FABRICATION, SELF-ASSEMBLY AND DYNAMICS OF ANISOTROPIC COLLOIDS

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BY

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THESIS

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Abstract

This work details the development of techniques to fabricate and study structured colloidal particles...

To Leigh.

Acknowledgements

Any scientific project which is not completely trivial is the work of many different people, and this project is no exception. First of all I would like to thank my advisor, Professor Jennifer Lewis: without her ideas and support this project would simply not exist, and her guidance has been crucial throughout my work. Professor Jacinta Conrad and Dr. Robert Shepherd were immensely important to this work, providing assistance and support throughout most of my graduate career. They taught me everything I know about working with colloidal materials and microfluidics, and were kind enough to answer many questions which I often could not even properly articulate. I owe special thanks to my undergraduate assistants, Alissa Cote, Stephen Menke, Fatima Salazar and Kundan Chaudhary: they all spent a lot of time on that microscope with me, and I can't imagine how I could have done without them. I would also like to thank the rest of the Lewis Group for many things, great and small and too numerous to mention, all of which made my life much easier; in particular Chris Hansen, John Vericella, David Lorang, Elizabeth Glogowski and Willie Wu. And Steve Kranz, who is taking over much of my work in the Lewis group, I thank and wish good luck.

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I know I've left people out, and to them I give my sincerest apologies. I could not list everyone without destroying the illusion that this work is, in fact, about colloids. The past few years have been hard and crazy and amazing, and I wouldn't trade them for anything. Thank you all.

Table of Contents

List of Figures

Chapter 1

Introduction

As a class of materials, self-assembled colloidal structures are of interest in applications as widely varied as photonic crystals **??**, photovoltaic devices **??**, and three-dimensional templates for tissue engineering scaffolds **??**. However, despite the wide interest in these structures, the range of possible structures made available by self-assembled spherical colloids is relatively narrow. Due to the isotropic nature of colloidal interactions, there are three basic structures available. **??** When the interparticle interaction is purely repulsive, such as in a hard-core interaction, two structures are available: a stable, ordered face-centered-cubic crystal structure(Fig. 1.1(a)) with a volume fraction of ??, and a dynamically-trapped disordered "glassy" state (Fig. 1.1(b)) with a slightly higher volume fraction of up to ??. Both of these structures are space-filling in the sense that there are no large gaps in the structure larger than the particle size. When the interparticle interaction is attractive, the particles may form an open, disordered "gel" structure (Fig 1.1(c)) with an essentially random arrangement and gap volumes which are potentially larger than the particle size **??**.

Many applications, such photonic crystals, would benefit from the availability of ordered structures with different geometries than fcc. One potential route for realizing different structures is to change the building block, replacing the isotropically-interacting spherical particles with some type of anisotropic particle. Here, we develop techniques for the fabrication of colliods with geometric and chemical anisotropy and begin to characterize the dynamical behavior and self-assembly of these particles.

1.1 Thesis Scope

The aim of this work is to develop techniques for the fabrication and characterization of anisotropic colloids, and begin to explore their dynamical and assembly characteristics. Fabrication is based on flow lithography techniques for producing polymeric particles **??**, and characterization is primarily based on fluorescence and

Figure 1.1: Spherical colloids with purely repulsive interactions may assemble into (a) ordered crystal structures with fcc geometry or (b) space-filling disordered "glass" structures. Attractive colloids assemble into (c) open "gel" structures.

confocal microscopy. The systems used are based on a combination of a hydrophobic monomer (tri(methylol propane) triacrylate) and hydrophilic monomers (poly(ethylene glycol) diacrylate and 20-mol ethoxylated tri(methylol propane) triacrylate). Single-component particles are used to study the effects of geometry on dynamical behavior in isolation, while multiple-component particles introduce the hydrophobic attraction for self-assembly. The solvents used are varied to explore this interaction, and include water, ethanol, dimethyl sulfoxide, isopropanol and toluene.

