Forward Through Backwards Time by RocketBoom

Optimal Thermodynamic Control and the Dynamic Riemannian Geometry of Ising magnets

Gavin Crooks
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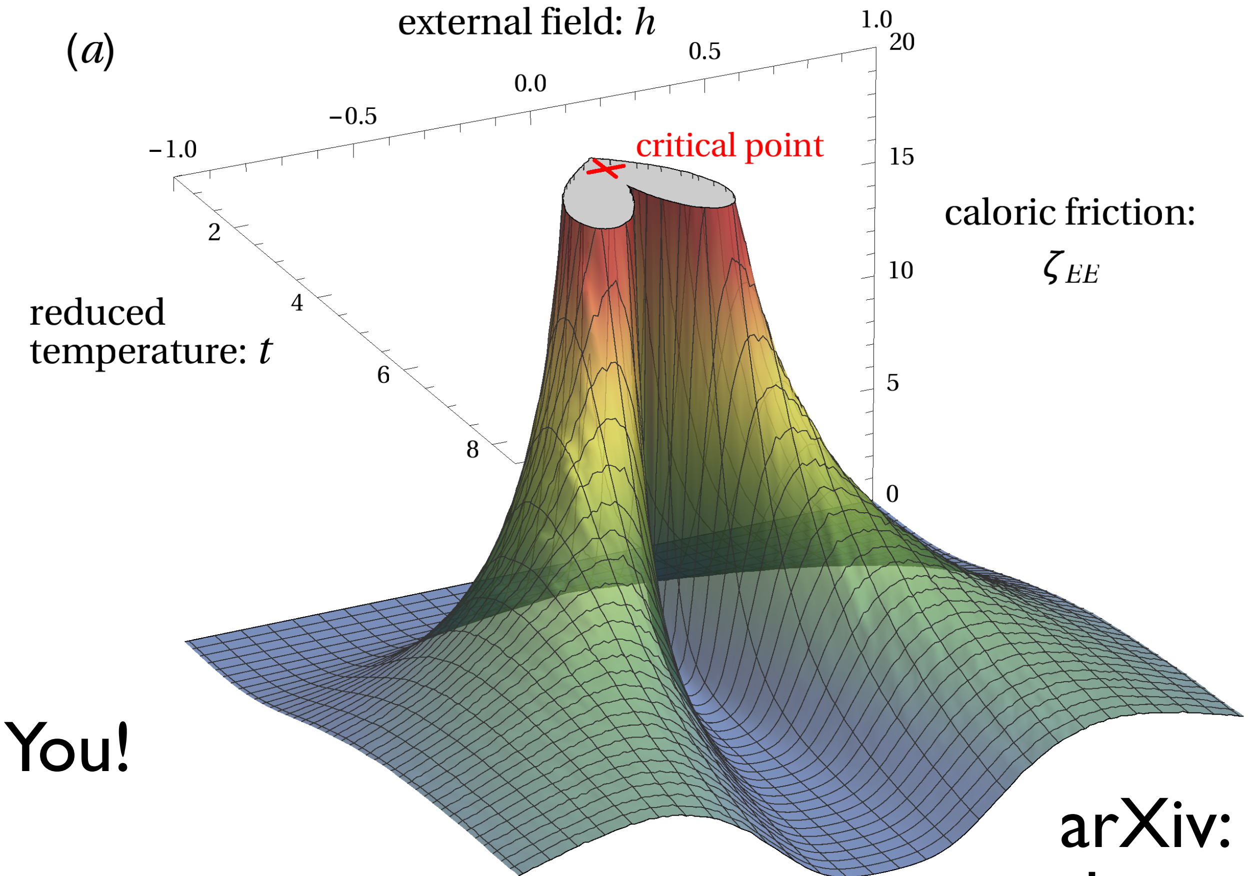

Funding:
Citizens Like You!
ARO
NSF, DOE

arXiv: 1510.06734
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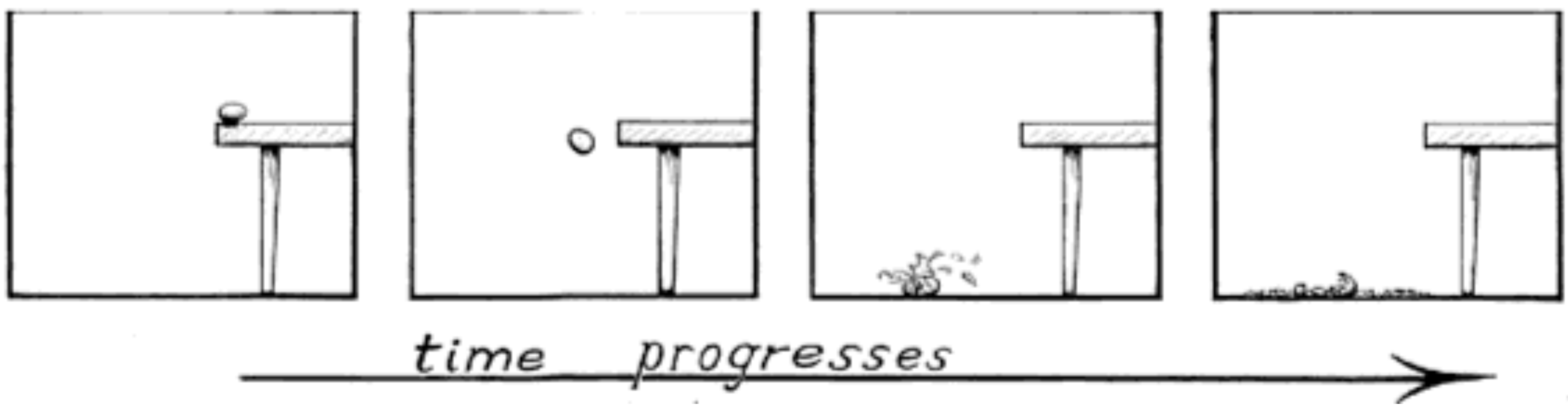
The 2nd Law of Thermodynamics

Clausius inequality (1865)

Entropy

$$\Delta S_{\text{total}} \geq 0$$

Entropy increases as time progresses



Cycles of time
R.Penrose (2010)

Once or twice I have been provoked and asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold. It was also negative. Yet I was asking something which is about the scientific equivalent of "Have you read a work of Shakespeare's?" -- C. P. Snow

Entropy and Disorder

$$S = \log\{\text{Number of configurations}\}$$

1 natural unit of entropy
equivalent to
1 kT of thermal energy

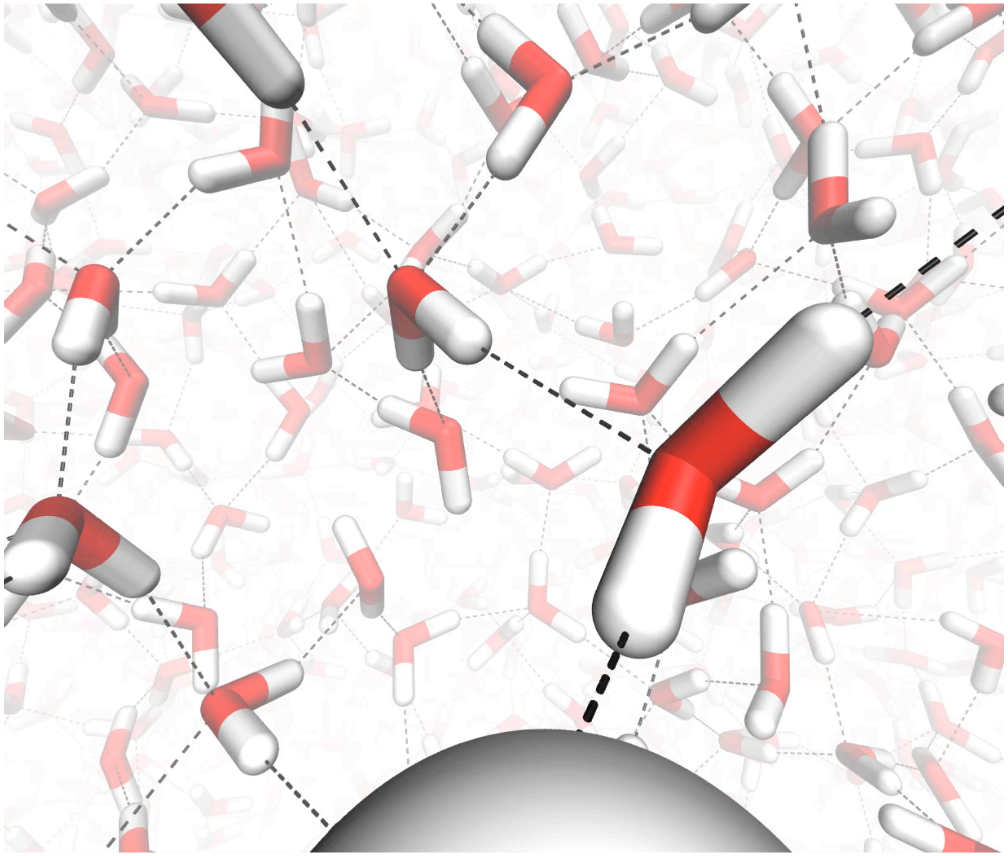
T : Temperature (ambient 300 Kelvin)
k : Boltzmann's constant

