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ChE Preliminary Exam Outline

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**Working title**: Studying non-equilibrium self-assembly in active, driven systems

**Intro/general motivation**:

* **Reconfigurable systems** hold great promise for enabling adaptive material applications such as next-generation self-healing materials, wet computing information storage, and responsive photonic devices
  + Existing examples of reconfigurable materials are limited to macroscale systems for printed or otherwise manually arranged particles
  + However, such methods are infeasible at the nanoscopic scales required for realization of the aforementioned applications
* **Equilibrium self-assembly** can be used to nanofabricate ordered structures by allowing atoms, molecules, or colloidal particles to sample many potential configurations through thermal fluctuations
  + The resulting self-assembled structure is the configuration that minimizes the free energy
  + In equilibrium systems, colloidal-scale self-assembly is a well-characterized process
  + Particle anisotropy, specifically shape, has been shown to determine the structure of self-assembled colloidal crystals, even in the absence of explicit inter-particle interactions
* **Experimentally**, many **synthetic colloidal systems** do not assemble reliably or robustly
* In contrast, **biologically assembled materials** often reliably assemble into metastable, non-equilibrium states that allow them to rapidly respond to external stimuli structurally and functionally
  + Many of these biological structures are stabilized by the constant input of energy from ATP, which provides the driving force for non-equilibrium self-assembly in these systems
* This robust self-assembly inspires engineers looking to design synthetic nanofabrication processes
  + However, the fundamental physics of such driven non-equilibrium self-assembly remains poorly understood
* By understanding the principles governing driven non-equilibrium self-assembly, we can eventually design pathways to robustly self-assembly reconfigurable, adaptive materials for nanoscale applications

**Background**:

* “Active matter” describes driven non-equilibrium systems in which a self-propulsive driving force is applied to each particle
  + These systems display a wealth of non-equilibrium behavior, such as a collective motion (e.g. swarming) and giant density fluctuations (e.g. clustering)
* Experimental and theoretical active matter research has focused primarily on the behavior and self-assembly of isotropic particles
  + While useful for defining the basic physics of these systems, such particles do not have a natural “alignment rule” allowing for torques to be effected on neighboring particles
  + However, anisotropic particles with shape *are* able to alter the orientations of neighboring particles, and we know that particle shape alone is sufficient to direct self-assembly in equilibrium systems
* Thus, a natural question arises: how does particle anisotropy, specifically shape, impact self-assembly in drive non-equilibrium systems?

***(Section on proposed work begins on next page)***

**Proposed work**: **Understand how particle anisotropy (specifically shape) impacts self-assembly in driven non-equilibrium systems**

* Computational capabilities allow the study of active systems on large enough time and length scales to be predictive
* Experimentally determining the key drivers of self-assembly is prohibitively time-consuming
* **Proposal**: Computationally develop an understanding of the drivers of non-equilibrium self-assembly to be able to guide experimental work towards systems of interest

**Timeline:**

I’ll put together a nice Gantt chart that ties all this together.

**1) AIM #1**: **Predict structures and formation kinetics of self-assembled anisotropic hard particle systems (2D)**

a) Collective motion onset versus shape (n-gons), driving force, density

b) Cluster structure versus equilibrium crystal structure

c) Theory for kinetics of collective motion that incorporates shape

d) *Anything needed beyond this kinetic theory to claim “prediction”?*

**Hypothesis and rationale for it:**

* Self-assembled structures in driven systems can be related to the system density, applied driving force, and anisotropy of the particles (cite isotropic systems)

**Key preliminary results**:

* Cluster onset diagrams for n-gons 4-8
* Cluster structure for n-gons 4-8
* (Maybe) Equilibrium structure for n-gons 4-8
* (Maybe) Isaac/my collision theory for general active particles, with some work on how it might be extended to take shape into account

**Experimental design/specific methods**:

* *Methods*: Active particles will be modeled using HOOMD-blue molecular dynamics, and open source software package built to run in parallel on GPUs and CPUs, and developed and maintained by the Glotzer lab. Anisotropic shape interactions are accounted for with a discrete element method, borrowed from the granular matter community (read up on this) and implemented in HOOMD-blue.
* *Analysis*: Clusters of active particles have previously been shown to assemble into “active crystals”. The emergence of clusters versus driving force and density can be compared with the sparse literature on anisotropic active particles, while structure can be checked against known equilibrium assemblies. Equilibrium self-assembly of anisotropic particles can be validated using hard-particle Monte Carlo in HOOMD-blue, by equating active driving force to system pressure.

