Thesis Outline (draft 2)

1. Literature Review

Nucleation

- Outline the distinction between:
    - Primary Nucleation: formation of a brand new crystal nucleus.
    - Secondary Nucleation: formation of additional nuclei in the vicinity of 'seed crystals'.
    - Homogeneous Nucleation: nucleation in the bulk solution, absent of surfaces of particulates.
    - Heterogeneous nucleation: nucleation around or against an interface.

Nucleation Theories

- Description of current nucleation theories:
    - Classical Nucleation: fundamental theorem of nucleation in any system, poorly predicts nucleation rates at large scale.
    - Multi-step Nucleation: extension of the classical model, solute forms an intermediate cluster of dense liquid from which nucleation can occur. The theory does a better job at explaining some nucleation events but no one model accurately describes the myriad of possible pathways seen in literature.
- One of the challenges behind describing nucleation is a lack of in situ methods that can discern the formation, and role of intermediate structures. The ability to reliably nucleate and monitor the first instances is highly sought after.

Nucleation methods:

- Discussion of the different methods used to induce nucleation via manipulation of supersaturation:
    - Cooling-nucleation
    - Evaporative-nucleation
    - Anti-solvent nucleation.

History of Optical tweezing:

- A short description of the early applications of optical tweezing, the working principle for optical tweezers, and how optical tweezing has been applied in recent years to induce local nucleation. This section will discuss the literature behind laser-induced nucleation (LIN) and the different phenomena associated with it.
    - Non-photochemical LIN (NPLIN): the use of a low-power pulsed laser can induce nucleation, there is not a single agreed upon theory about why this occurs due to the difficulty in modelling and measuring the interaction between the solute and electric field.
    - High-intensity LIN (HILIN): high intensity laser pulses can induce cavitation within the solution, there is still a lot of debate around how the cavitation occurs, and how tuning the parameters of the input laser can have any influence on the final crystalline product.
    - Optical Trapping LIN: nucleation via the use of a focused optical trap, its not clear how the potential induces nucleation

Other applications of Optical Tweezers

- Discussion of the different applications of optical tweezers such as: force measurements, micro-manipulation, and local measurement of fluid properties (viscosity, temperature, etc).

Fluid shearing and nucleation

- One of the factors not discussed prior in the chapter is the impact that fluid shearing has on nucleation, it is well known that agitation can indirectly result in nucleation events. While the large scale effects can be measured, and the microscopic description has been discussed, there has been no attempt to try and investigate if localised shearing at a microscopic level has any impact on the likelihood of nucleation. Optical tweezers are already used to probe the local fluid viscosity via rotating or translating target particles, it stands to reason that they can also be used to shear the fluid in a local area and induce nucleation.

2. Theory and Methods

Langevin Equation

- Description of the Langevin equation, its differences compared to the Einstein and Fick models of diffusion, and how it can be applied to the motion of an optically trapped particle.

Optical Tweezing Calibration techniques

- Discussion of the different methods used to calibrate and characterise the motion of an optically trapped particle.
  - Equipartition method
  - Potential well analysis
  - Auto-correlation analysis
  - Power Spectrum analysis

Scattering theories

- In order to properly characterise the motion of an optically trapped particle you need to understand which scattering regime you fall into, this section discusses the following scattering theories.
  - Lorenz-Mie Theory: The full solution to the scattering problem, being a solution to the Maxwell equations and capable of describing the forces applied to a target particle in an electric field.]
  - Rayleigh Scattering: An extension to Lorenz-Mie Theory that approximates the target as a dipole moment.
  - Ray-Optics: Another extension to Lorenz Mie Theory but now describes the electric field as a array of rays all incident on the target.
- Also show comparisons of force approximations of each theory.

Simulating the forces on an optically trapped particle

- Unlike with Rayleigh or Ray-optics, the Lorenz Mie theory requires an accurate description of the scattered electromagnetic field in order to calculate the total momentum transferred to the target. This section outlines the different methods used to compute the scattered field, including.
  - Generalised Lorenz-Mie Theory: provides a full description of the incident and scattered fields, the incident field can describe the electric field for a beam of any arbitrary shape but is computationally taxing for simulating complex particles.
  - T-Matrix method: describes the scattered field by matching the boundary conditions across the target's surface, difficult to apply to complex media such as birefringent materials.
  - Discrete Dipole Approximation: approximates the target particle as an array of dipoles of any configuration, computationally taxing as the number of dipoles increases with r^3.

Simulation code

- Brief description of the code initially developed by Vigilante *et al* to simulate the motion of spherical aggregates, how forces are computed and analysed.

Simulation of a Quadrant Photo Diode.

- Outline describing the underlying theory of a quadrant photo diode (QPD), how it was applied to the simulation software, and how it compares to previous works looking at simulated QPD signals.

Simulation of light scattering detection system

- Outline of scattering code used to detect scattering from an arbitrarily oriented dimer, and how the signals are converted into an approximation of the dimer's instantaneous orientation.

