Modeling and Overcoming Thermodynamic-Kinetic Tradeoffs for Self-Assembling Colloidal Chains

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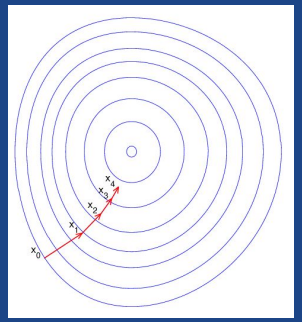
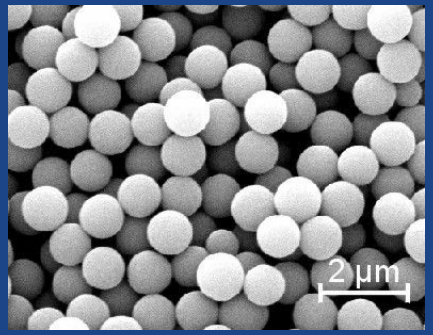
Thesis Defense
April 29th, 2021

Overview of Topics

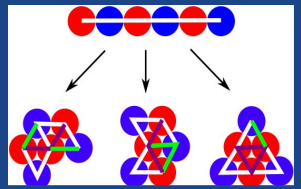


1. Numerical Optimization

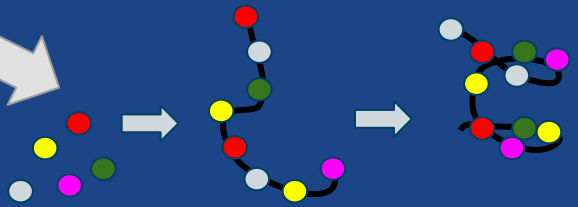


Colloids

3. Hydrodynamics



2. Equilibrium Self Assembly



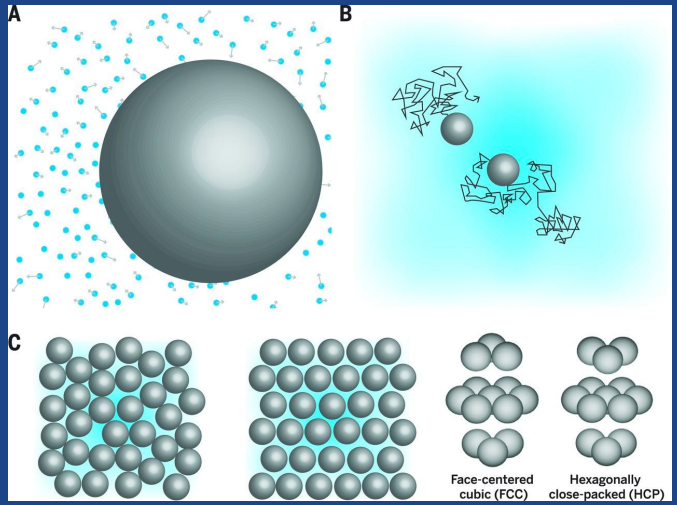
4. Non-equilibrium Self Assembly

Colloids - What are they?

- Particles, typically around 100nm - 1 micron in diameter, dispersed in a fluid.
  - Everyday Examples: Milk, Jam, Clouds, Paint



- Why are they interesting?
  - Size!
    - Small enough and big enough
  - Exhibit interesting phenomena
    - “Big Atoms”
    - Self-Assembly

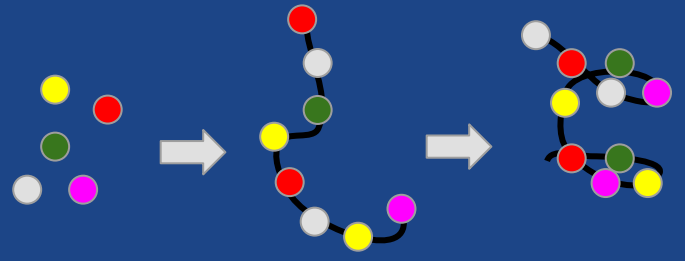


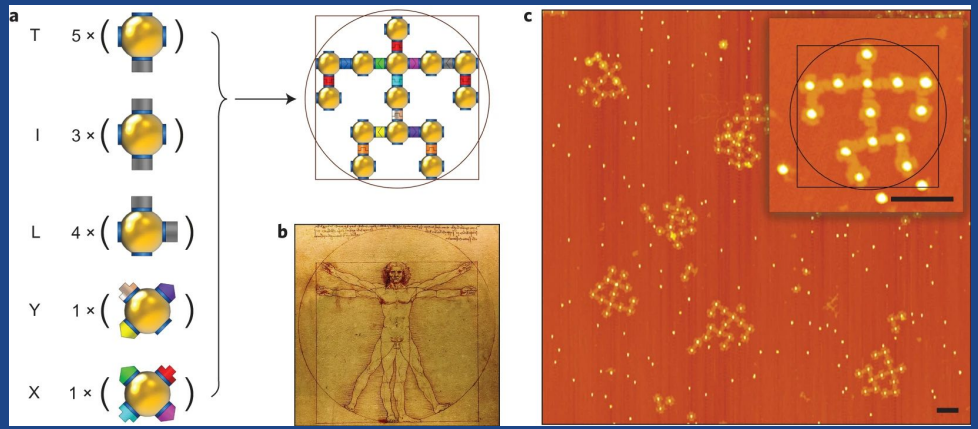
Manoharan, 2015. Colloidal Matter.

Applications of Self-Assembly

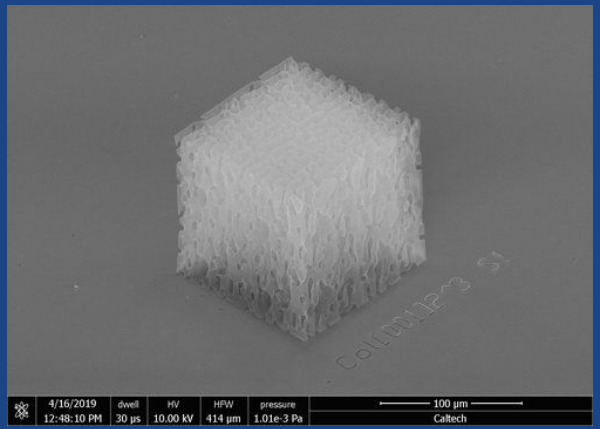
Self Assembly:

Spontaneous organization of a collection of individual units into a well-defined structure, without human (external) intervention.





Oleg Gang. Nature, 2016



Greer Lab, CalTech 2020

Model Self-Assembling System - Colloidal Chains

Big Questions:

1) How do we model this system?

2) How important are hydrodynamic interactions?

3) How can we design this system to form a desired target state, both quickly and with high yield?

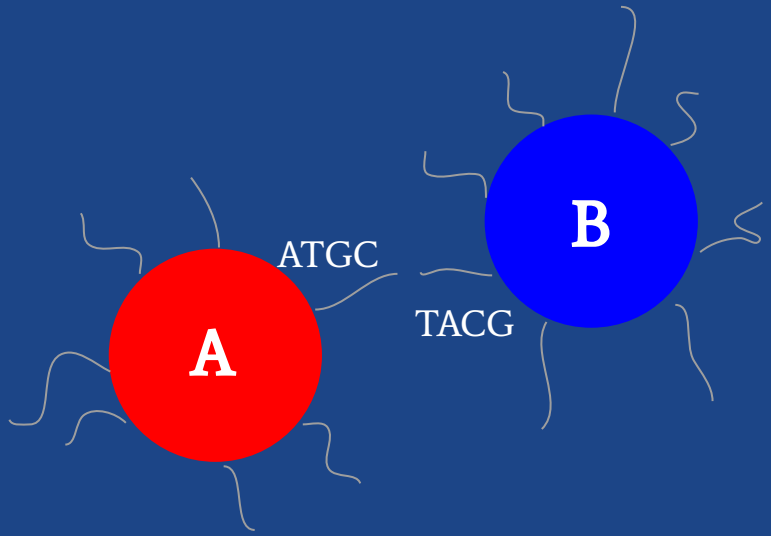
Movie courtesy of Solomon Barkley, Manoharan Lab, Harvard.

How do colloids interact?

$$dX_t = -\frac{D}{k_B T}\nabla U(X_t)dt + \sqrt{2D}dW_t$$

What goes into $U(X_t)$?

- Excluded Volume - Short range repulsive
- Electrostatics - Long range attractive/repulsive
- Van der Walls - Short range attractive
- Steric - Short range attractive/repulsive
- Selective DNA bonds - Short range attractive



Canonical Potentials

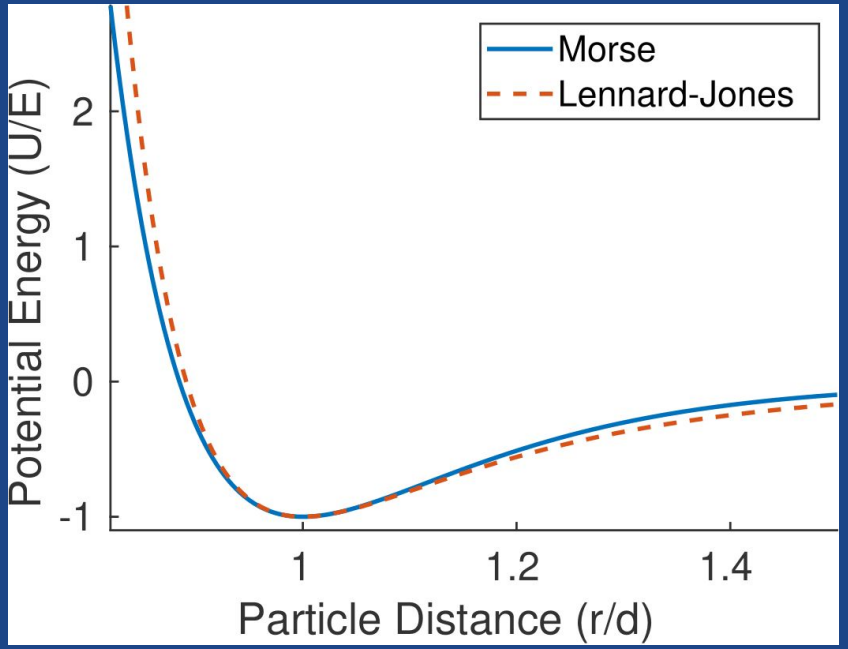
$$U_M(r) = E\left(e^{-2\rho(\frac{r}{d}-1)} - 2e^{-\rho(\frac{r}{d}-1)}\right),$$

$$U_{\mathrm{LJ}}(r) = \frac{E}{m}\left(m\left(\frac{d}{r}\right)^{2m} - 2m\left(\frac{d}{r}\right)^{m}\right)$$

$E =$ Well Depth

$\rho, m \sim$ Well Width

How does the choice of potential affect the interactions? What about parameters?