1.2 Thesis Organization

A review of the relevant literature on the fabrication of anisotropic colloids, their experimental and simulated self-assembly, and their characterization using particle tracking techniques is included in chapter two. Chapter three details algorithms and software developed in the course of this study to analyze microscopy images containing anisotropic colloids. Chapter four investigates the fabrication, behavior and self-assembly of simple rod-shaped colloids in both single-component and "Janus" forms, while chapter five investigates colloids with more exotic geometries. The main conclusions are presented in chapter six. Appendices are included which present experimental techniques developed for but not used in the final study, including novel microfluidic devices for studying concentrated colloids and a variant of the fabrication technique.

Chapter 2

Literature Review

2.1 Introduction

This literature review begins with an introduction to current work on the design and classification of anisotropic colloidal particles, and examples of real-world systems incorporating colloidal anisotropy. This is followed by a discussion of current techniques for the fabrication of anisotropic colloids, the theory of their self-assembly and experimental results. Flow lithography is then reviewed in detail to explore different forms of anisotropy which may be targeted by this technique. Finally we review the current state-of-the-art in the characterization of colloidal suspensions by particle tracking in microscopy image data, and potential extensions of this technique for tracking anisotropic particles.

2.2 Anisotropic and Patchy Colloids

2.2.1 Dimensions of Anisotropy

While the self-assembly of colloidal particles can produce structures with a variety of potential applications **??**, the range of structures which may be produced by conventional spherical colloids is limited. One way to address this is to introduce colloidal particles which incorporate one or more forms of anisotropy, in which the particle is altered such that the interaction between two or more particles becomes non-uniform depending on their relative orientations. These alterations may be based on the shape of the particles, the chemical makeup, or some combination of the two.

In a 2007 article in *Nature Materials* **??**, Glotzer and Solomon propose a system of anisotropy dimensions shown in Fig. 2.1. These include shape-based dimensions such as aspect ratio, faceting, branching, shape gradient and roughness (Fig. 2.1(B,C,E,G,H)) and dimensions based on the presence of multiple chemistries such as surface coverage, pattern quantization and chemical ordering (Fig. 2.1(A,D,G)). These dimensions do not necessarily represent an exhaustive list of the types of anisotropy which are theoretically possible, but are an observational list of anisotropy types which have been observed in the recent literature. For example, rod-

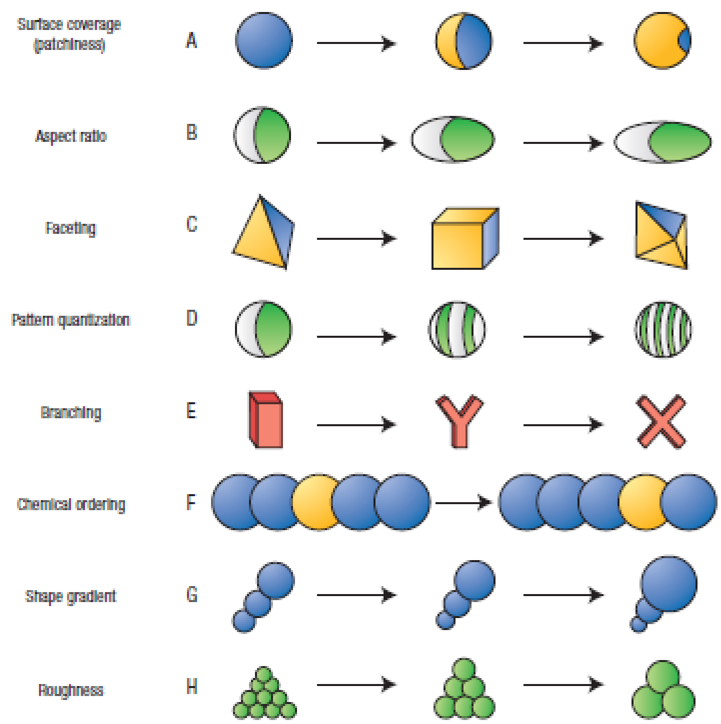

Figure 2.1: Anisotropy dimensions proposed by Glotzer and Solomon **??** to classify different forms of particle anisotropy.

shaped or ellipsoidal particles of moderate aspect ratio have been fabricated by a wide variety of techniques including lithography **??** and particle distortion **??**; branched tetrapods have been fabricated of gold **??** and CdTe **??**; and chemically patterned particles have been produced through microfluidic means **??** as well as by conventional photolithography **??**. This list of dimensions may therefore be seen as a useful framework for classification: by combining multiple dimensions, more complex types of particles may be developed (Fig. **??**), or a complex particle may be classified in terms of which dimensions it includes. New forms of anisotropy may be identified as those which cannot be decomposed into dimensions already identified.

