Chapter 1

Introduction

Crystallisation is one of the oldest forms of phase separation used by humanity[46], put simply, it is the formation and growth of a new structured phase within a disordered bulk phase. This has applications in a number of industries such as pharmaceuticals, food production, and electronics [39]. Where the extraction of dilute materials can help improve product quality while keeping production costs low. The industrialisation of crystallisation has allowed engineers to reliably and efficiently induce the crystal formation within a bulk phase. However, while on a large scale crystallisation is seemingly an understood physical process, just a small amount of investigation into the literature reveals that at a micro scale there is yet to be unifying theory that can accurately explain the process of crystallisation [18]. Of which there two primary areas of focus, nucleation and crystal growth. The latter focusing on how an already stable crystal grows and how it takes on its final shape. Whereas the former is more concerned with which factors contribute to its formation in order to control crystal growth.

The focus of this research is partly based around investigating the impact of a focused electromagnetic (EM) field can influence the nucleation process by inducing shear flow within the bulk phase. This in hope that the localised EM field can be used to study different phenomena in nucleation in order to develop a better understanding of the underlying mechanisms.

1.1 Nucleation

Nucleation is an example of a binary phase separation, where a dilute phase is miscible in a bulk phase, more often called the solute and solvent respectively. Because of thermodynamics, the two can only remain in equilibrium while below a specific concentration (C_{eq}) - below which the chemical potential μ for a miscible solution is greater than the potential required to separate the two phases. Once C_{eq} is exceeded there is a chemical potential difference driving the solution to separate the two phases. Since different combinations of solute and solvent will have different equilibrium concentrations, researchers often instead measure the ratio between the solute and solvent by using 'supersaturation', one form of measuring supersaturation is shown below [37]:

$$S(T) = \frac{C_{sol}}{C_{eq}(T)} \tag{1.1}$$

Where C_{sol} is just the solute concentration, and $C_{eq}(T)$ is the equilibrium concentration at temperature T. While the solution remains supersaturated there is a chemical potential driving force for the solute to coalesce and separate from the solution as an ordered solid, the first formation of the crystal is referred to as the nucleus and understanding its formation of has been the focus of researchers for decades now. Typically, for an industrial crystallisation process the working principle is based on controlling and manipulating the supersaturation of the system. Of course nucleation events in a variety of different situations which each require their own classification.

1.1.1 Primary & Secondary nucleation

From an industrial perspective, the nucleation process can be broadly categorised into either primary of secondary nucleation. The former describes the formation of an initial nucleus within the bulk phase, absent of any external stimuli. Primary nucleation is therefore considered stochastic as there is no reliable means of predicting where a nucleus may form, or how long it will take. The only reliable indicator being that higher supersaturations will result in faster nucleation rates. At a small scale one can estimate the nucleation rate by making repeated measurements of sample solutions

and seeing how many have nucleated after a given time, giving us a Poisson probability distribution.

$$P(t) = 1 - exp\left[-JV(t - t_g)\right] = \frac{M^*(t)}{M} \qquad (1.2)$$

Where J is the nucleation rate, t_g is the 'growth time', V is the volume of the individual samples, and $M^*(t)$ & M are the number of nucleated samples and the total number of samples used respectively. While this is useful for studying the effects of different parameters at a small scale, for industrial applications there are to many external factors for primary nucleation to be the only