Sticky Limit

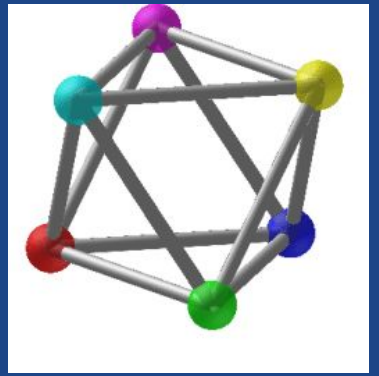
Take the limit as $E \to \infty$ and $\rho \to \infty$ with

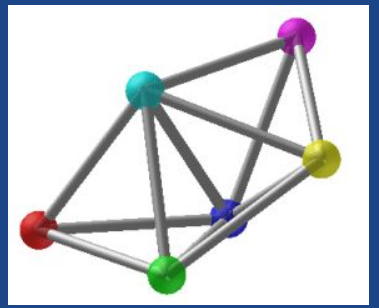
$$\kappa = \sqrt{\frac{\pi}{\beta E \rho^2}} e^{\beta E} = c \text{ fixed}$$

In this limit, both potentials become delta functions at the particle diameter.

The local minima of potential energy become clusters with a maximal number of contacts.

Enumerated for small enough N by [Arkus 2011, Hoy 2012, Holmes-Cerfon 2017].



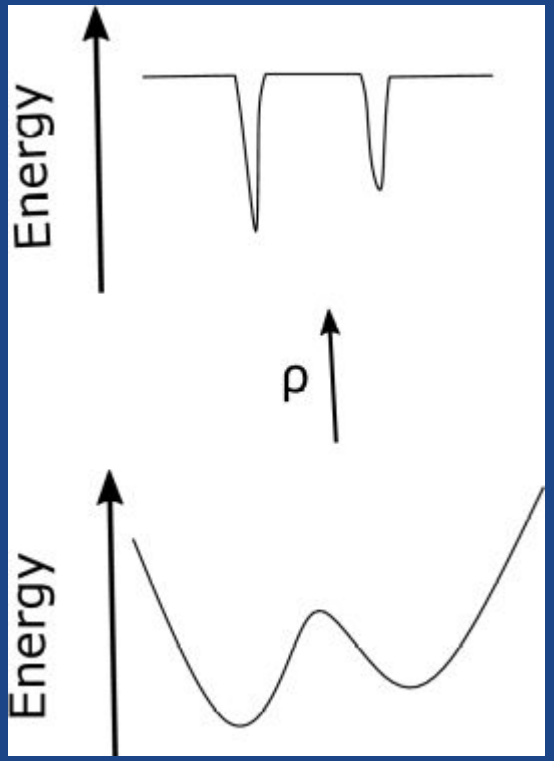


Numerical Continuation Algorithm

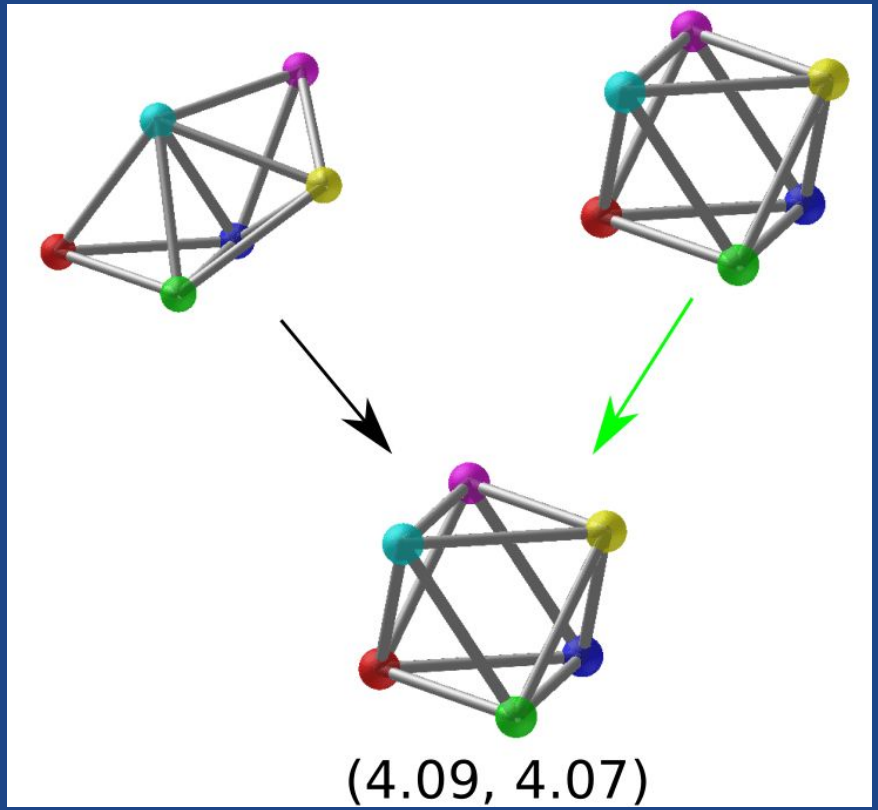
- Begin with set of SHS clusters
- Choose initial potential mimicking a delta function (Morse/LJ, Range 50)
- Minimize potential energy (CG/BFGS)
- Decrease ρ by 0.01, set E such that κ remains constant.
- Perform energy minimization with previous cluster as the initial guess.
- Output clusters
- Stop when ρ=1

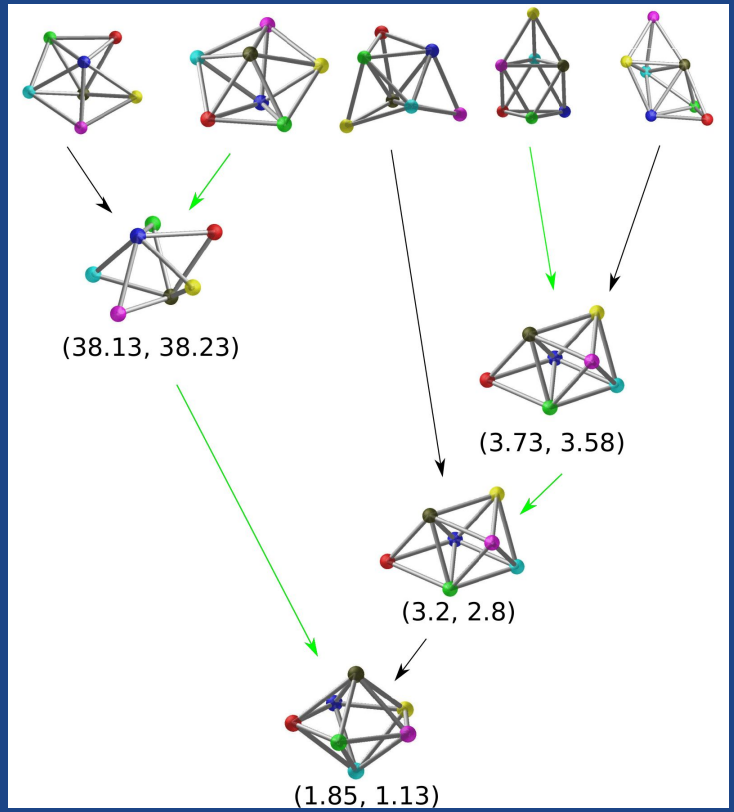
Loop

Perform for both Morse and LJ potentials, for 3 different κ values.

