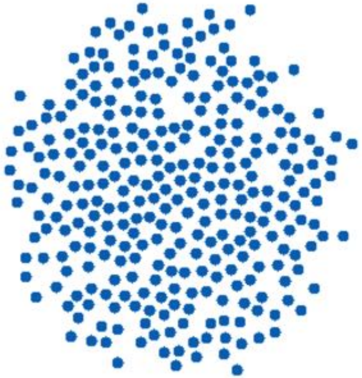

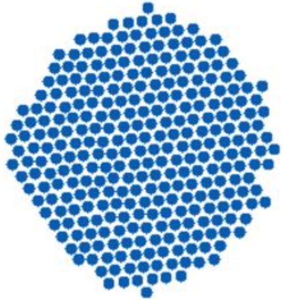

Control of Self-Assembly

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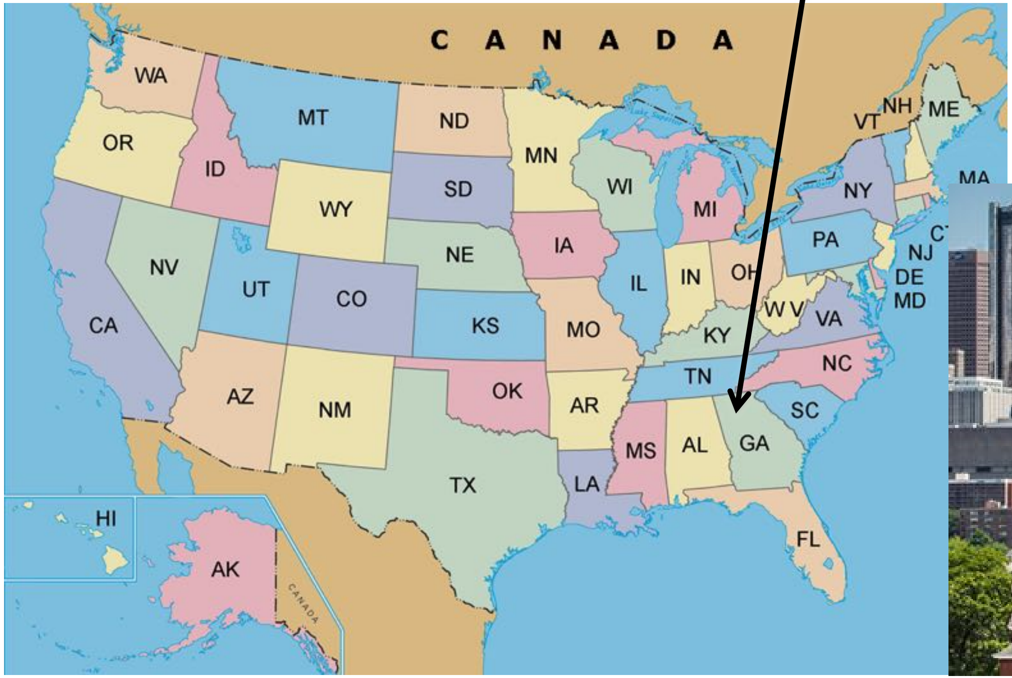
April 24, 2019

Dynamics and Control of Process Systems

Georgia Institute of Technology

Atlanta, GA USA

GEORGIA TECH

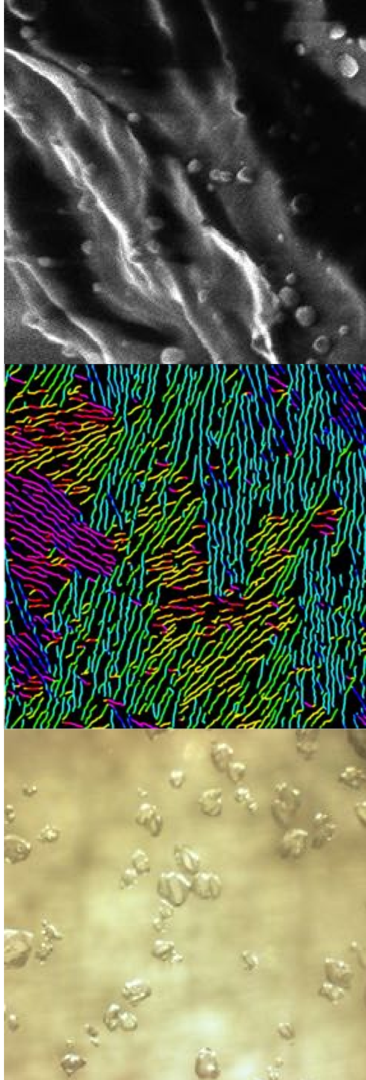


Control of Self-Assembly

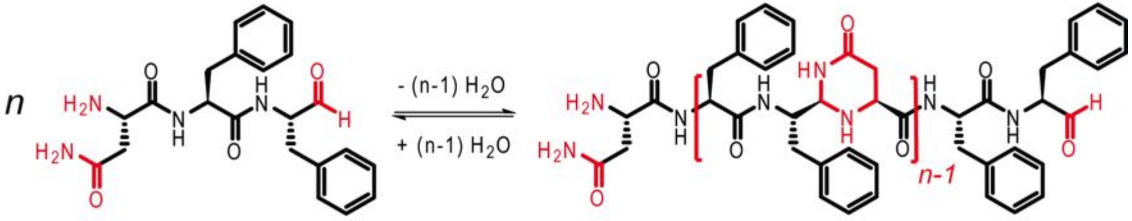
- Many-body dynamic system
- Symmetries due to indistinguishable particles
- Covalent and non-covalent interactions
- Interactions can be manipulated with external fields
- Desired state
  - – Metastable kinetic trap
  - – Low-energy crystalline state

Chemistry → Process → Structure → Property

"Control of self-assembly in micro- and nano-scale systems," J. Paulson, A. Mesbah, X. Zhu, M. Molaro, R. Braatz, *Journal of Process Control*, **27**, 64-75 (2015).

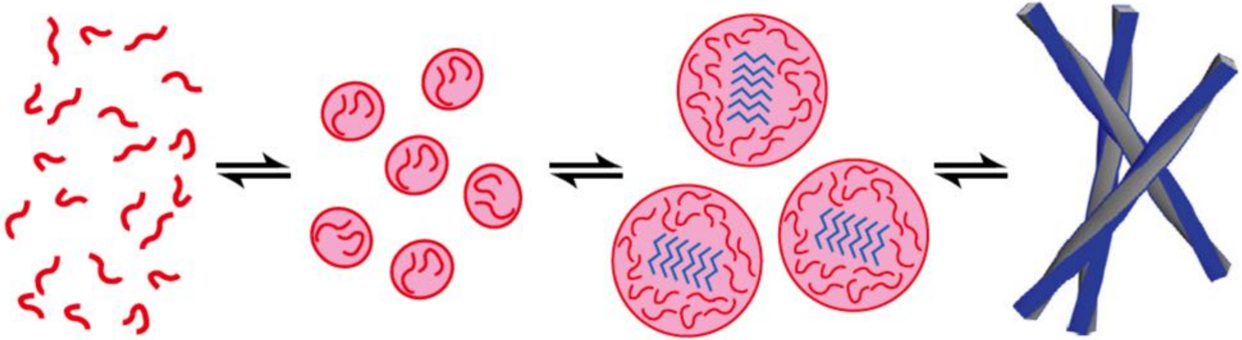


Self-assembly in biological function and selection



NFF-CHO monomer

NFF-CHO oligomers

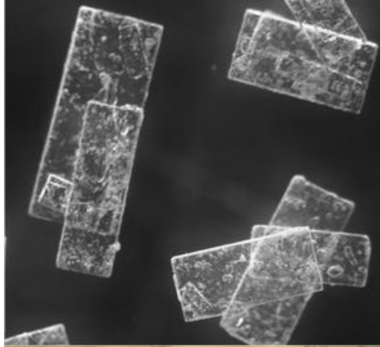


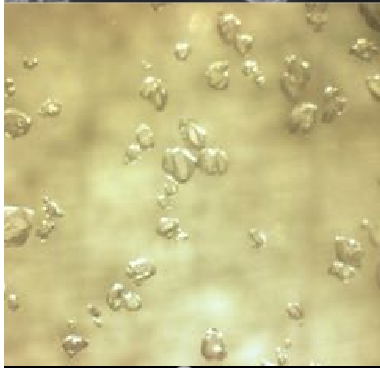
"Design of multi-phase dynamic chemical networks," C. Chen, J. Tan, M. C. Hsieh, T. Pan, J. T. Goodwin, A. K. Mehta, M. A. Grover, D. G. Lynn, *Nature Chemistry*, **9**(8), 799-804 (2017).

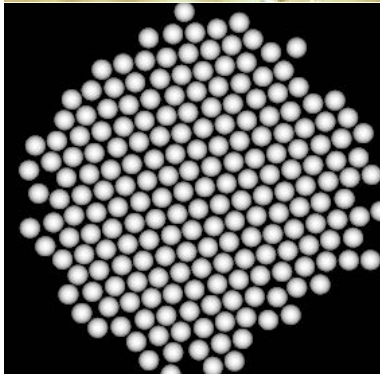
Motivation: Crystallization

- Crystalline ordered state is desired for
  - Separation (nuclear waste)
  - Purification (pharmaceutical)
  - Materials processing (optical and electronic properties)
- Low-energy thermodynamic ground state
- Defects can occur as kinetic traps
- Feedback can help overcome the “inherent” tradeoff between thermodynamics and kinetics.

“Model identification and control strategies for batch cooling crystallizers,” S. Miller and J. Rawlings, *AIChE Journal*, **40**(8), 1312-1327 (1994).







