* 22.2 (Nov. 2021), pp. 1476–1499. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.1c01084.

[6] John W. Mullin. *Crystallization*. 4th ed. Description based on publisher supplied metadata and other sources. Oxford: Elsevier Science Technology, 2001. 1611 pp. ISBN: 9780080530116.

[7] Gregory D. Botsaris. "Secondary Nucleation — A Review". In: *Industrial Crystallization*. Springer US, 1976, pp. 3–22. ISBN: 9781461572589. DOI: 10.1007/978-1-4615-7258-9_1.

[8] Jamshed Anwar, Shahzeb Khan, and Lennart Lindfors. "Secondary Crystal Nucleation: Nuclei Breeding Factory Uncovered". In: *Angewandte Chemie International Edition* 54.49 (Mar. 2015), pp. 14681–14684. ISSN: 1521-3773. DOI: 10.1002/anie.201501216.

[9] S. G. Agrawal and A. H. J. Paterson. "Secondary Nucleation: Mechanisms and Models". In: *Chemical Engineering Communications* 202.5 (Jan. 2015), pp. 698–706. ISSN: 1563-5201. DOI: 10.1080/00986445.2014.969369.

[10] J. Frenkel. "A General Theory of Heterophase Fluctuations and Pretransition Phenomena". In: *The Journal of Chemical Physics* 7.7 (July 1939), pp. 538–547. ISSN: 1089-7690. DOI: 10.1063/1.1750484.

[11] M Volmer and Weber. "Keimbildung in ubersattigten Gebilden". In: *Zeitschrift fur Physikalische Chemie* 119U.1 (Jan. 1926), pp. 277–301. ISSN: 0942-9352. DOI: 10.1515/zpch-1926-11927.

[12] S. Karthika, T. K. Radhakrishnan, and P. Kalaichelvi. "A Review of Classical and Nonclassical Nucleation Theories". In: *Crystal Growth &; Design* 16.11 (Oct. 2016), pp. 6663–6681. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.6b00794.

[13] Murad Gharibeh, Yoojeong Kim, Uta Dieregsweiler, et al. "Homogeneous nucleation of n-propanol, n-butanol, and n-pentanol in a supersonic nozzle". In: *The Journal of Chemical Physics* 122.9 (Mar. 2005). ISSN: 1089-7690. DOI: 10.1063/1.1858438.

[14] Peter G. Vekilov. "The two-step mechanism of nucleation of crystals in solution". In: *Nanoscale* 2.11 (2010), p. 2346. ISSN: 2040-3372. DOI: 10.1039/c0nr00628a.

[15] W T Lee, E K H Salje, and Martin T Dove. "Effect of surface relaxations on the equilibrium growth morphology of crystals: platelet formation". In: *Journal of Physics: Condensed Matter* 11.38 (Sept. 1999), pp. 7385–7410. ISSN: 1361-648X. DOI: 10.1088/0953-8984/11/38/316.

[16] S.-T. Yau and Peter G. Vekilov. "Direct Observation of Nucleus Structure and Nucleation Pathways in Apoferritin Crystallization". In: *Journal of the American Chemical Society* 123.6 (Jan. 2001), pp. 1080–1089. ISSN: 1520-5126. DOI: 10.1021/ja003039c.

[17] Alexander E.S., Van Driessche, Matthias Kellermeier, et al. *New Perspectives on Mineral Nucleation and Growth*. Springer International Publishing, 2017. ISBN: 9783319456690. DOI: 10.1007/978-3-319-45669-0.

[18] J. R. Savage and A. D. Dinsmore. "Experimental Evidence for Two-Step Nucleation in Colloidal Crystallization". In: *Physical Review Letters* 102.19 (May 2009), p. 198302. ISSN: 1079-7114. DOI: 10.1103/physrevlett.102.198302.