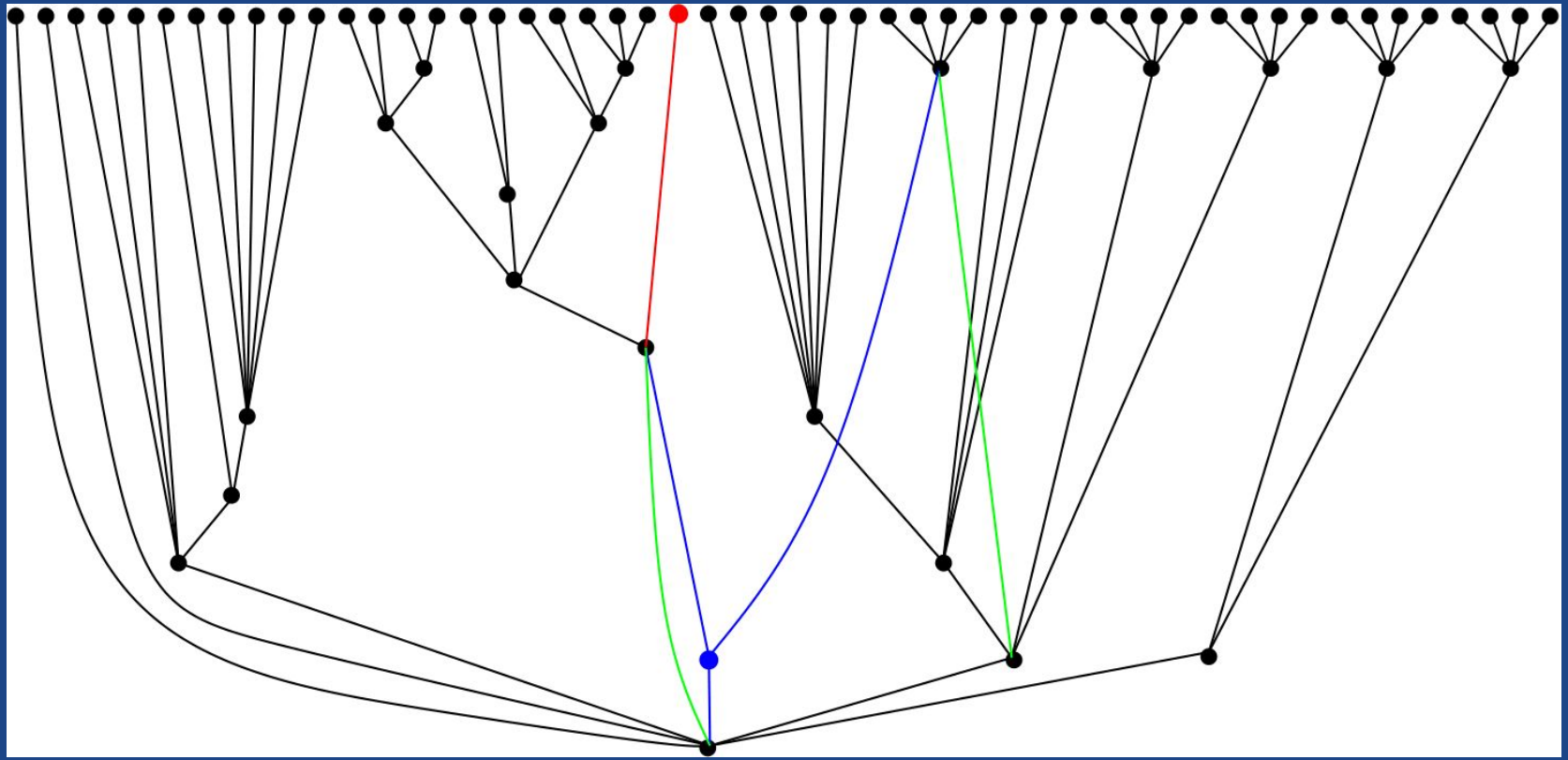


Results - 6 and 7 Sphere Clusters





Results - 9 Sphere Clusters

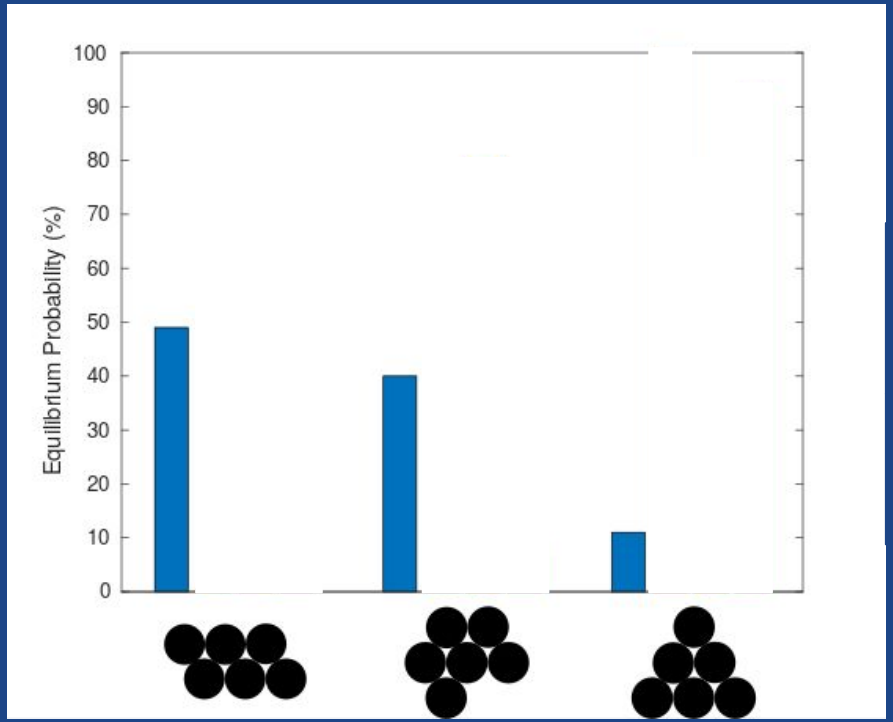


Conclusions on Interaction Potentials

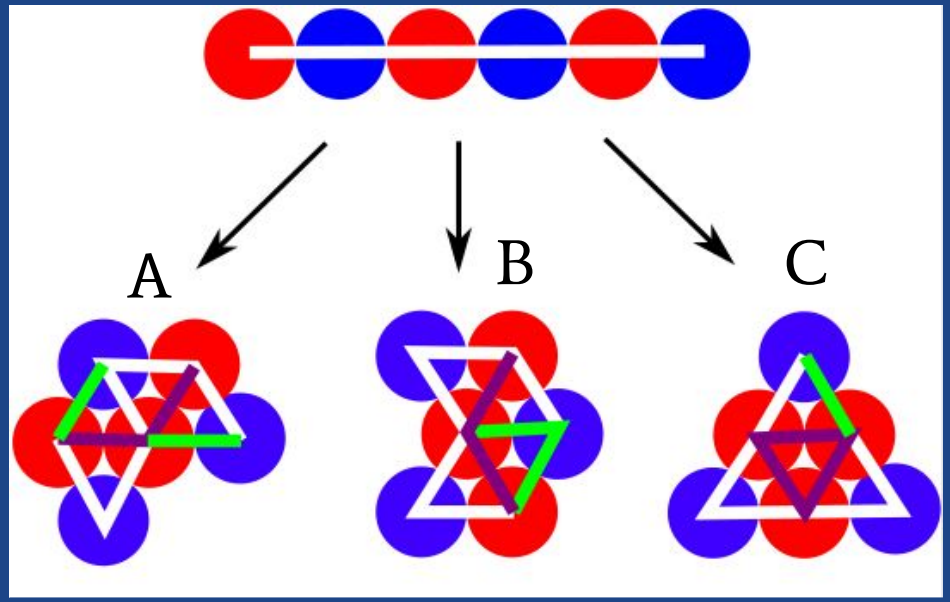
- As long as interactions are sufficiently short-ranged, the choice of potential does not appreciably affect the potential energy landscape.

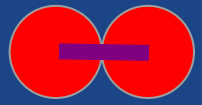
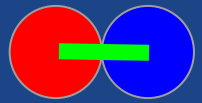
- Models going forward will assume a Morse potential with range parameter 40, which is above the range in which the first bifurcation occurs for up to 10 particles.

Equilibrium Self-Assembly of 6 Disk Chains

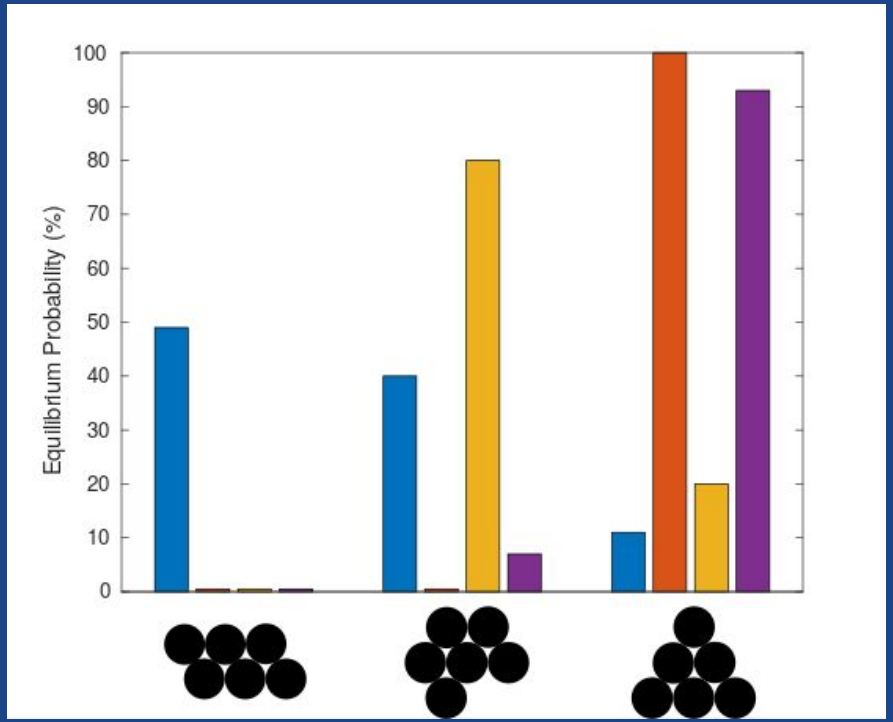


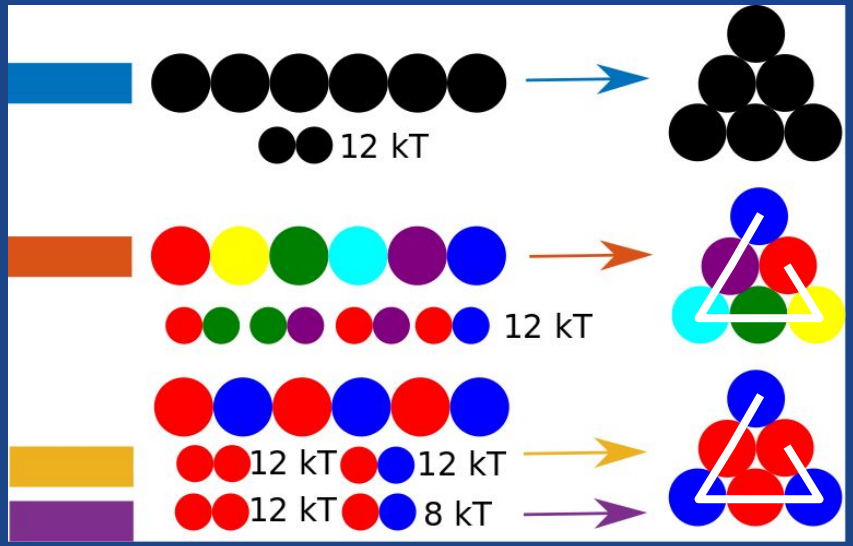
Bond Counting



Bond	A	B	C
	2	2	3
	2	2	1

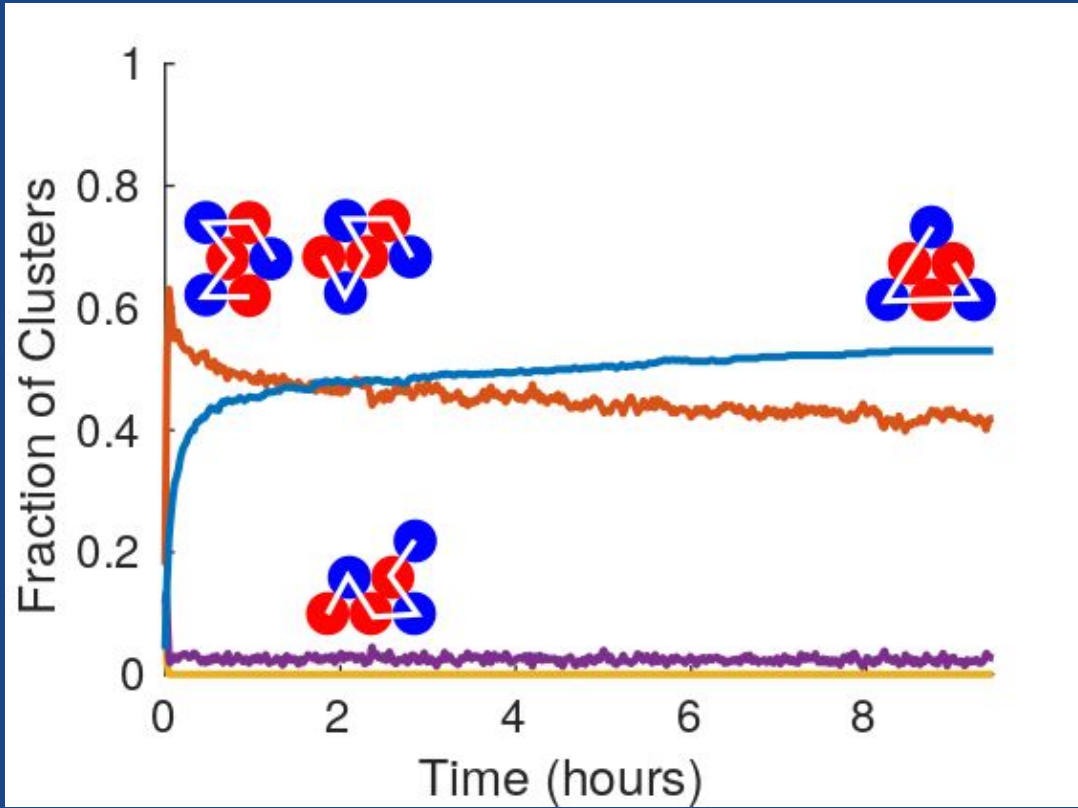
High Equilibrium Yield Design?