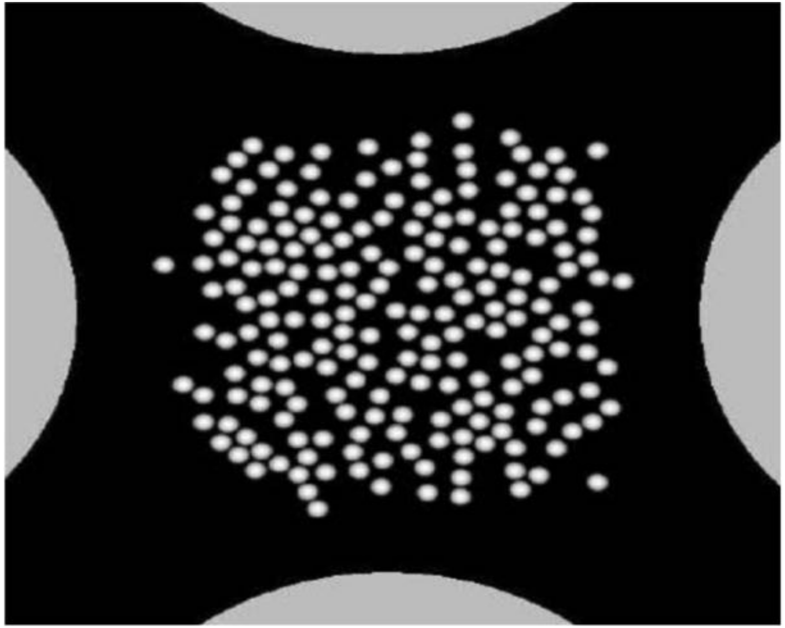
Experimental approaches to crystallization control

- Open-loop dynamic inputs
  - Linear (batch cooling crystallization)
  - Toggling (switching magnetic fields)
- Closed-loop feedback
  - Model-free (Direct nucleation control, PID control)
  - Model-based (Population balance and MPC / Markov-state model and dynamic programming)

"Feedback controlled colloidal self-assembly," J. Juarez and M. Bevan, *Advanced Functional Materials*, **22**, 3833-3839 (2012).
"Nonlinear model-based control of a semi-industrial batch crystallizer using a population balance modeling framework," A. Mesbah, Z. Nagy, A. Huesman, H. Kramer, P. Van den Hoff, *IEEE Transactions on Control Systems Technology*, **20**, 1188-1201 (2012).

Case Studies

Colloidal Crystallization

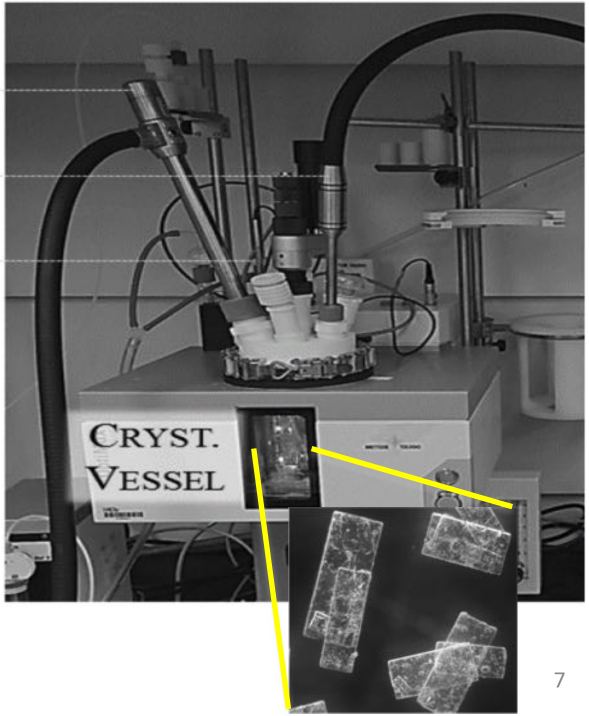


Salt Crystallization

FBRM

ATR-FTIR

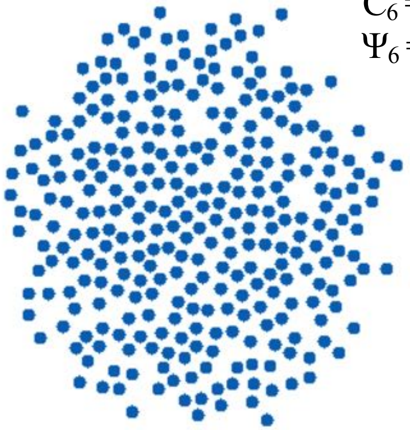
Temperature



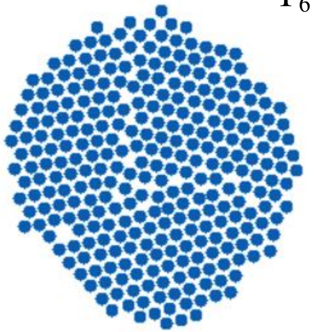
Challenges for Control of Self-Assembly

- large state dimension
- stochastic and nonlinear dynamics
- limited actuation
- limited sensors for real-time measurements

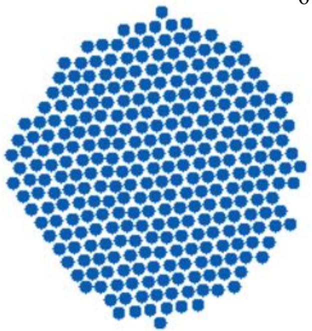
$C_6 = 1.76$
$\Psi_6 = 0.04$



$C_6 = 5.15$
$\Psi_6 = 0.33$



$C_6 = 5.55$
$\Psi_6 = 0.99$



Methodology

1. Selection of variables that characterize the aggregate state of the system and can be measured in real time
2. Application of machine learning to develop an empirical model of the system dynamics in terms of the evolution of the selected aggregate state metrics
3. Application of dynamic programming to obtain optimal state-feedback control policies

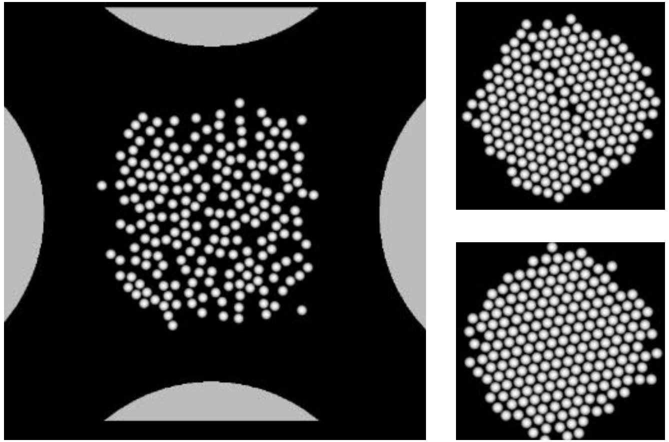
C. Oguz and M. A. (Grover) Gallivan. Optimization of a thin film deposition process using a dynamic model extracted from molecular simulations. *Automatica*, **44**(8): 1958–1969 (2008).

Motivation: Colloidal Crystallization

Rapid high-throughput production of nanostructured materials is challenging.

- Low-defect metamaterials needed for optoelectronics
- Self-assembly has a greater potential for scale-up (compared to top-down placement)
- Challenge
  - defects form as kinetic traps
- Idea
  - use feedback to intervene…

    only when necessary

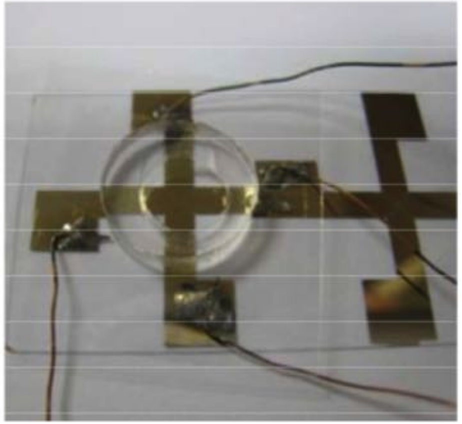


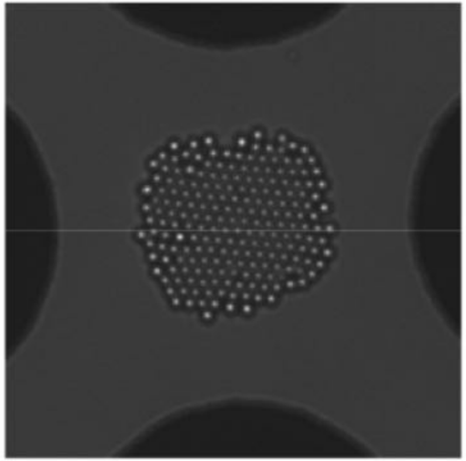
van Blaaderen *et al*. *Nature* 2003,
Velev *et al*. *Langmuir* 2009

Colloidal assembly batch process

AC electric field exerts forces on the particles

- Quadrapole electrode
- ~300 SiO_2 ~3 μm diameter spheres in water
- Quasi 2-D assembly (voltage < 2 V)
- *kT*-scale interactions enable <u>reversible</u> assembly
- Particle-field interactions are frequency dependent
  - Pull toward center at 1 MHz AC
  - Push away from center at 0.1 MHz AC
- Real-time monitoring with optical video microscopy
  - Image processing to extract particle locations