[19] Pieter Rein ten Wolde and Daan Frenkel. "Enhancement of Protein Crystal Nucleation by Critical Density Fluctuations". In: *Science* 277.5334 (Sept. 1997), pp. 1975–1978. ISSN: 1095-9203. DOI: 10.1126/science.277.5334.1975.

[20] K. Geoffrey Soga, John R. Melrose, and Robin C. Ball. "Metastable states and the kinetics of colloid phase separation". In: *The Journal of Chemical Physics* 110.4 (Jan. 1999), pp. 2280–2288. ISSN: 1089-7690. DOI: 10.1063/1.477881.

[21] W. Ostwald. "Studien über die Bildung und Umwandlung fester Körper: 1. Abhandlung: Übersättigung und Überkaltung". In: *Zeitschrift für Physikalische Chemie* 22U.1 (Feb. 1897), pp. 289–330. ISSN: 0942-9352. DOI: 10.1515/zpch-1897-2233.

[22] Zhiyu Liao and Klaas Wynne. "A Metastable Amorphous Intermediate Is Responsible for Laser-Induced Nucleation of Glycine". In: 144 (2022), pp. 6727–6733. ISSN: 0002-7863. DOI: 10.1021/jacs.1c11154.

[23] Kecheng Cao, Johannes Biskupek, Craig T. Stoppiello, et al. "Atomic mechanism of metal crystal nucleus formation in a single-walled carbon nanotube". In: *Nature Chemistry* 12.10 (Aug. 2020), pp. 921–928. ISSN: 1755-4349. DOI: 10.1038/s41557-020-0538-9.

[24] Huanyu Ye, Zhihong Zhang, and Rongming Wang. "Nucleation and Growth of Nanocrystals Investigated by In Situ Transmission Electron Microscopy". In: *Small* 19.49 (Aug. 2023). ISSN: 1613-6829. DOI: 10.1002/smll.202303872.

[25] Peng Tan, Ning Xu, and Lei Xu. "Visualizing kinetic pathways of homogeneous nucleation in colloidal crystallization". In: *Nature Physics* 10.1 (Dec. 2013), pp. 73–79. ISSN: 1745-2481. DOI: 10.1038/nphys2817.

[26] Jens Baumgartner, Archan Dey, Paul H. H. Bomans, et al. "Nucleation and growth of magnetite from solution". In: *Nature Materials* 12.4 (Feb. 2013), pp. 310–314. ISSN: 1476-4660. DOI: 10.1038/nmat3558.

[27] Miguel A. Durán-Olivencia and James F. Lutsko. "Mesoscopic nucleation theory for confined systems: A one-parameter model". In: *Physical Review E* 91.2 (Feb. 2015), p. 022402. ISSN: 1550-2376. DOI: 10.1103/physreve.91.022402.

[28] Aaron R. Finney and Matteo Salvalaglio. "Molecular simulation approaches to study crystal nucleation from solutions: Theoretical considerations and computational challenges". In: *WIREs Computational Molecular Science* 14.1 (Nov. 2023). ISSN: 1759-0884. DOI: 10.1002/wcms.1697.

[29] David B. Williams and C. Barry Carter. *Transmission Electron Microscopy.* Springer US, 2009. ISBN: 9780387765013. DOI: 10.1007/978-0-387-76501-3.

[30] P. E. Champness. *Electron Diffraction in the Transmission Electron Microscope.* Aug. 2020. DOI: 10.1201/9781003076872.

[31] N. Duane Loh, Soumyo Sen, Michel Bosman, et al. "Multistep nucleation of nanocrystals in aqueous solution". In: *Nature Chemistry* 9.1 (Oct. 2016), pp. 77–82. ISSN: 1755-4349. DOI: 10.1038/nchem.2618.

[32] Edward T. Broadhurst, Hongyi Xu, Max T. B. Clabbers, et al. "Polymorph evolution during crystal growth studied by 3D electron diffraction". In: *IUCrJ* 7.1 (Jan. 2020), pp. 5–9. ISSN: 2052-2525. DOI: 10.1107/s2052252519016105.