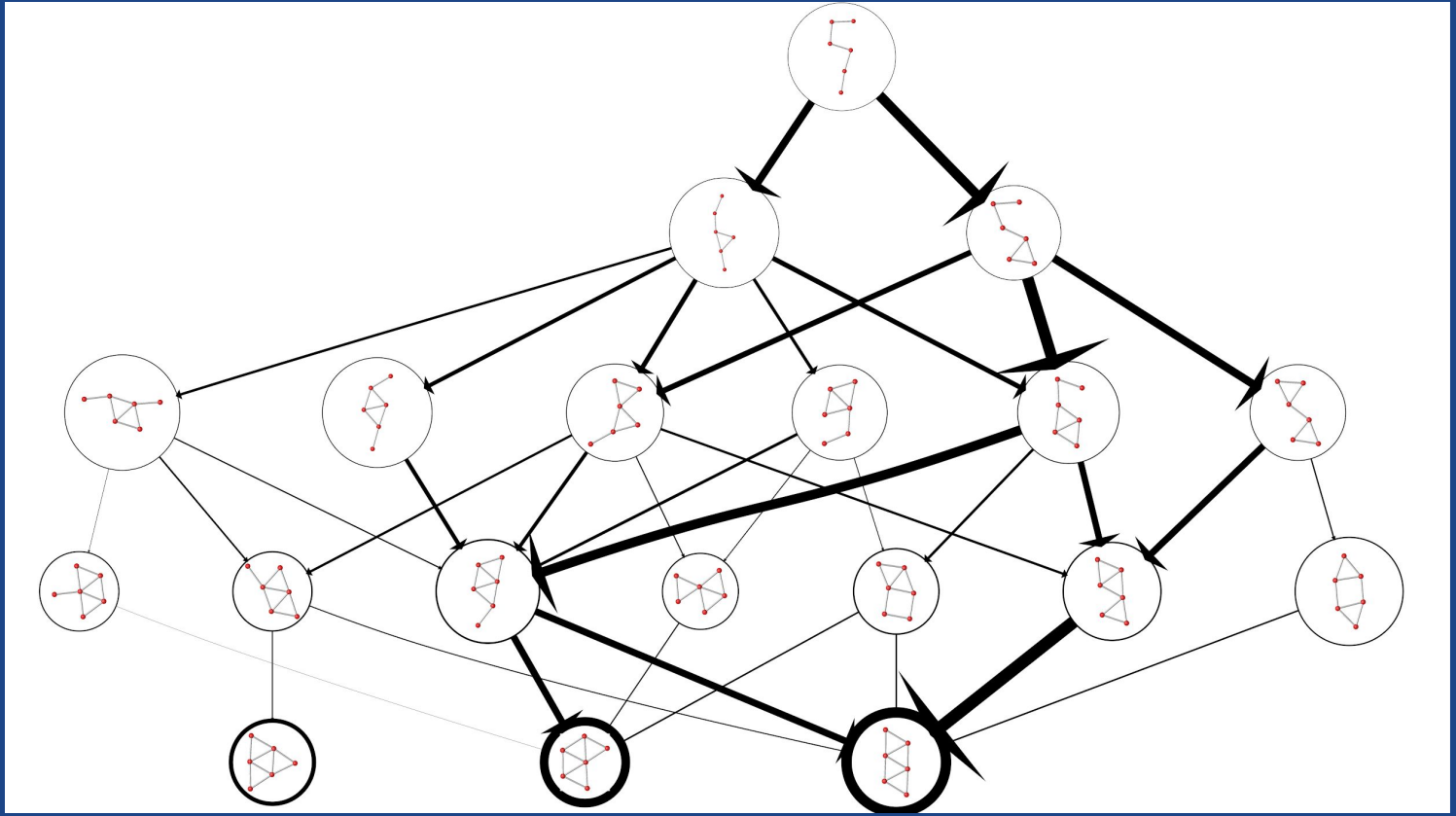


Does it work?

- Simulate with Brownian Dynamics
  - Close-ranged Morse Potential
- Only about 50% yield after 8 hours (real time)
  - Extrapolating the rate, 90% yield will take ~40-50 hours
- Why? Kinetic trapping by Chevron
  - Time scale for breaking Red-Red bond ~ exp(E)



Incorporating Kinetics - Markov Model



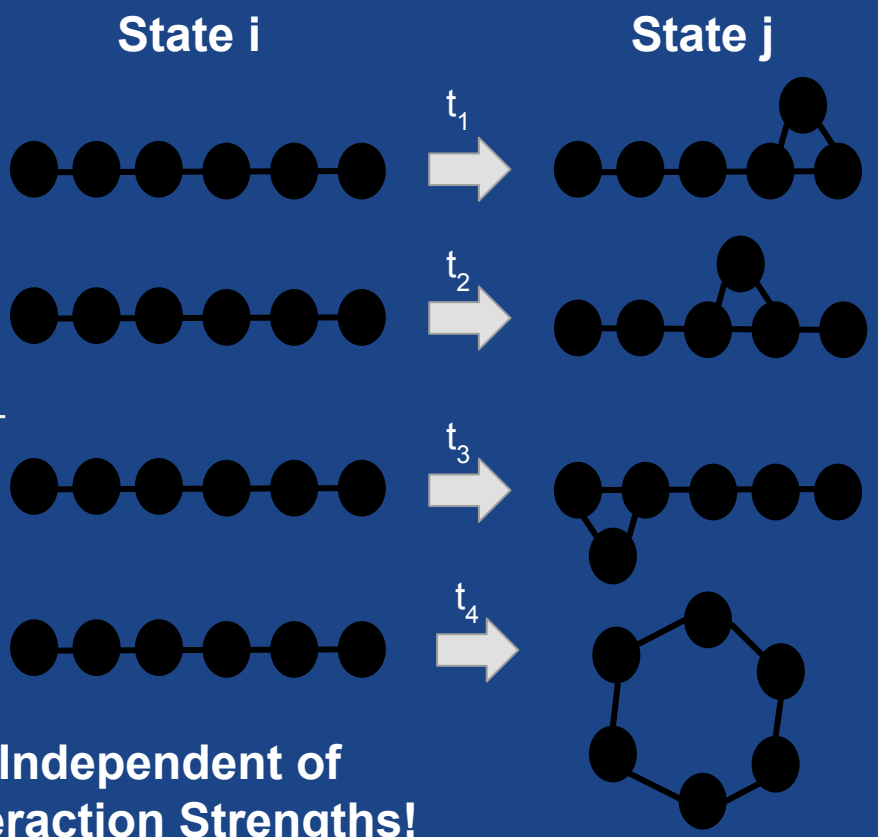
Forward Rate Estimation

Use Reflecting Brownian Dynamics to sample the exit time out of state i, and keep counts of the number of times state j is visited.

Mean First Exit Time: $\hat{\tau} = \frac{\delta t}{\sum_{k=1}^{M} t_k} \sum_{k=1}^{M} \frac{t_k(t_k+1)}{2}$

Transition Probability: $\hat{P}_{ij} = \frac{c_j}{N}$

Transition Rate: $\hat{T}_{ij} = \frac{\hat{P}_{ij}}{\hat{\tau}}$



Independent of Interaction Strengths!

Backward Rates

- Estimating the rate of bond breakage is hard.
  - Instead, invoke detailed balance

$$T_{ji} = \frac{\pi_i}{\pi_j} T_{ij}$$

π depends on E !

- Reweighting Scheme:

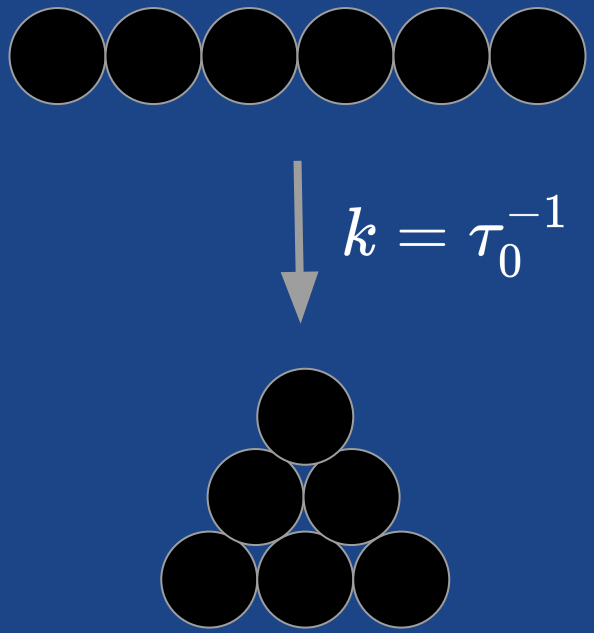
$$\frac{\pi_i(E)}{\pi_j(E)} = \frac{\pi_i(E_0)}{\pi_j(E_0)} e^{-\beta(E-E_0)}$$

- Equilibrium probabilities at the reference value are estimated exactly in the sticky limit via an MCMC on manifolds algorithm. [Zappa, Holmes-Cerfon, Goodman, 2017]

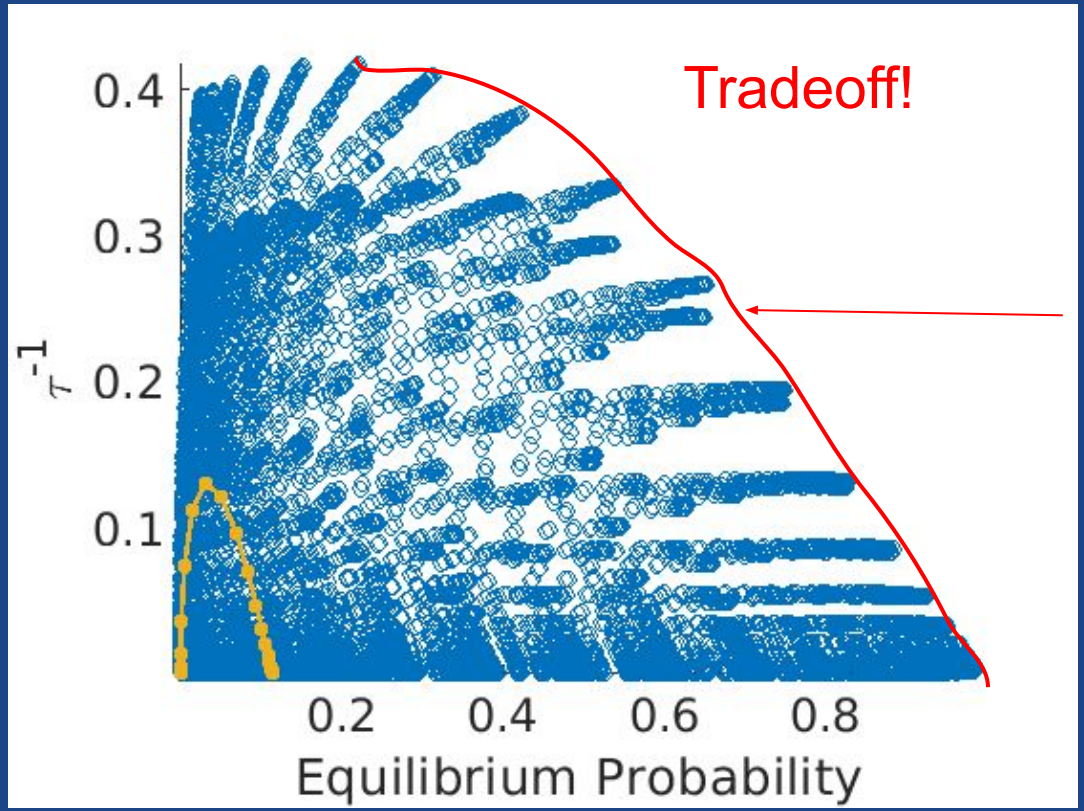
Markov Chain Model Outputs

1. Equilibrium Probabilities for each ground state
   a. Must be estimated once for one parameter set.
   b. Re-weighting scheme allows fast computation for any parameter set.
2. Average transition rates to each ground state.
   a. Can be computed using the transition rate matrix, T, by solving a linear system.

