Dissipation and control in nonequilibrium transformations

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KITP: Nanoparticle Assemblies

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Stanford University

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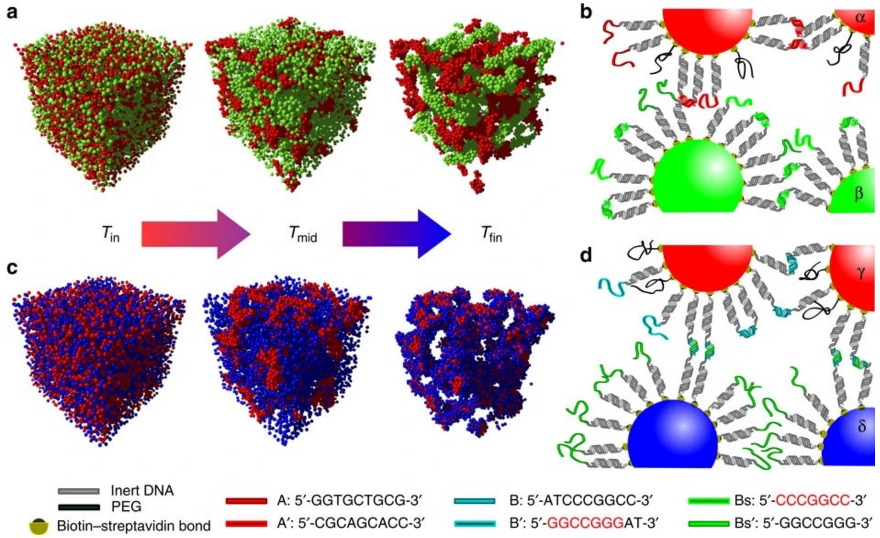
Equilibrium design strategies for self-assembly

Specificity



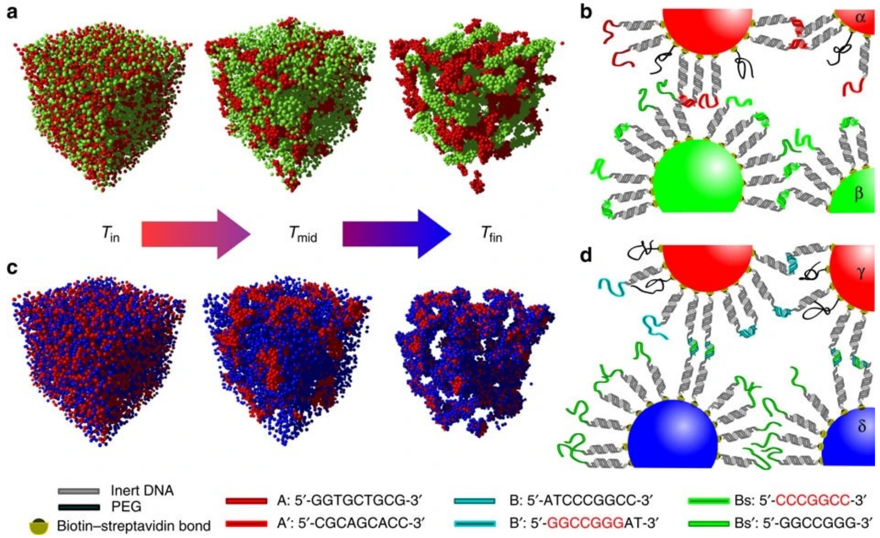
Di Michele et al. *Nat Commun* **4**, 2007 (2013)

Constrained intermolecular organization
Tunable and specific interactions

Equilibrium design strategies for self-assembly

Specificity

Simplicity



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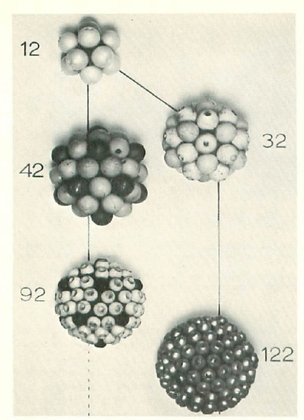


FIGURE 11. The arrangement of hexamer and pentamer morphological units in the lower members of the two icosahedral classes P = 1 (at left) and P = 3 (at right). The units are necessarily in close-packed array on the surface. The numbers of morphological units in the two classes are:
P = 1. 12, 42, 92, 162, 252 . . . . . See Table 1
P = 3. 32, 122, 272 . . . .
In some of the models, the 5-coordinated and 6-coordinated units are shown in different shades.

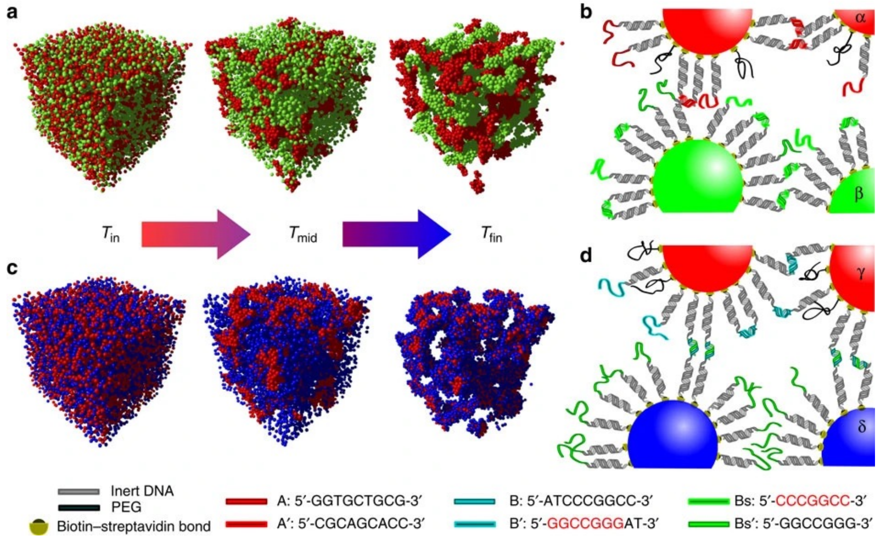
Caspar and Klug. CSH 27. (1962)

Constrained intermolecular organization
Tunable and specific interactions

Few kinetic traps
Unique assembled structure

Equilibrium design strategies for self-assembly

Specificity



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Constrained intermolecular organization
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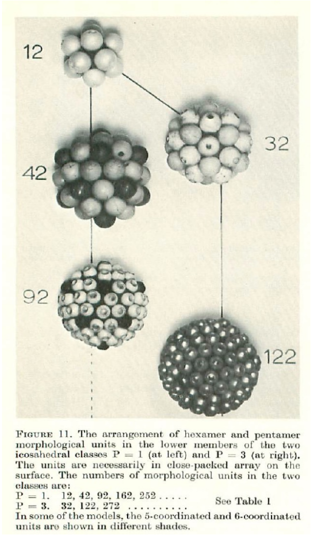
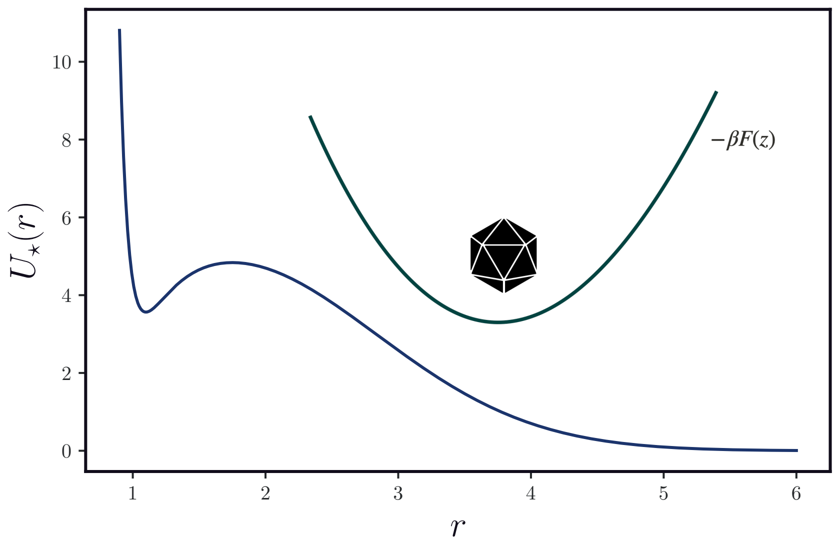


Caspar and Klug. CSH 27. (1962)

Few kinetic traps
Unique assembled structure

Realizability



Infeasible intermolecular interactions
Strong material constraints

Can we overcome these limitations with external control?

PHYSICAL REVIEW LETTERS **130,** 107101 (2023)

Unified, Geometric Framework for Nonequilibrium Protocol Optimization

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Physics-informed graph neural networks enhance scalability of variational nonequilibrium optimal control

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Probing the theoretical and computational limits of dissipative design

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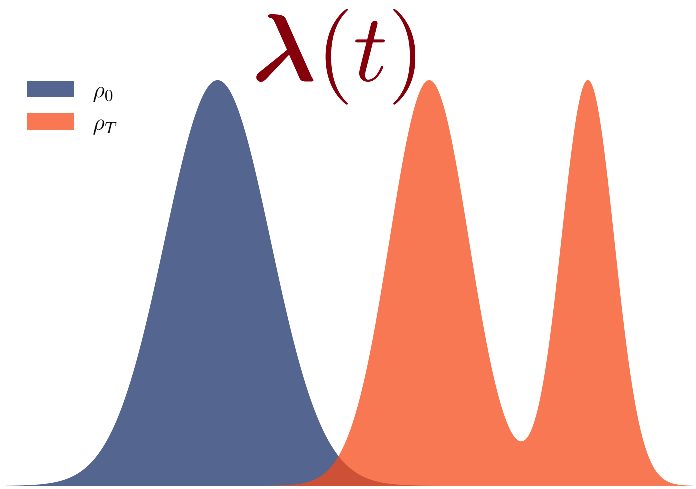
Part I: Measuring dissipation

A parallel set of concerns?

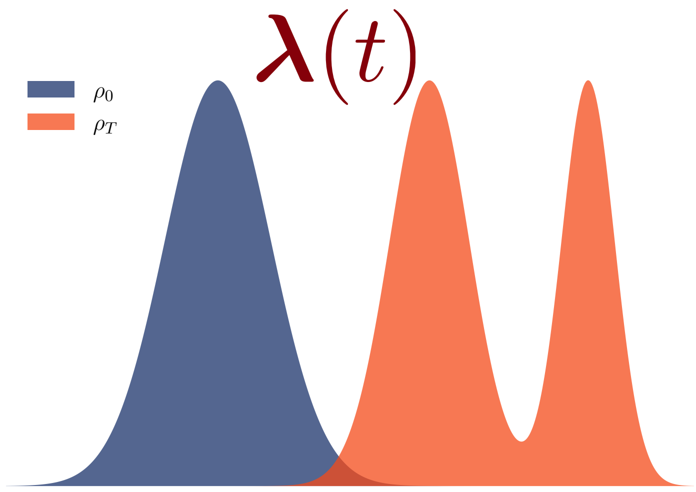
Energetic Costs



External input energy to maintain the desired steady state?

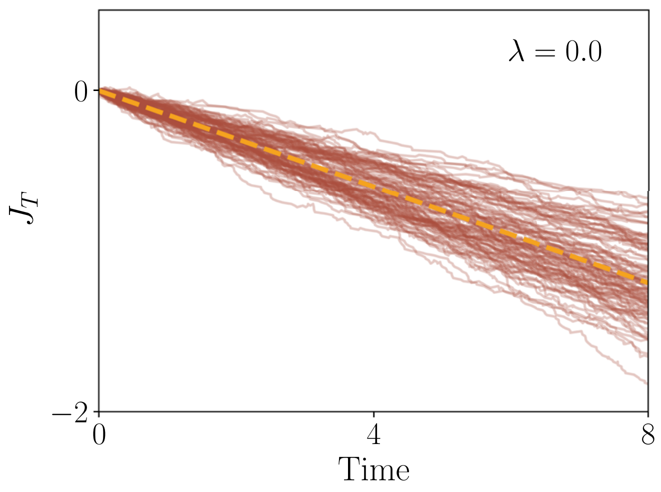
A parallel set of concerns?