[33] A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, et al. *Observation of a single-beam gradient force optical trap for dielectric particles.* DOI: 10.1887/0750309016/b1142c30.

[34] A. Ashkin. "Applications of Laser Radiation Pressure". In: *Science* 210.4474 (Dec. 1980), pp. 1081–1088. ISSN: 1095-9203. DOI: 10.1126/science.210.4474.1081.

[35] Po-Wei Yi, Wei-Hsiang Chiu, Tetsuhiro Kudo, et al. "Cooperative Optical Trapping of Polystyrene Microparticle and Protein Forming a Submillimeter Linear Assembly of Microparticle". In: *The Journal of Physical Chemistry C* 125.34 (Aug. 2021), pp. 18988–18999. ISSN: 1932-7455. DOI: 10.1021/acs.jpcc.1c05796.

[36] Jonghoon Ahn, Zhujing Xu, Jaehoon Bang, et al. "Optically Levitated Nanodumbbell Torsion Balance and GHz Nanomechanical Rotor". In: *Physical Review Letters* 121.3 (July 2018), p. 033603. ISSN: 1079-7114. DOI: 10.1103/physrevlett.121.033603.

[37] Fernando Monteiro, Sumita Ghosh, Elizabeth C. van Assendelft, et al. "Optical rotation of levitated spheres in high vacuum". In: *Physical Review A* 97.5 (May 2018), p. 051802. ISSN: 2469-9934. DOI: 10.1103/physreva.97.051802.

[38] B. A. Garetz, J. E. Aber, N. L. Goddard, et al. "Nonphotochemical, Polarization-Dependent, Laser-Induced Nucleation in Supersaturated Aqueous Urea Solutions". In: *Physical Review Letters* 77.16 (Oct. 1996), pp. 3475–3476. ISSN: 1079-7114. DOI: 10.1103/physrevlett.77.3475.

[39] Bruce A. Garetz, Jelena Matic, and Allan S. Myerson. "Polarization Switching of Crystal Structure in the Nonphotochemical Light-Induced Nucleation of Supersaturated Aqueous Glycine Solutions". In: *Physical Review Letters* 89.17 (Oct. 2002), p. 175501. ISSN: 1079-7114. DOI: 10.1103/physrevlett.89.175501.

[40] Xiaoying Sun, Bruce A. Garetz, and Allan S. Myerson. "Supersaturation and Polarization Dependence of Polymorph Control in the Nonphotochemical Laser-Induced Nucleation (NPLIN) of Aqueous Glycine Solutions". In: *Crystal Growth &; Design* 6.3 (2006), pp. 684–689. ISSN: 1528-7483. DOI: 10.1021/cg050460+.

[41] Rohit Kacker, Sanjana Dhingra, Daniel Irimia, et al. "Multiparameter Investigation of Laser-Induced Nucleation of Supersaturated Aqueous KCl Solutions". In: *Crystal Growth &; Design* 18.1 (Dec. 2017), pp. 312–317. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.7b01277.

[42] Brandon C. Knott, Michael F. Doherty, and Baron Peters. "A simulation test of the optical Kerr mechanism for laser-induced nucleation". In: *The Journal of Chemical Physics* 134.15 (Apr. 2011). ISSN: 1089-7690. DOI: 10.1063/1.3574010.

[43] Andrew J. Alexander and Philip J. Camp. "Single Pulse, Single Crystal Laser-Induced Nucleation of Potassium Chloride". In: *Crystal Growth &; Design* 9.2 (Dec. 2008), pp. 958–963. ISSN: 1528-7505. DOI: 10.1021/cg8007415.