As an example of a particle which combines many types of anisotropy, consider the "barcoded" particles described in *Tan et al.* **??** for DNA analysis (Fig 2.3). These particles have multiple aspect ratios (dimension B); faceting, due to the flat top and bottom surfaces (C); and pattern quantization due to the three different chemistries included (D). An additional form of anisotropy, the barcoding, may be seen as a new dimension or as a more complex instance of pattern quantization. While these particles are larger than typical colloidal dimensions, they illustrate these principles vividly and it is reasonable to suspect they may be miniaturized.

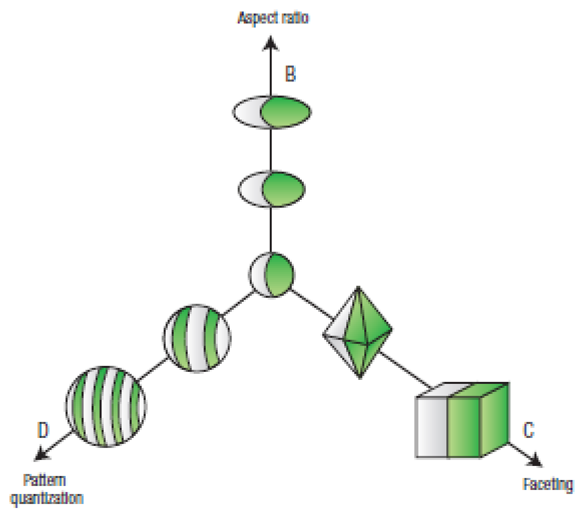

Figure 2.2: Multiple anisotropy dimensions may be combined to yield more complex types of particles. ??

2.2.2 Theory of self-assembly

2.2.3 Fabrication of anisotropic colloids

- Fabrication of Janus spheres: Granick, etc
- Fabrication of rods
- Fabrication of Janus rods
- Faceted particles (crystal growth etc)
- Flow lithography
- PRINT particles
- Glotzer work on spherical patchy colloids
- Other self-assembly of spherical colloids
- Review self-assembly of non-spherical patchy colloids: focus on Janus rods

2.2.4 Experimental self-assembly

- Hydrophobic/hydrophilic: Granick, clusters
- Charge-based assembly

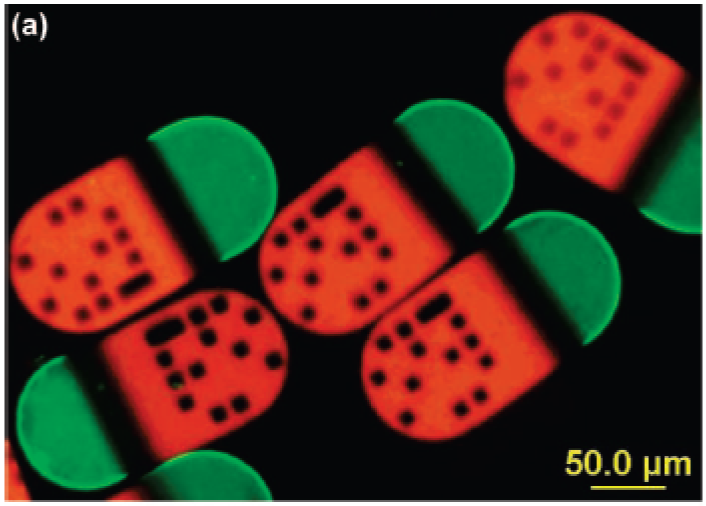

Figure 2.3: "Barcoded" PEG-DA particles which incorporating a DNA probe and fluorescent dyes ??.