Energetic Costs



External input energy to maintain the desired steady state?

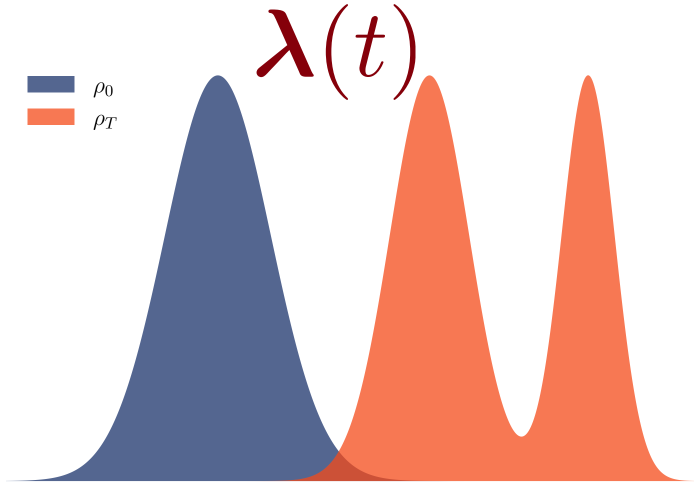
Speed of Control



Finite time thermodynamic cost. Limitations on speed?

A parallel set of concerns?

Energetic Costs



External input energy to maintain the desired steady state?

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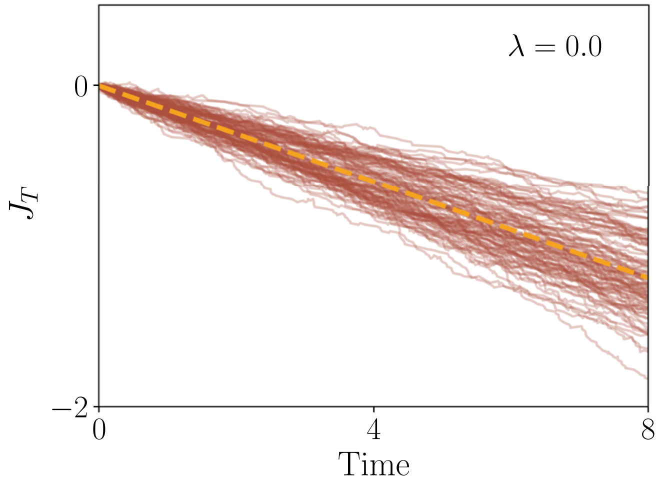
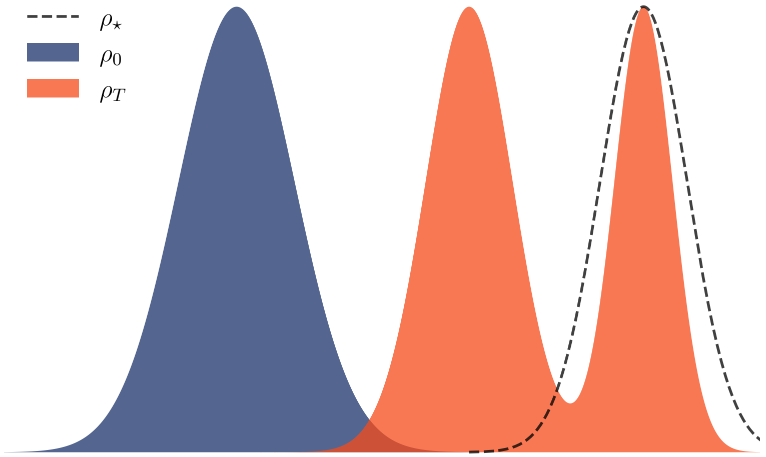


Finite time thermodynamic cost. Limitations on speed?

Accuracy of Outcome



How closely did we realize the desired transformation?

Measuring dissipation in nonequilibrium transformations

$$\boldsymbol{\lambda}(t)$$ Control parameters → $$\boldsymbol{\Theta}(\boldsymbol{x}, t) = -\partial_{\boldsymbol{\lambda}} U(\boldsymbol{x}, \boldsymbol{\lambda}(t))$$

Conjugate response

Work

$$W[\boldsymbol{X}(t)] = -\int_0^{t_\mathrm{f}} \boldsymbol{\Theta}(\boldsymbol{X}(t, \boldsymbol{x}_0)) \cdot \dot{\boldsymbol{\lambda}}(t) dt$$

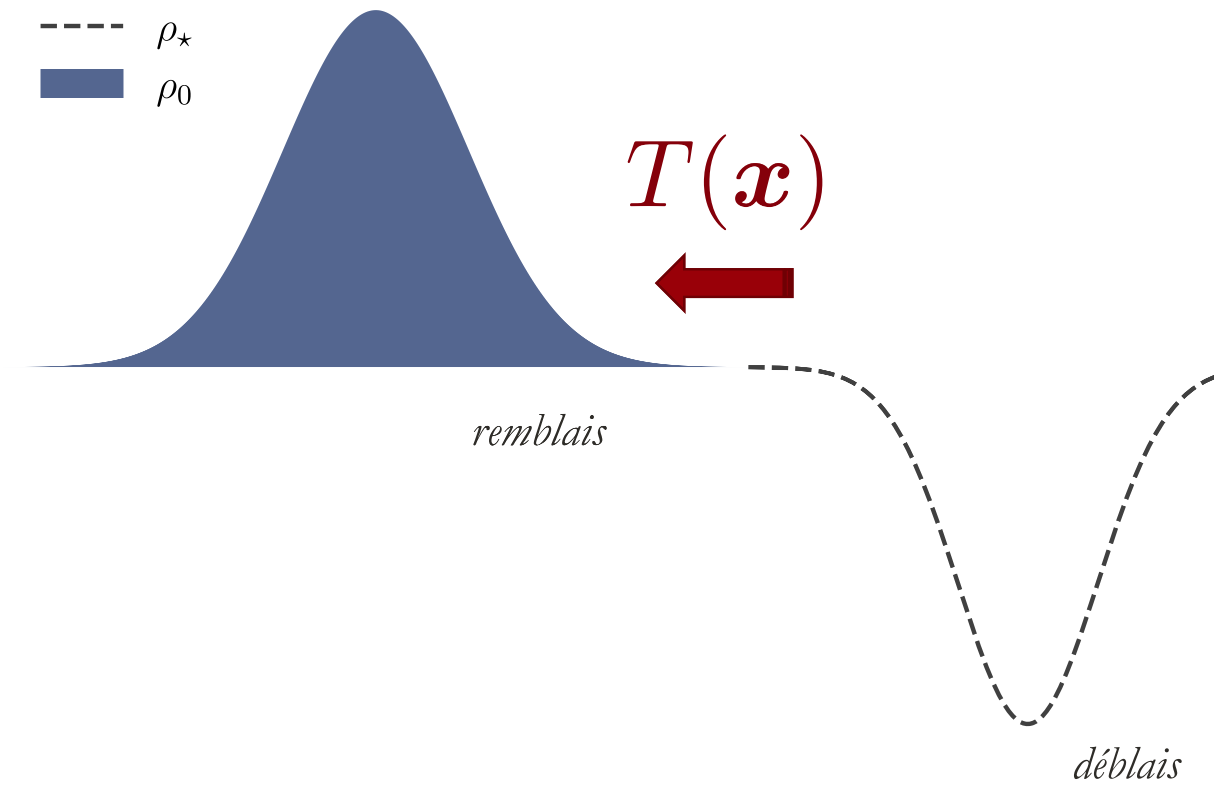
Heat

$$\mathcal{Q}[\boldsymbol{X}(t)] = -\int_0^{t_\mathrm{f}} \nabla U(\boldsymbol{X}(t, \boldsymbol{x}_0)) \circ d\boldsymbol{X}(t)$$

Dissipation

$$\Delta\Sigma = \beta(\langle W - \Delta U \rangle) = \beta \langle \mathcal{Q} \rangle$$

Dissipation the language of *optimal transport*



Monge Problem

$$\mathcal{W}_2^2(\rho_A, \rho_B) = \inf_T \int_\Omega |\boldsymbol{x} - T(\boldsymbol{x})|^2 \rho_A(\boldsymbol{x}) d\boldsymbol{x}$$

$$\rho(\cdot, 0) = \rho_A, \quad \rho(\cdot, t_\mathrm{f}) = \rho_B.$$

No explicit protocol!

$$\boldsymbol{X}(t; \boldsymbol{x}) = (1 - \frac{t}{t_\mathrm{f}})\boldsymbol{x} + \frac{t}{t_\mathrm{f}} T(\boldsymbol{x})$$

Optimal transport and dissipation

$$\dot{\boldsymbol{x}} = -\nabla U(\boldsymbol{x}, \boldsymbol{\lambda}(t)) + \sqrt{2\beta^{-1}}\boldsymbol{\eta}(t) \qquad \partial_t \rho + \nabla \cdot (\boldsymbol{v}\rho) = 0$$

$$\Delta\Sigma_{\text{tot}} = \int_0^{t_{\text{f}}} \beta(t) \int_\Omega \boldsymbol{v}^T(\boldsymbol{x}, t)\boldsymbol{v}(\boldsymbol{x}, t)\rho(\boldsymbol{x}, t)\, d\boldsymbol{x}\, dt$$

Benamou-Brenier optimal transport: minimize with respect to the velocity field

$$\boldsymbol{\lambda}_* = \underset{\boldsymbol{\lambda}:[0,t_{\text{f}}]\to\mathbb{R}^k}{\text{argmin}} \ \Delta\Sigma_{\text{tot}}[\boldsymbol{\lambda}] \text{ subj. to } \rho(\cdot, 0) = \rho_A, \quad \rho(\cdot, t_{\text{f}}) = \rho_B$$

Linear response regime yields classic results

Perturb around the instantaneous equilibrium:

$$\rho(\boldsymbol{x}, t) = \rho_0(\boldsymbol{x}, t) + \epsilon\rho_1(\boldsymbol{x}, t) + \mathcal{O}(\epsilon^2)$$

First order correction satisfies,

$$\partial_t \rho_1(\boldsymbol{x}, t) = \mathcal{L}_0^\dagger \rho_1(\boldsymbol{x}, t) + \mathcal{L}_1^\dagger \rho_0(\boldsymbol{x}, t)$$

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$$\partial_t \rho_1(\boldsymbol{x}, t) = \mathcal{L}_0^\dagger \rho_1(\boldsymbol{x}, t) + \mathcal{L}_1^\dagger \rho_0(\boldsymbol{x}, t)$$

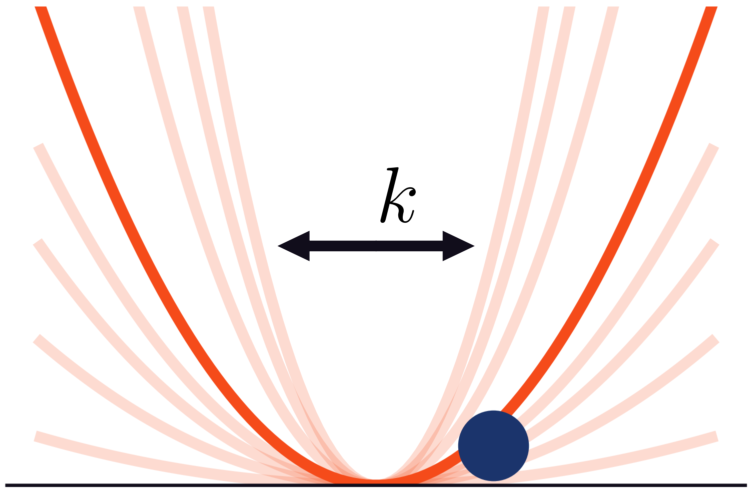
Computing the contribution to the dissipation from the protocol,