In contrast, secondary nucleation is the result of a initial seed crystal inducing further nucleation within the bulk solution [12], in absence of a seed crystal nucleation is near impossible. The research of Secondary Nucleation is fascinating for its own merits; is it speculated that the supersaturation barrier is non-existent [14], and furthermore there are a multitude of mechanisms that can induce secondary nucleation making it imperative that researchers can control the nucleation rate at an industrial scale.
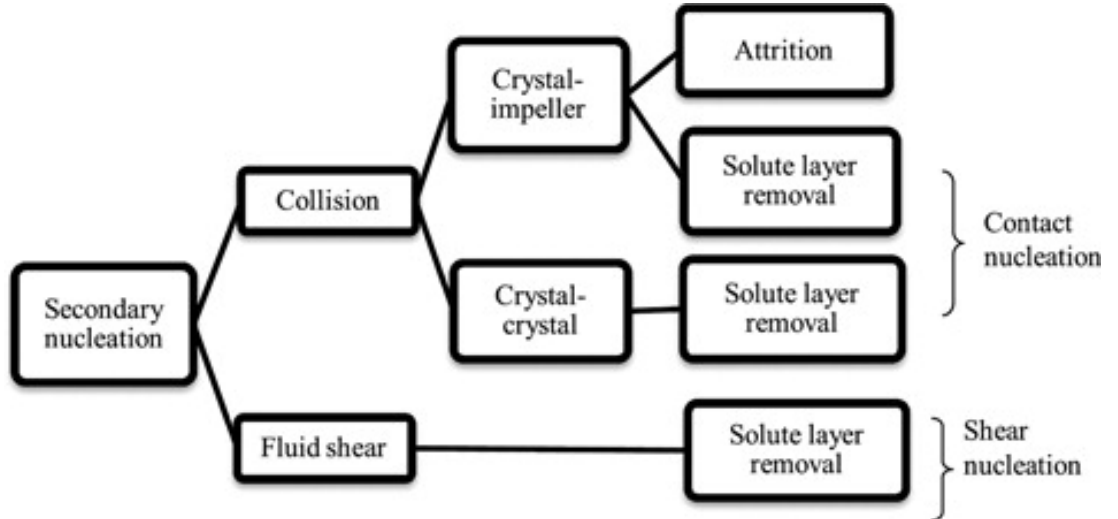

Figure 1.1: Secondary Nucleation mechanisms, classified by Agrawal and Paterson [1]

1.2 Nucleation Theories

1.2.1 Classical Nucleation Theory (CNT)

Sometimes referred to as 'Gibs Nucleation Theory' the original theory was first formed from the works of Volmer and Weber, and Frenkel [17, 55]. While initially it was more focused into describing droplet formation in condensing vapours it was extrapolated to describe crystallisation. The central premise of classical theory is that nucleation occurs stochastically due to collisions between individual solute molecules, ions, or atoms. At the same time the bulk phase is resistant to the formation of a new phase. The competition between these random collisions and the bulk solution can be used to predict the probability of a newly formed nucleus.

Consider a supersaturated solution, after some time enough individual sub units collide, forming a nucleus of volume $4\pi r^3/3$. The newly formed phase has a lower chemical potential than the surrounding solution, reducing the free energy of the system. Simultaneously, the formation of a new interface is resited by the bulk phase due to surface tension. The net free energy of the system for a nucleus of radius r is given as [28]:

$$\Delta G = \frac{-4\pi r^3}{3v} k_B T \ln(S) + 4\pi r^2 \sigma_{inf} \tag{1.3}$$

Where v is the approximate volume of an individual molecule, k_B is the Boltzmann constant, and σ_{inf} is the interfacial tension of the bulk solution. This assumes that the nucleus will have a spherical morphology so that the surface tension σ_{inf} is a scalar value. Looking at (1.3) suggests that there must be some critical size r where the free energy gain from the nucleus exceeds the surface tension of the surrounding fluid. Plotting the free energy of the system against nucleus size reveals a critical size above which the gain in free energy exceeds the interfacial tension. Furthermore it shows how increasing the supersaturation of the system reduces said barrier.