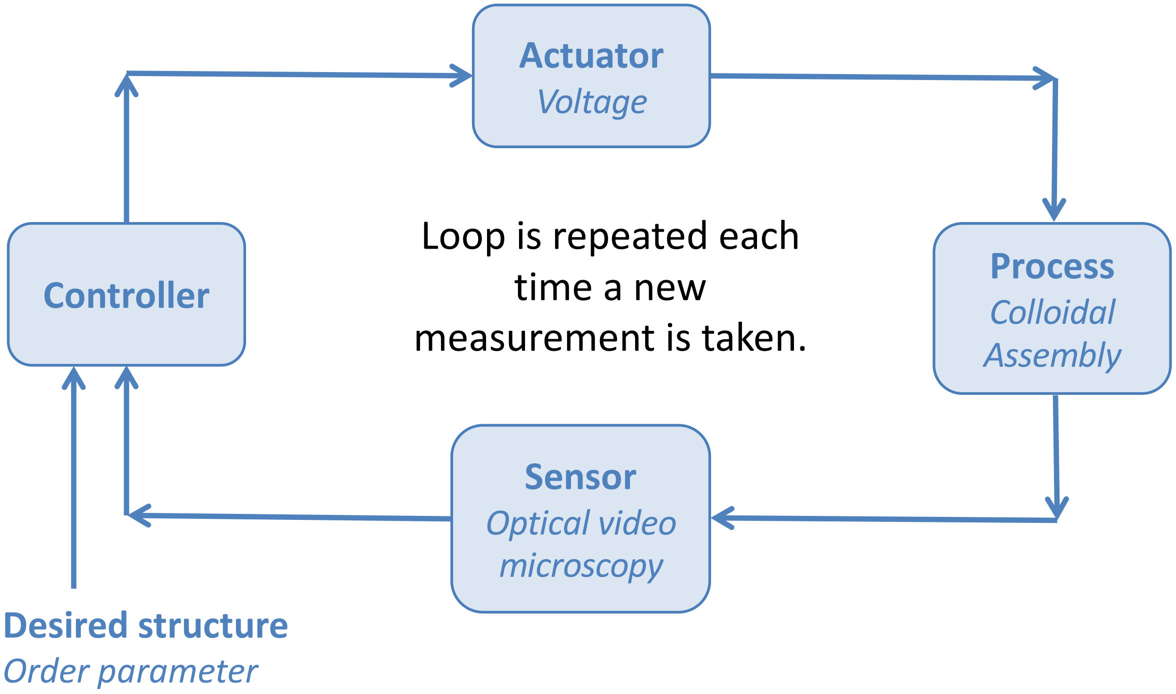


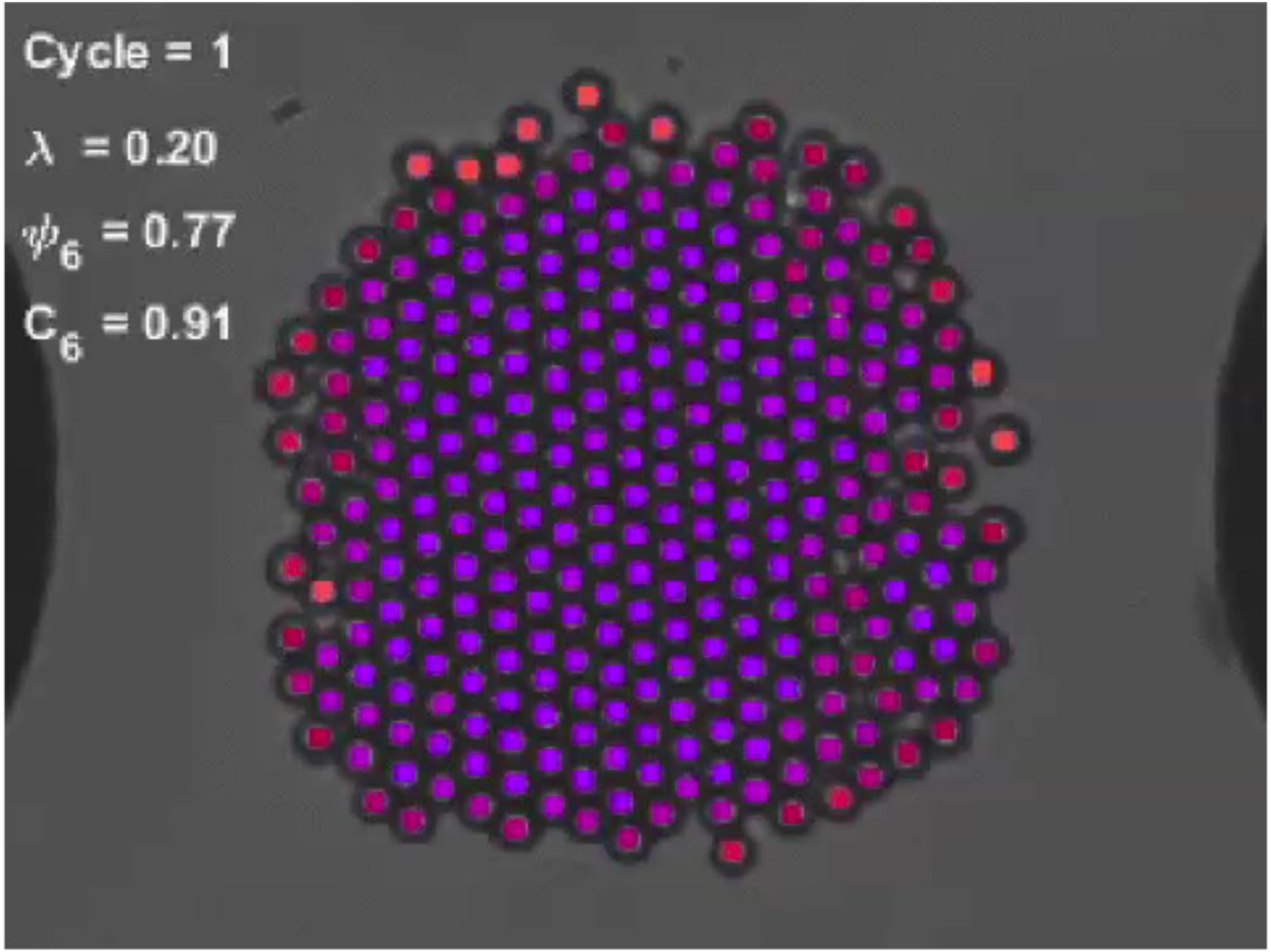


Bevan lab at JHU

Feedback control system

Real-time measurement enables immediate correction to the process

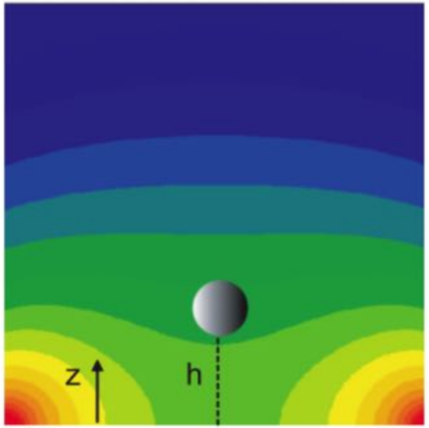



Cycle = 1
λ = 0.20
ψ_6 = 0.77
C_6 = 0.91

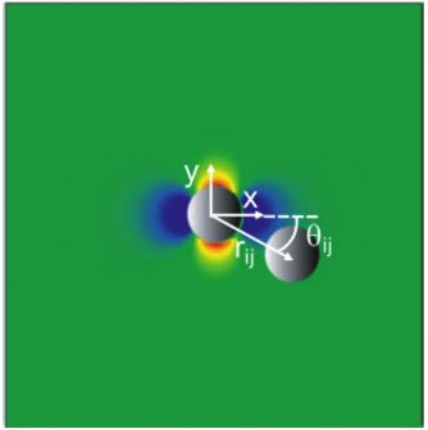
Many-body simulation

Classical mechanics describes forces and particle motion

- Particle-field interactions
  - Induced dipole in an inhomogeneous field
- Particle-particle interactions
  - Electrostatic
  - Dipole-dipole
- Stochastic
  - Random Brownian motion due to solvent fluctuations
- Integrate the equation of motion on each particle
- Model parameters: geometry and material properties



(b)



"Interactions and microstructures in electric field mediated colloidal assembly," J. Juarez and M. Bevan, *Journal of Chemical Physics*, **131**, 134704 (2009).

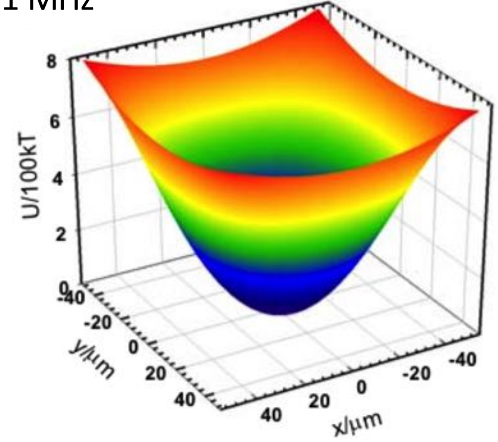
Reduced-order state

Due to symmetries, the state dimension can be reduced.

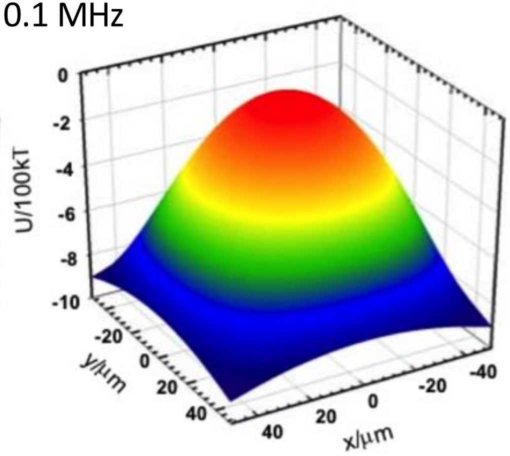
- Direction of force on particles can be changed via frequency
- Free energy surfaces calculated from long-time sampling of experiments
- C_6 is an order parameter: a measure of crystallinity