- Magnetic assembly
- DNA-based assembly

2.3 Flow Lithography

- Doyle: continuous-flow lithography
- Stop-flow lithography
- Multiple-stream particles
- Applications: biomolecules, etc
- Recent elaborations: lock-release, phase mask, etc

2.4 Particle Tracking

- Crocker and Grier: IDL particle tracking
- Solomon: rod particle tracking

Figure 2.4: Janus spheres fabricated by emulsion technique ??.

Figure 2.5: PMMA rods are fabricated by (a) embedding PMMA spheres in PDMS, (b) stretching the PDMS while heated and allowing it it to cool, and (c) dissolving the PDMS to reveal ellipsoidal rods.

- Other relevant tracking?
- Basic review of morphological image processing

Figure 2.6: Small clusters of Janus spheres; wormlike chains; Granick

Figure 2.7: Multi-panel figure: other assembly

Figure 2.8: Particle tracking illustration

Figure 2.9: Solomon rod tracking

Figure 2.10: Illustrate morphological processing

Chapter 3

Computerized Tracking of Anisotropic Colloids

3.1 Introduction

Figure 3.1: Illustration of Solomon technique

Figure 3.2: SFL particles as 2D extruded objects; flat fluorescence

- Desirable to locate anisotropic particles in microscopy images to study dynamics and assembly.
- Previous work in this area: Crocker and Grier, Solomon
- Can't use Solomon method: fluorescence is too flat for SFL particles. 2D-extruded objects. (Figure to illustrate.)
- Must develop new algorithms which can work on these particles.

3.2 Algorithms

Figure 3.3: Image processing flowchart

- Tracking algorithm for rods
  - Image cleanup using erosion, opening
  - Particle segmentation using watershed transform
  - Particle skeleton (backbone) using distance transform plus rank-order filter
  - Calculation of center-of-mass, oritentation according to Solomon
  - Time-series tracking according to Blair and Dufrense

Figure 3.4: Example image: cleanup, segmentation, skeleton, track

Figure 3.5: Schematic comparison of 2D/3D

  - Difference between 2D and 3D version of algorithm

- Tracking algorithm for arbitrary shapes
  - Initial steps same as for rods: cleanup, segmentation
  - "Skeletonization" as above, but producing a more complex skeleton than for rods
  - Calculate center-of-mass as with rods
  - Choose a sample skeleton as the "canonical" particle skeleton
  - Isolate particles into individual windows
  - To measure orientation: rotate canonical skeleton image in small increments. For each one, AND together the rotated skeleton and the sample skeleton. Maximize pixel sum of ANDed image.
  - Faster in 2D than in 3D
  - Implementation not finished!

3.3 Implementation

- Rod tracking implemented in 2D in Matlab.
- Go over the details of the matlab implementation
- Rod tracking implemented in 3D in Matlab, but with major bugs.
- Arbitrary tracker not yet fully implemented, using Matlab.

3.4 Assessment

- Identify issues caused by morphological image processing for these algorithms.
- Estimate errors in particle segmentation
- Estimate error of rod COM and orientation calculations.
- Estimate error of skeleton-based orientation calculations.

Figure 3.6: Schematic explanation of “template” technique for tracking arbitrary shapes

Figure 3.7: Example images for “template” tracking

Figure 3.8: Example particle trackes

Figure 3.9: Cartoons to show possible errors

Chapter 4

Assembly and Dynamics of Rod-Shaped Colloids

4.1 Introduction

Figure 4.1: Colloidal rod examples

- Natural rod systems
- Systems studied by Solomon
- Janus colloids: Granick
- Interest in Janus rods

4.2 Experimental Procedure

4.2.1 Stop-Flow Lithography

Figure 4.2: Photo of SFL setup; SFL flowchart; example experiment

- Microscope setup
- Pressure system–Rob
- LabView controller for SFL
- Design of microfluidic devices for up to 3-stream SFL
- Fabrication of microfluidic devices

Figure 4.3: Examples of SFL masks used in rod experiments

4.2.2 Mask Design

- Demagnification using 60X objective
- Design parameters
- Rod aspect ratios used