$$T_G\vec{\tau} = -1, \quad \vec{\tau}(G) = 0$$



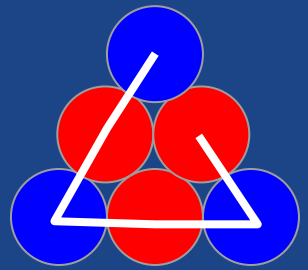
Markov Model Output - Triangle, 2 Types



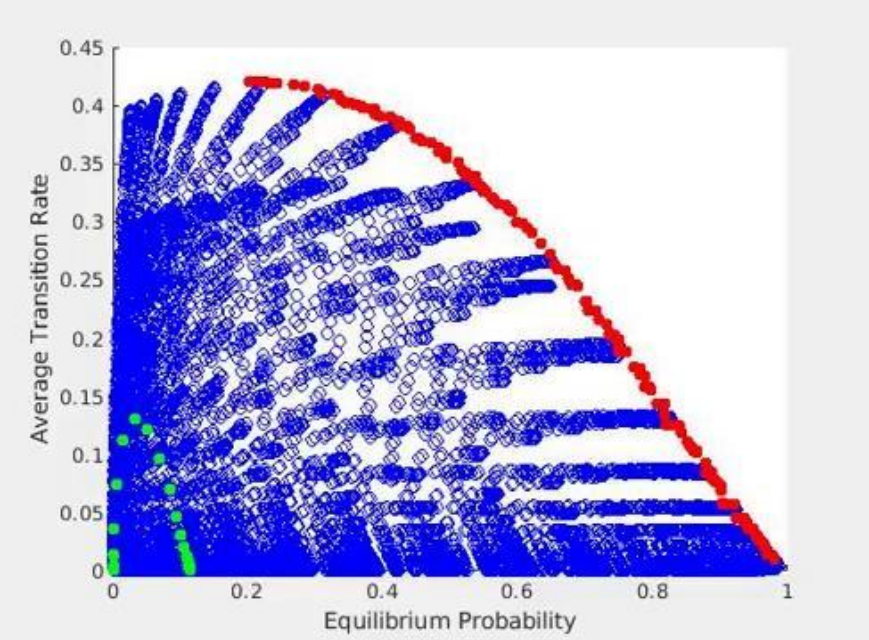
Compute (π_i, τ^{-1}) for many different choices of $\vec{E} = (E_{AA}, E_{AB}, E_{BB})$

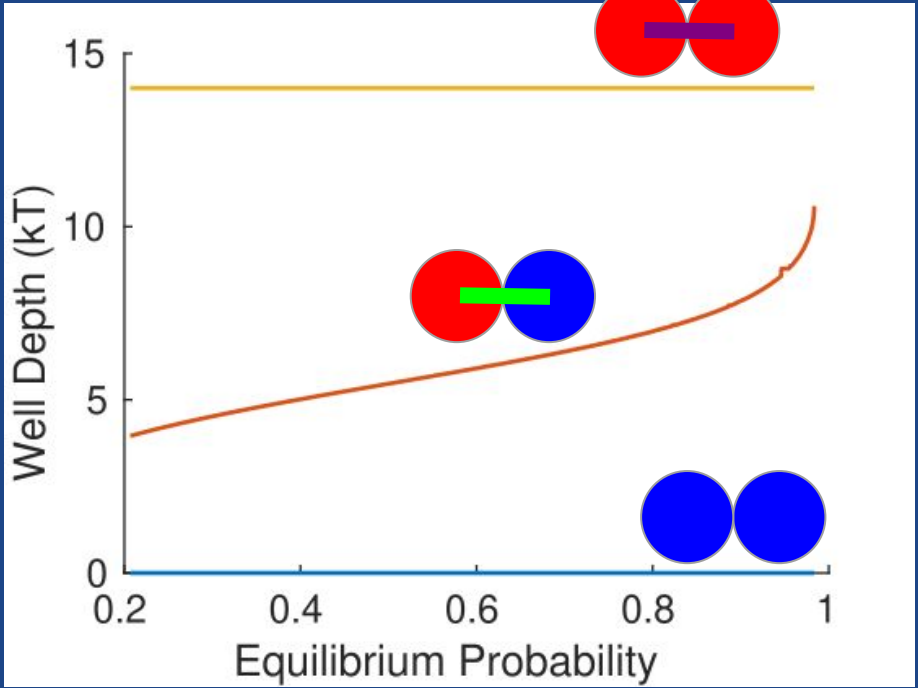
Pareto front:

No objective can be increased without decreasing another



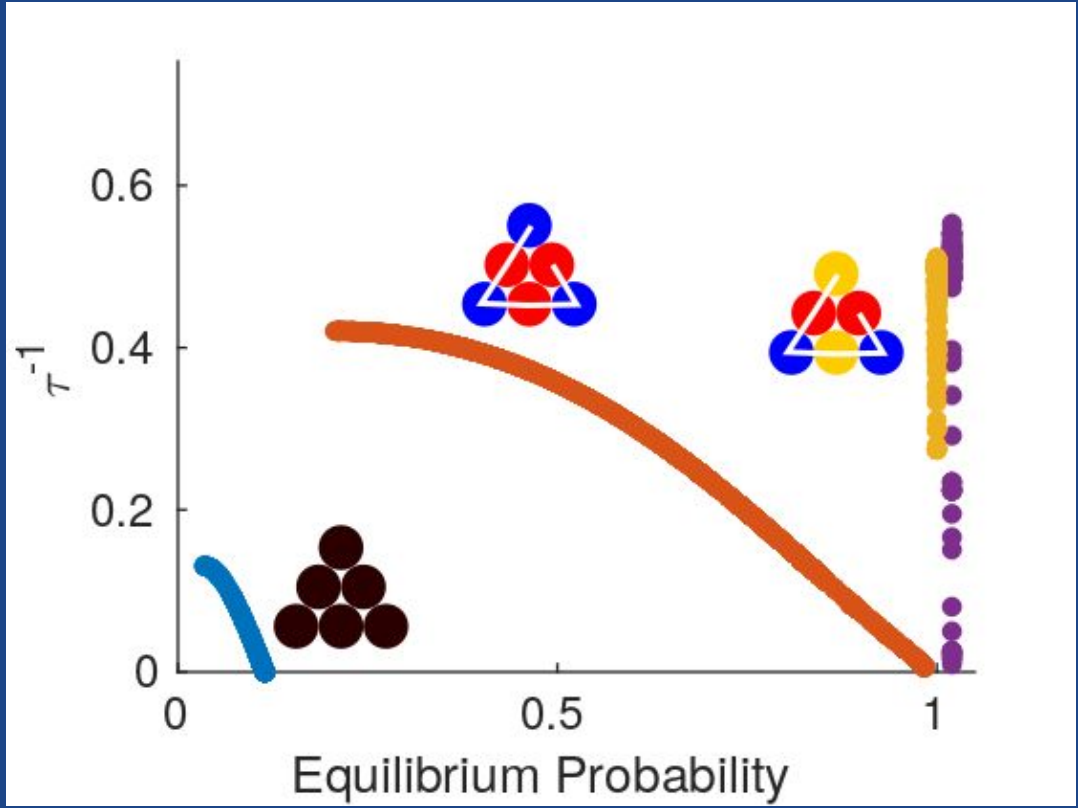
Genetic Algorithm for Computing Pareto Fronts



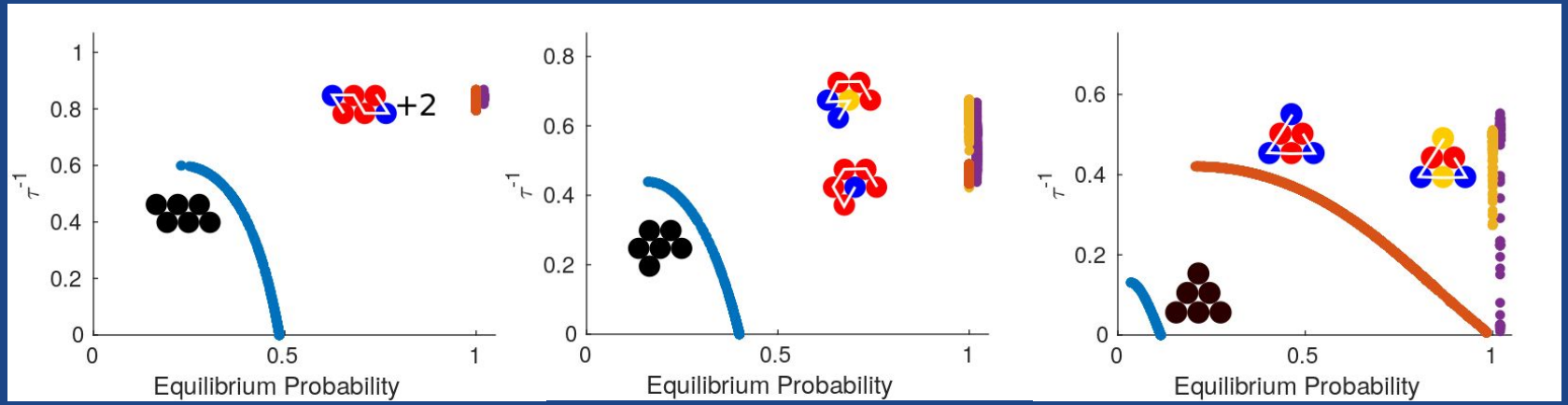


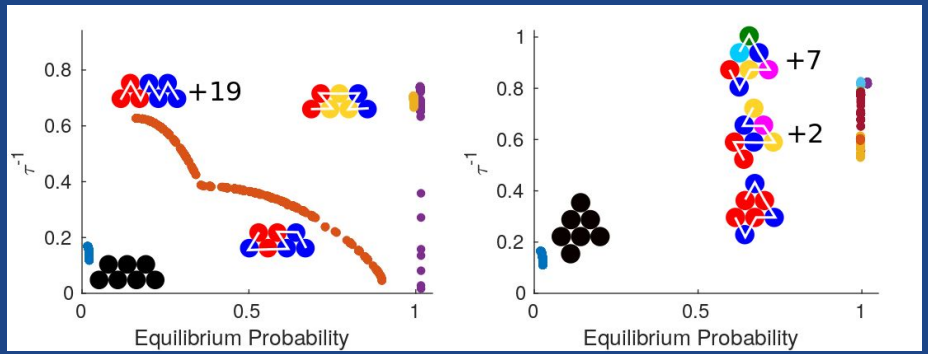
Determining the Minimum Number of Species