1 kT = 25 meV
= 2.5 kJ/mol

average kinetic energy = 1.5 kT

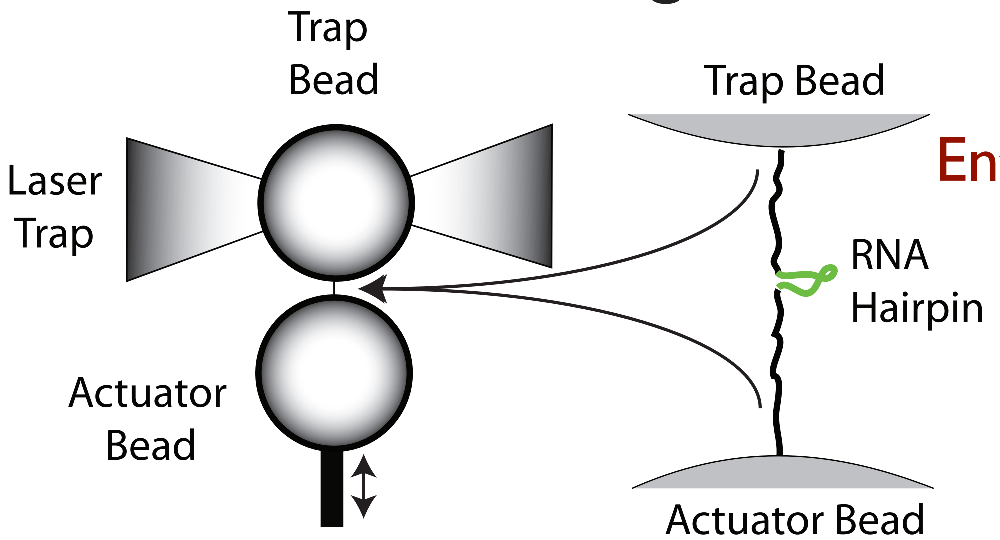
Thermodynamic Equilibrium

The future is the direction of time in which entropy increases

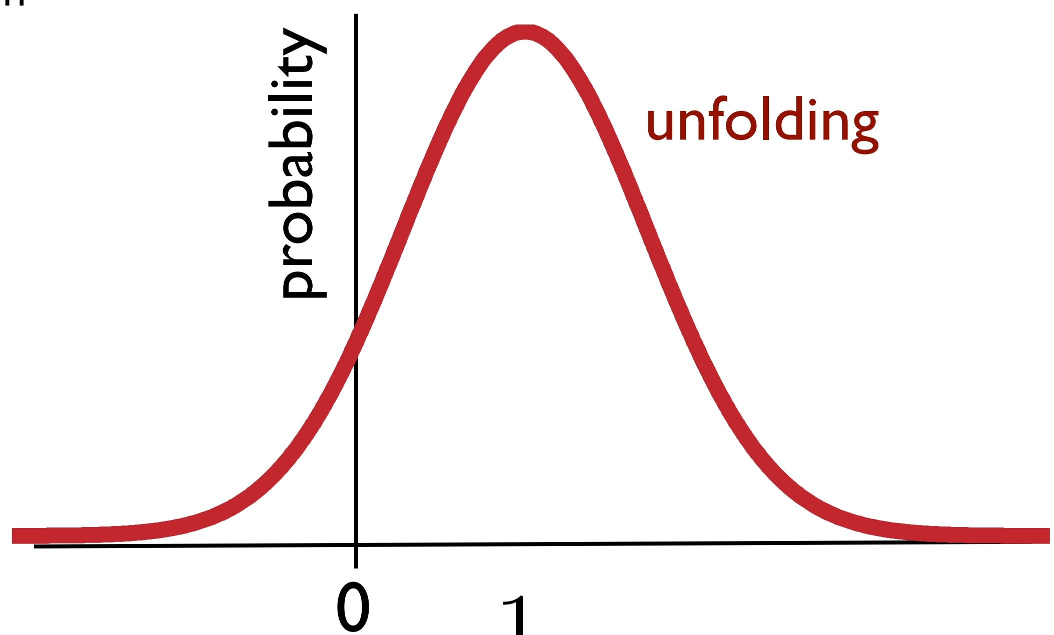


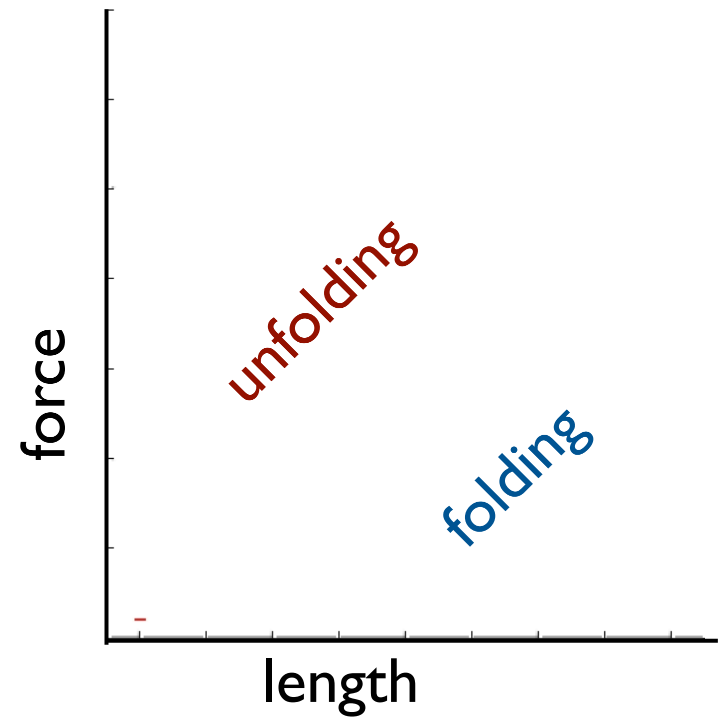
No change in Entropy. No Arrow of time.
Future, past and present are indistinguishable

Unfolding of RNA hairpins. (circa 2000)



Entropy sometimes goes down!





$$\Delta S_{\text{total}} = \frac{1}{T}(W - \Delta F)$$

total entropy change · temperature · work · free energy change

The (improved) 2nd Law of Thermodynamics

Clausius inequality
(1865)

$$\langle \Delta S_{\rm total} \rangle \geq 0$$

equality only for
reversible process

Jarzynski identity
(1997)

$$\left\langle e^{-\Delta S_{\rm total}} \right\rangle = 1$$

equality far-from-equilibrium

$$\Delta S_{\rm total} = \frac{1}{T}(W - \Delta F)$$

Fluctuation Theorems:

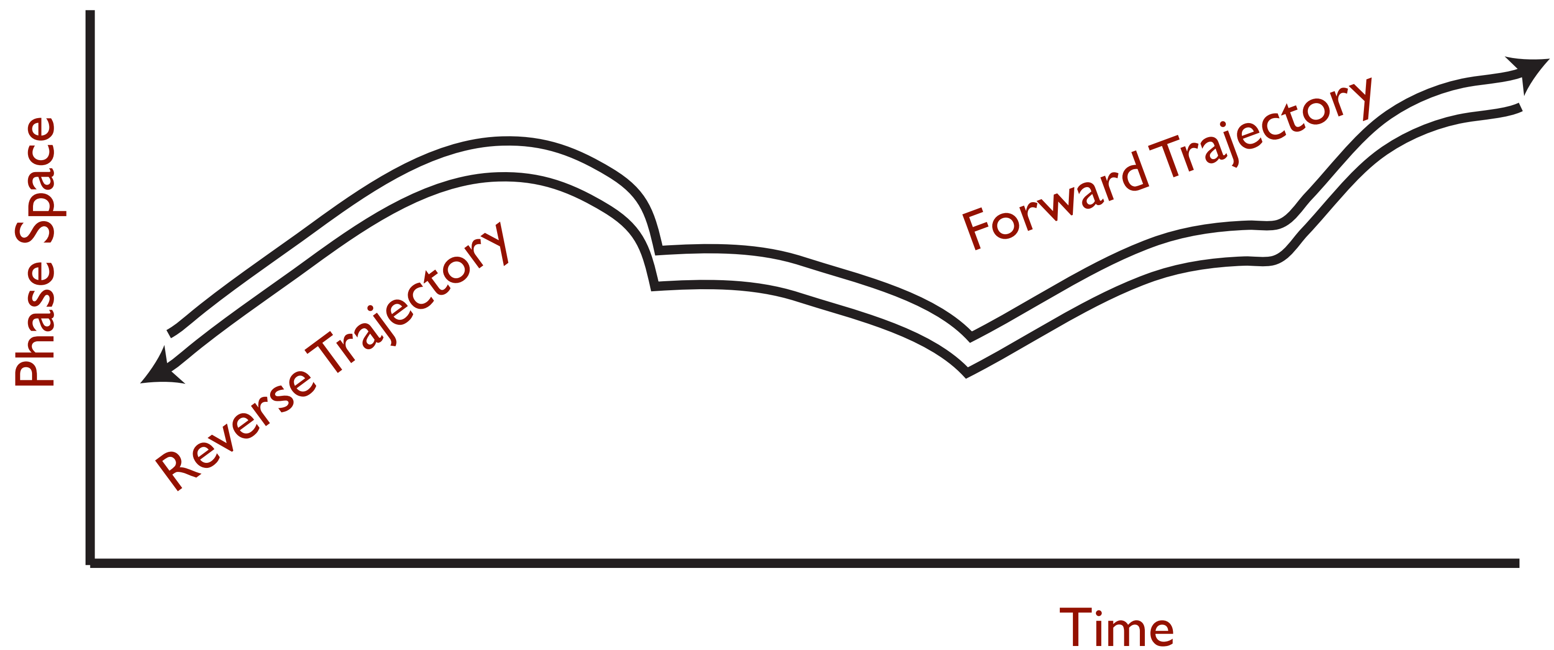
Dissipation (entropy increase) breaks time-reversal symmetry

$$\frac{P[\text{trajectory}]}{P[\text{time reversed trajectory}]} = e^{\text{dissipation}} = e^{\beta W - \beta \Delta F}$$