The maximum value of ΔG_{tot} is the free energy barrier that any newly formed nucleus needs to overcome in order to stabilise. The nucleation rate (the volume of
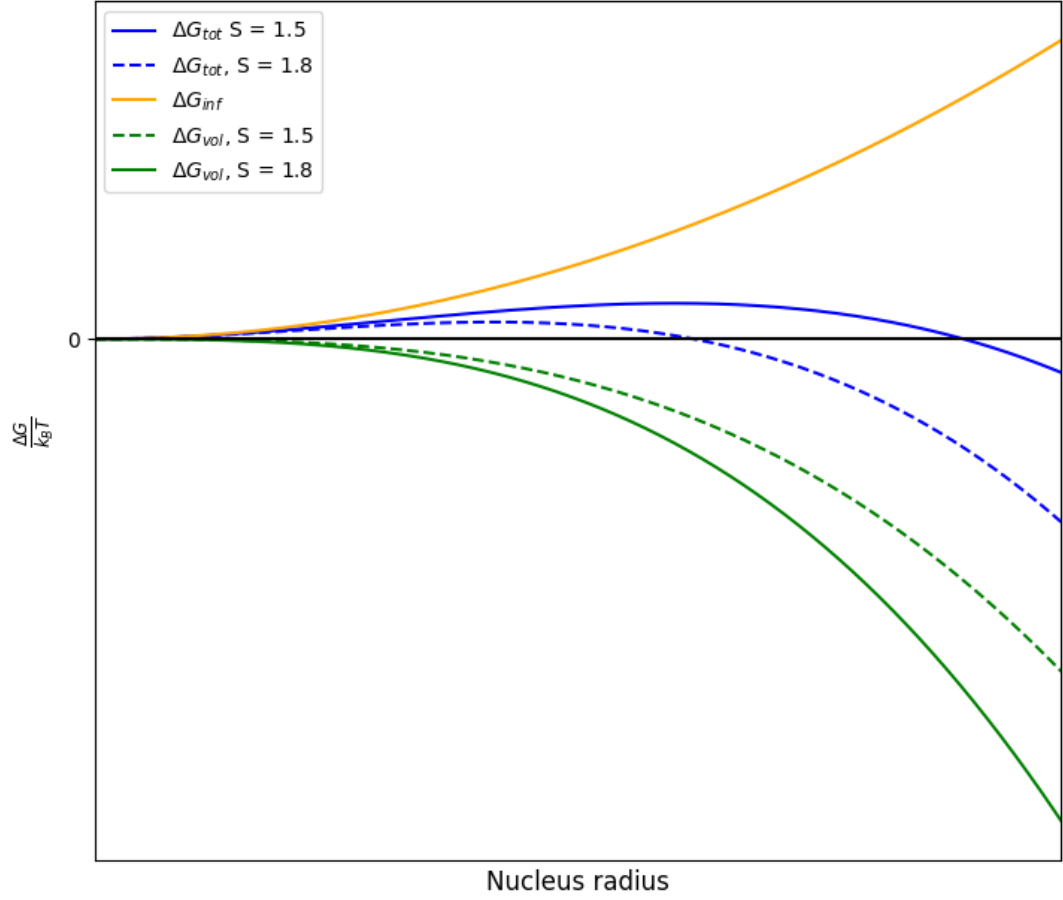
Figure 1.2: Free energy diagram of a newly formed nucleus according to the Classical Nucleation Theory. The total free energy (blue) is due to the competition between the volume free energy gain (green) and the interfacial free energy cost (orange). Dotted lines are for a higher supersaturation than the solid lines, the interfacial energy cost is independent of supersaturation.

new crystalline material formed per unit time), is therefore commonly defined as being dependent on the energy barrier ΔG^*:

$$J = A \; exp \left[-\frac{\Delta G^*}{k_B T} \right] \tag{1.4}$$

Where A is a pre-factor that can be fine tuned to the exact demands of the system (typically involving Zeldovich Factor, Z) the free energy barrier can be found by finding the turning point of ΔG_{tot}.

CNT is often regarded as a good description of the macro system, its obvious that for all crystallization systems there is an inherent energy barrier that dictates the nucleation rate. Where it falters is in its predictive ability, both in estimating nucleation rates [21, 54], and in the structure of newly formed nuclei [31, 59]. Recent studies suggest classical nucleation is merely one of many possible pathways that can be taken to produce a structured crystalline phase. Prompting the development of alternative theories to better describe the nucleation process.