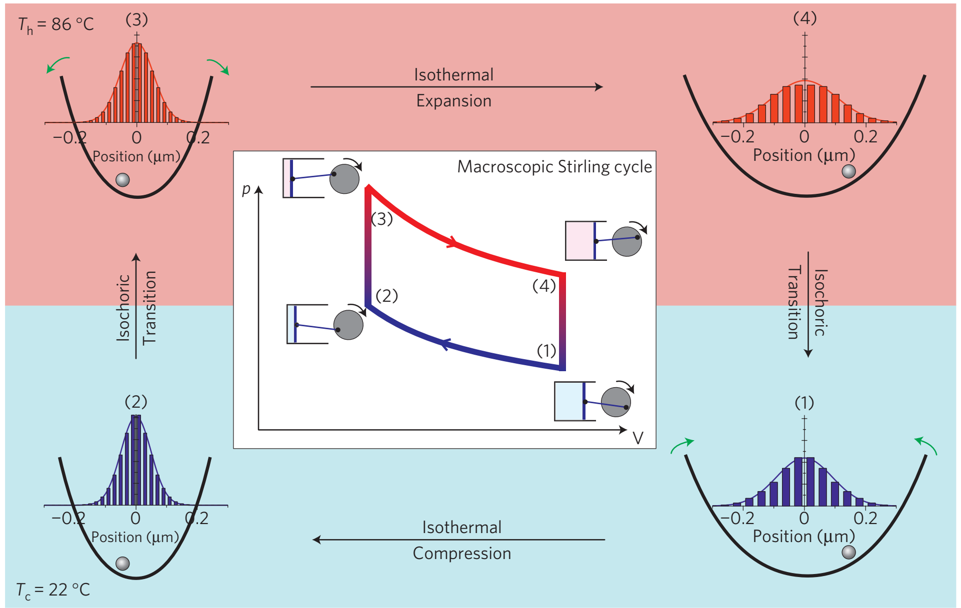
$$\begin{aligned} -\langle W \rangle &= \int_\Omega \int_0^{t_\mathrm{f}} \dot{\boldsymbol{\lambda}}(t) \cdot \partial_{\boldsymbol{\lambda}} U(\boldsymbol{x}, \boldsymbol{\lambda}(t)) \rho(\boldsymbol{x}, t) \; d\boldsymbol{x} \; dt \\ &= \beta \int_\Omega \int_0^{t_\mathrm{f}} \dot{\boldsymbol{\lambda}}^T(t) \boxed{\left(\int_0^\infty \delta \boldsymbol{\Theta}(\boldsymbol{x}^{\boldsymbol{\lambda}}(s), t) \delta \boldsymbol{\Theta}^T(\boldsymbol{x}_0^{\boldsymbol{\lambda}}, t) ds \right)} \rho_0(\boldsymbol{x}_0^{\boldsymbol{\lambda}}, t) \dot{\boldsymbol{\lambda}}(t) \; d\boldsymbol{x}_0^{\boldsymbol{\lambda}} \; dt \end{aligned}$$

A different perspective on efficiency

Minimal nanoscale engine

Control parameters: force constant of optical trap, temperature





[Blickle and Bechinger. *Nat Phys* 8 (2012)](#)

Protocol optimization via gradient descent

Optimization scheme: differentiating through dynamics to update parametric maps representing T and k

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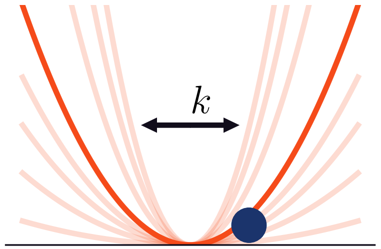
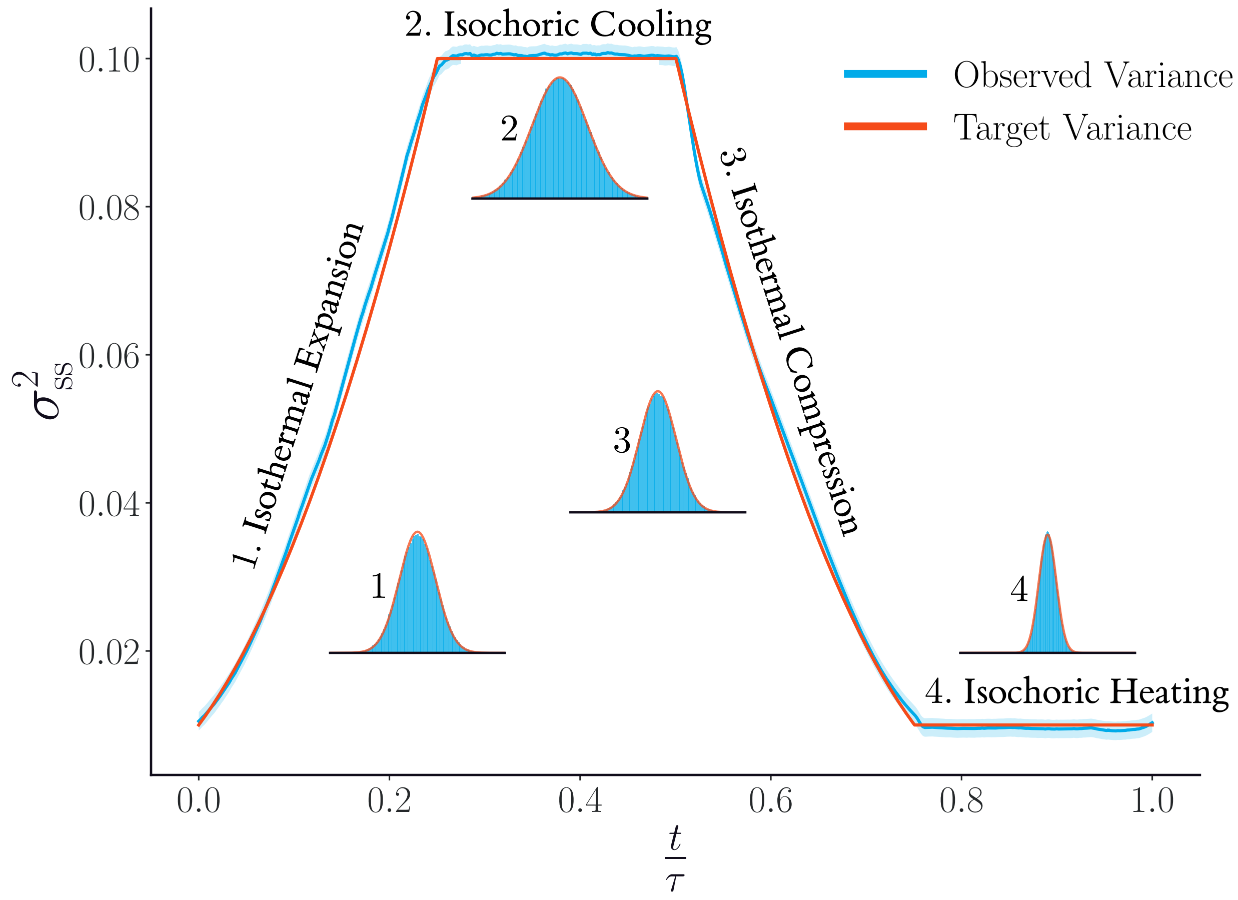
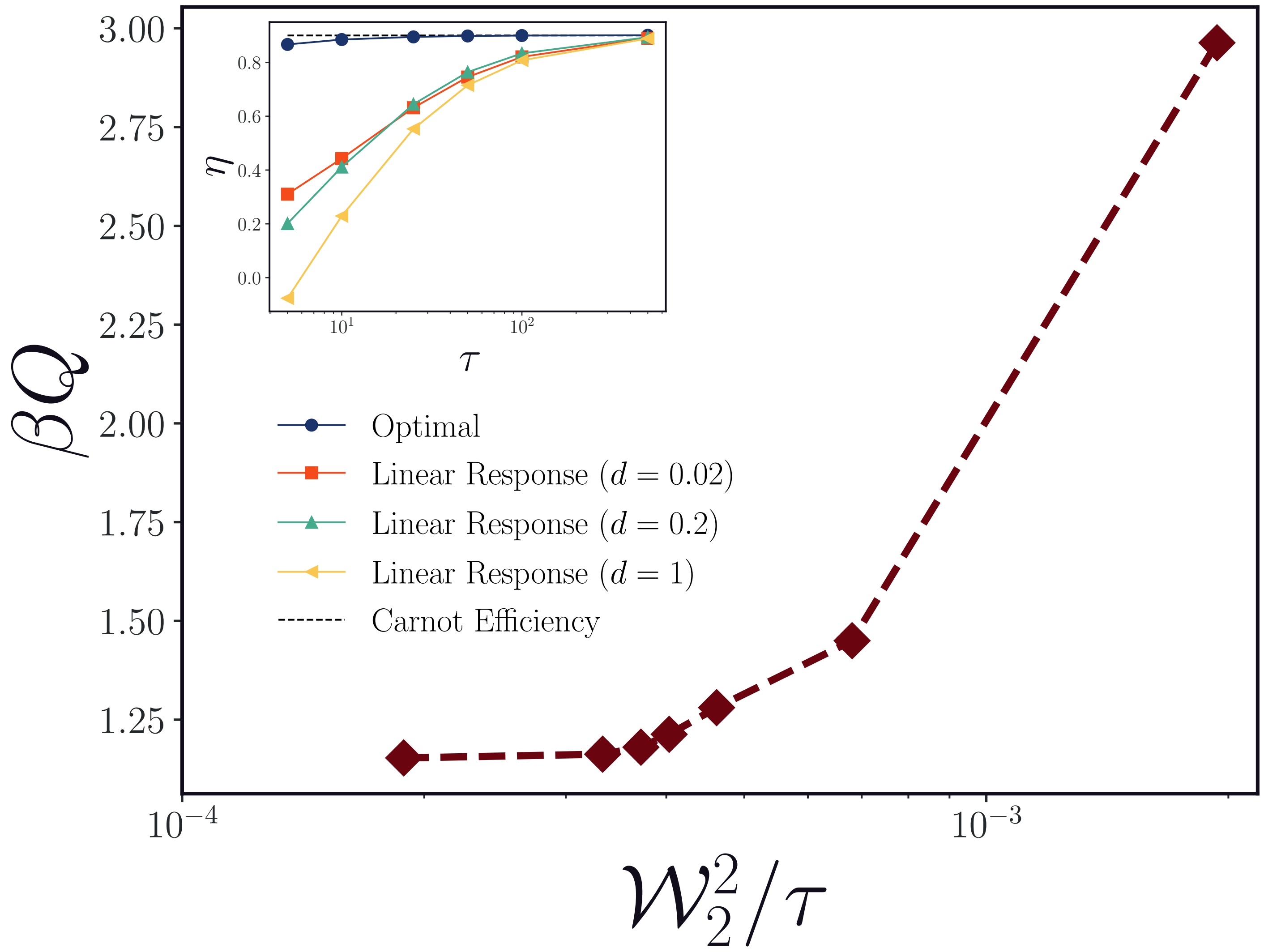
Algorithm 1 Automatic Differentiation to Optimize $\boldsymbol{\lambda}_*$

Initialize protocol $\boldsymbol{\lambda}_*$
for $e = 1, \ldots, n_{\text{epochs}}$ **do**
  Initialize state $\boldsymbol{x}_0$
  for $t < \tau$ **do**
    $\boldsymbol{X}^{\boldsymbol{\lambda}}(t + \Delta t) = \boldsymbol{X}^{\boldsymbol{\lambda}}(t) + \dot{\boldsymbol{X}}^{\boldsymbol{\lambda}}(t)\Delta t$
    $t \leftarrow t + \Delta t$
    if end of interval **then**
      Compute $\mathfrak{L}(t)$ and update $\boldsymbol{\lambda}_*$
      Clear gradient information
    end if
  end for
end for