Work

Free Energy Change

Inverse Temperature

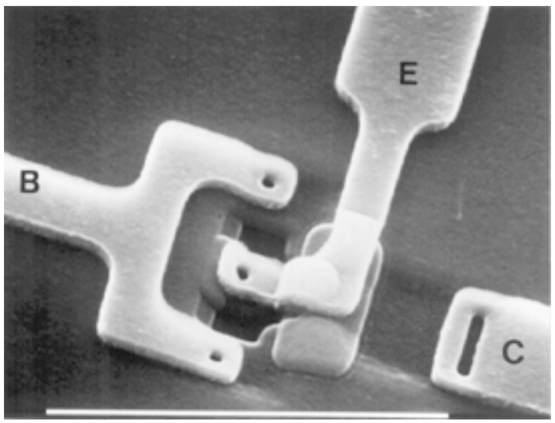


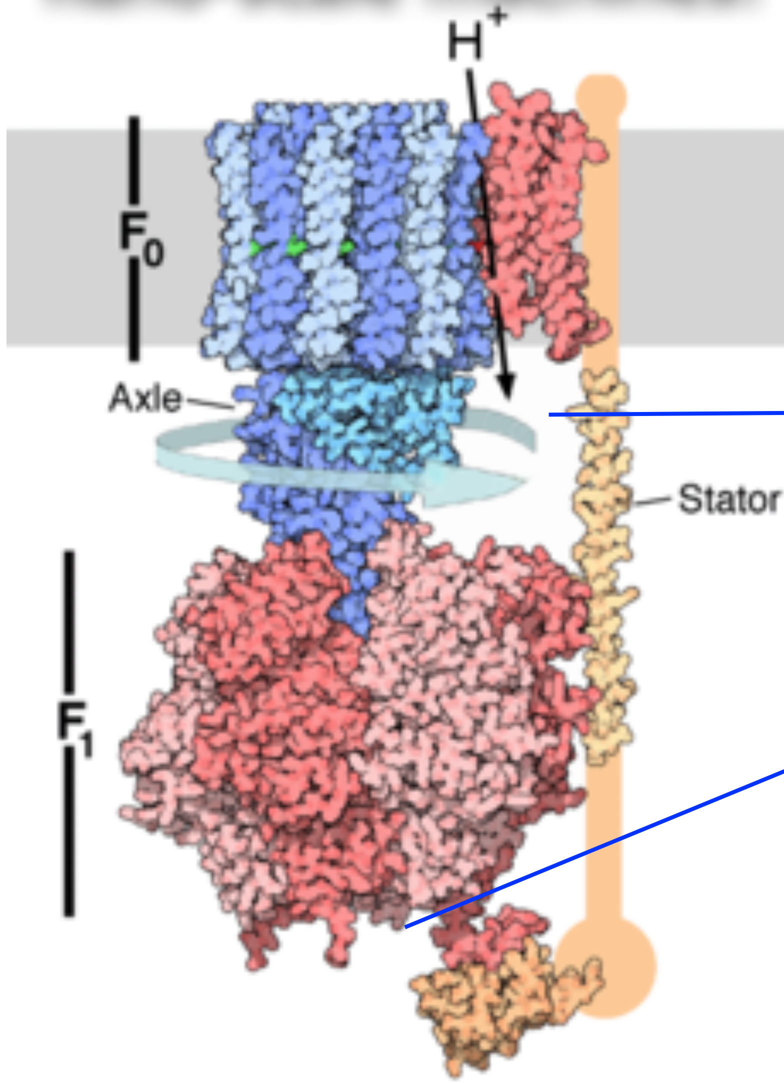
What have we learned?

$$\langle e^{-\Delta S_{\mathrm{total}}} \rangle = 1$$

- There are exact, general relations valid far-from-equilibrium
- *Trajectories* are the primary objects (rather than *states*)
- Fluctuations matter
- Entropy change breaks time *quantitatively* reversal symmetry
- Directly relevant at small dissipation (less than about 10 kT)
- Information flow is as important as work and heat flow.

What are the fundamental operational principles of nano-scale machines?





ATP synthase

proton gradient

mechanical energy

chemical energy

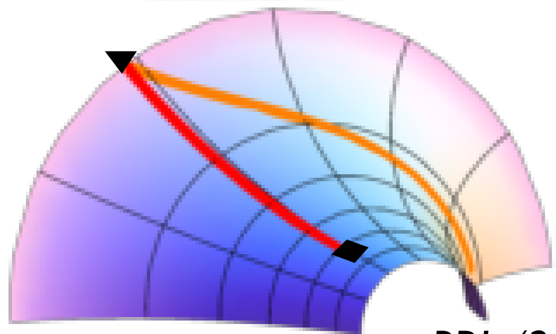
Free Energy ATP = 20 kT
= 0.5 eV

Recent Projects

Coupled Systems & the Thermodynamics of prediction

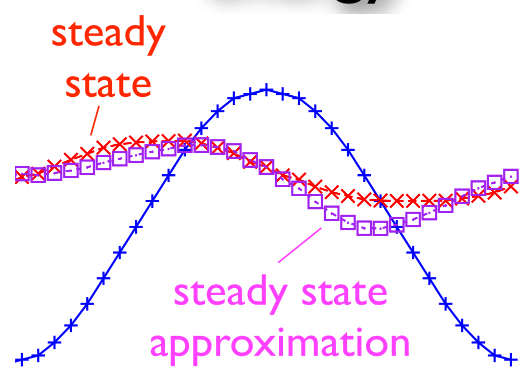
PRL (2012)

Geometry of thermodynamic control



PRL (2012)
PRE (2012)

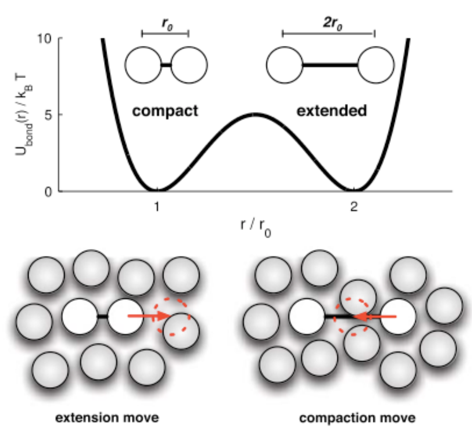
Measurement of nonequilibrium free energy



PRL (2012)

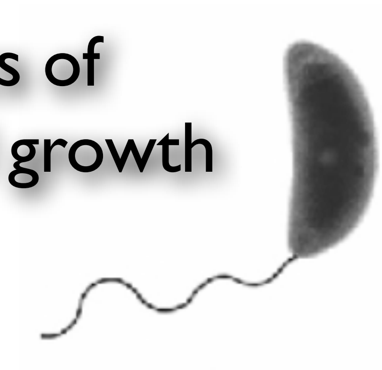
Nonequilibrium simulation

PNAS (2011) PRX (2013)
JPC (2014)