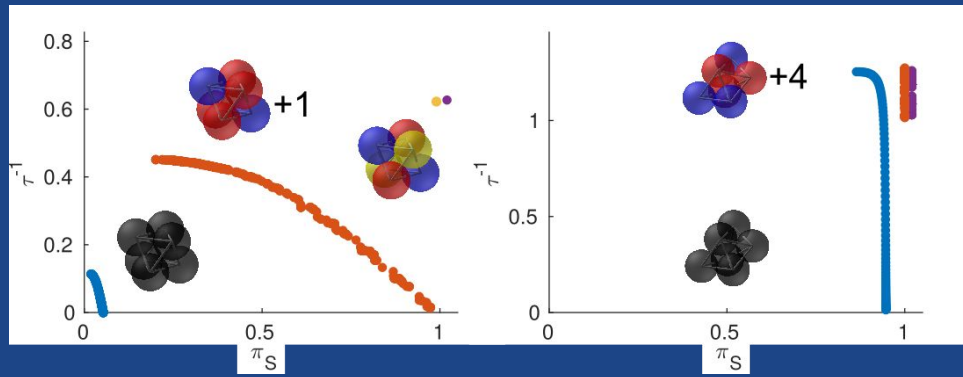
- Allow particle species to be an inheritable property for the genetic algorithm.
- Fix number of types as m. Increase m until assembly efficiency is comparable to m=6.
- Nearly vertical fronts -> tradeoff eliminated!



Applying to Other Structures

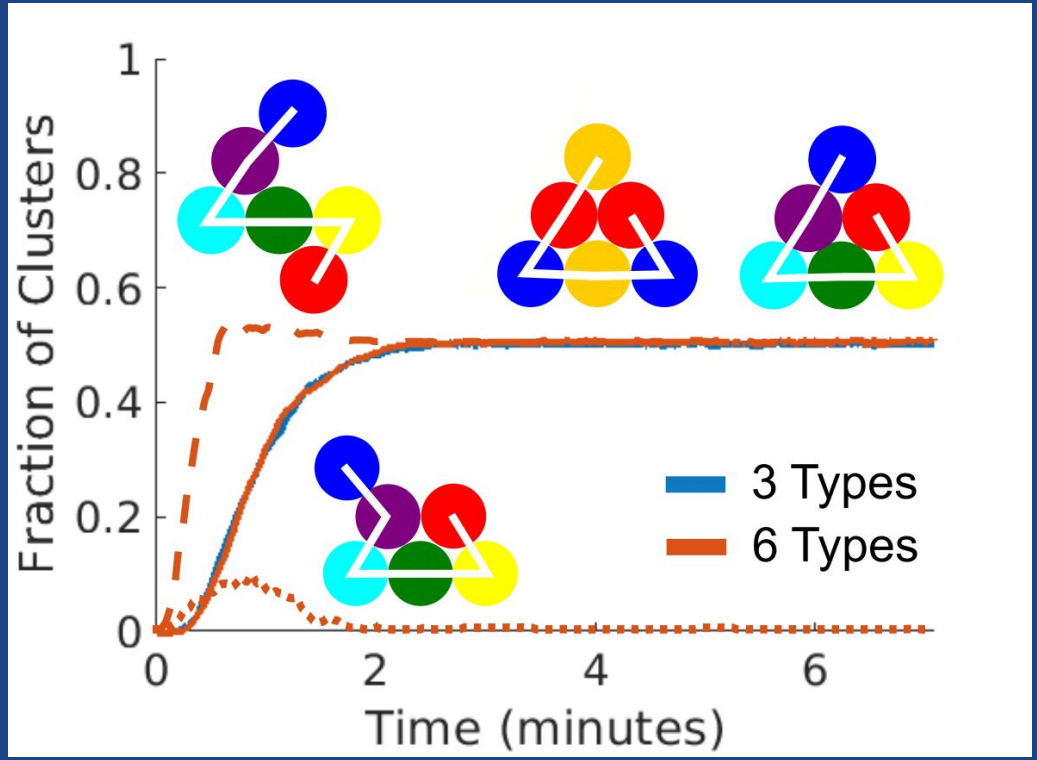






Verification through Simulation

- Perform 400 Brownian dynamics simulations using optimal triangle parameters determined by the genetic algorithm.
- Similar dynamics for 3 and 6 types, but why only 50% yield?
- Model drawback: lumping by adjacency matrix.
- Takeaway: 100% yield is not possible with isotropic interactions.



Conclusions on Equilibrium Self-Assembly

- I used a coarse-grained Markov model along with a genetic algorithm to identify thermodynamic-kinetic tradeoffs for the self assembly of colloidal chains.
- By constructing Pareto fronts, I was able to determine the minimal design complexity to achieve assembly that is as efficient as possible, within the confines of isotropic interactions.
- Brownian dynamics simulations showed we cannot achieve yields near 1 with isotropic interactions; orientation dependent interactions are necessary.
    - A possibility for future work is to come up with a sampling approach to identify these tradeoffs, which would naturally capture the traps neglected by this model.

Brownian Dynamics (Plus Hydrodynamics)

$$\frac{d\boldsymbol{Q}}{dt} = \underbrace{\boldsymbol{\mathcal{M}}\boldsymbol{F}}_{\text{Det. Drift}} + \underbrace{(k_B T)\partial_{\boldsymbol{Q}} \cdot \boldsymbol{\mathcal{M}}}_{\text{Stochastic Drift}} + \underbrace{\sqrt{2k_B T}\boldsymbol{\mathcal{M}}^{1/2}\boldsymbol{\mathcal{W}}(t)}_{\text{Brownian Increment}}$$

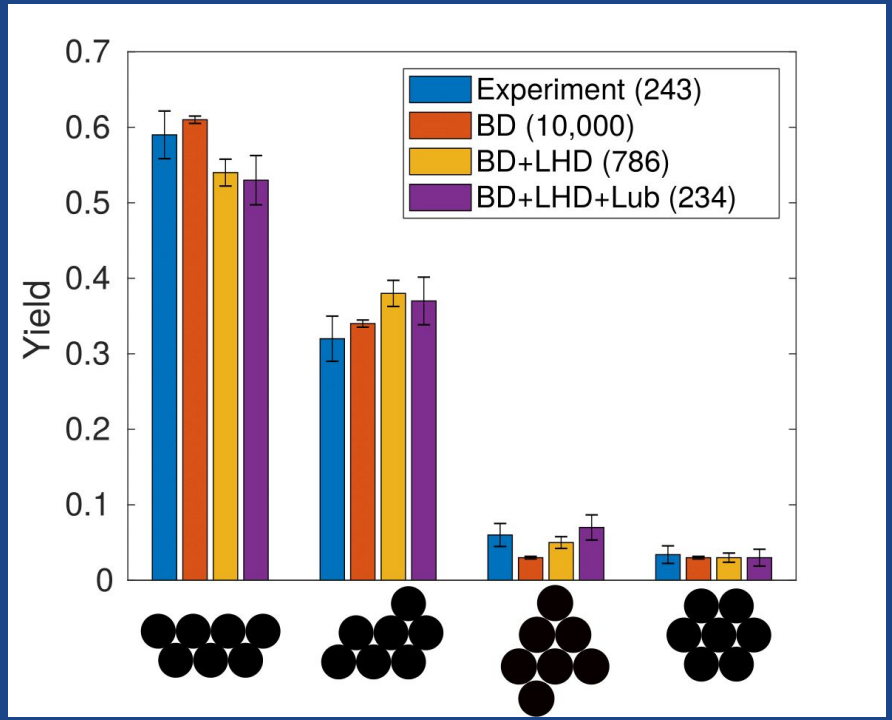
3 Choices for the Mobility Matrix:

1) Identity -> Typical Brownian Dynamics
2) Far-field Hydrodynamic Interactions (RPY Tensor)
3) Far-field + Short-Ranged Lubrication Corrections [1]

[1] Brennan Sprinkle, Ernest B. van der Wee, Yixiang Luo, Michelle Driscoll, and Aleksandar Donev. Driven dynamics in dense suspensions of microrollers. Soft Matter, 16:7982 – 8001, 2020.

Comparing Simulation Yields

- Hydrodynamics has a noticeable effect on the ground state yields.
- Note: Sample size still too small to choose a “best” model.
- Also have access to full trajectory information.
  - How else can we compare simulation results?

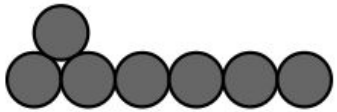
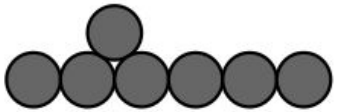
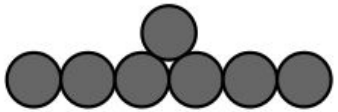


BD trajectories courtesy of Andreas Neophytou, University of Birmingham.