1.2.2 Two Step Nucleation

The two step nucleation theory is an extension to the CNT that suggests that prior to nucleation, the solute will cluster together. This was shown via colloid simulations showed that short range (such as in proteins [58, 22]) interactions allow for the formation of a liquid-liquid metastable phase from which a new solid phase could form [4, 28]. Several papers later reported the presence of stable liquid-like clusters that formed prior to nucleation [45, 58, 48]. The formation of these clusters can be understood by Oswald's rule; which says that any crystallising system does not immediately take the path to the lowest possible energy state but instead first transitions to the state with the smallest free energy barrier [40]. Further phase transitions can still occur but this pathway minimises the overall free energy cost. Initially it was suspected that the formation of the dense liquid phase was a result of stochastic density fluctuations in the system. However, simulations suggest that the the local bond order is a stronger driving force than the local density [52]. Studies into two step nucleation in Glycine solutions have noted that the solutions need to be aged before the presence of clusters was detected. This suggests that there exist further barriers to the formation of clusters in some systems, this has lead to instead calling this phenomena as Multi-step Nucleation.

1.2.3 Non-classical Nucleation

The current research into two step nucleation (or now more commonly referred to as multi-step nucleation theory) is developing a robust framework to describe what nucleation pathway will occur given the initial conditions. Reviews of all currently

documented nucleation pathways identified highlighted the fact the need for a the development of *in situ* techniques that can induce nucleation locally but can also reliably identify the nucleation pathway across a broad range of experimental conditions [28, 18].

1.3 Crystallisation methods

1.3.1 Cooling Crystallisation

For some binary mixtures the supersaturation is heavily dependent on the solution temperature, therefore a simple method of producing crystals is by cooling the mixture to induce crystal formation. At ambient temperatures the solute concentration is too high to be fully incorporated into the solution ($S \gg 1$), after heating however the solute is fully dissolved into the solution ($S < 1$). Now as the mixture is allowed to cool to room temperature the supersaturation will increase until crystal formation begins, the rate of cooling drastically influencing the size and number of crystals produced.

If dT/dt is high then the final product will consist of large crystal and be low in number, as the nucleation rate is directly related to the supersaturation only a handful of nuclei can form before the remaining solute grows onto the surface. If dT/dt is low then the final product will consist of smaller crystals and be far more numerous, as the supersaturation is so large that the new nuclei are forming continuously. Between these two extremes, one can define the meta-stable zone width, a region in the temperature-concentration phase space where both nucleation and crystal growth can be reliably controlled. The lower limit being given by the solubility curve of the binary mixture, and the upper limit being defined by the metastable zone.

The viability of cooling crystallisation is dependent on the meta-stable zone width, too narrow and the process is difficult to control, too wide and the crystal growth rate may be insufficient for the desired outcome.
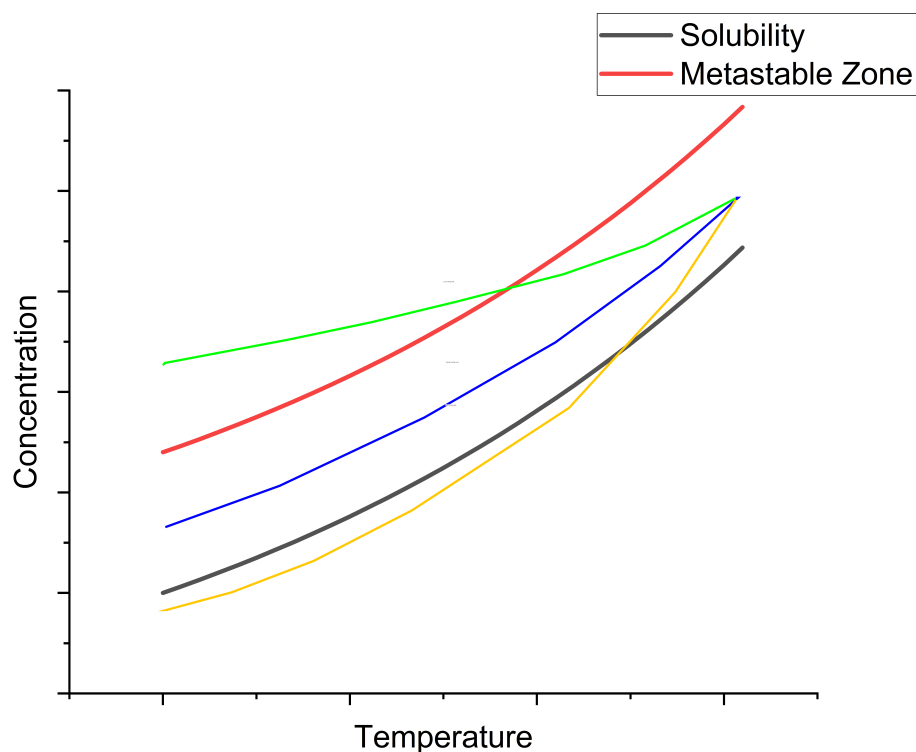
Figure 1.3: Typical Concentration vs Temperature plot with the solubility curve (black) and metastable zone (red). 3 different cooling curves are shown as well: a high rate of cooling (orange) shows the mixture quickly dropping below the solubility curve resulting in no new nuclei forming; a low rate of cooling (green) shows the mixture exceeding the metastable zone, where now nucleation occurs freely; and a typical cooling rate (blue) shows how a typical cooling crystalliser will operate, sitting in the middle of the other two curves.