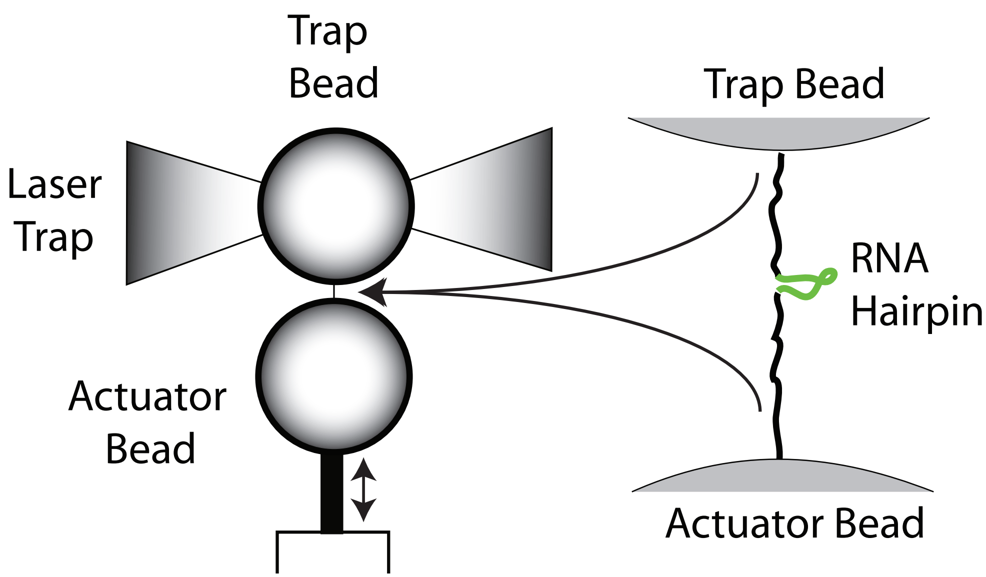


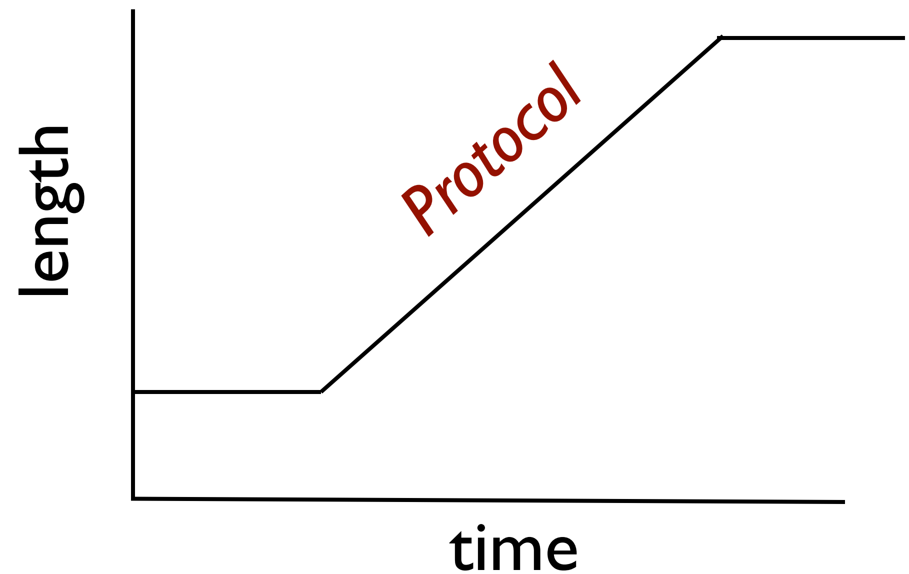
Dynamics of bacterial cell growth

PNAS (2014)
PRL (2014)



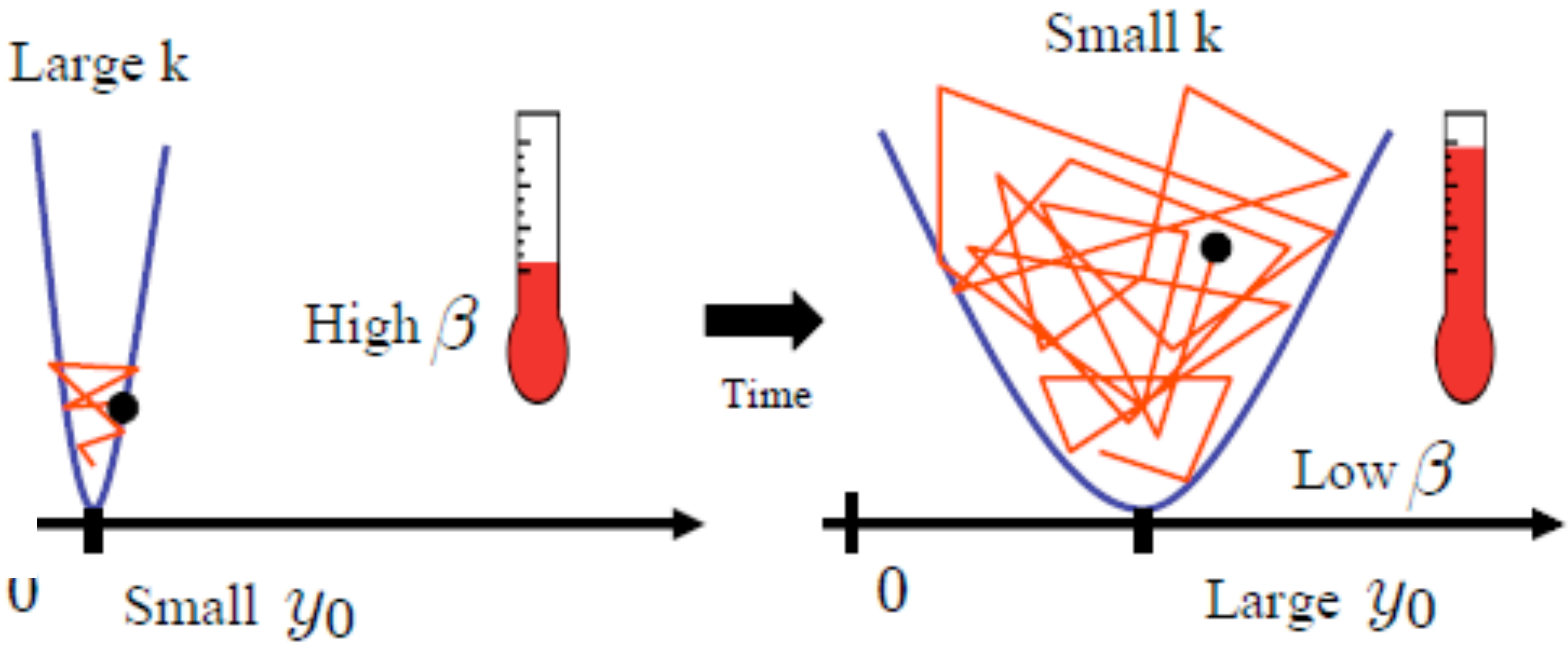
Optimal thermodynamic control of molecular scale systems





Which finite-time experimental protocols minimize dissipation?

Exact minimum dissipation protocols



Control trap position: Schmiedl & Seifert PRL (2007)

Geometry of thermodynamic control

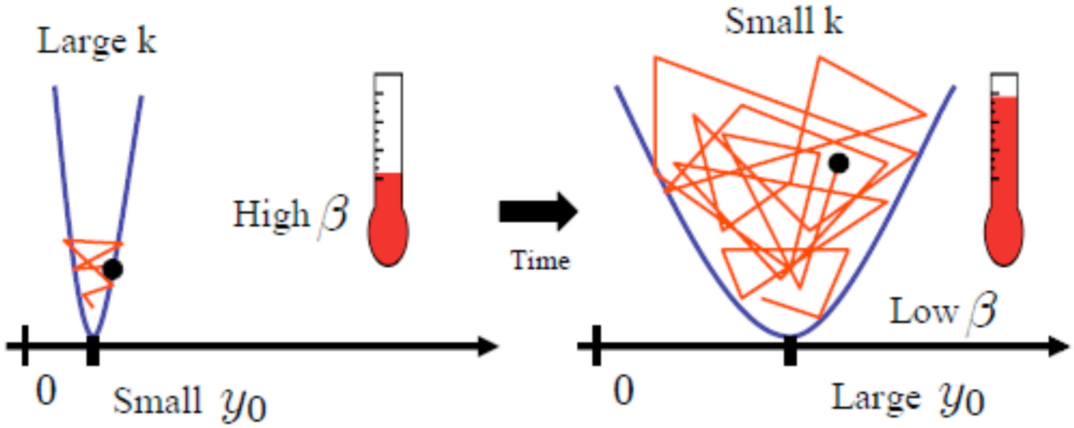
- Finite time thermodynamics with linear response friction tensor
- Riemannian metric, minimum dissipation paths are *geodesics*

Prof. David Sivak
(Simon Fraser U.)

nonequilibrium excess power imposed by protocol Λ

linear response friction tensor

$$\mathcal{P}^{\text{ex}}_{\Lambda}(t_0) = \left[\frac{\mathrm{d}\boldsymbol{\lambda}^T}{\mathrm{d}t}\right]_{t_0} \cdot \zeta\big(\boldsymbol{\lambda}(t_0)\big) \cdot \left[\frac{\mathrm{d}\boldsymbol{\lambda}}{\mathrm{d}t}\right]_{t_0}$$



F. Weinhold (1975), Peter Salamon and Steven Berry (1983), Sivak & Crooks PRL (2012)

Combine linear response and thermodynamic geometry

$$p(x|\lambda) = e^{\beta F(\lambda) - \beta E(x,\lambda)}$$

free energy

inverse temperature

controllable parameters

$$\zeta(\lambda)_{ij} = \beta \int_0^\infty dt \, \langle \delta X_j(0) \delta X_i(t) \rangle_\lambda$$

positive semi-definite symmetric matrix
i.e. thermodynamic metric tenser

correlations of conjugate variables

nonequilibrium
excess power

linear response
friction tensor

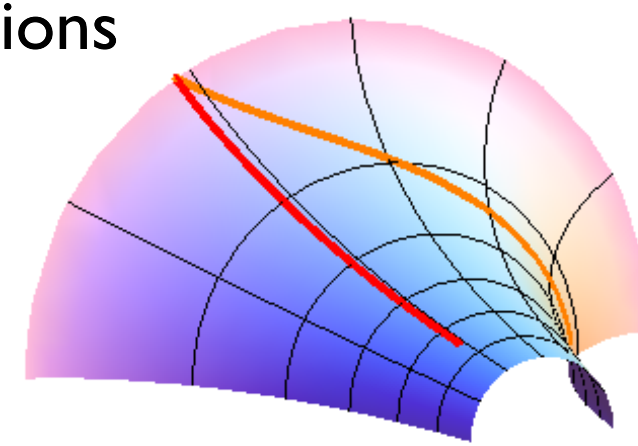
$$\mathcal{P}^{\text{ex}}_\Lambda(t_0) = \left[\frac{\mathrm{d}\boldsymbol{\lambda}^T}{\mathrm{d}t}\right]_{t_0} \cdot \boldsymbol{\zeta}\big(\boldsymbol{\lambda}(t_0)\big) \cdot \left[\frac{\mathrm{d}\boldsymbol{\lambda}}{\mathrm{d}t}\right]_{t_0}$$

imposed by protocol Λ

Sivak & Crooks PRL (2012)