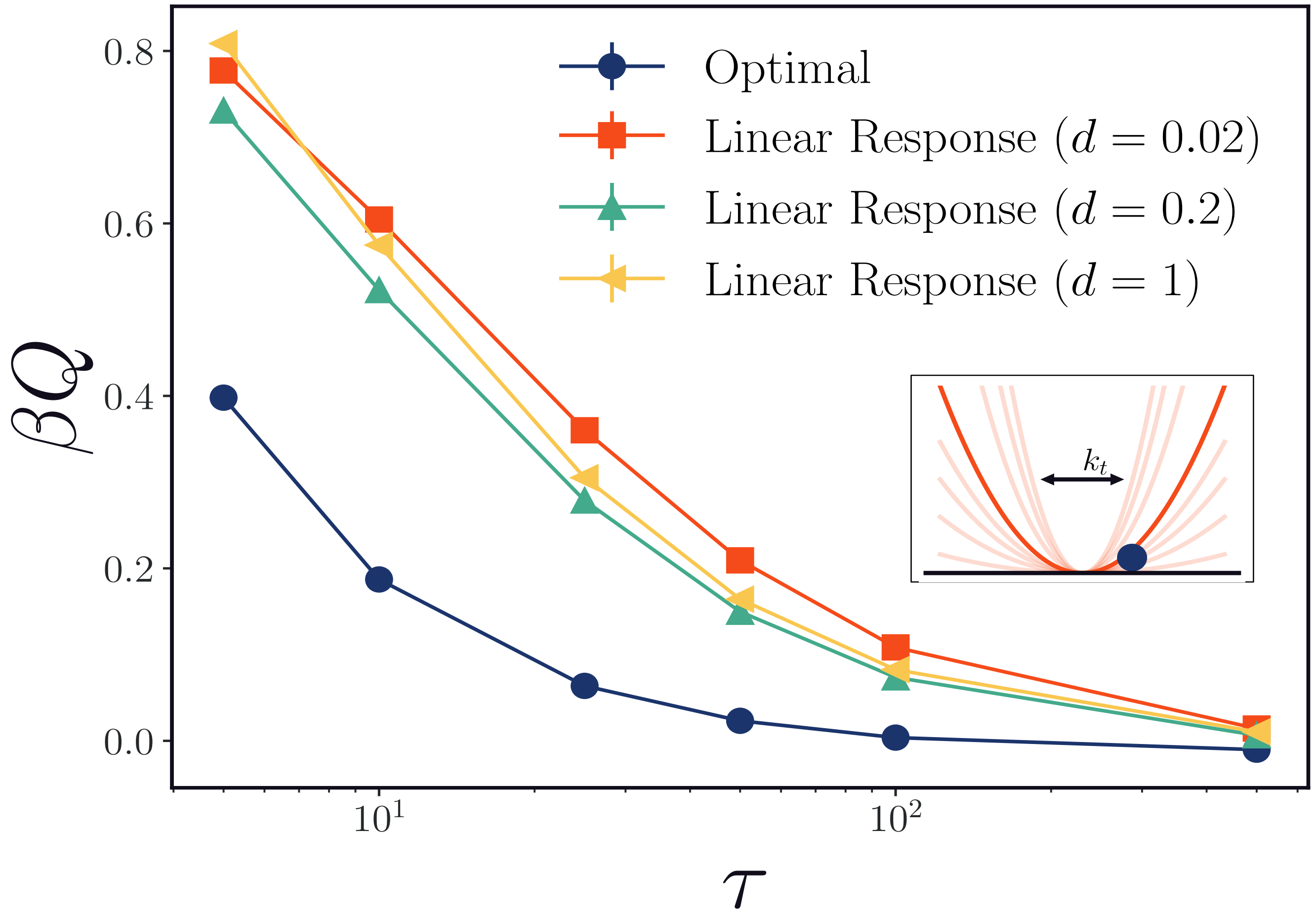




High efficiency beyond linear response

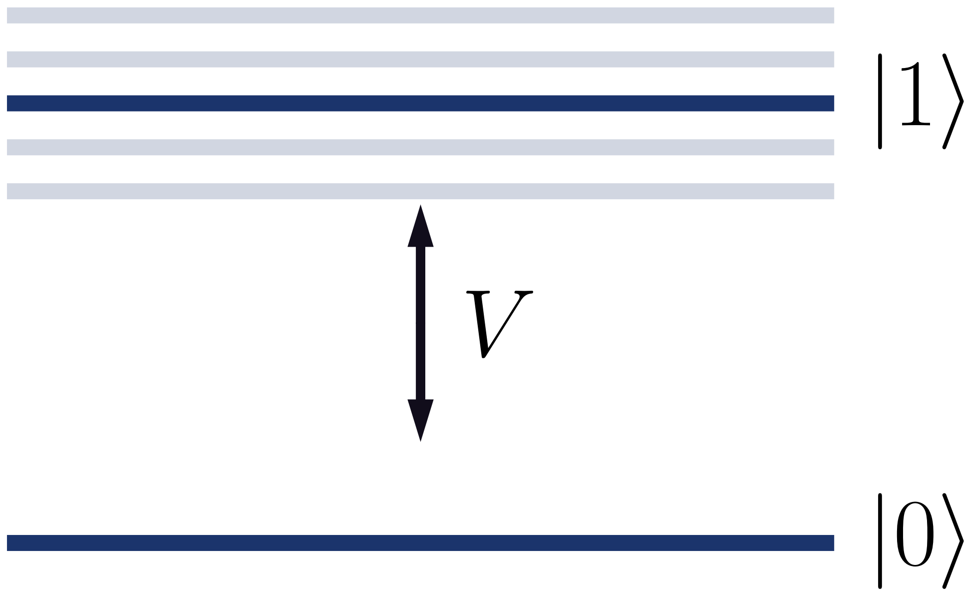


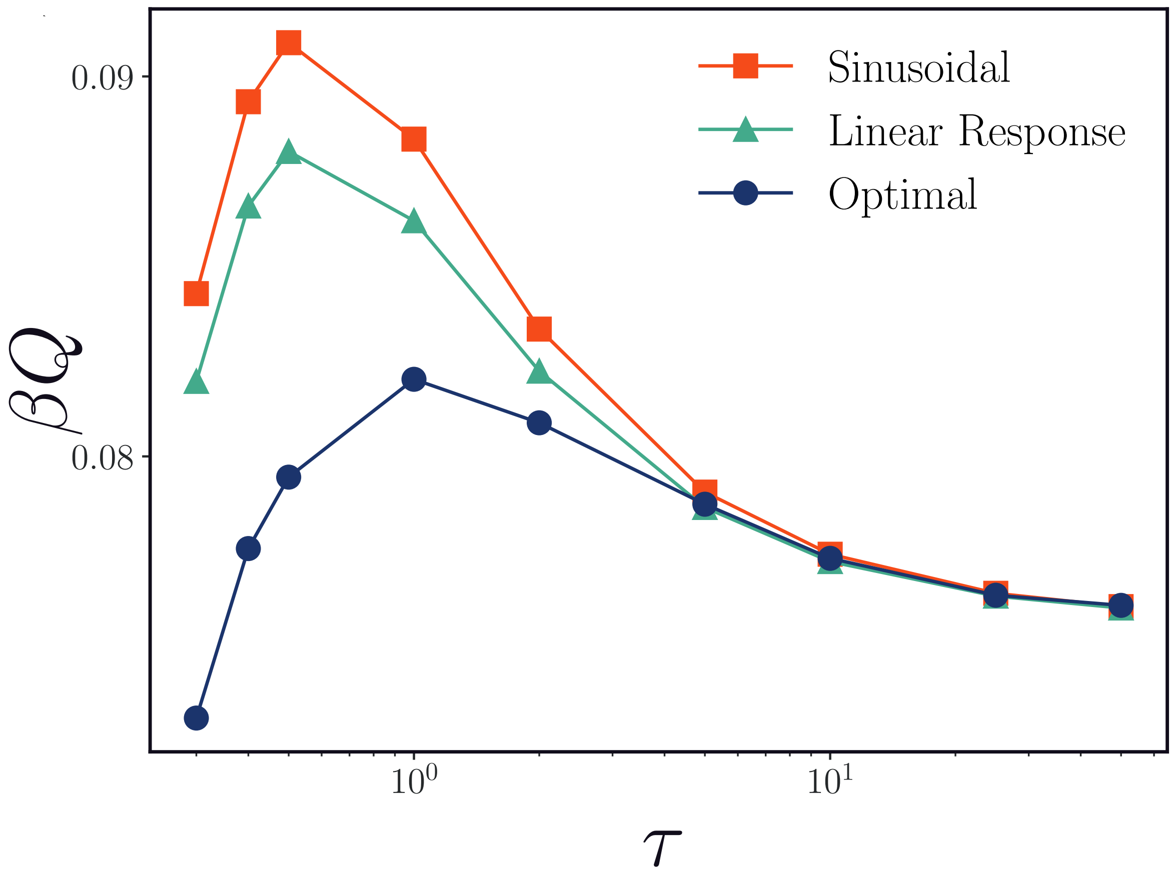
Fast driving highlights breakdown of linear response



Framework holds for open quantum systems

$$H_v = -\frac{\hbar\Omega}{2}\left(\epsilon\sigma_x + \sqrt{V^2 - \epsilon^2}\sigma_z\right)$$