[44] Vikram Korede, Nagaraj Nagalingam, Frederico Marques Penha, et al. "A Review of Laser-Induced Crystallization from Solution". In: *Crystal Growth & Design* 23.5 (2023), pp. 3873–3916. DOI: 10.1021/acs.cgd.2c01526. eprint: https://doi.org/10.1021/acs.cgd.2c01526. URL: https://doi.org/10.1021/acs.cgd.2c01526.

[45] Martin R. Ward, Alasdair M. Mackenzie, and Andrew J. Alexander. "Role of Impurity Nanoparticles in Laser-Induced Nucleation of Ammonium Chloride". In: *Crystal Growth &; Design* 16.12 (Nov. 2016), pp. 6790–6796. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.6b00882.

[46] Hiroshi Y. Yoshikawa, Yoichiroh Hosokawa, and Hiroshi Masuhara. "Explosive Crystallization of Urea Triggered by Focused Femtosecond Laser Irradiation". In: *Japanese Journal of Applied Physics* 45.1L (Dec. 2005), p. L23. ISSN: 1347-4065. DOI: 10.1143/jjap.45.l23.

[47] Anamaria Soare, Rory Dijkink, Marcos Rodriguez Pascual, et al. "Crystal Nucleation by Laser-Induced Cavitation". In: *Crystal Growth &; Design* 11.6 (Apr. 2011), pp. 2311–2316. ISSN: 1528-7505. DOI: 10.1021/cg2000014.

[48] Eleanor R. Barber, Nina L. H. Kinney, and Andrew J. Alexander. "Pulsed Laser-Induced Nucleation of Sodium Chlorate at High Energy Densities". In: *Crystal Growth &; Design* 19.12 (Oct. 2019), pp. 7106–7111. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.9b00951.

[49] Kenji Ikeda, Mihoko Maruyama, Yoshinori Takahashi, et al. "Selective crystallization of the metastable phase of indomethacin at the interface of liquid/air

bubble induced by femtosecond laser irradiation". In: *Applied Physics Express* 8.4 (Mar. 2015), p. 045501. ISSN: 1882-0786. DOI: 10.7567/apex.8.045501.

[50] Xi-Lin Wang, Jing Chen, Yongnan Li, et al. "Optical orbital angular momentum from the curl of polarization". In: *Physical Review Letters* 105.25 (Dec. 2010), p. 253602. ISSN: 1079-7114. DOI: 10.1103/physrevlett.105.253602.

[51] Yasuyuki Tsuboi, Tatsuya Shoji, and Noboru Kitamura. "Optical Trapping of Amino Acids in Aqueous Solutions". In: *The Journal of Physical Chemistry C* 114.12 (Dec. 2009), pp. 5589–5593. ISSN: 1932-7455. DOI: 10.1021/jp9072334.

[52] Ken-ichi Yuyama, Teruki Sugiyama, and Hiroshi Masuhara. "Millimeter-Scale Dense Liquid Droplet Formation and Crystallization in Glycine Solution Induced by Photon Pressure". In: *The Journal of Physical Chemistry Letters* 1.9 (Apr. 2010), pp. 1321–1325. ISSN: 1948-7185. DOI: 10.1021/jz100266t.

[53] Ken-ichi Yuyama, Thitiporn Rungsimanon, Teruki Sugiyama, et al. "Formation, Dissolution, and Transfer Dynamics of a Millimeter-Scale Thin Liquid Droplet in Glycine Solution by Laser Trapping". In: *The Journal of Physical Chemistry C* 116.12 (Mar. 2012), pp. 6809–6816. ISSN: 1932-7455. DOI: 10.1021/jp210576k.

[54] Omar Y. Gowayed, Tahany Moosa, Angelica M. Moratos, et al. "Dynamic Light Scattering Study of a Laser-Induced Phase-Separated Droplet of Aqueous Glycine". In: 125 (2021), pp. 7828–7839. ISSN: 1520-6106. DOI: 10.1021/acs.jpcb.1c02620.