Geometry of thermodynamic control

- Linear response friction tensor yields a Riemannian metric
- Metric tensor measures friction in *control space*
- Optimal (minimum dissipation) protocols:
  - are geodesics in control space
  - independent of protocol duration
  - constant excess power
  - dissipation inversely proportional to protocol duration
  - minimize time for fixed dissipation
  - minimize error for free energy calculations



Rotskoff & Crooks (2015)
Sivak & Crooks (2012)
Peter Salamon and Steven Berry (1983)

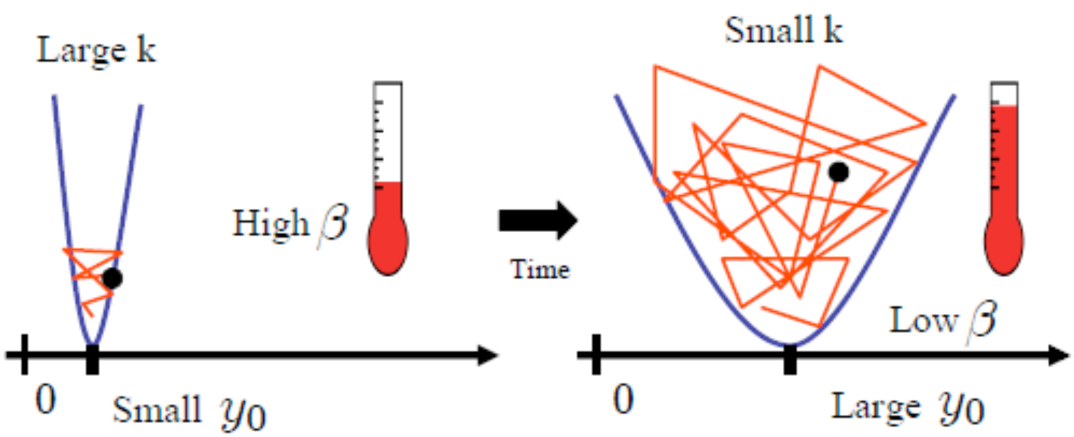
Thermodynamic Geometry of a Harmonic Trap

- Finite time thermodynamics with linear response friction tensor
- Riemannian metric, minimum dissipation paths are *geodesics*

nonequilibrium excess power imposed by protocol Λ

linear response friction tensor

$$\mathcal{P}^{\mathrm{ex}}_{\Lambda}(t_0) = \left[\frac{\mathrm{d}\boldsymbol{\lambda}^T}{\mathrm{d}t}\right]_{t_0} \cdot \zeta\big(\boldsymbol{\lambda}(t_0)\big) \cdot \left[\frac{\mathrm{d}\boldsymbol{\lambda}}{\mathrm{d}t}\right]_{t_0}$$



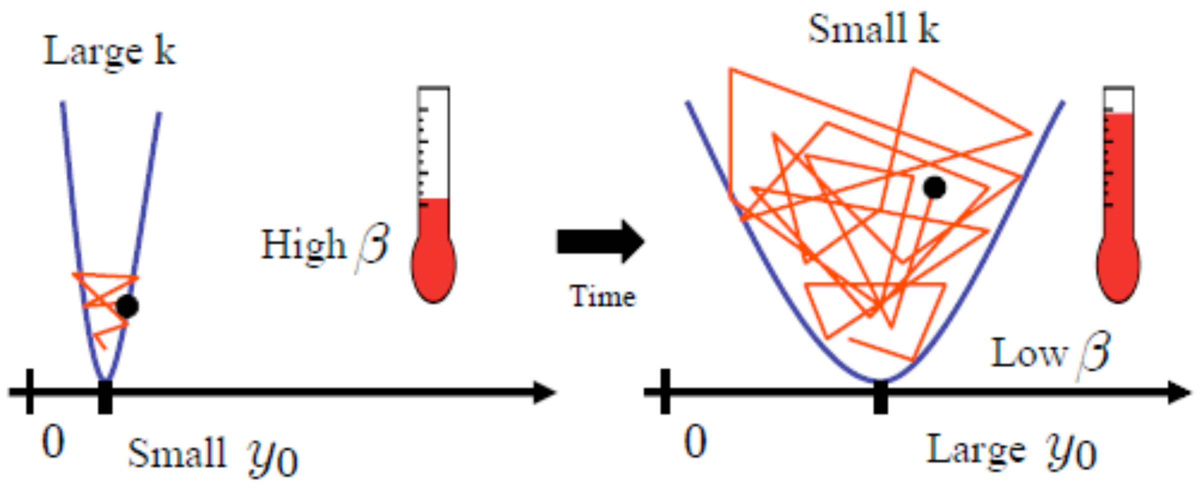
Sivak & Crooks, *Phys. Rev. Lett.*, 2012
Zulkowski, Sivak, Crooks & DeWeese *Phys. Rev. E* 2012