  $C_6 = 6$ is a hexagonal structure

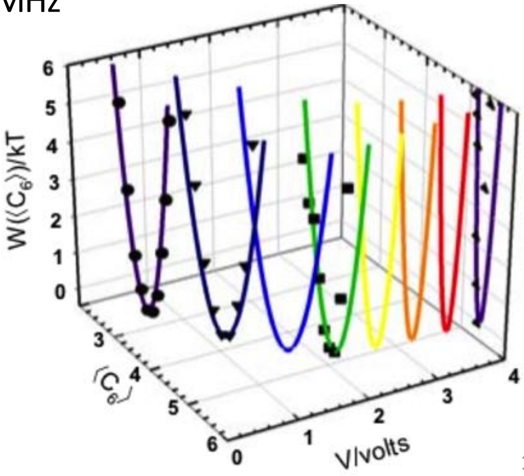
1 MHz



0.1 MHz



1 MHz



Implementation of model-free control

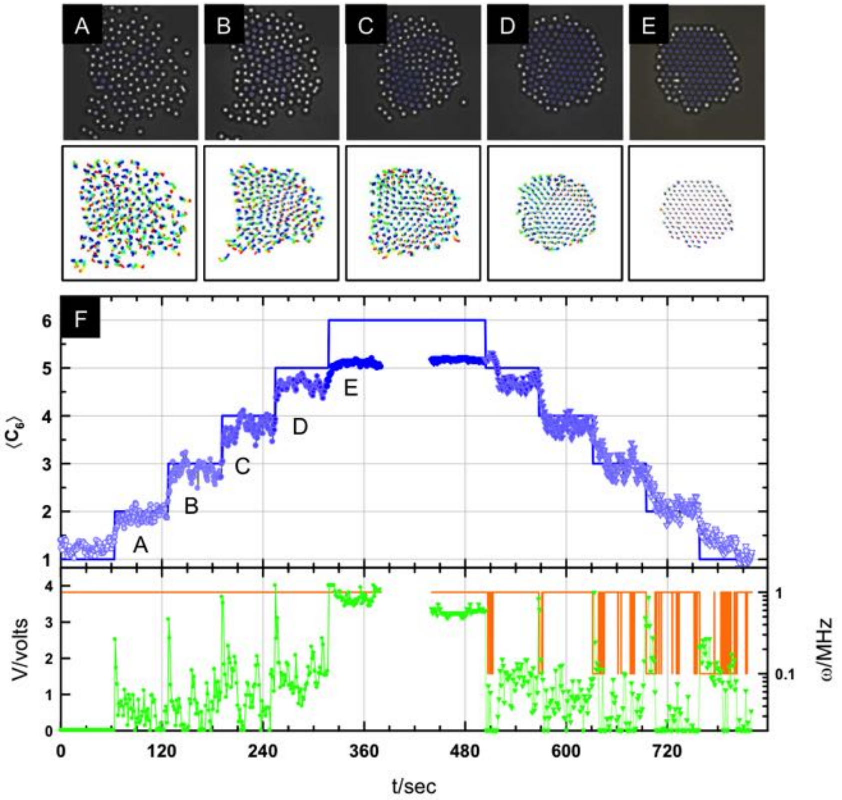
Corrective action is proportional to the error in C_6

$$[V,\omega]=\begin{cases} -K\Delta\langle C_6\rangle, 0.1MHz & \Delta\langle C_6\rangle < -0.25 \\ K\Delta\langle C_6\rangle, 1.0MHz & \Delta\langle C_6\rangle \geq -0.25 \end{cases}$$

$$\Delta\langle C_6\rangle = \langle C_6\rangle_{des} - \langle C_6\rangle_{meas}$$

$$K = 4V_{pp}$$

- Switch between two controllers
  - assembly
  - disassembly
- Controller gain K is chosen empirically
- Proportional control: steady state error

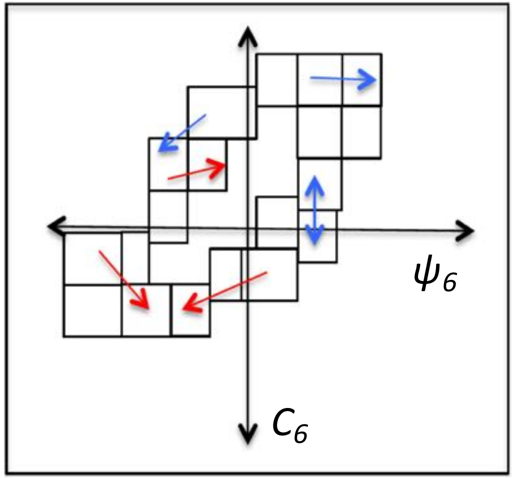


Juarez and Bevan, *Adv. Fun. Matl.* (2012)

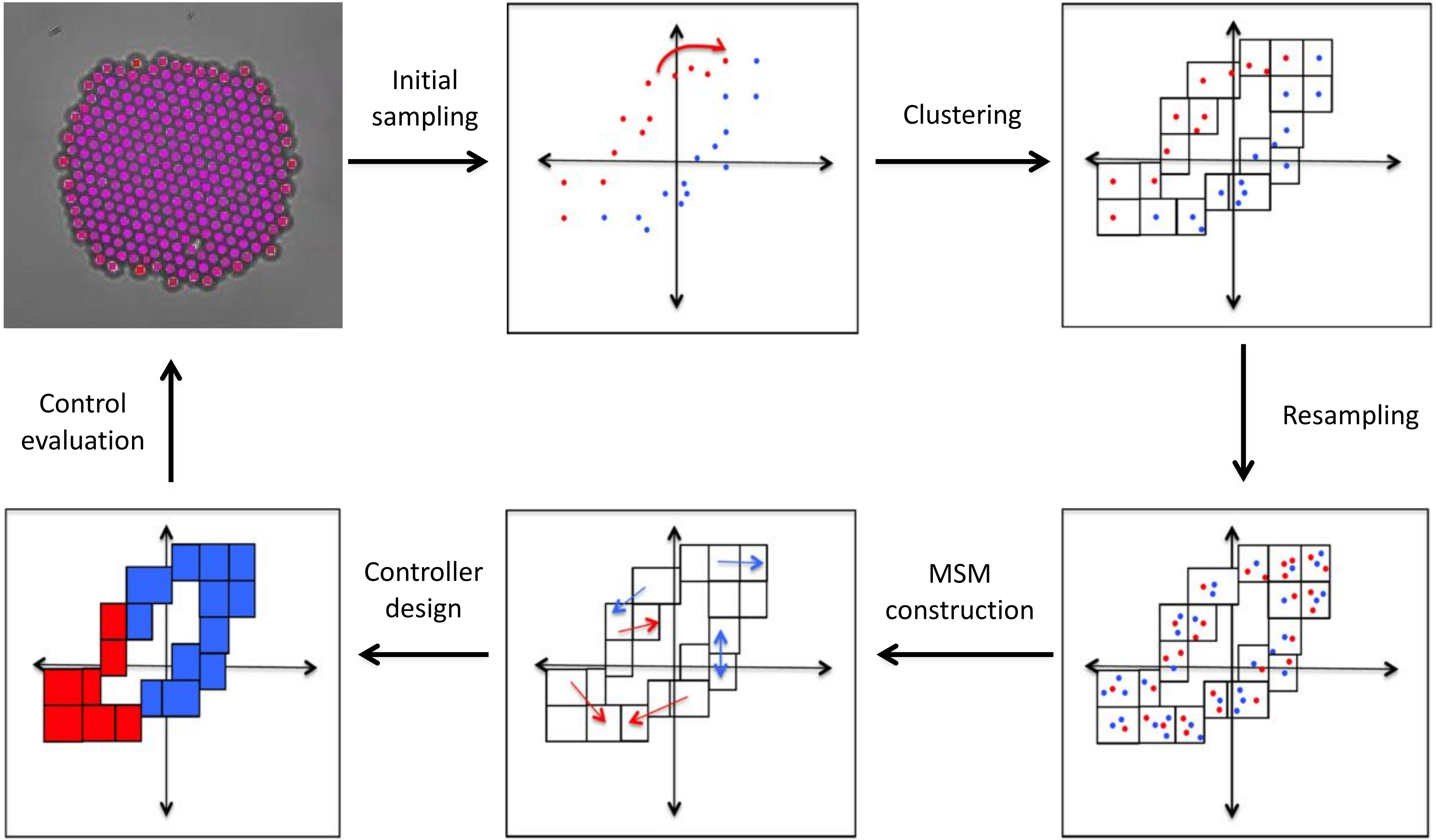
Markov state model

Use detailed simulation to learn reduced-order model

- Discrete state space *S*, action space *A*, and time *T:*
  - C_6 = [0,6] into 120 states
  - ψ_6 = [0,1] into 50 states
  - Transition time: Δt = 100 s
  - *A* = {0.1V, 0.2V, 0.3V, 0.95V}, V=2.0 volts
- Markov transition matrix *P(a)*:
  - $P(a)_{ij}$: probability for the system to be in state *j* from state *i*, after transition time Δt, given action *a*



"The construction and application of Markov state models for colloidal self-assembly process control," X. Tang, M. Bevan, M. Grover, *Molecular Systems Design and Engineering*, 2, 78-88 (2017).


Initial sampling
Clustering
Resampling
MSM construction
Controller design
Control evaluation

Model-based control

At each point in time, apply the voltage to best achieve the long-term objective.

Optimal control:

$$J_i(x) = E\left\{\sum_{t=i}^{H-1} c(x_t, u_t) + h(x_H) \mid x_i = x\right\}$$

$c(x_t, u_t)$ is cost function at stage t, $h(x_H)$ is terminal cost

Define $J_i^*(x) = \inf_{u \in U} J_i(x)$, $u^*(x) = \arg\left\{\inf_{u \in U} J_i(x)\right\} = \arg J_i^*(x)$

Bellman's Principle:

$$J_i^*(x) = \inf_{u \in U}\left\{E[c(x,u,w)] + E[J_{i+1}^*(f(x,u,w))]\right\}$$

$$J_H^*(x) = E[h(x_H)]$$

J. Yong and X. Y. Zhou, Stochastic Controls: Hamiltonian Systems and HJB Equations, Springer, 1999, NY.

"Optimal design of a colloidal assembly process," Y. Xue, D. Beltran-Villegas, X. Tang, M. Bevan, M. Grover, *IEEE Transactions on Control Systems Technology*, **22**(5), 1956-1963 (2014).