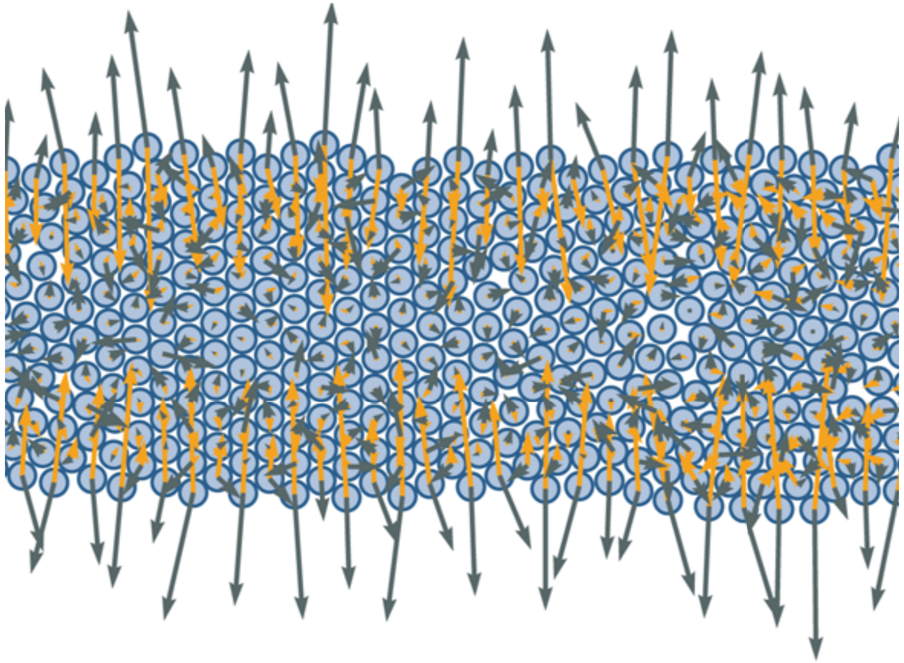


Part II: Inexact knowledge

Active matter systems: testing ground for control

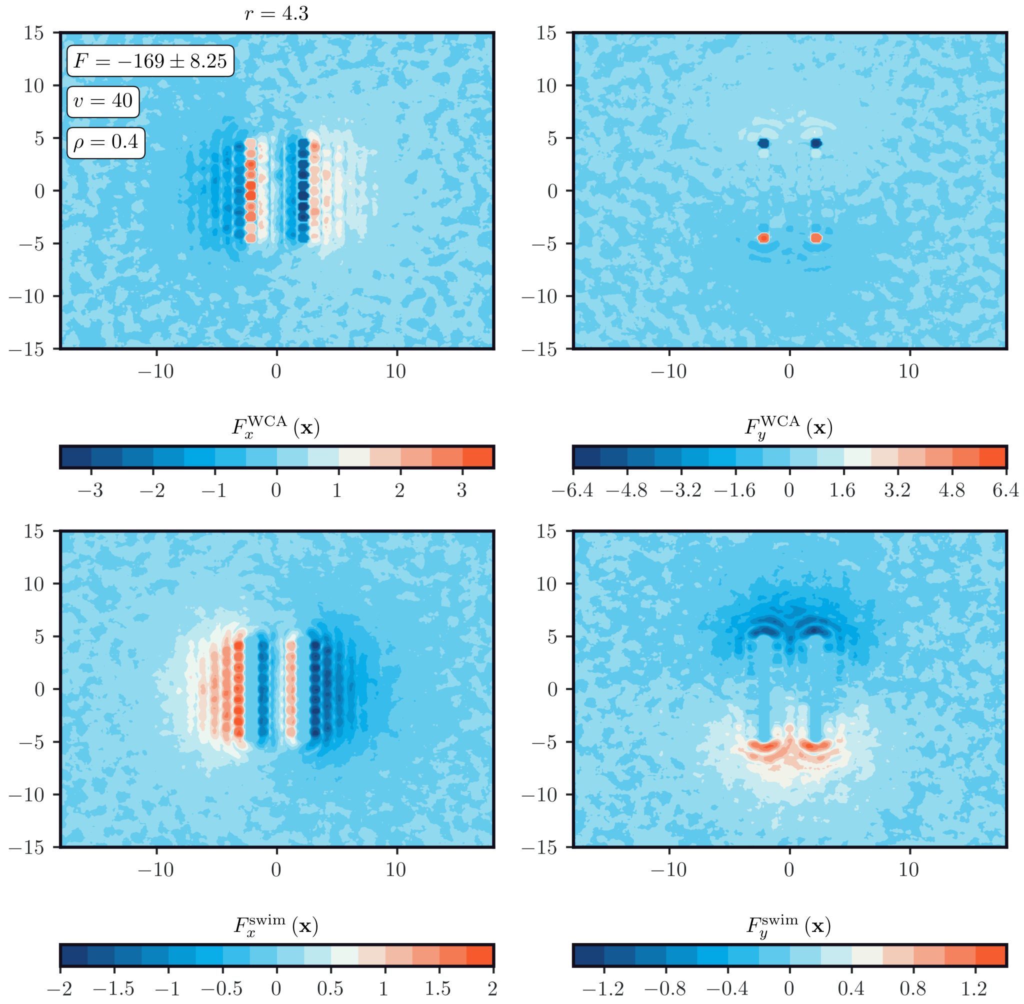
$$dX_t^{(i)} = [-\mu \frac{\partial U(\boldsymbol{X}_t)}{\partial \boldsymbol{x}^{(i)}} + v\boldsymbol{b}_t^{(i)}]dt + \sqrt{2D_t}d\boldsymbol{W}_t^{(i)},$$

$$\boldsymbol{b}^{(i)} = [\cos\phi_t^{(i)}, \sin\phi_t^{(i)}]^\top, \quad d\phi_t^{(i)} = \sqrt{2D_r}d\boldsymbol{W}_t^{\phi^{(i)}}.$$

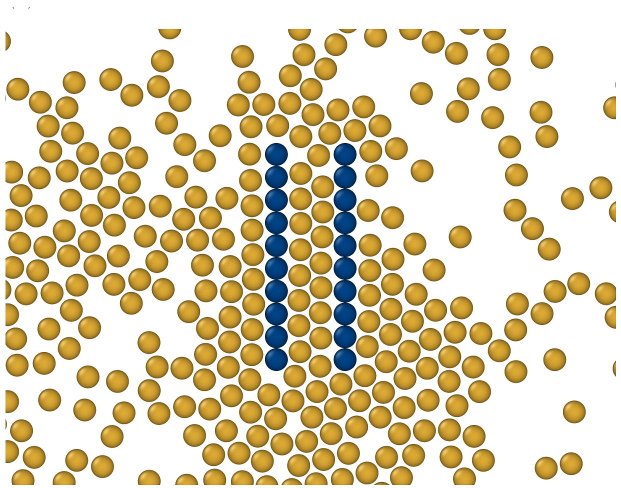


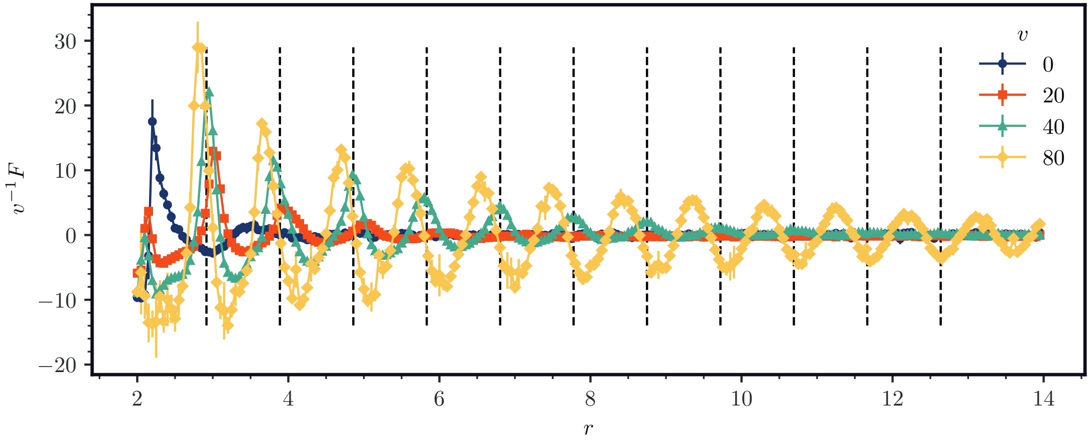
Palacci et al. *Science* 339 6122 (2013).

Potential for control of passive solutes

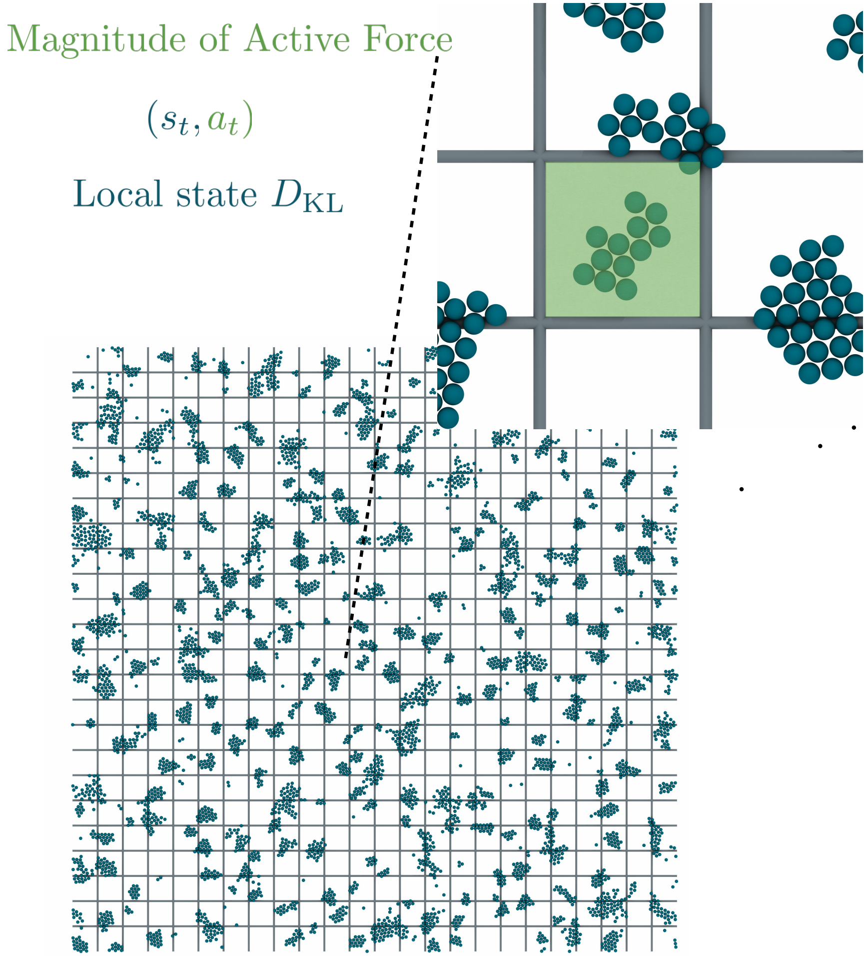


Active Casimir effect





Controlling dynamical clustering in ABPs



Controlling dynamical clustering in ABPs

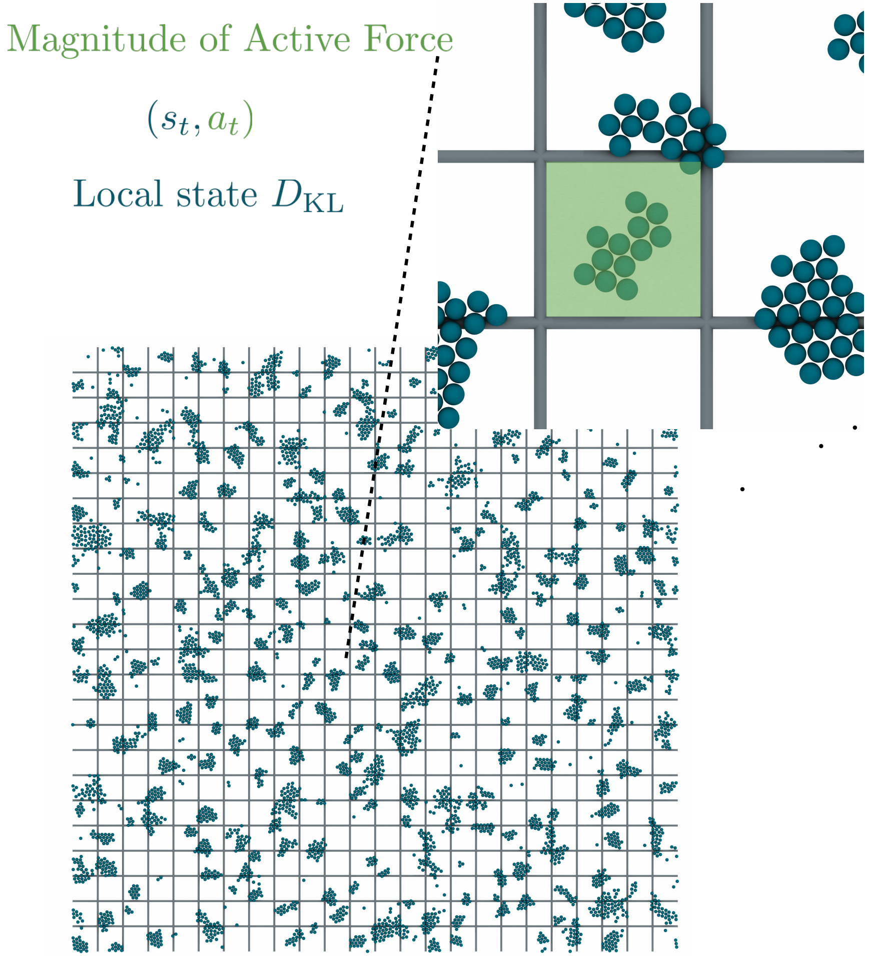
Cannot measure whole distribution!

$$u_* = \underset{u}{\mathrm{argmin}} \, |\mathbb{E}_u f - f_*|$$

Another formulation of the Wasserstein distance:

$$\mathcal{W}_1(\rho_u, \rho_*) = \max_g \min_u |\mathbb{E}_u g - \mathbb{E}_* g|$$