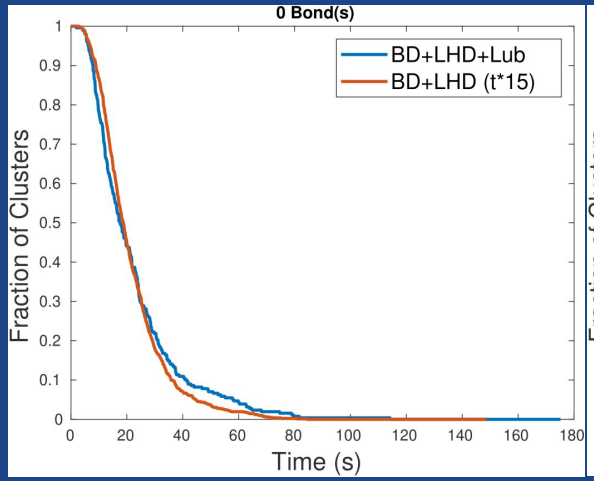
Effect of Hydrodynamics on Pathways

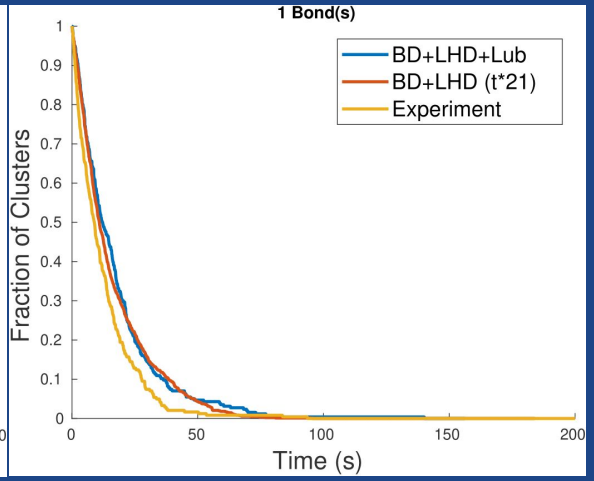
Most Probable Path:

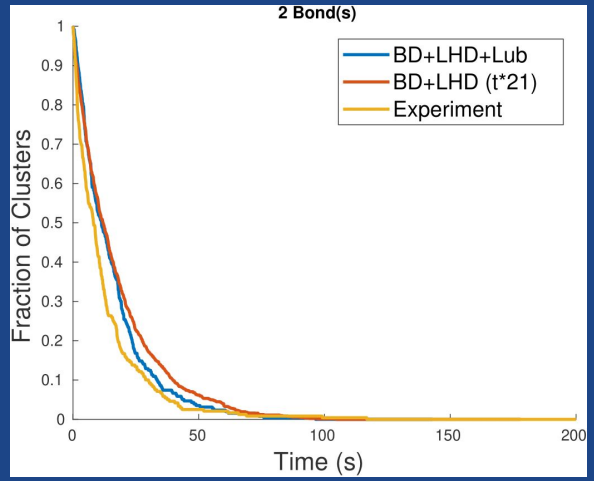
Probability Distribution of 1-bonded states:

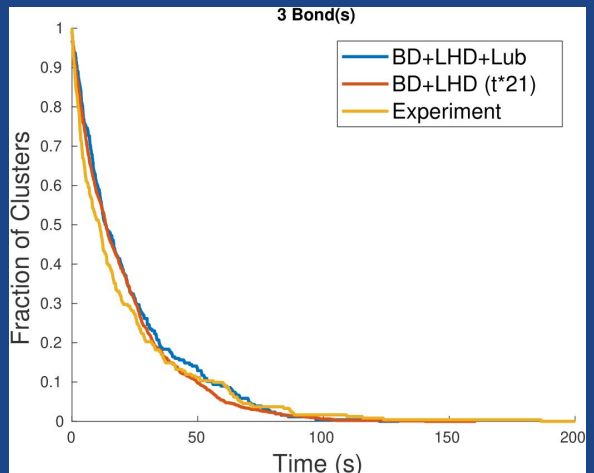
			
Brownian Dynamics	0.63 ± 0.005	0.27 ± 0.004	0.10 ± 0.003
Far-Field HD	0.50 ± 0.018	0.34 ± 0.017	0.15 ± 0.013
Far-Field HD + Lubrication	0.48 ± 0.033	0.37 ± 0.032	0.12 ± 0.021

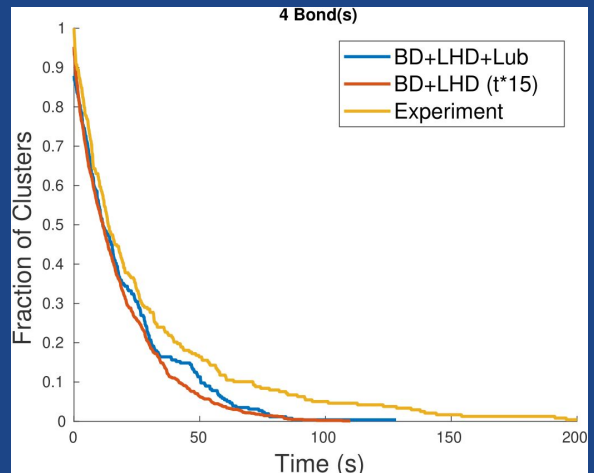
Distribution of Dwell Times











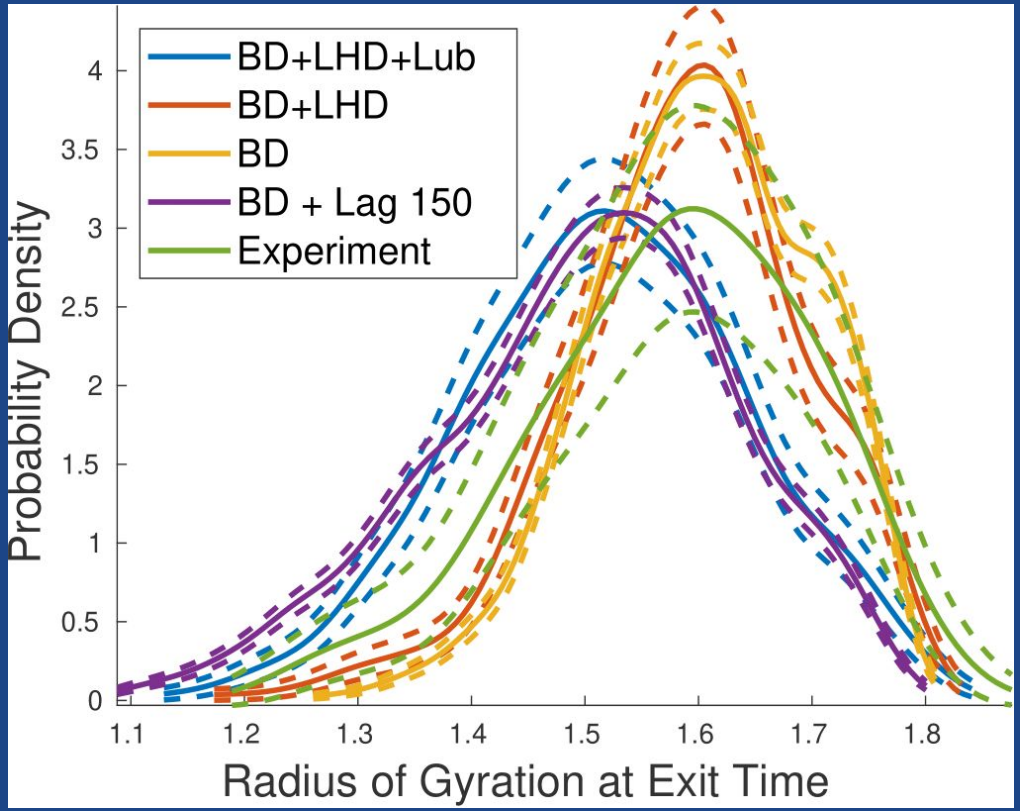
Comparing First Hitting Time Distributions

- Compare actual clusters via an order parameter.
  Ex: Radius of Gyration

$$R_g^2 = \frac{1}{N}\sum_{i=1}^{N} r_i^2$$

- Simulations with lubrication forces favor more compact structures at first bond time.

- Could be result of increased time until bond formation?



Conclusions on Hydrodynamics

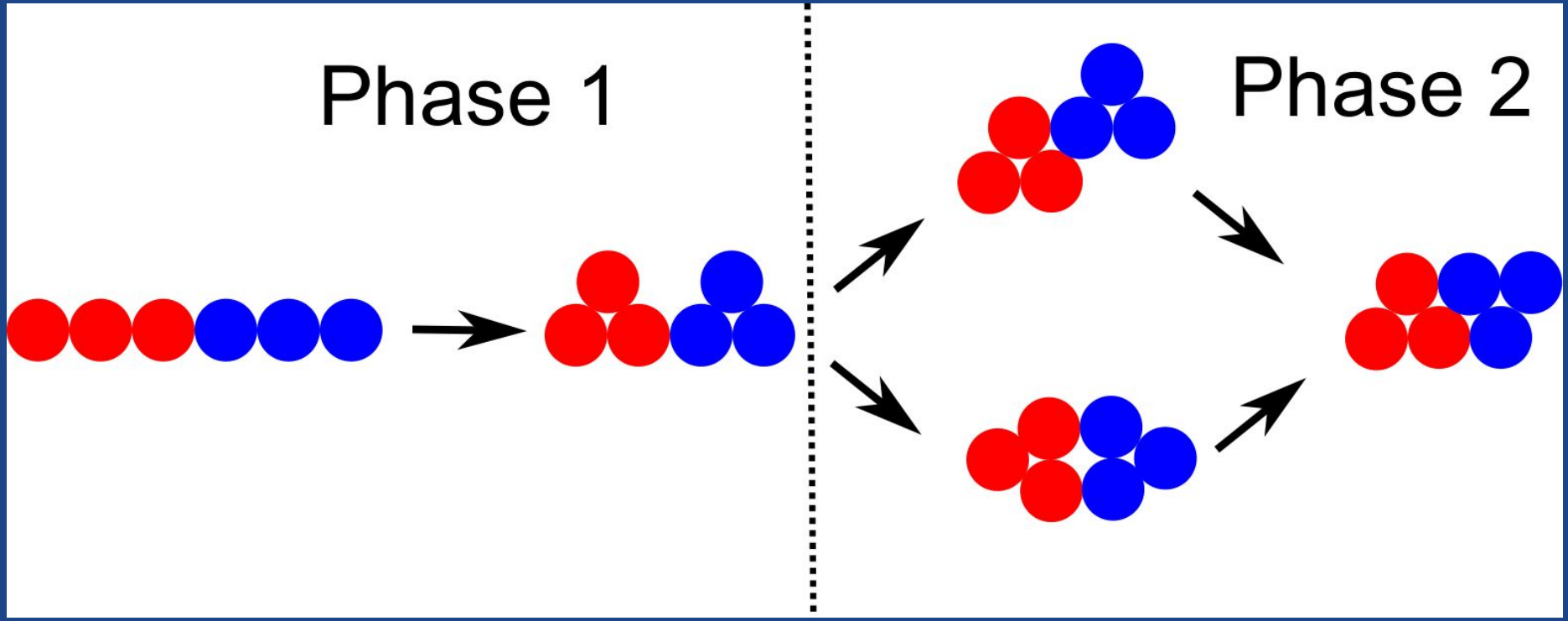
- We performed hydrodynamics simulations of the self assembly of 7-disk colloidal chains and compared to experiment and plain BD.
  - Hydrodynamics had a non-negligible effect on ground state yields, potentially due to the suppression of triangle formation at the end of the chain.
  - More data is necessary to make a comparison among models.
- Short-ranged hydrodynamics led to an increase in the time for bond formation
  - A possible explanation is an additional effective energy barrier for bond formation induced by lubrication. This warrants further study.
- The dynamics with short-ranged lubrication were found to be sensitive to the pair potential.
  - Simulation would benefit from an in-depth study of the pair potential between colloids.

Non-Equilibrium Protocols for Colloidal Self-Assembly

- Equilibrium self-assembly is typically plagued by thermodynamic-kinetic tradeoffs
- Tradeoffs can be eliminated by increasing the complexity of the design space.