Optimal policy for colloidal control

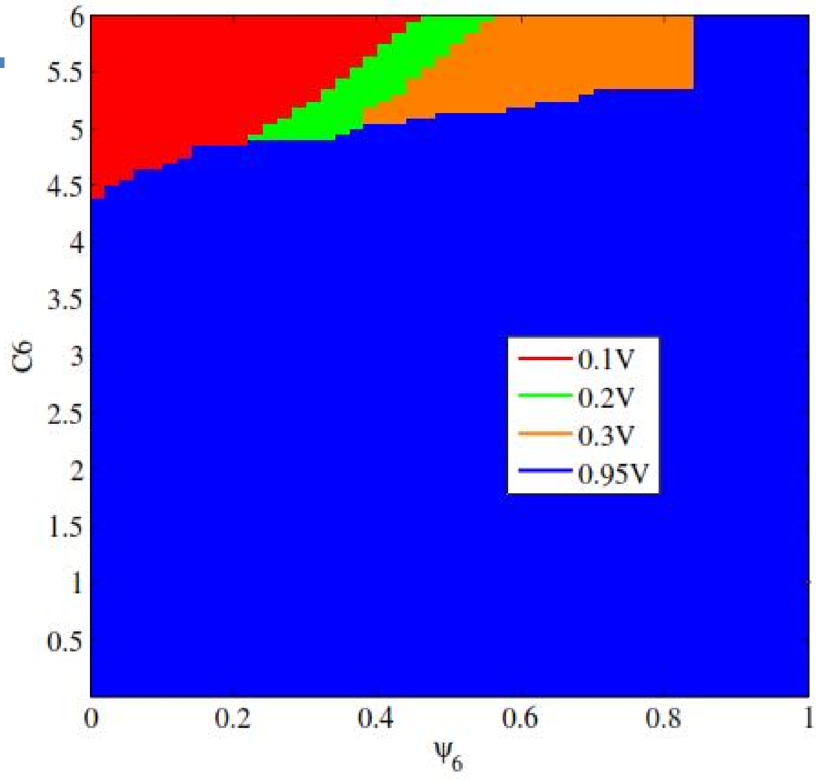
Relax assembly only when necessary to heal defects

- Markov Decision Process (MDP)
  - Characterized by {*T, S, A, P_a*}
- Objective function: infinite-horizon MDP
- Dynamic programming with policy iteration

$$J_u(x) = E\{\sum_{k=0}^{\infty} \gamma^k R(x_k, u_k)\}$$

$$R(x_k, u_k) = \psi_6^2$$

$$\gamma = 0.99$$

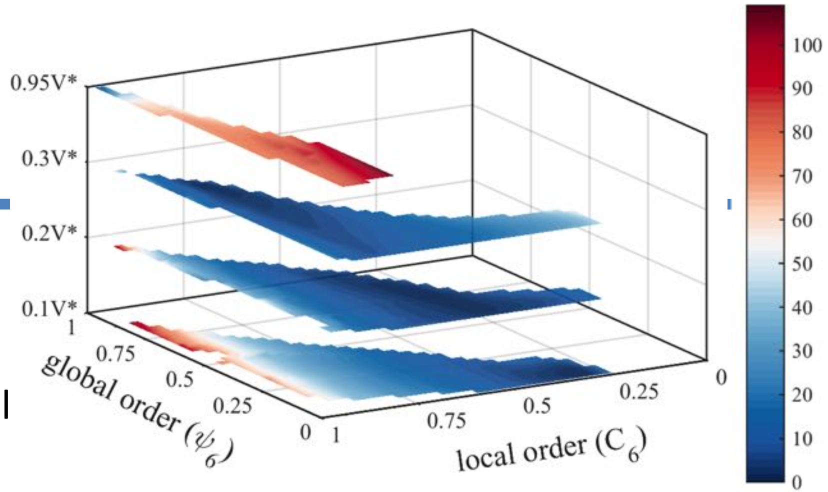


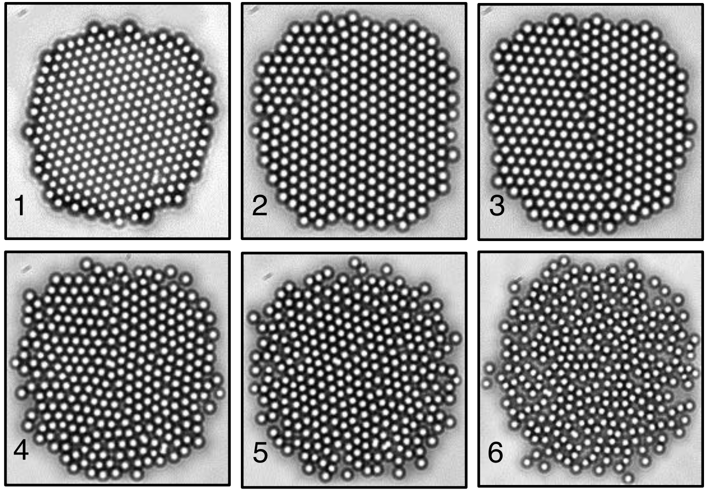
X. Tang, B. Rupp, Y. Yang, M. A. Grover, and M. A. Bevan, "Optimal feedback controlled assembly of perfect crystals," *ACS Nano,* **10**(7), 6791–6798 (2016).

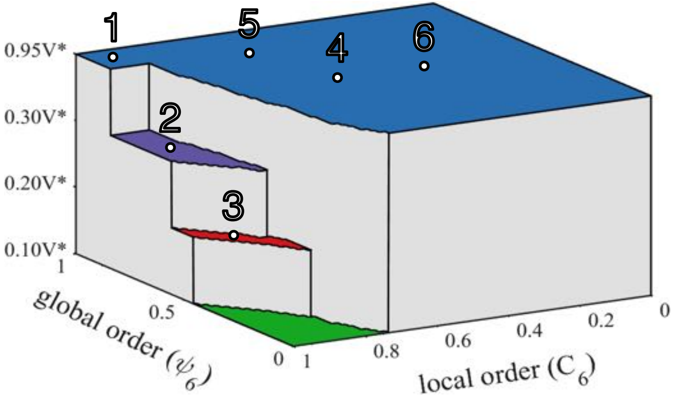
Physical interpretation

Partially melt any defected crystals

- Free energy landscape shows equilibrium
- Apply high voltage to fluid for rapid condensation
- In defected crystal state, apply lower voltage to heal the defect



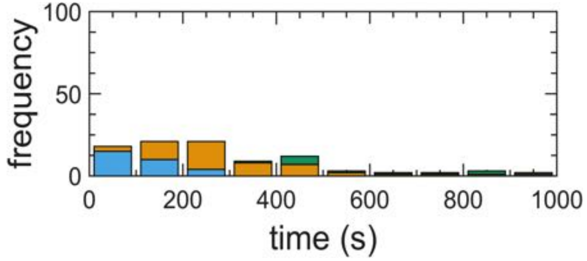


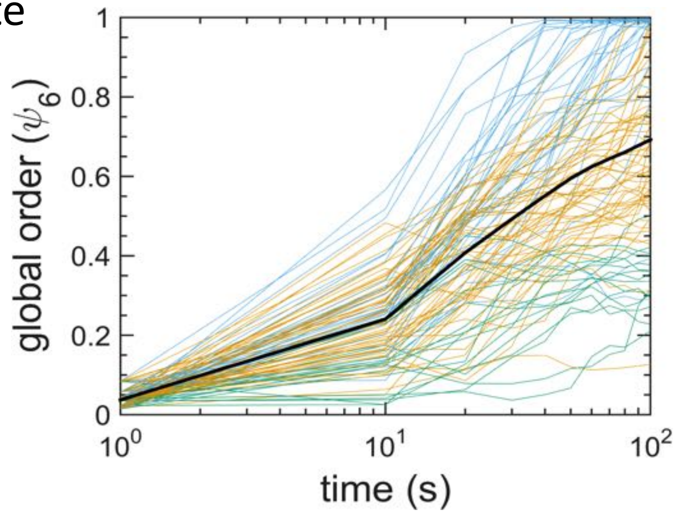


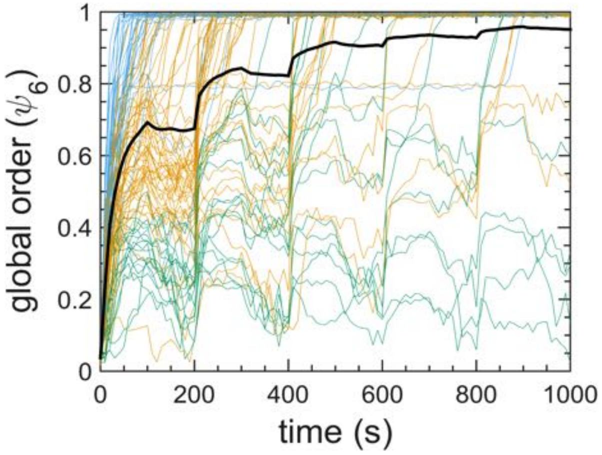
Results in Brownian Dynamics simulation

Assembly is achieved for 93%, compared to 62% for quench

- Realizations that travel through a grain boundary state are most likely to fail
- Stochastic nature is highly significant
- After 1000 s, most have achieved crystalline state



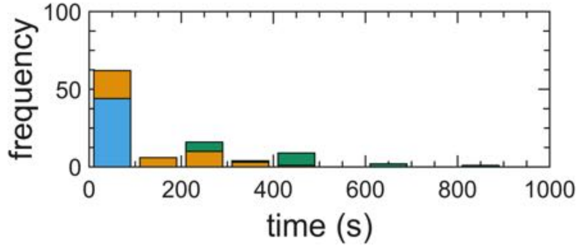


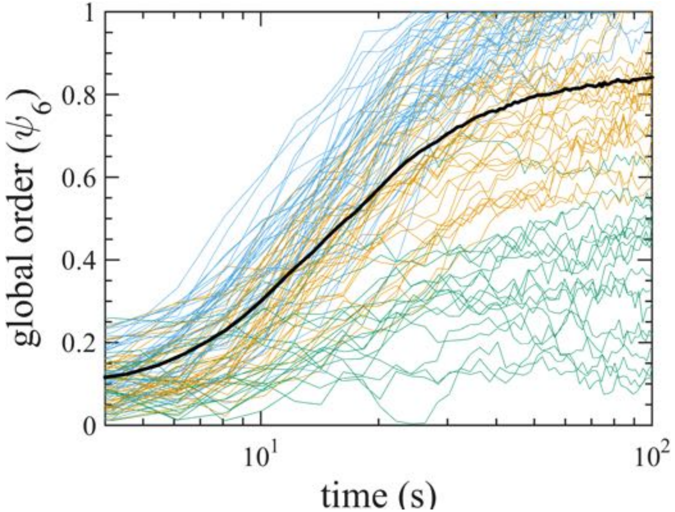


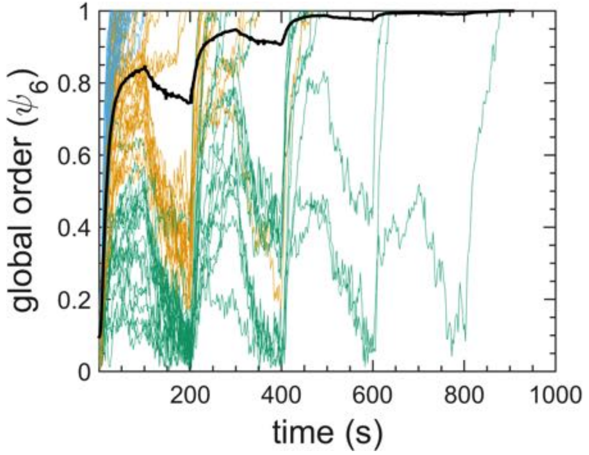
Experimental results

Assembly is achieved for 100 out of 100 cases

- Optimal feedback policy facilitates rapid assembly
- Similar (but better) performance compared to simulation
- Some parameters shift from BD to experiment