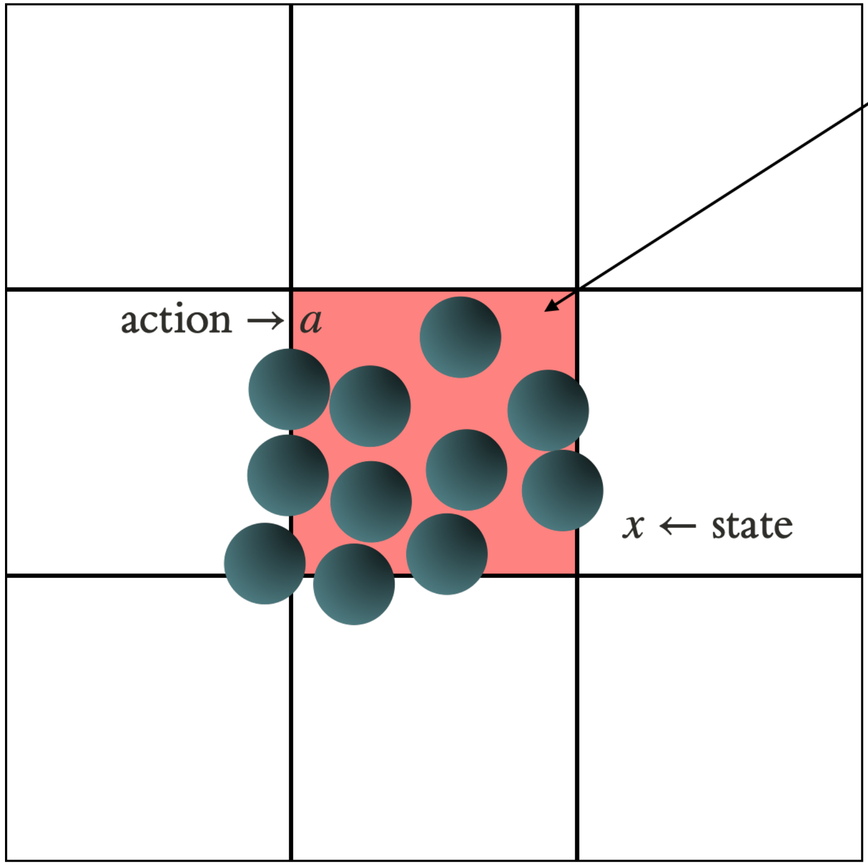
$$\min_u |\mathbb{E}_u f - f_*| \leq \mathcal{W}_1(\rho_*, \rho_u)$$



Multi-agent reinforcement learning

Requires moderately heavy machinery: *Multi-agent* Deep Reinforcement Learning

Independent agents for local control



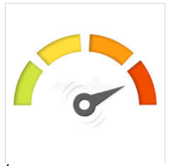
Idea of RL, learn to "act"

$Q^u(x, a) \leftarrow$ describes average future "reward"

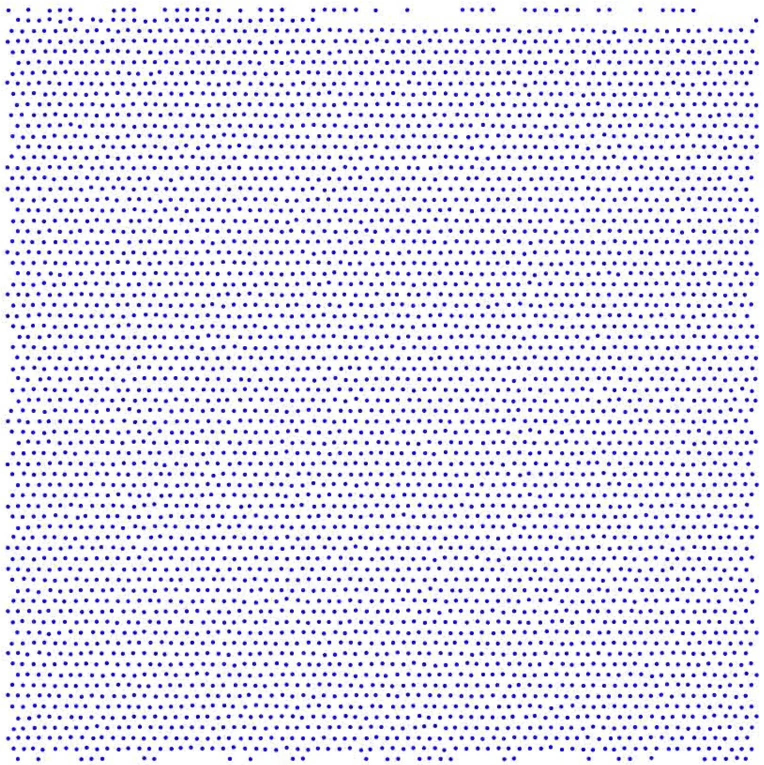
$$Q^u(x, a) = \mathbb{E}_u^{x_0}\left[\mathscr{C}(x_{t+\tau}; a_t) + \sum_{k=1}^{\infty} \gamma^k \mathscr{C}(x_{t+\tau(k+1)})\right]$$