[55] Martin B. Sweatman, Nasser D. Afify, Carlos A. Ferreiro-Rangel, et al. "Molecular Dynamics Investigation of Clustering in Aqueous Glycine Solutions". In: *The Journal of Physical Chemistry B* 126.25 (June 2022), pp. 4711–4722. ISSN: 1520-5207. DOI: 10.1021/acs.jpcb.2c01975.

[56] Alexis I. Bishop, Timo A. Nieminen, Norman R. Heckenberg, et al. "Optical Microrheology Using Rotating Laser-Trapped Particles". In: *Physical Review Letters* 92.19 (May 2004), p. 198104. ISSN: 1079-7114. DOI: 10.1103/physrevlett.92.198104.

[57] Rae M. Robertson-Anderson. "Optical Tweezers Microrheology: From the Basics to Advanced Techniques and Applications". In: *ACS Macro Letters* 7.8 (Aug. 2018), pp. 968–975. ISSN: 2161-1653. DOI: 10.1021/acsmacrolett.8b00498.

[58] Richard A. Beth. "Mechanical Detection and Measurement of the Angular Momentum of Light". In: *Physical Review* 50 (1936), pp. 115–125. URL: https://api.semanticscholar.org/CorpusID:126010764.

[59] Graham D. Bruce, Paloma Rodríguez-Sevilla, and Kishan Dholakia. "Initiating revolutions for optical manipulation: the origins and applications of rotational dynamics of trapped particles". In: *Advances in Physics: X* 6.1 (Dec. 2020). ISSN: 2374-6149. DOI: 10.1080/23746149.2020.1838322.

[60] V. Svak, O. Brzobohatý, M. Šiler, et al. "Transverse spin forces and non-equilibrium particle dynamics in a circularly polarized vacuum optical trap". In: *Nature Communications* 9.1 (Dec. 2018). ISSN: 2041-1723. DOI: 10.1038/s41467-018-07866-8.

[61] Johannes Courtial and Miles J. Padgett. "Limit to the orbital angular momentum per unit energy in a light beam that can be focussed onto a small particle". In: *Optics Communications* 173.1-6 (2000), pp. 269–274. ISSN: 0030-4018. DOI: 10.1016/s0030-4018(99)00619-7.

[62] Konstantin Y. Bliokh, Aleksandr Y. Bekshaev, and Franco Nori. "Extraordinary momentum and spin in evanescent waves". In: *Nature Communications* 5.1 (Mar. 2014). ISSN: 2041-1723. DOI: 10.1038/ncomms4300.

[63] Simon J. Parkin, Robert Vogel, Martin Persson, et al. "Highly birefringent vaterite microspheres: production, characterization and applications for optical micromanipulation". In: *Optics Express* 17.24 (Nov. 2009), p. 21944. ISSN: 1094-4087. DOI: 10.1364/oe.17.021944.

[64] Yoshihiko Arita, Joseph M. Richards, Michael Mazilu, et al. "Rotational Dynamics and Heating of Trapped Nanovaterite Particles". In: *ACS Nano* 10.12 (Dec. 2016), pp. 11505–11510. ISSN: 1936-086X. DOI: 10.1021/acsnano.6b07290.

[65] J. Millen, T. Deesuwan, P. Barker, et al. "Nanoscale temperature measurements using non-equilibrium Brownian dynamics of a levitated nanosphere". In: *Nature Nanotechnology* 9.6 (May 2014), pp. 425–429. ISSN: 1748-3395. DOI: 10.1038/nnano.2014.82.

[66] Paloma Rodríguez-Sevilla, Yoshihiko Arita, Xiaogang Liu, et al. "The Temperature of an Optically Trapped, Rotating Microparticle". In: *ACS Photonics* 5.9 (Aug. 2018), pp. 3772–3778. ISSN: 2330-4022. DOI: 10.1021/acsphotonics.8b00822.