**Complications/alternative strategies**: These Brownian simulations take a long time to run; force.active is currently not MPI compatible; maybe do them in NVT, could be easier to calculate?

**2) AIM #2**: **Evaluate material reconfigurability as a means of tailoring nanofabrication and information storage for nanoscale applications**

*Ideas on non-equilibrium self-assembly*

a) Change shape throughout a simulation—does the activity stabilize the original structure, or does cluster structure change?

b) In a dense system of passive particles, can we use active particles to change the self-assembled structure? How many do we need to have an effect? Is there a critical volume fraction of one type of particle that will lead to this transition?

c) Are there self-assembled structures that are only stable at higher pressure (probably have to go to 3D for this), and can we use some number of active particles in the system to effect an active pressure that can stabilize the system?

**Hypothesis and rationale for it**:

* If non-equilibrium self-assembly of active particles is dependent upon their anisotropy and driving force (Aim #1), then reconfiguring the particle’s shape and driving force should allow the active crystal structure to transition to a new steady state structure.
* *Importance*: If reconfigurability in non-equilibrium allows us to reach otherwise inaccessible structures, this would be of further interest as a nanofabrication approach. Additionally, reconfigurability-induced switching of a material’s structure could be explored as a way of storing information (“memory”) in a material. Such work could be extended as a potential solution for wet computing information storage.

**Key preliminary results**: N/A

**Experimental design/specific methods**:

* All simulations can be carried out as in Aim #1, with particle shape or driving force reconfiguration attempted after system is at steady state.
* *Analysis*: From Aim #1, we will already know the expected crystal structure of a set of anisotropic shapes with which these results can be compared.

**Complications/alternative strategies**: TBD

**3) AIM #3**: **Evaluate the impact of hydrodynamics on active anisotropic self-assembly**

a) TBD

**Hypothesis and rationale for it**:

* Incorporating hydrodynamic forces will affect the active crystal kinetics of formation, but not the structure formed
* Understanding how hydrodynamics may impact the self-assembly can serve as preparation for experimentally realizing self-assembly of active anisotropic particles

**Key preliminary results**: N/A

**Experimental design/specific methods**:

* Hydrodynamic effects are neglected in Aims #1 and #2 to isolate the effect of particle anisotropy on self-assembly. They can be approximated by the inclusion of small “solvent” particles using HOOMD-blue.
* *Analysis*: The assembly diagrams from Aim #1 can be replicated, with the inclusion of hydrodynamics. These results can be verified experimentally as proof of concept for designed non-equilibrium self-assembly.

**Complications/alternative strategies**: TBD

**REFERENCE: Other projects of interest**

*These either don’t fit the story in this prelim so well, or seem too “out there” to talk about during a prelim exam. Some could probably be re-worked into a decent prelim section.*

Other active matter ideas with shape

* Using some subset of driven particles in a self-assembling system to help the system avoid kine­­­­­=tic traps
* In biological systems, ATP acts on proteins to phosphorylate them and make them highly reactive; typically this puts them in an unfavorable configuration, which they resolve by reconfiguring in some way (e.g. Na/K pumps) and then release the P

Low-hanging fruit

* Extend all this to 3D
* Evaluate the impact of hydrodynamics on active anisotropic self-assembly

Use kirigami self-assembly as a means of studying structural entropy

* Can we define nets that have more “information” than others?
* Can we define pathways that have more “information” than others?

Novel mechanisms

* Ratcheting/local symmetry breaking leading to a global driving force?

Biomimicry

* Minimum sufficient cell model
* Model of durotaxis?

Colloidal robots

* “Terminator vicsek model”
* “Intelligent” active matter with shape
* Designing behavior into a particle with shape
* Patchy colloidal robots ala the MIT sand robots, build up a driving force so that across the system appears randomly distributed