3. Experimental work: Effects of shearing on supersaturated solutions

Experimental set up:

- Description and explanation of optical trapping setup, with particular focus on.
  - 4f correlator and galvano-mirror set up
  - Quadrant Photo Diode
  - Beam expander.

Calibration of trapping set up:

- Basic power spectrum analysis of silica micro-beads at varying laser powers for characterisation of trap set up.
  - Compare between pure water and glycine solutions to show impact of increased viscosity.
- Power fall off from laser driver to trapping objective.

Birefringent micro-spheres as micro-rotors

- Description of synthesis method for production of vaterite micro-spheres and liquid crystal droplets
- Power spectra showing rotational frequency appearing as a peaks in the power spectrum.
- Relationship between particle size and rotational frequency for both vaterite and liquid crystals

Micro rotors in supersaturated solutions

- Table of different supersaturated solutions, and rotational speed achieved (if any) using and liquid crystals
- Explanation of why no nucleation was achieved.
- Calculation of theoretical fluid flow that would need to be achieved in order to match literature values for optimal fluid flow.

Influence of moving beam path on nucleation and crystal growth

- Instead of manipulating the particle directly we look at how moving the beam through a supersaturated solution can effect the crystal growth of a newly formed nucleus. This section would include frames from a high speed camera that shows the crystal front matching the path of the focused beam. No further experiments are possible due to time constraints but notable takeaways are:
  - Supersaturation plays a critical role, even low supersaturated solutions will nucleate rapidly and the crystal growth is too fast for the beam path to influence anything. Sub-saturated solutions however will dissolve a newly formed nucleus and as such the crystal growth is localised around the beam focus.

- The beam path can influence how quickly the crystal front grows, an elongated beam path that extends out past the main crystal mass will accelerate the growth of the crystal far more than a circular beam path constrained to the main crystal mass.
- Proximity to the interface is also crucial, while it can increase the likelihood of nucleation the nucleus will get stuck against the interface and escape the influence of the beam.

4. Computational work 1: Non-Langevin dynamics of simple spherical aggregates

- Brief intro discussing why spherical aggregates are often difficult to model in an optical trap.

Orientational and positional dependence of trapping force

- Discussing how a typical micro sphere will have a single stable equilibrium position in which it can be trapped, demonstration of how this can be easily be computed both by using analytical methods or iterative approaches.

Equilibrium position of differently sized dimers

- Demonstration of the increased complexity that arises from the addition of a second micro-sphere by means of a second equilibrium trapping position. Not only are these equilibrium positions dependent on the initial orientation of the dimer but they can also have wildly different trap strengths despite being relatively close spatially.

Searching for off-axis trapping positions

- There is no rule saying that any spherical aggregate should have a single stable orientation, in truth looking at the torque for different orientations indicates there should be a large array of possible trapping configurations. This section discusses that just by varying the initial position or orientation of our target dimer can result in it taking widely different paths towards the trap focus, and even may result in it trapping in an off-axis orientation.

Interaction of spherical aggregates with circularly polarised light

- Discussion of the unique phenomena that arises when dimers are trapped using circularly polarised light, unlike typical micro-spheres whose motion is largely unaffected by the change in polarisation, dimer's experience a continuous torque about their long axis that is similar to how birefringent particles rotate.

5. Computational work 2: Detection and characterisation of spherical aggregate dynamics

- Brief outline on the literature behind instantaneous monitoring of an asymmetric particles dynamics, also highlighting the fact that non-spherical particles are poorly described by Langevin dynamics.

Comparison between QPD and analytical force approximations

- Using power spectrum analysis to characterise the behaviour of simple dimer in an optical trap in a similar manner to what a QPD would pick up. The fitted curve gives a somewhat accurate description for symmetric dimers but quickly diverges from the exact results given by the T-matrix method.

Detection of Rotational motion via QPD signals

- Unlike birefringent materials whose scattering creates a periodic signal, homogeneous spheres give off no such periodicity, as such we look at the time-averaged probability flux of the QPD quadrant signals to determine the if there is indeed rotational motion that creates a drift in the QPD signals. This would allow a user to confirm if the rotational motion of an asymmetric trapped object is periodic or stochastic.

Instantaneous rotational motion via fibre detection feedback

- Instantaneous orientation can be inferred from a trapped object utilising a combination of Bayesian statistics and machine learning, in this section we show the results of this work and discuss why no algorithm can perfectly infer orientation (or any time-dependent parameter) due to the inherent difficulty of mapping between signal and parameter space.

6. Conclusions and Future work

- Optical tweezers have the potential to study and characterise a whole host of asymmetric particles who interact completely differently depending on the beam polarisation. Unlike typical birefringent materials whose rotation is dependent on the synthesis method and morphology, asymmetric particles have the potential to be finely tuned micro-rotors with different rotational modes based on orientation or position.
- The most promising work is the use of a galvano-mirror to influence the crystal growth front of a newly formed nucleus. There is a lot of literature focusing on the effects into optical traps in highly supersaturated solutions, or dilute solutions, but very little research has been conducted looking at how optical traps if properly built there is he possibility that the crystal growth can be precisely controlled via a dual beam trap, one to grow the crystal, the other to maintain the trapping position/orientation.