- Alternative: introduce a non-equilibrium driving to facilitate assembly
  - Example: a time-dependent temperature for a folding experiment
  - Bond strength depends sensitively on temperature
  - Rates are now implicitly characterized by the experimental time
  - Potentially more experimentally accessible than creating more particle types

Idealized Non-Equilibrium Assembly Example



Time-Dependent Protocol Optimization

Goal:

$$\begin{cases} \max_{\theta(t)} P_B(T) \\ \text{subject to} \\ \partial_t \vec{p}(t) = \vec{p}(t) L(\theta(t)), \\ \vec{p}(0) = \vec{p}_0 \end{cases}$$

Approach:

$$\frac{\delta \vec{p}(t)}{\delta \theta(s)} = \vec{R}(t,s)$$

$$\partial_t \vec{R}(t,s) = \vec{R}(t,s) L(\theta(t)) + \vec{p}(t) L'(\theta(t)) \delta(t-s)$$

$$\frac{\delta P_B(T)}{\delta \theta(t)} = \sum_{i \in B} R_i(T,t) = 0$$

$$\theta^{n+1}(t) = \theta^n(t) + h \sum_{i \in B} R_i(T,t)$$

Time-Dependent Protocol Optimization - Adjoint Algorithm

Primal Equation:

$$\partial_t \vec{p}(t) = \vec{p}(t) L(\theta(t)),$$
$$\vec{p}(0) = \vec{p}_0$$

Adjoint Equation:

$$\partial_t \vec{\mu}^T(t) = -L(\theta(t)) \vec{\mu}^T(t),$$
$$\vec{\mu}^T(T) = \vec{b}^T$$

Time Derivative of Inner Product:

$$\partial_t \left(\vec{R}(t,s) \vec{\mu}^T(t) \right) = \partial_t \vec{R}(t,s) \vec{\mu}^T(t) + \vec{R}(t,s) \partial_t \vec{\mu}^T(t)$$

$$= \left(\vec{R}(t,s) L(\theta(t)) + \vec{p}(t) \frac{\delta L(\theta(t))}{\delta \theta(s)} \right) \vec{\mu}^T(t) - \vec{R}(t,s) L(\theta(t)) \vec{\mu}^T(t)$$

$$= \vec{p}(t) \frac{\delta L(\theta(t))}{\delta \theta(s)} \vec{\mu}^T(t)$$

$$\int_0^T \vec{p}(t) \frac{\delta L(\theta(t))}{\delta \theta(s)} \vec{\mu}^T(t) dt = \frac{\delta P_B(T)}{\delta \theta(s)}$$

Dissipative Penalty Term

- Protocols may develop steep gradients or fast oscillations
  - Potentially unrealizable in a physical experiment. Ex: Instantaneous temperature control

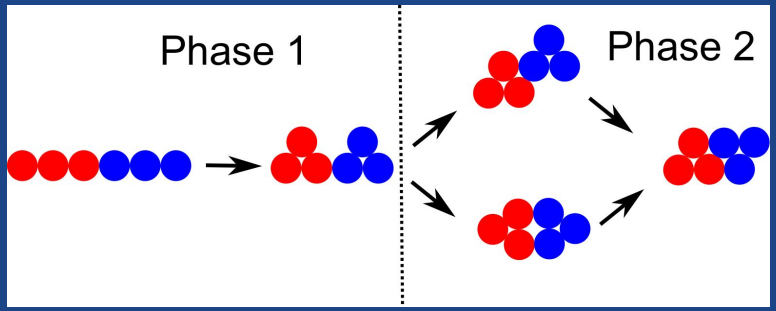
- Introduce penalty term to favor smooth solutions

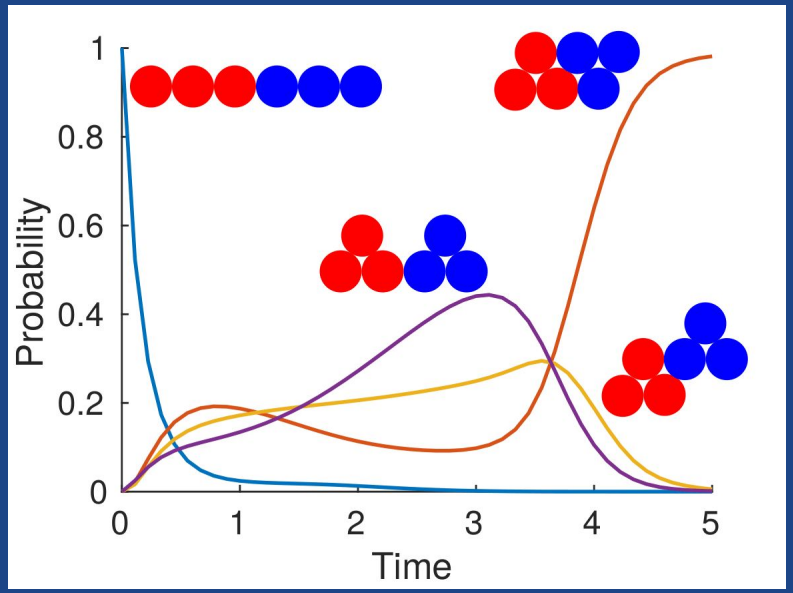
$$P(\theta(t)) = -\lambda/2 \int_0^T |\dot{\theta}(t)|^2 dt$$

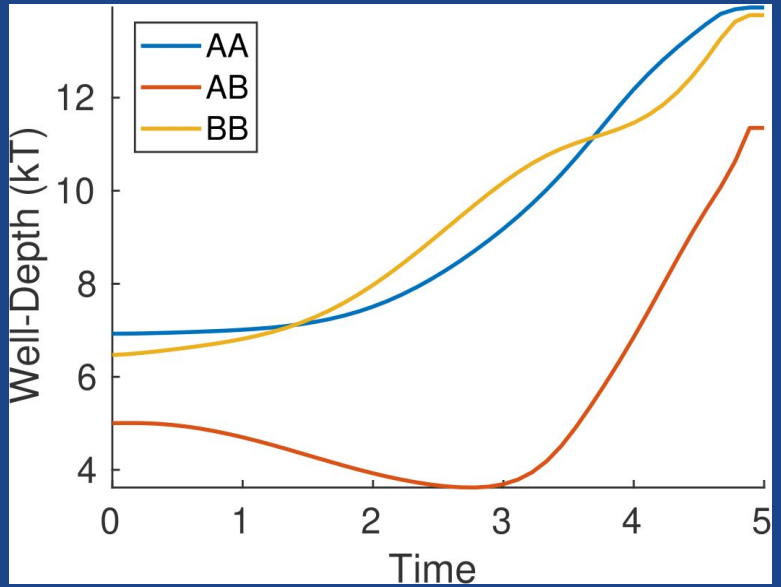
- Gradient descent update then becomes equivalent to solving a heat equation with source term in some artificial optimization time, τ. Use Neumann BCs.

$$\theta_\tau(t) = G(T,t) + \lambda\theta_{tt}(t)$$

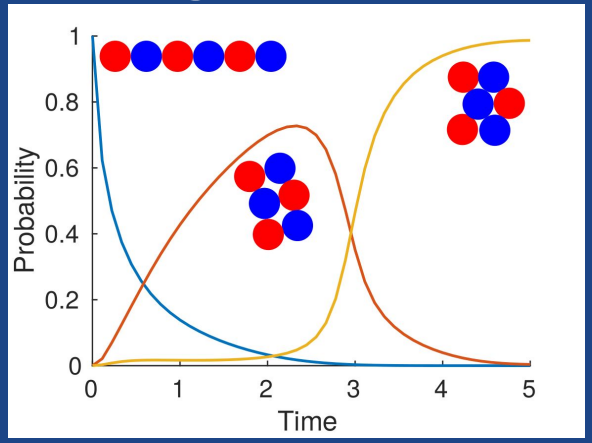
Assembling the Parallelogram

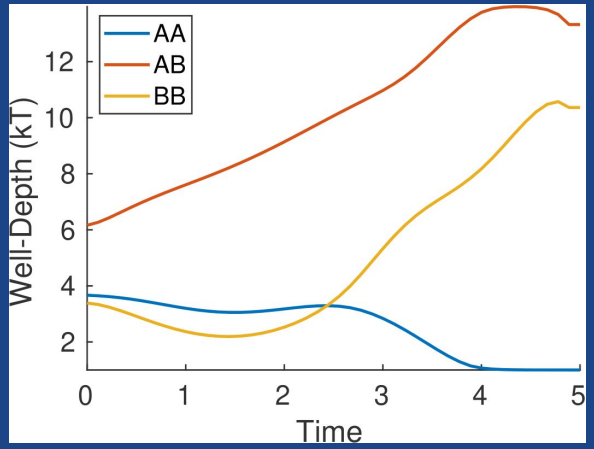


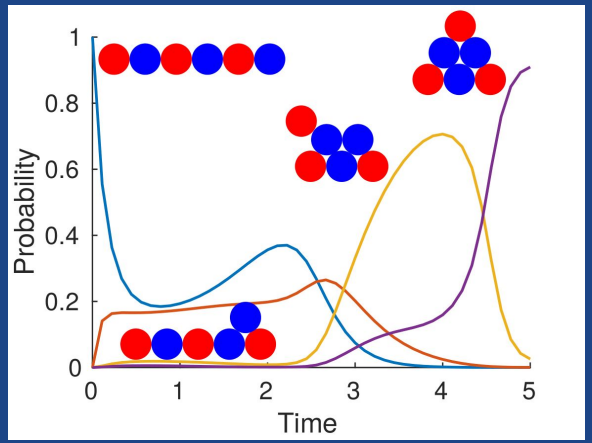


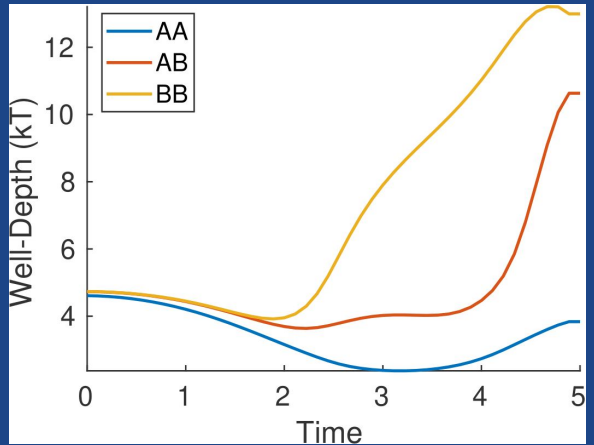


Assembling Other 6-Disk Clusters









Conclusions on Non-Equilibrium Self-Assembly

- I've presented a method for computing an optimal time dependent protocol to maximize the probability of a target state, for dynamics governed by a Markov jump process.
  - Applying the algorithm to the self-assembly of 6-disk chains, we found protocols to form each ground state with high yield, including a previously known procedure for the parallelogram.
  - The transition matrix is constructed under the same assumptions as for the equilibrium self-assembly problem, so the same issues are present regarding isotropic interactions.

- We have also derived an analogous adjoint algorithm for dynamics governed by an SDE. In this case, we also have a formula to approximate gradients by sampling for higher dimensional problems.
  - Still need to apply it to test problems and compare to other methods. Ex: CMA-ES, Miskin Optimizer

Thank You!