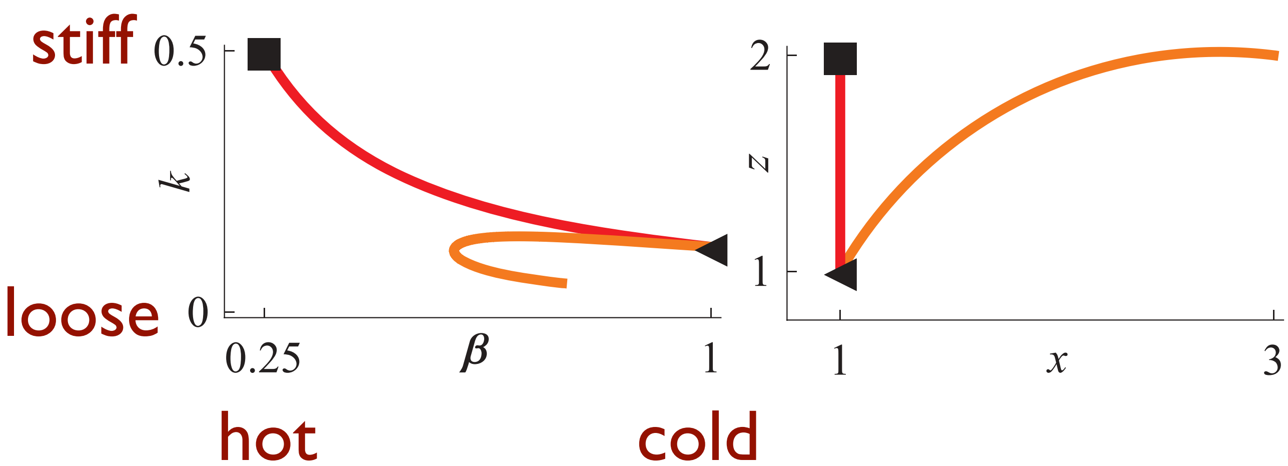
David Sivak

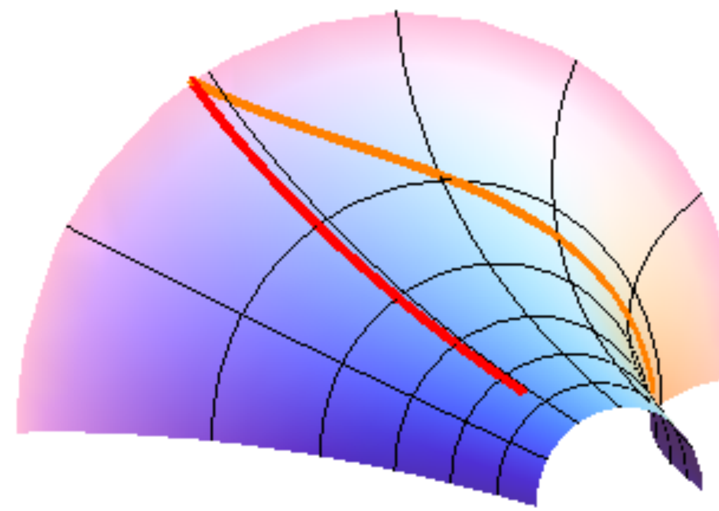
Michael DeWeese

Patrick Zulkowski

Thermodynamic Geometry of a Harmonic Trap



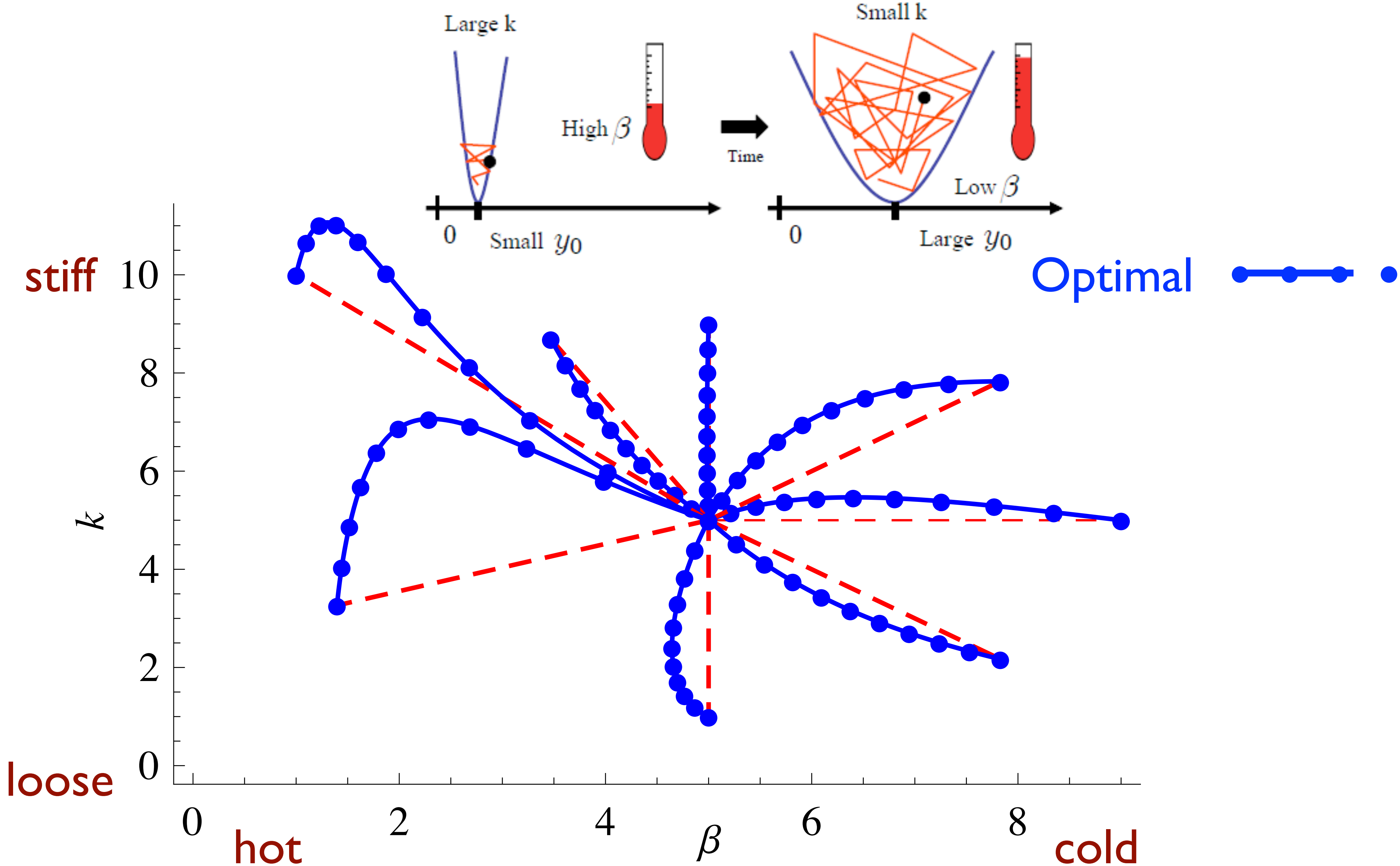




Hyperbolic geometry

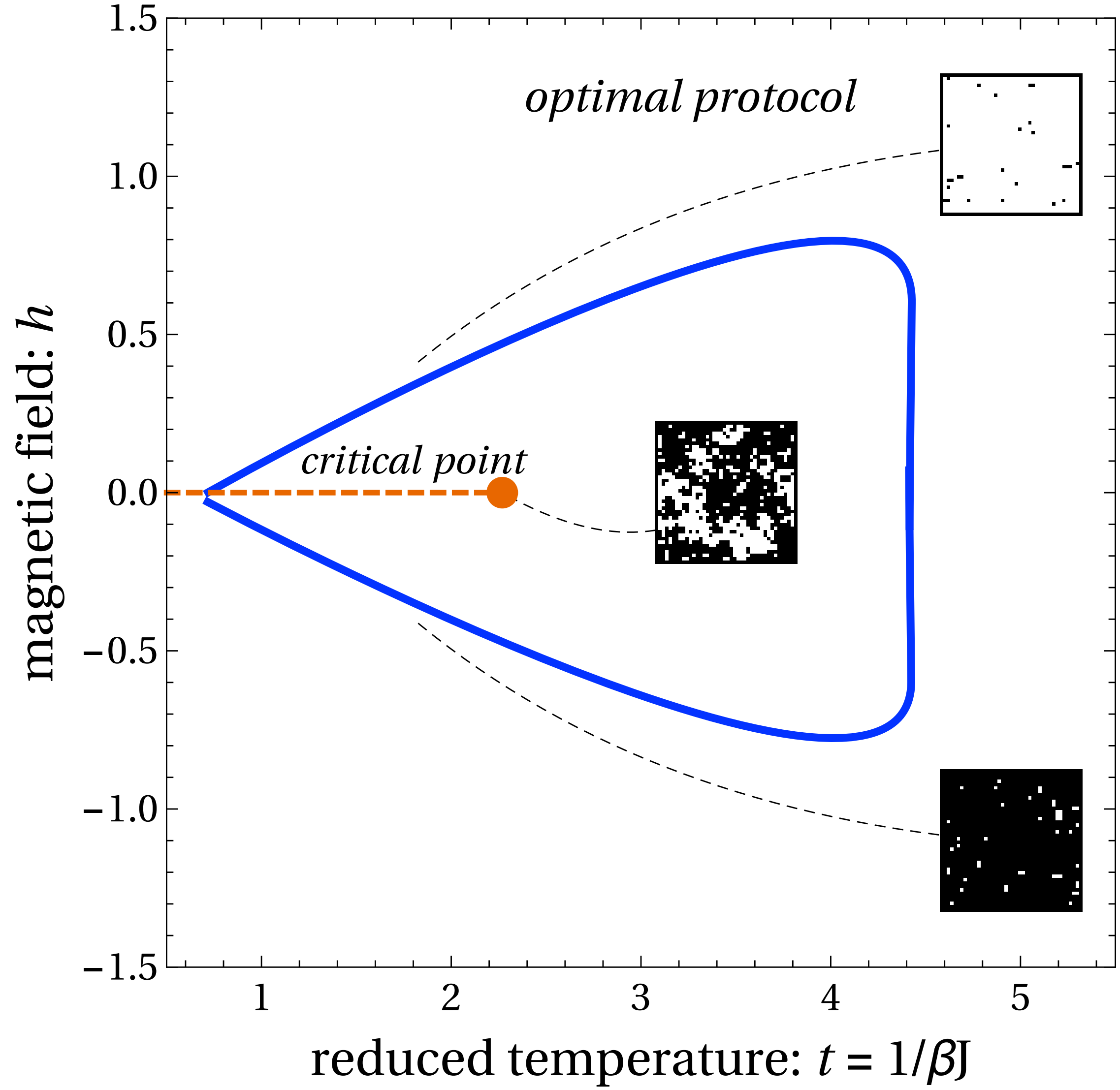
Zulkowski, Sivak, Crooks & DeWeese *Phys. Rev. E* 2012