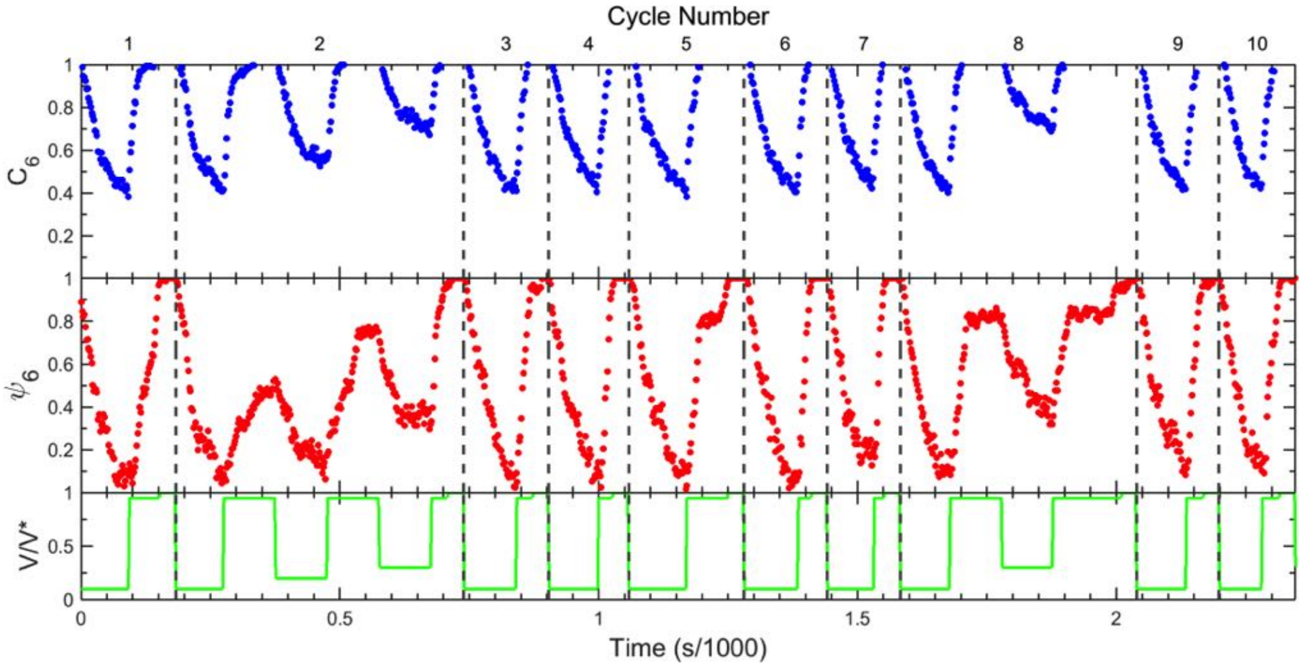




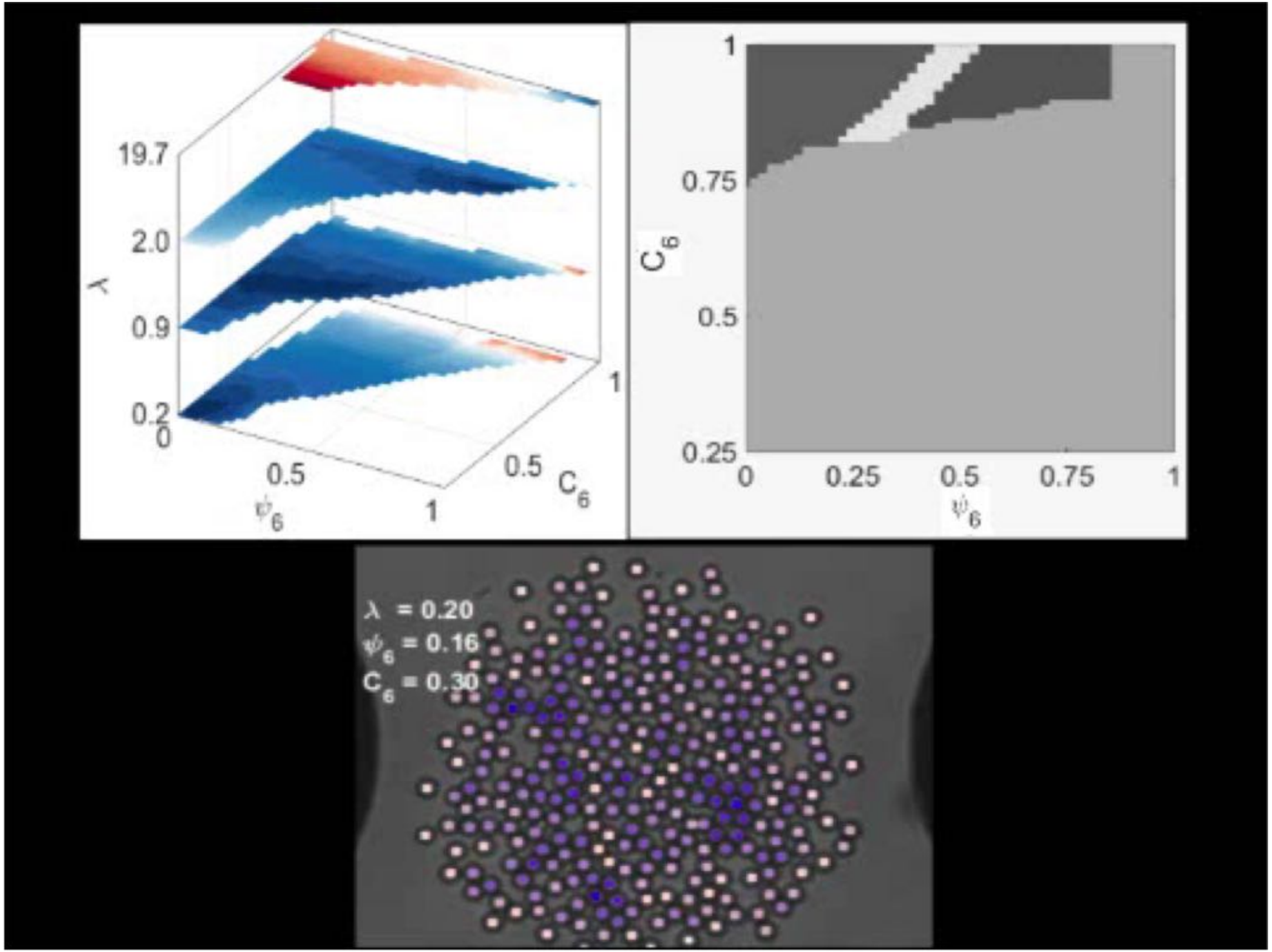


Control actions

The system is stochastic, so each trial is different.

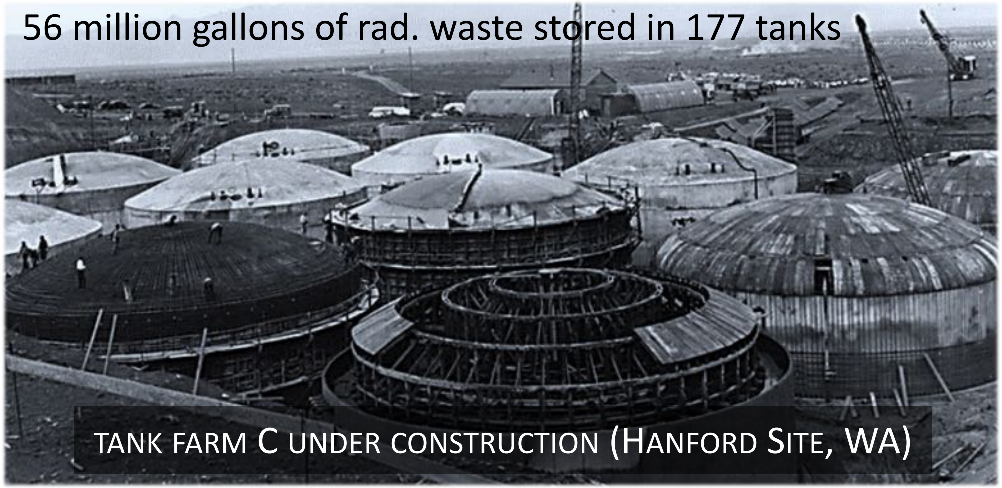


Only two out of these ten trials required intervention.