[67] René Reimann, Michael Doderer, Erik Hebestreit, et al. "GHz Rotation of an Optically Trapped Nanoparticle in Vacuum". In: *Physical Review Letters* 121.3 (July 2018), p. 033602. ISSN: 1079-7114. DOI: 10.1103/physrevlett.121.033602.

[68] Qi Zhu, Nan Li, Heming Su, et al. "Dynamic Analysis and Simulation of an Optically Levitated Rotating Ellipsoid Rotor in Liquid Medium". In: *Photonic Sensors* 12.2 (Sept. 2021), pp. 105–116. ISSN: 2190-7439. DOI: 10.1007/s13320-021-0639-0.

[69] B. M. Mihiretie, P. Snabre, J. -C. Loudet, et al. "Optically driven oscillations of ellipsoidal particles. Part I: Experimental observations". In: *The European Physical Journal E* 37.12 (Dec. 2014). ISSN: 1292-895X. DOI: 10.1140/epje/i2014-14124-0.

[70] E. Higurashi, H. Ukita, H. Tanaka, et al. "Optically induced rotation of anisotropic micro-objects fabricated by surface micromachining". In: *Applied Physics Letters* 64.17 (Apr. 1994), pp. 2209–2210. ISSN: 1077-3118. DOI: 10.1063/1.111675.

[71] Jaehoon Bang, T. Seberson, Peng Ju, et al. "Five-dimensional cooling and nonlinear dynamics of an optically levitated nanodumbbell". In: *Physical Review Research* 2.4 (Oct. 2020), p. 043054. ISSN: 2643-1564. DOI: 10.1103/physrevresearch.2.043054.

[72] Yogesha, Sarbari Bhattacharya, and Sharath Ananthamurthy. "Precise characterization of micro rotors in optical tweezers". In: *arXiv: Soft Condensed Matter* (2011). URL: https://api.semanticscholar.org/CorpusID:118262469.

[73] R. Bar-Ziv, A. Meller, T. Tlusty, et al. "Localized Dynamic Light Scattering: Probing Single Particle Dynamics at the Nanoscale". In: *Physical Review Letters* 78.1 (Jan. 1997), pp. 154–157. ISSN: 1079-7114. DOI: 10.1103/physrevlett.78.154.

[74] A. Meller, R. Bar-Ziv, T. Tlusty, et al. "Localized Dynamic Light Scattering: A New Approach to Dynamic Measurements in Optical Microscopy". In: *Biophysical Journal* 74.3 (Mar. 1998), pp. 1541–1548. ISSN: 0006-3495. DOI: 10.1016/s0006-3495(98)77866-x.

[75] Federica Mura and Alessio Zaccone. "Effects of shear flow on phase nucleation and crystallization". In: *Physical Review E* 93.4 (Apr. 2016), p. 042803. ISSN: 2470-0053. DOI: 10.1103/physreve.93.042803.

[76] Robin Debuysschère, Bart Rimez, Alessio Zaccone, et al. "Experimental and Theoretical Investigation of Nonclassical Shear-Induced Nucleation Mechanism for Small Molecule". In: *Crystal Growth &; Design* 23.7 (June 2023), pp. 4979–4989. ISSN: 1528-7505. DOI: 10.1021/acs.cgd.3c00232.

[77] David Richard and Thomas Speck. "The role of shear in crystallization kinetics: From suppression to enhancement". In: *Scientific Reports* 5.1 (Sept. 2015). ISSN: 2045-2322. DOI: 10.1038/srep14610.

[78] Amrita Goswami, Indranil Saha Dalal, and Jayant K. Singh. "Seeding method for ice nucleation under shear". In: *The Journal of Chemical Physics* 153.9 (Sept. 2020). ISSN: 1089-7690. DOI: 10.1063/5.0021206.

[79] A. Mersmann. *Crystallization Technology Handbook*. CRC Press, May 2001. ISBN: 9780203908280. DOI: 10.1201/9780203908280.