Optimal Protocols

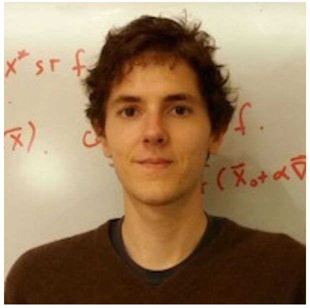


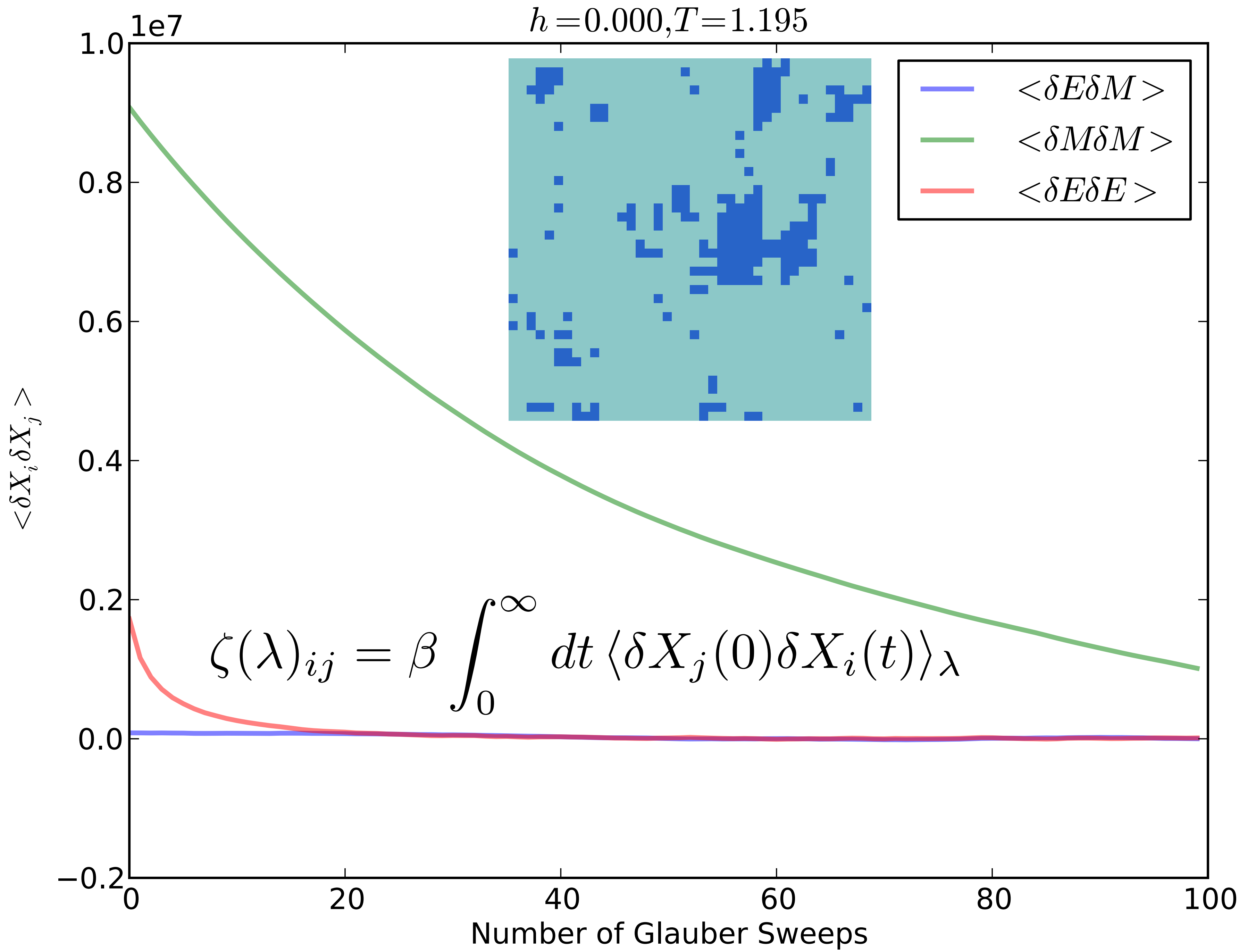
The Ising Model

$$H(\sigma) = -J \sum_{<ij>} \sigma_i \sigma_j - h \sum_i \sigma_i$$



Grant Rotskoff

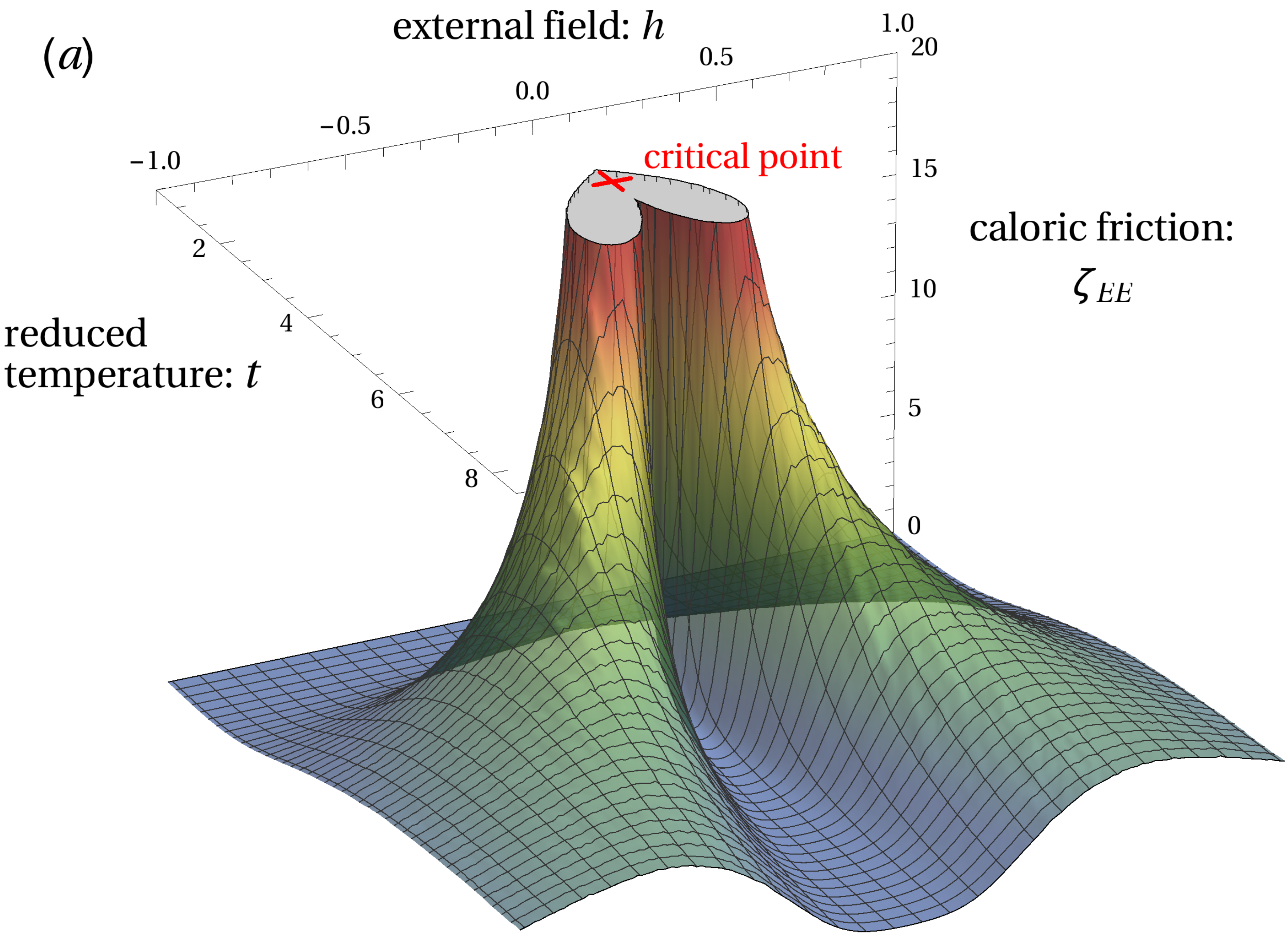




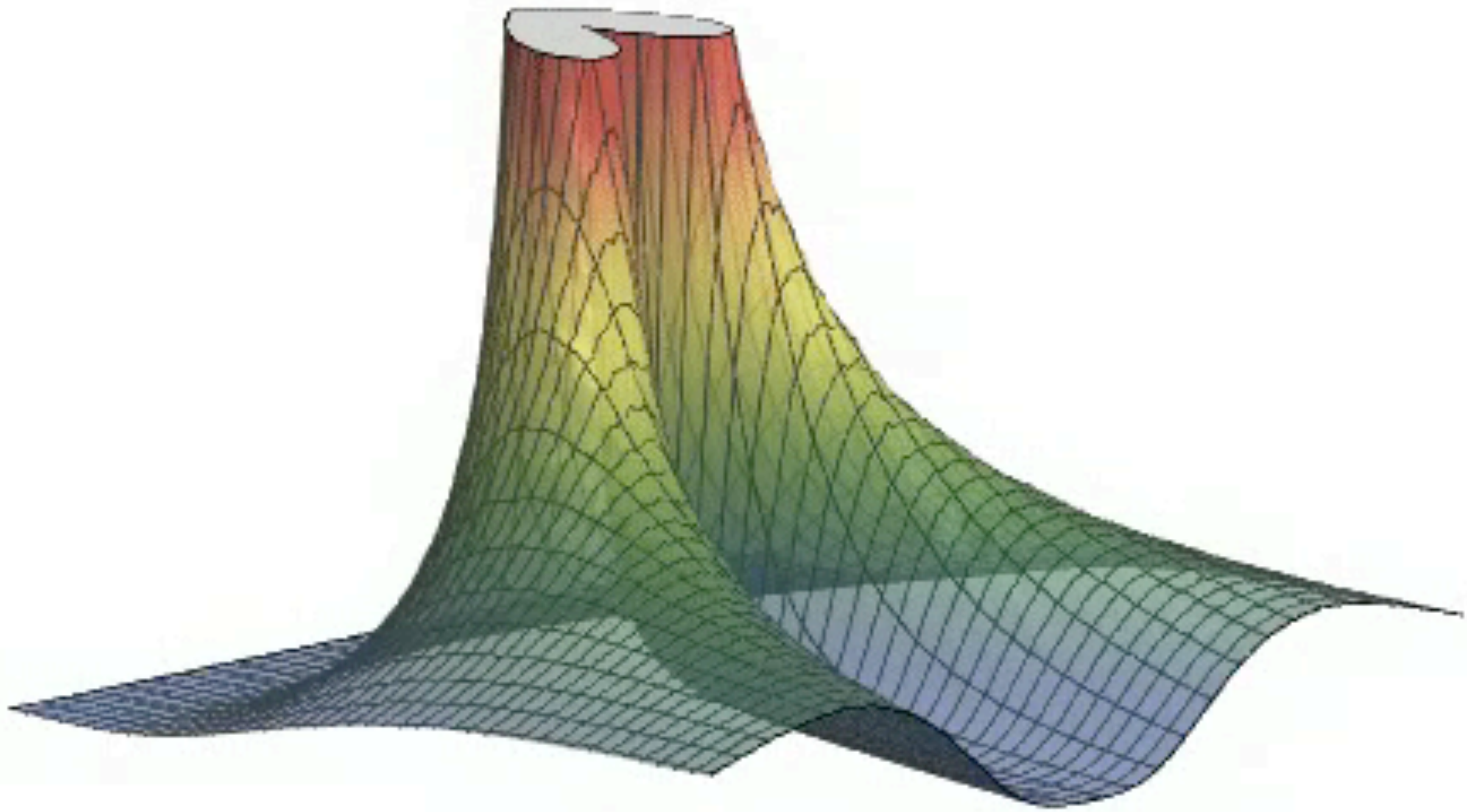
$$\zeta(\lambda)_{ij} = \beta \int_0^\infty dt\, \langle \delta X_j(0)\delta X_i(t)\rangle_\lambda$$