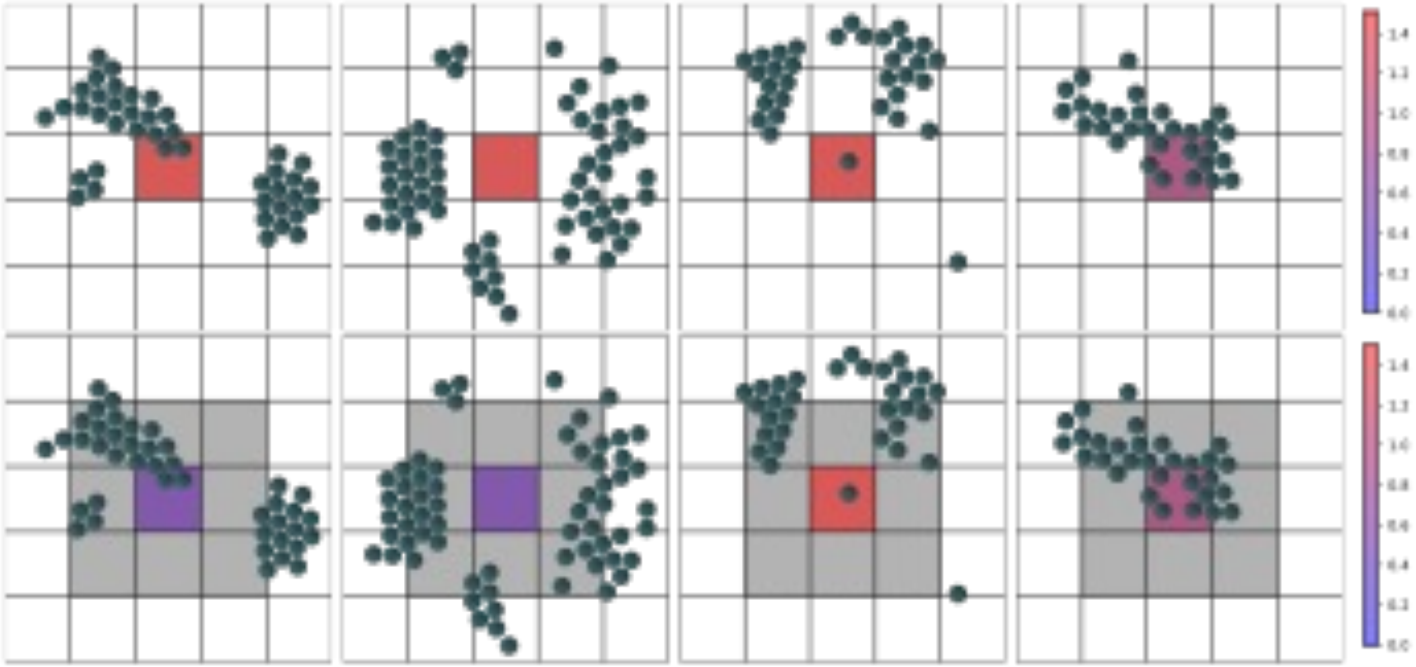
Choose "action" that maximizes Q

An action sets current intensity of light

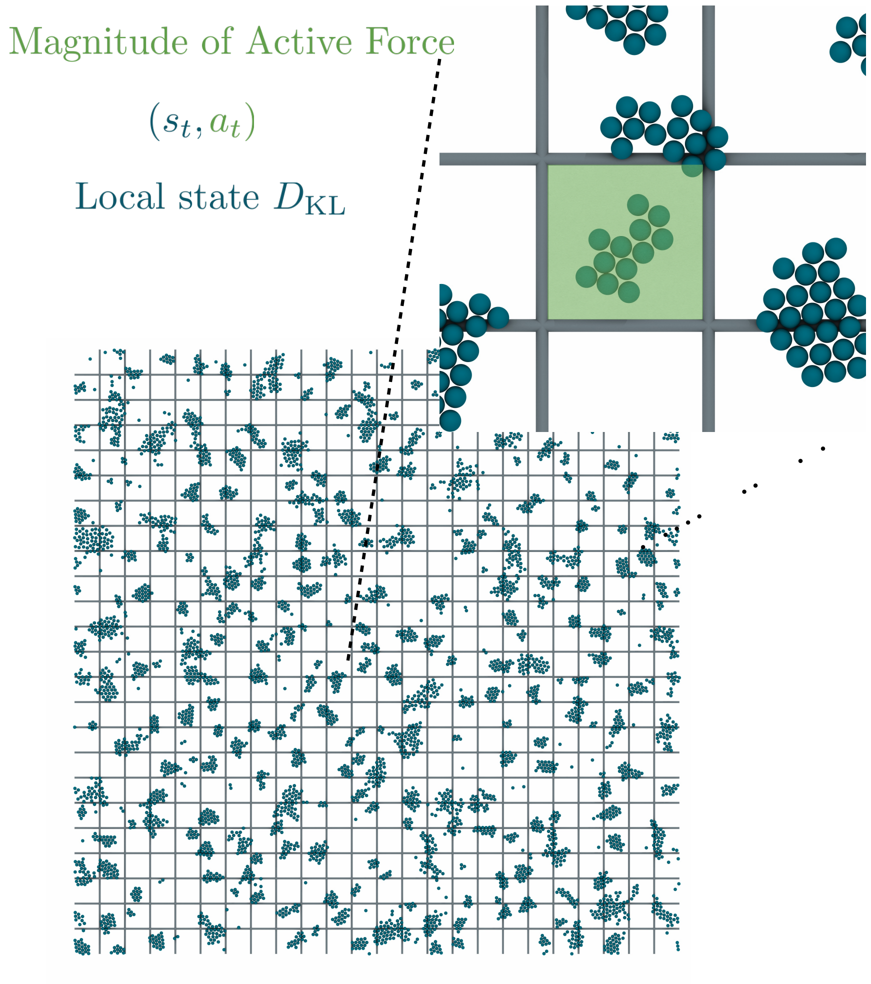


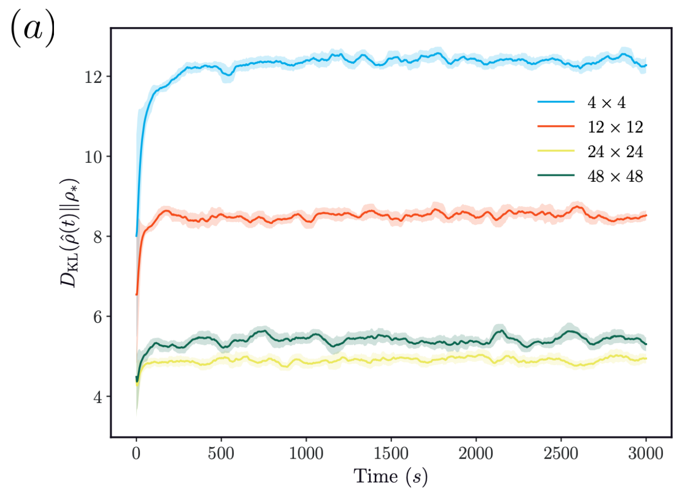
Partially decentralized control

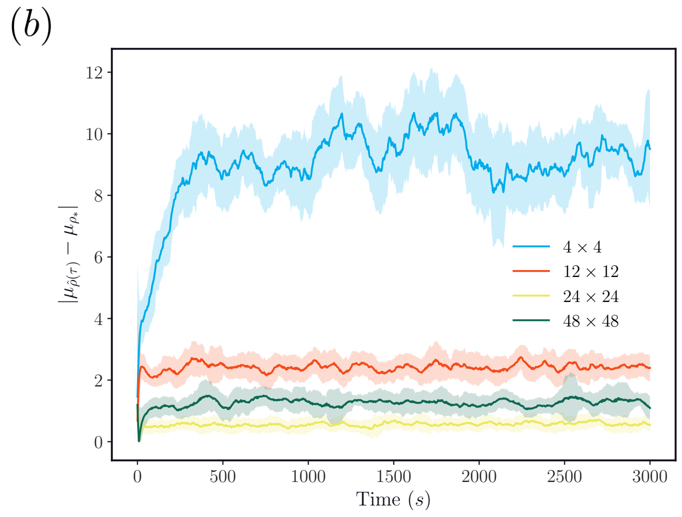




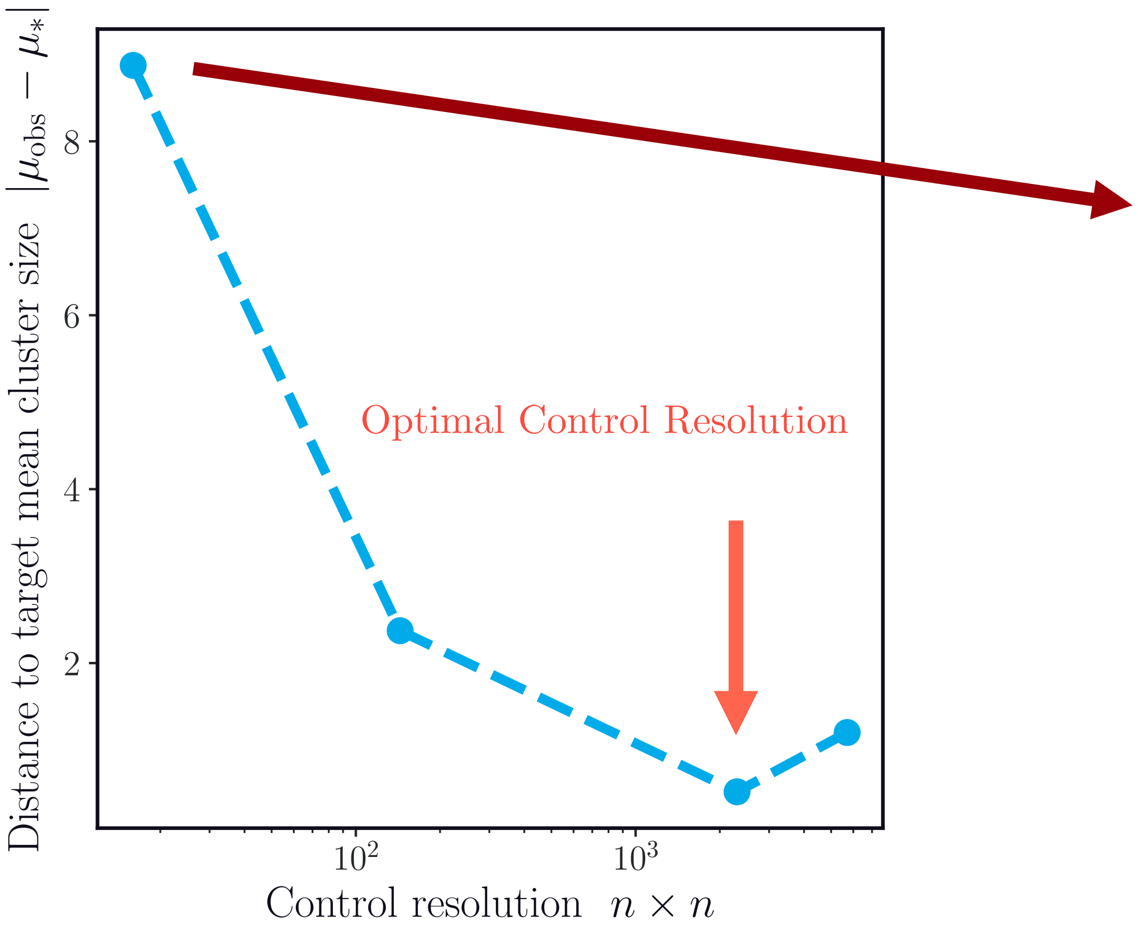
Performance varies with control resolution

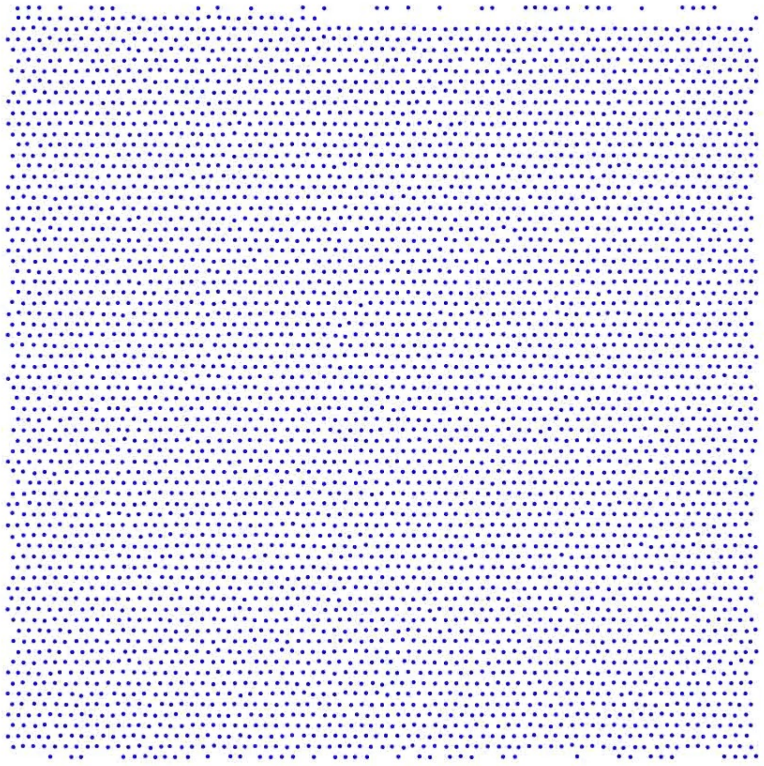






Distributional control depends on natural length scales





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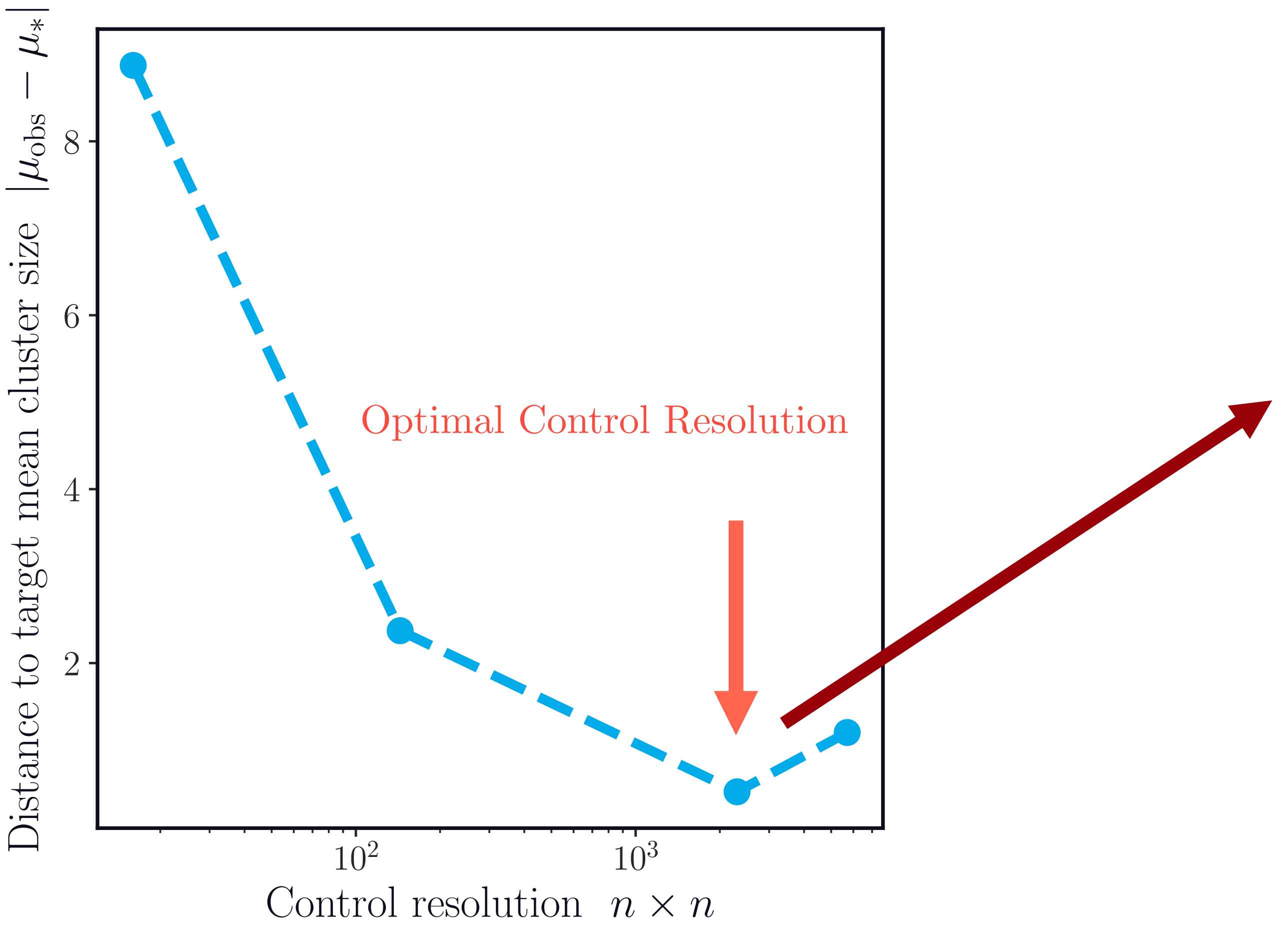
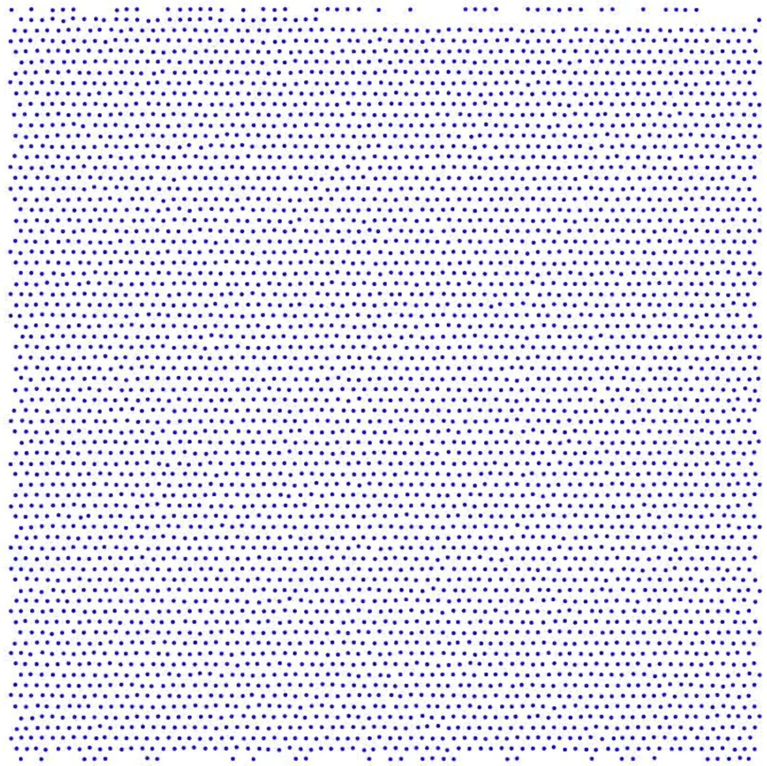
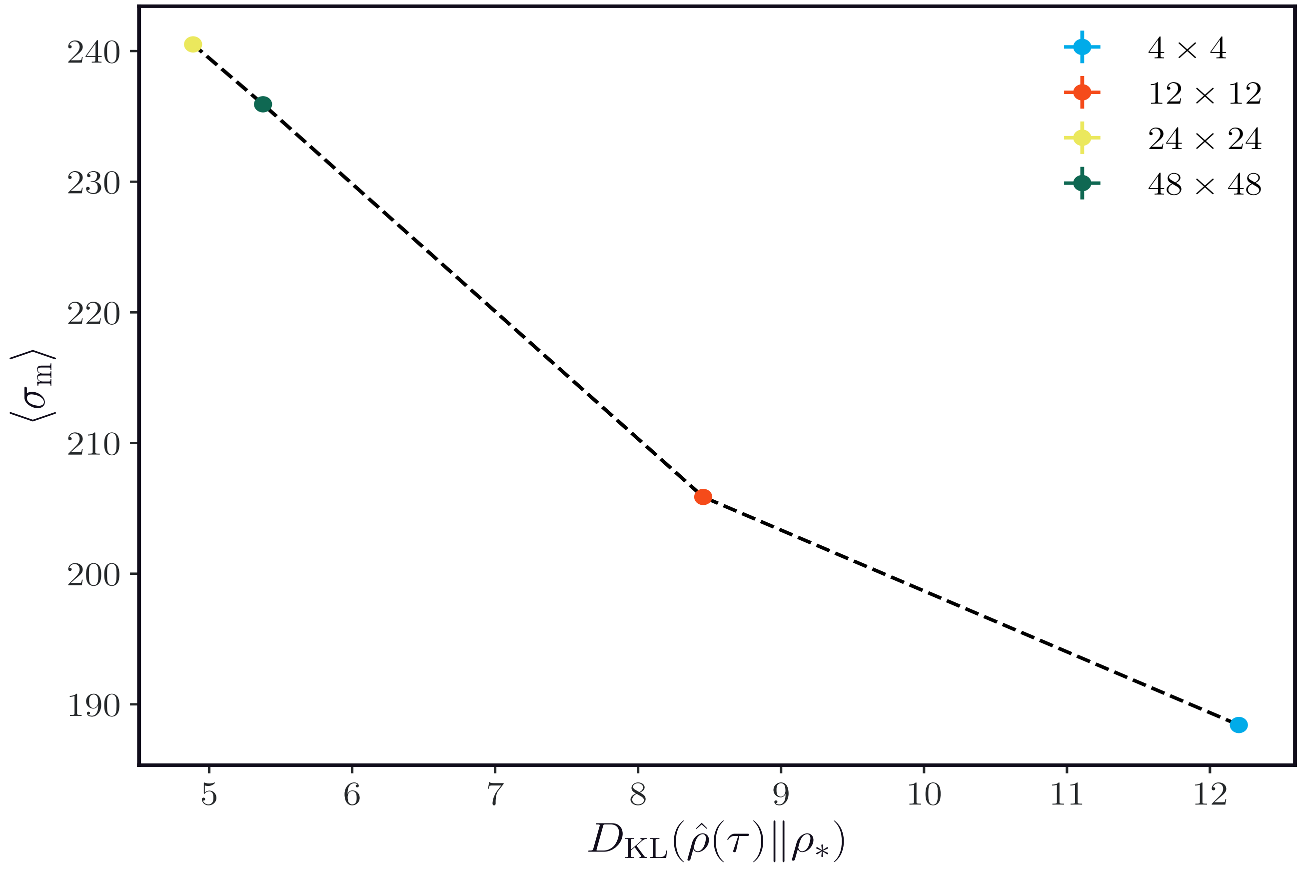