1.3.2 Evaporative Crystallisation

In situations where control of the final product size or shape is not the main focus, often the cheapest method of producing a crystalline product is simply to allow the solvent evaporate and separate from the solute. Depending on the total volume of solvent to evaporate this process can take on time scale of several days to complete.

1.3.3 Anti-solvent Crystallisation

Anti-solvent crystallisation is a more involved separation method , by adding a new solvent that is miscible with the old solvent but is immiscible with the solute, the solute's effective solubility is decreased. As such, the solution becomes supersaturated. This has the trade off in that the overall mass ratio between the solvent and solute is now lower. Careful measurement of the anti-solvent is required in order to ensure that the decrease in solubility is not out matched by the decrease in mass ratio. Anti-solvent crystallisation is not as common due to the fact that not all solutions will have an ideal anti-solvent candidate.

1.4 Optical Tweezers

1.4.1 Background

Optical tweezing has been a field of applied optics ever since the 1970s when Ashkin [7] first showed that focused light was capable of trapping micron sized particles due to light exerting 'radiation pressure'. The working principle was that a light source such as a laser could trap small objects within a 2D plane, as long as the light source had an approximately Gaussian profile. Soon after, Ashkin showed that the introduction of a microscope objective would allow one to focus the light source to a diffraction limited point that would stably trap small objects within a confined volume [6]. This allowed Ashkin and others to study biological material and would later be used to probe microscopic properties such as the formation of colloidal aggregates [60] to the drag forces exerted by a pure vacuum [2, 36]. Due to the predictable behaviour of light, optical tweezers have become essential for measuring and exerting precise forces on the magnitude of pico-newtons allowing one to probe the material properties of the smallest materials.

1.4.2 Gaussian Beams

A Gaussian Beam is a simplistic approximation of a laser beam, in short it is an unbounded plane wave whose intensity of the electromagnetic field falls off from the

centre similar to a normal distribution. This is perfectly fine for beams with a divergence angle of $0°$, but later studies into focused beams has shown that the assumption of a Gaussian intensity profile is inaccurate. A study conducted by Lock and Gouesbet found that as the Gaussian beam was focused the fall off in the electric field would consequentially induce additional electromagnetic fields [33]. As a result the shape of the beam profile diverges from a Gaussian profile for focused beams. Regardless, for optical trapping experiments it is useful to approximate a Gaussian beam as many descriptions of lasers are simply combinations of plane waves (with varying amplitudes and wave vectors). More information on electromagnetic theory is covered in chapter 2 but for now any mention of a focused laser can be thought of as a Gaussian beam, unless specified otherwise.

1.4.3 Literature related to laser induced nucleation

From as early as 1996 it has been known that laser irradiation is a viable method of inducing nucleation within a supersaturated solution [19]. 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 [20]. Future research has found nucleation can be induced by 1 of 3 routes.