4.2.3 Particle Collection

- Considerations for collection
- Solvents used
- Pipettes
- Fluorosilane coatings

4.2.4 Diffusion Measurements

- Confocal microscopy setup
- Space and time resolution requirements
- Fluorescence requirements

4.3 Results and Discussion

Figure 4.4: Resolution test mask; image of resulting particles

4.3.1 Resolution

- Limiting factors for SFL resolution: mask design, optics, flow effects
- Resolution limits constrained by 60X lens–need to redo this (1 hour work)
- Resolution limits for Janus rods–interface effects

Figure 4.5: Image of rod tracking

Figure 4.6: Plots of translational and rotational diffusion data

4.3.2 Translational and Rotational Diffusion

- Particle collection–PEGDA vs TMPTA
- Compare particle/solvent/surface effects
- 2D diffusion size series: TMPTA in toluene (additional experiments may be required)
- Analyze diffusion data for rods (partially done).

Figure 4.7: Show fabricated Janus rods of various sizes.

Figure 4.8: Assembly of rods in various solvents

4.3.3 Self-Assembly of Janus Rods

- Fabrication of Janus rods: various sizes (figure)
- Comparison of self-assembly in various solvents (figure)
- Small clusters vs large structures
- Alignment of assembled rods
- Image segmentation for analyzing structures
- Some more good-looking images may be required

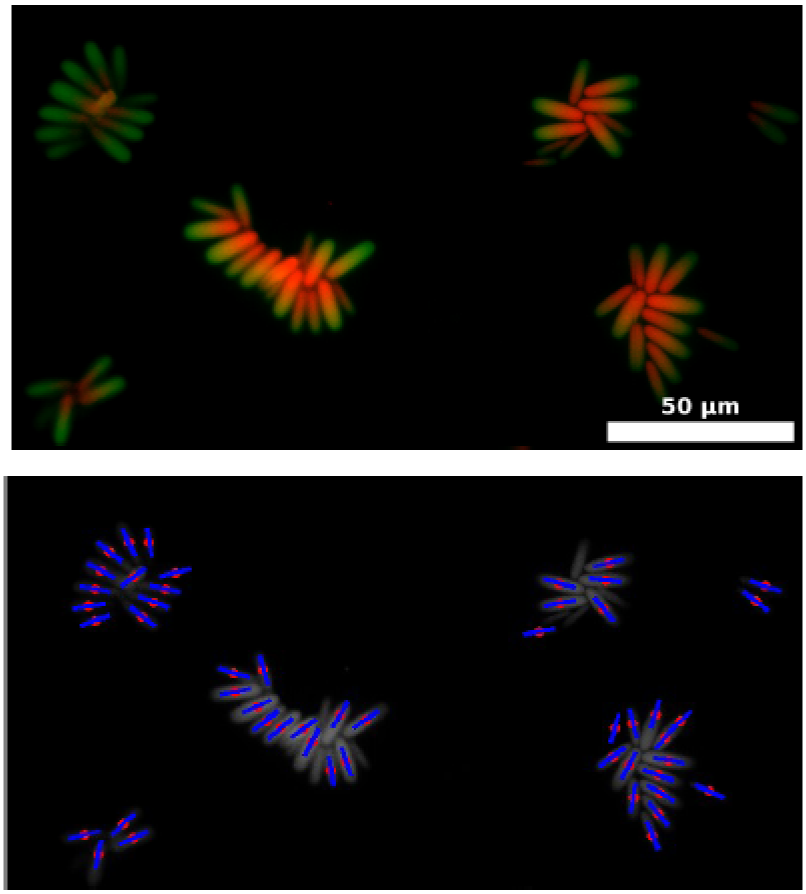

Figure 4.9: (a) Janus rods which have self-assembled into ordered clusters are identified and separated, and (b) their positions and orientations are labeled.