19.7
2.0
0.9
0.2
0
λ
0.5
ψ6
1
0.5
C6
1
0.75
0.5
0.25
0
0.25
0.5
0.75
1
λ = 0.20
ψ6 = 0.16
C6 = 0.30

Motivation: salt crystallization

Nuclear waste separation

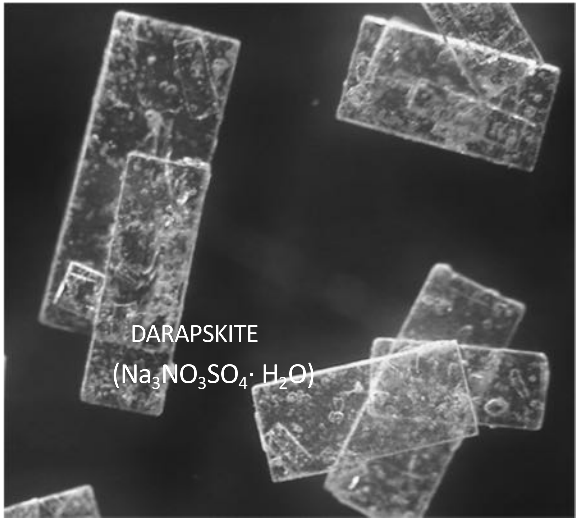


- U.S. Department of Energy cleanup
  - Remove, **vitrify**, and re-encase
  - Motivates research on separations operations

Lab crystallization system

waste simulant:

$NaNO_3$ and $NaSO_4$ in water



FBRM

ATR-FTIR

TEMPERATURE

CRYSTALLIZATION VESSEL

DATA ACQUISITION AND CONTROL

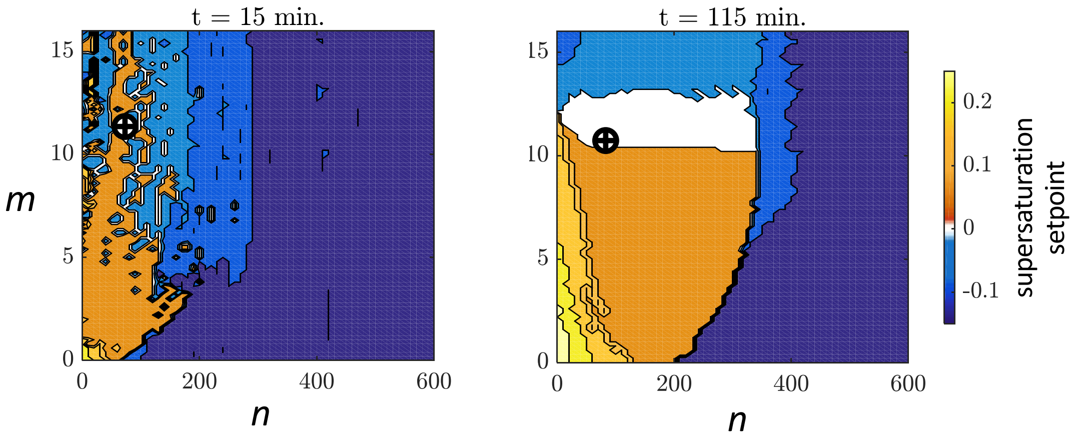
Experimental results

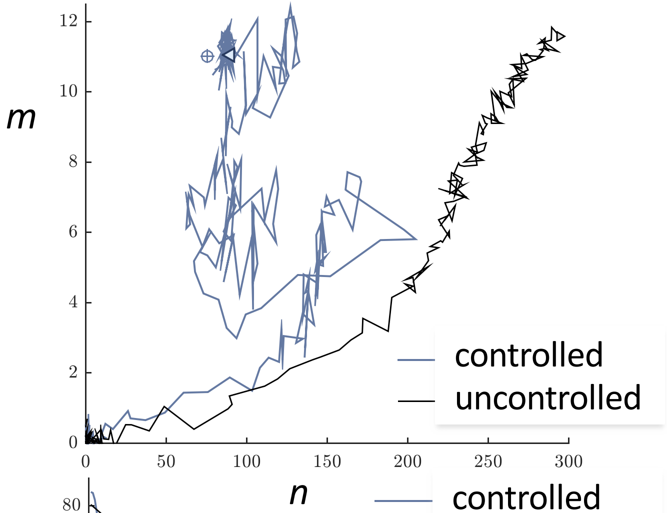
Achieve target at final time

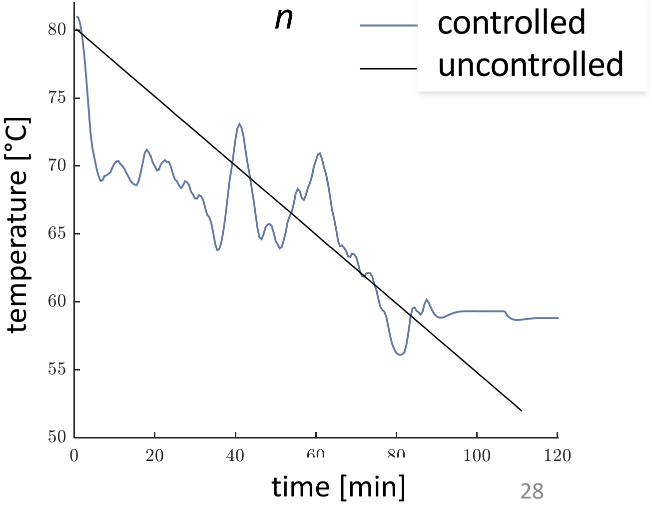
$$\underset{u_0,\ldots,u_{t+\mathcal{T}-1}}{\text{minimize}}\{\sum_{\tau=t}^{t+\mathcal{T}-1}[(t_\tau/t_N)^\gamma d(\mathbf{x}_\tau,\mathbf{x}^\oplus)+\rho\varepsilon(u_\tau)] + (t_\tau/t_N)^\gamma d(\mathbf{x}_{\tau+\mathcal{T}},\mathbf{x}^\oplus)\}$$

$$\text{subject to}\quad \mathbf{x}_{r+1}=F(\mathbf{x}_\mathcal{T},u_\mathcal{T})\Delta t+\mathbf{x}_\mathcal{T},\ \tau=t,\ldots,N-1$$