1.4.3.1 Non-Photochemical Laser Induced Nucleation

Non-photochemical laser induced nucleation (NPLIN) involves irradiating a solution with a pulsed laser [19, 20, 49]. 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 [27]. In addition, 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 [20]. Several papers have debated the exact mechanism that induces

NPLIN [20, 29]. 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 [20]. If enough molecules are co-aligned the free energy barrier is reduced to allow for ambient nucleation [29]. An alternative theory is the dielectric polarisation effect, in conditions that are unfavourable to cluster formation the polarising effect can stabilise the clusters [3]. As the cluster concentration rises so does the likelihood of nucleation [54]. 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 [30], such as acetamide which is similar to urea which does nucleate when irradiated [57]. 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.

1.4.3.2 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 [61, 47, 9]. 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 [26], this is not a universal method however, as it has also been shown that laser power can influence the crystal polymorph [56]. 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 [30]. It has been suggested that in theory any solution can undergo HILIN [30], 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.

1.4.3.3   Trapping Induced Nucleation

Lastly, there is trapping induced nucleation, this is where optical tweezers come into play. 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 [53]. 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 [63, 62]. 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 DLS analysis to the dense liquid region showed that it was populated by clusters that would consolidate together upon being focused by the optical trap [24]. 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 [51]. 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 [63]. 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 [63]. Whereas allowing a solution to age results in the formation of amorphous precursors that when irradiated will nucleate immediately [32]. 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 [32]. 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 [62, 24].

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 lenses 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. An common method is by apply a torque to a trapped particle, creating a micro-rotor that can can generate fluid flow.

1.4.4 Optical Torque

It has long been known that electromagnetic fields can transfer linear and angular momentum [10]; 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 [13, 50], 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 [6]. 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 [13, 15].

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 [50, 11]. This has sparked debate if SAM is even a physical quantity as it does not aid in the transport of energy directly [11] 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 all together 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, if the crystal lattice has different refractive indices for varying polarisations of light. For circularly polarised light this inhomogeneity results in a high degree of SAM being transferred to the target object [41, 5], this has been exploited to rotate microspheres as fast as 1000 Hz while suspended in a bulk medium [5] as well as a means of measuring the local temperature and shear response of said medium [35, 44]. Calculating the optical torque applied to a birefringent material is given via:

$$\tau_{opt} = -\frac{\epsilon}{2\omega_{laser}}E_0^2 sin(kd(\Delta n))cos2\theta sin2\phi$$
$$+ \frac{\epsilon}{2\omega_{laser}}E_0^2(1 - cos(kd(\Delta n))sin2\phi) \tag{1.5}$$

Where 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 is due to the target particle being aligned with the EM amplitude, when aligned $\theta = 0$ meaning the entire term is negligible for particle's with a stable orientation. For sphere's this is always the case as they lack a distinctive major axis. The second term is due purely to the polarisation of the optical trap, for

circularly polarised light $\phi = \pi/4$ thus maximising the torque transferred to the target particle. Eq. (1.5) 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. The common feature for shape induced birefringence is that all of these particles are aligned in the plane of polarisation. Often the optical torque experienced is far greater than similar spherical particles that are birefringent. Currently spherical dimers are being rotated in vacuums to measure quantum forces and torques [2, 42]. There are some cases 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 either clockwise or counter-clockwise [25].

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 [13], often in typical suspension trapping situations (where the particle is suspended in a fluid) the translational 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 [2]. This has lead to 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 [8].

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.

1.5   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 [38, 16, 43] and ice crystal formation [23]; however, no experimental work into these systems has been conducted to prove this is the case. 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 [16] 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 [38, 34] 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.

1.6 Significance of Thesis

As I have hoped to make clear in the above introduction, the current state 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 [18]. 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 nucleation, as the laser output can be concentrated to a small area. In this project we want to consider another application of optical tweezers, their ability to rotate micro-rotors to generate fluid flow. Such a method has not been tried before and would allow for us to consider how fluid flow impacts nucleation dynamics at the micro-level.

1.7 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 succeeded by experimental work where we instead using a galvano-mirror to 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.

In addition, computer simulations studying the dynamics of asymmetric dimers and their applications as complex micro-rotors are discussed in chapter 4. The latter results are interesting as a potential insight into how optical torque is transferred to anisotropic objects.

Chapter 1. Introduction

Lastly 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.

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