Chapter 5

Assembly and Dynamics of Exotic Colloids

5.1 Introduction

Figure 5.1: Glotzer anisotropy dimensions targeted by complex SFL

- Motivation for working on more complex shapes
- Reference Glotzer anisotropy dimenions
- Bring back three-stream SFL concept from lit review

5.2 Experimental Procedure

5.2.1 Device Design

Figure 5.2: Schematic for 3-stream channel, and constriction channel

- Design for three-stream SFL microfluidic device: explain considerations
- Channel-constriction design

5.2.2 SFL with Multiple Co-Flowing Streams

- **Alterations necessary to SFL protocol with three streams**
  - Timing considerations
  - Pressure considerations

5.3 Results and Discussion

5.3.1 SFL limitations

Figure 5.3: Show stable parallel interface vs droplet forming

- Multiple streams result in SFL slowdown
- Theoretical constraints on how closely interfaces can be spaced
- Empirical comparsion on interface spacing

5.3.2 Particles produced

Figure 5.4: Figure showing 2, 3, 4 patch particles

Figure 5.5: Figure showing boomerangs, and self-assembly concept

- Family of particles produced
- Branched (multi-patch) particles (figures)
- Boomerang fabrication and concept

5.3.3 Diffusion Measurements

- Confocal measurements of 2D diffusion for various shapes–not systematically done
- Diffusion results

5.3.4 Self-Assembly

- Some self-assembly observed for two-patch rods
- Little self-assembly observed for larger, less mobile particles
- Surface effects may affect observed assembly

Figure 5.6: Diffusion results for complex particles

Figure 5.7: Show two-patch self-assembly

Figure 5.8: Show samples with little assembly; schematic of surface effects

Chapter 6

Conclusions

- Fabrication of shape and chemical anisotropic colloids by stop-flow lithography
- Computer-based tracking of rod-shaped colloids
- Computer-based tracking of arbitrary-shaped colloids
- Fabrication of Janus rods
- Demonstrated self-assembly of Janus rods
- Fabrication of more complex colloids

6.1 Future work

- Microfluidic devices to study self-assembly (see appendix)
- High-concentration studies
- Mixtures of spherical and non-spherical colloids

Appendix A

Microfluidic Devices for Studying Self-Assembly

A.1 Introduction

- SFL is low-scale technique for fabricating very small particles
- Most interesting physics occurs at higher concentrations
- SFL yields are low once particles are transferred out of device
- Single microfluidic system to fabricate and study particles is desirable

A.2 Experimental Procedure

A.2.1 Device Design and Fabrication

Figure A.1: Overall design

Figure A.2: Post filters; Channel-height filters

- Design capable of multi-stream fabrication
- Design capable of concentrating particles in a small container
- Multi-layer SU-8 master fabrication
- Initial filter design: posts
- Final filter design: channel height
- Concentrator geometries
- System to exchange solvents and clean particles

A.2.2 Proposed Protocol

Figure A.3: Cartoon of proposed protocol

- Fabricate particles in channel
- Particles collect in concentration chamber
- When finished, cure fab channel shut
- Rinse particles
- Agitate to break up structure
- Image

A.3 Results and Discussion

A.3.1 Concentrator results

Figure A.4: Janus particles in concentrator

Figure A.5: Failed devices

- Particle fabrication: slowed by pressure
- Particle concentration by filters
- Solvent exchange: challenges due to pressure buildup
- Aggregates refuse to break up: suggested explanations
- Device failures

A.4 Future directions

- Suggestions on device design
- Suggestions for other uses of these devices

Appendix B

Grayscale Stop-Flow Lithography

B.1 Introduction

- SFL particle height set by channels; low versatility
- Allow height variation within channel?
- Give examples of grayscale lithography

B.2 Experimental Procedure

B.2.1 Design of Grayscale Filters

Figure B.1: Plot transmission vs filter thickness

- Construct mixed-PDMS filters

B.2.2 Grayscale Stop-Flow Lithography

Figure B.2: Cartoon of grayscale SFL fabrication

- Placement in SFL beam path
- Experimental optimization

B.3 Results and Discussion

B.3.1 Resulting particles

- Achieved height variation

- Particle swelling issues observed

B.4 Future work

- True grayscale masks