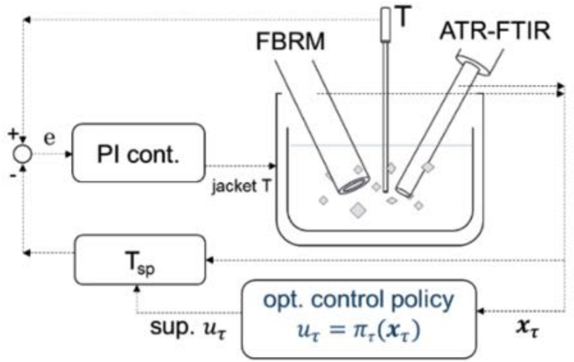
$$\mathbf{x}_t=\hat{\mathbf{x}}_t$$

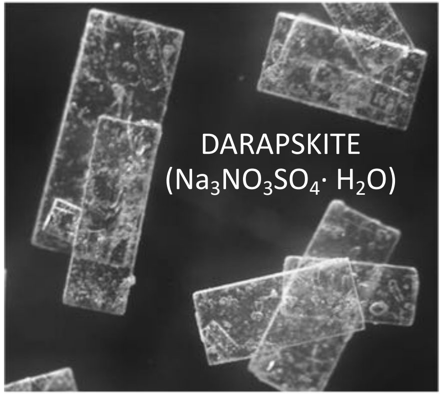


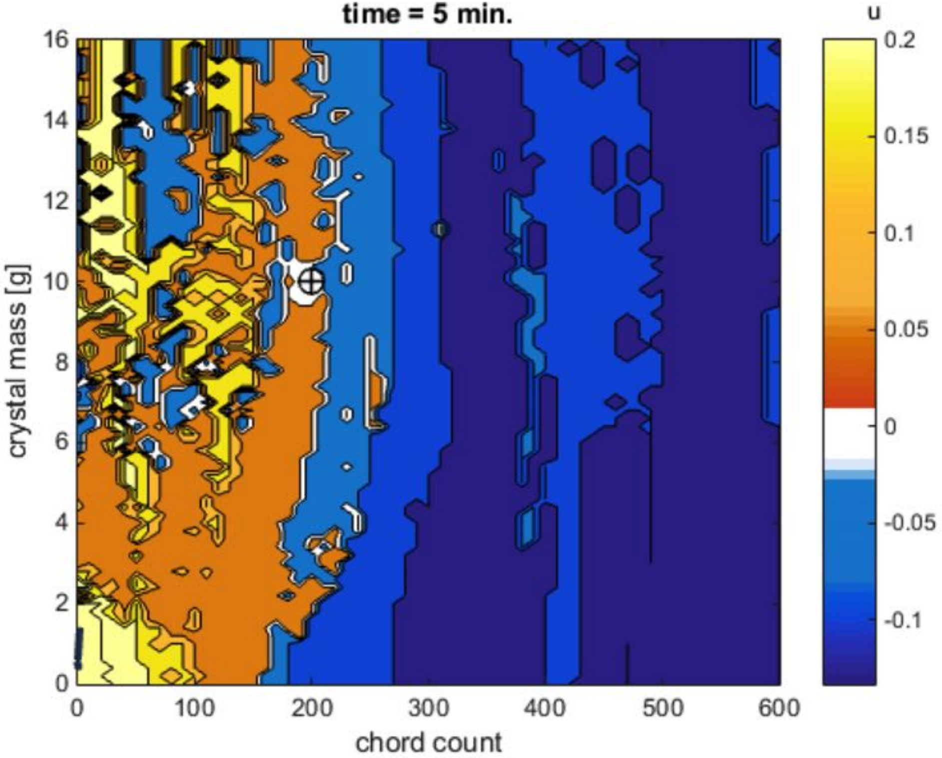




Visualization of the experiments

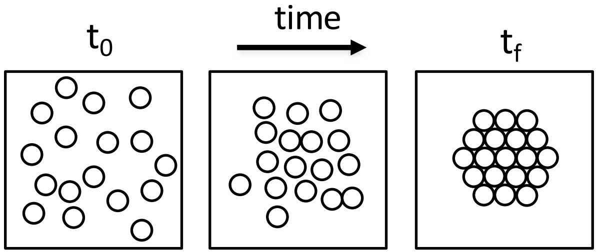




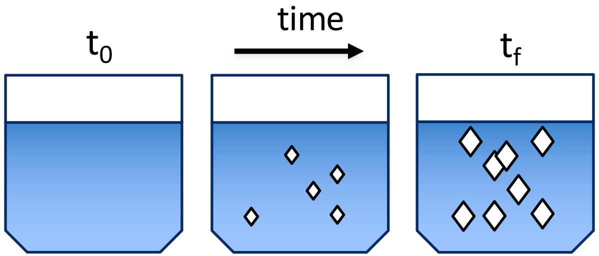


1. Selection of Aggregate Variables

Colloidal Crystallization

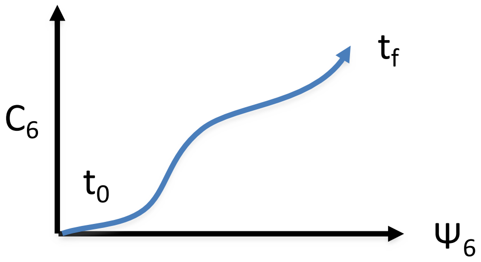


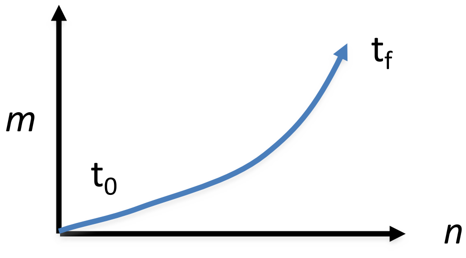
Salt Crystallization



local order parameter: C_6
global order parameter: Ψ_6

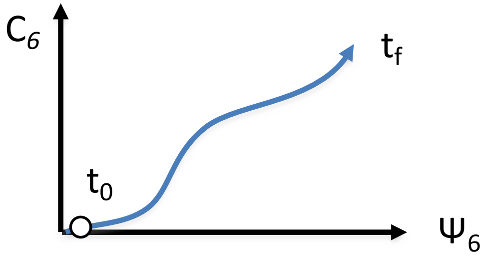
total crystal mass: *m*
total crystal number: *n*



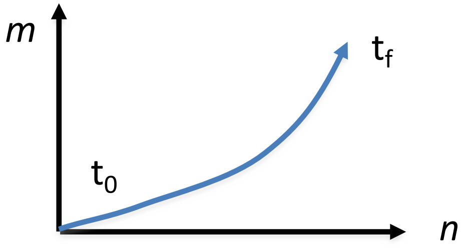


2. Learning the Dynamics

Colloidal Crystallization

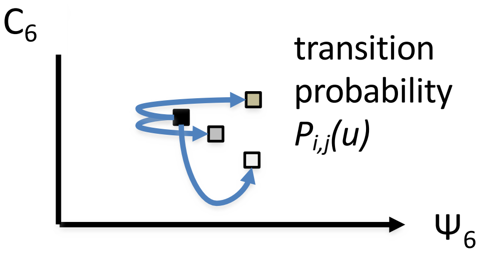


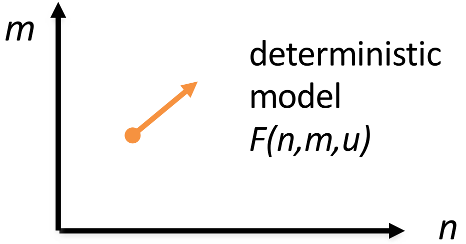
Salt Crystallization



Discretize the space, time, actions
Construct probability transition matrices from simulated data

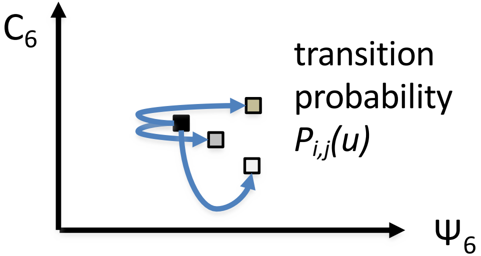
Discretize the space, time, actions
Construct a semi-empirical deterministic mapping from experimental data



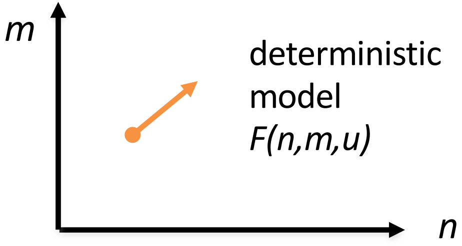


3. Control Policy Calculation

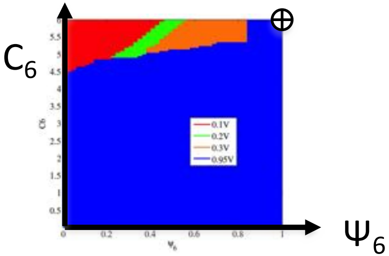
Colloidal Crystallization

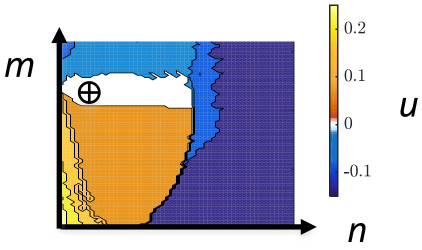


Salt Crystallization



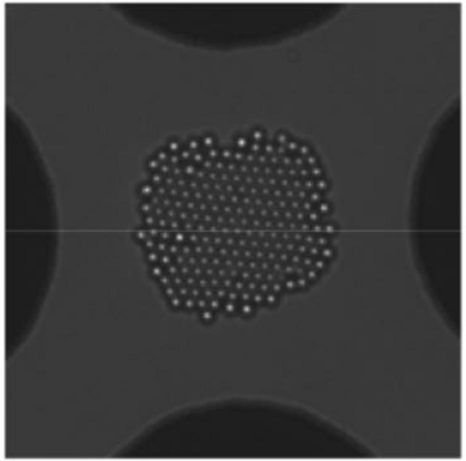
Calculate state feedback policy using dynamic programming

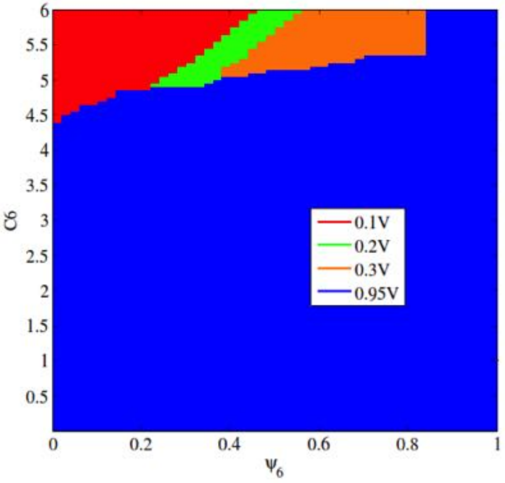




Conclusions

- Optimal feedback control of self-assembly is feasible
- Model-based optimal control promises to optimize self-assembly
- Remaining challenges include
  - Robustness of policy to model error
  - Selection of reduced-order state
- Technology for real-time imaging is continuing to develop
  - 3D imaging with confocal microscopy
  - Smaller length scales (*in situ* TEM)
- Optical microscopy may not be practical for manufacturing
  - the insights enable us to better understand the capability and limitations of directed self-assembly
  - simpler sensors can also be related to order-parameters in a manufacturing setting





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- Prof. Yoshiaki Kawajiri (GT)

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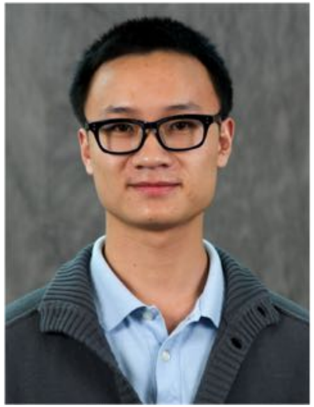
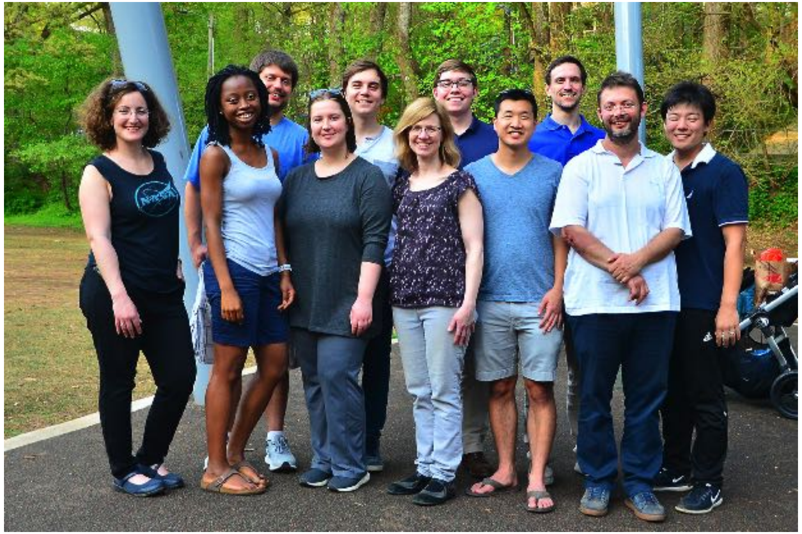
Yuzhen Xue

Xun Tang



Daniel Griffin



Select Publications

- X. Tang, B. Rupp, Y. Yang, M. A. Grover, and M. A. Bevan, “Optimal Feedback Controlled Assembly of Perfect Crystals,” *ACS Nano,* **10**(7), 6791–6798 (2016).
- D. J. Griffin, M. A. Grover, Y. Kawajiri, and R. W. Rousseau, “Data-Driven Modeling and Dynamic Programming Applied to Batch Cooling Crystallization,” *Industrial & Engineering Chemistry Research*, **55**(5) 1361–1372 (2016).
- M. A. Grover, D. J. Griffin, X. Tang, Control of Self-Assembly with Dynamic Programming, *Proceedings of the Dynamics and Control of Process Systems,* Florianopolis, Brazil, April 2019.