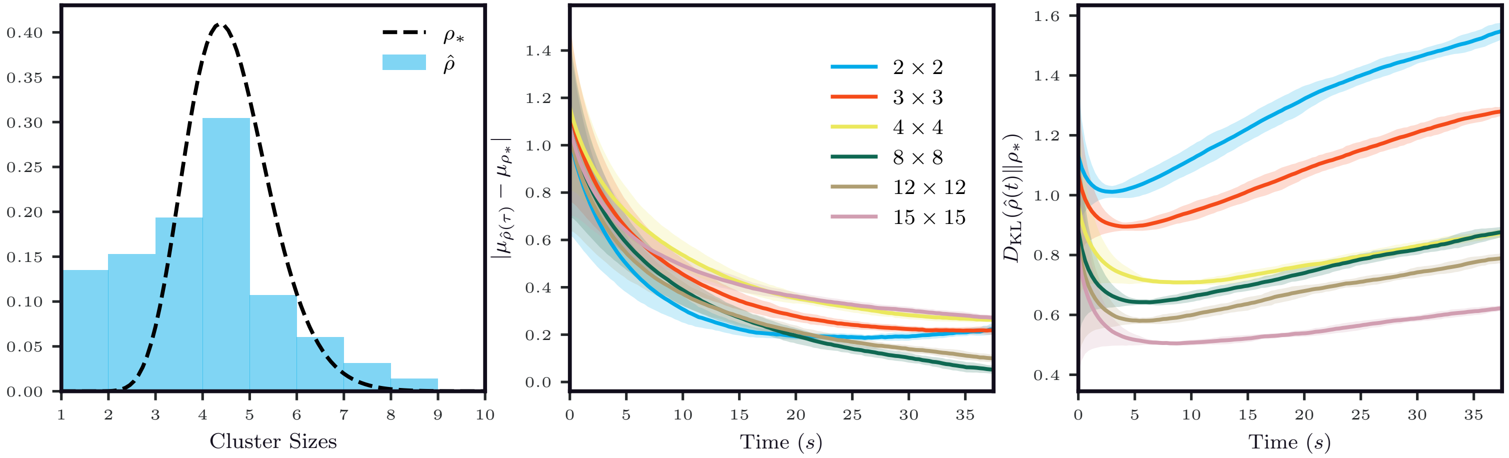


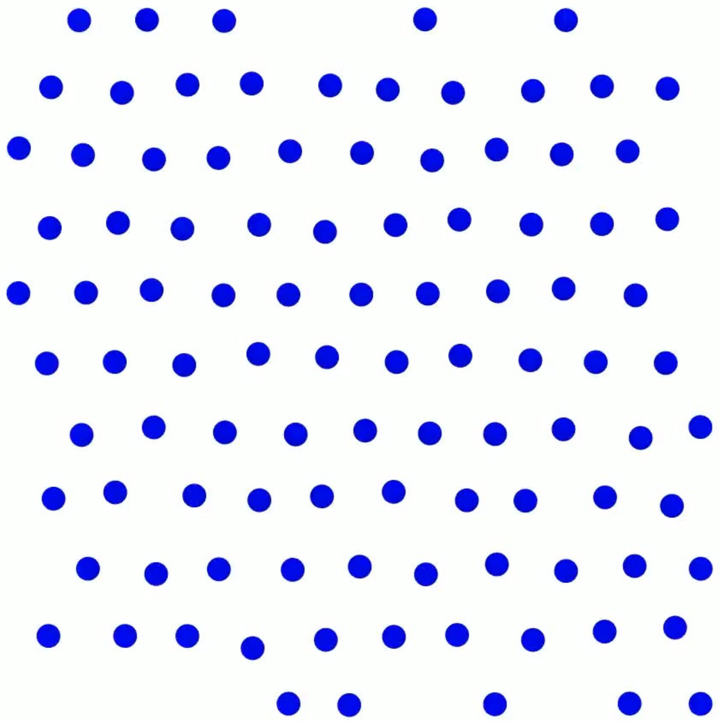
Dissipation is a proxy for accuracy



And accuracy is a proxy for dissipation!

Feedback guided annealing

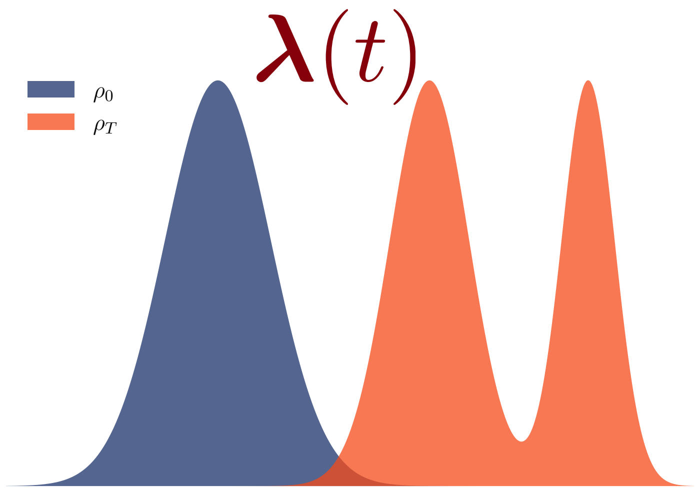




Coarse temperature control with feedback improves targeted assembly

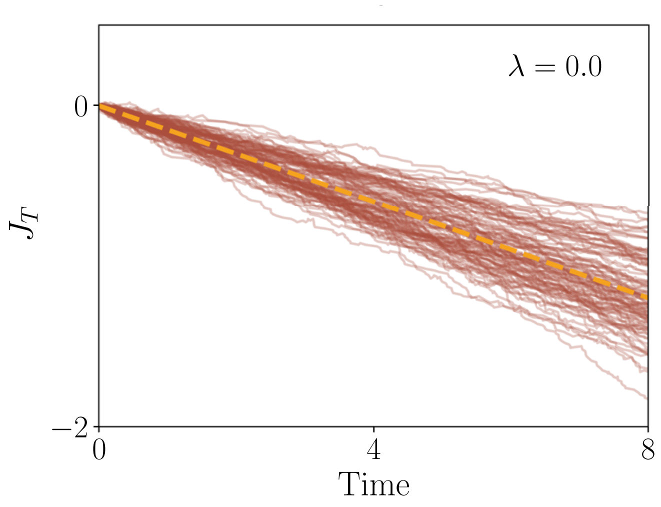
A parallel set of concerns?

Energetic Costs



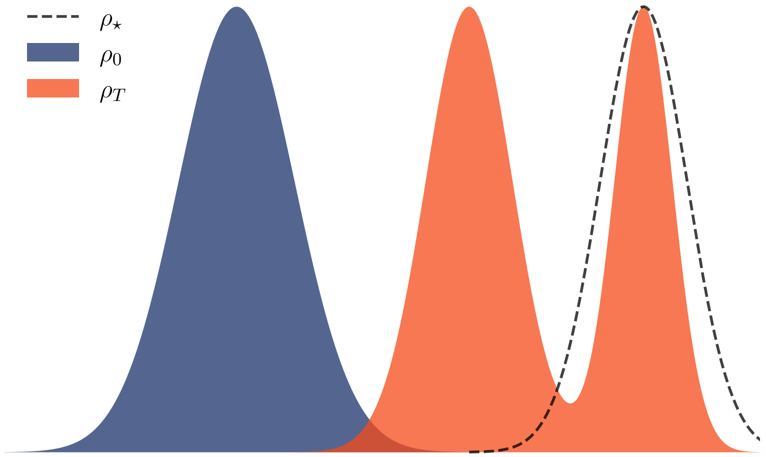
External input energy to maintain the desired steady state?

Speed of Control



Finite time thermodynamic cost. Limitations on speed?

Accuracy of Outcome



How closely did we realize the desired transformation?

Thanks!

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