Energy-Energy

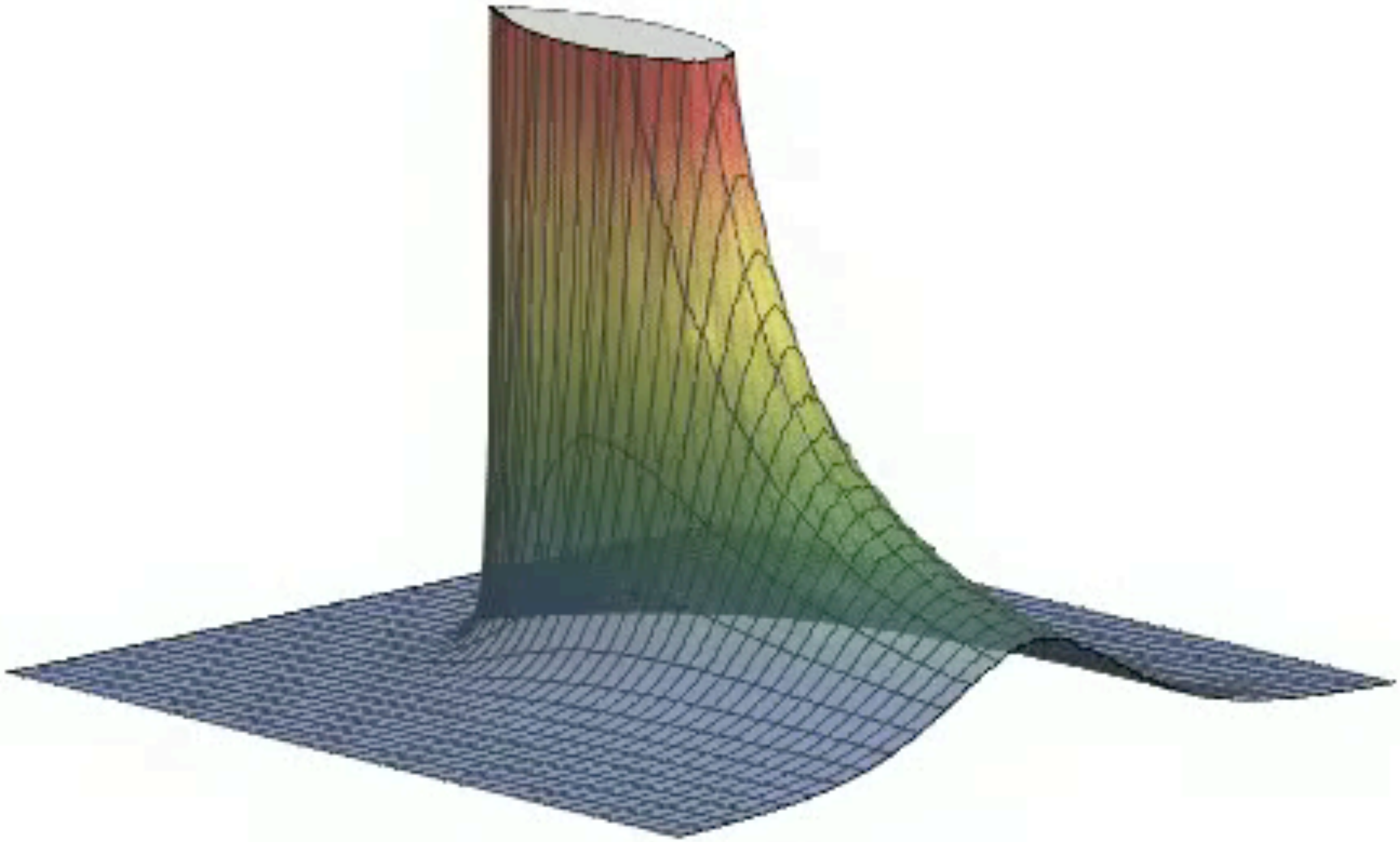
$$\zeta(\lambda)_{ij} = \beta \int_0^\infty dt \, \langle \delta X_j(0) \delta X_i(t) \rangle_\lambda$$



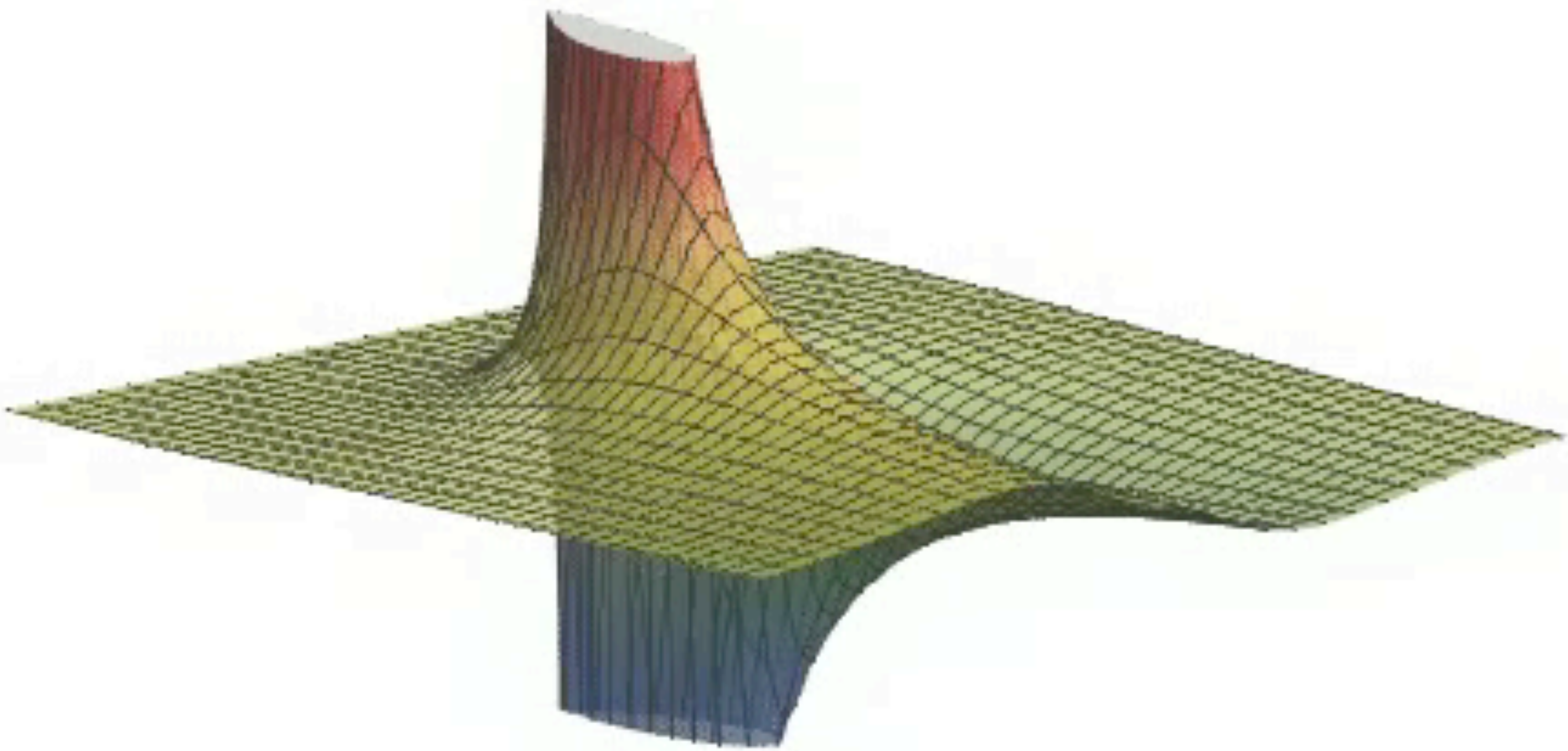
Energy-Energy



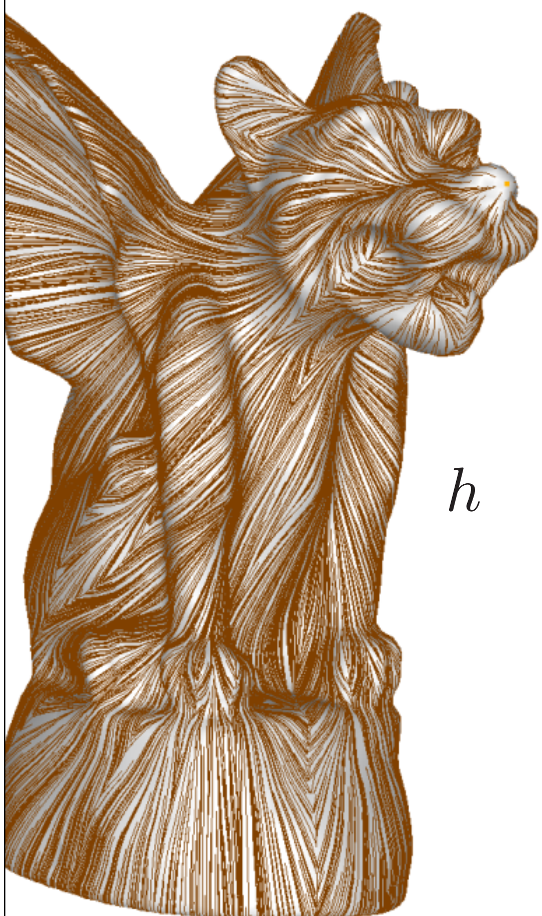
Magnetization-Magnetization



Energy - Magnetization



Fast Marching for Finding Geodesics on a Mesh.



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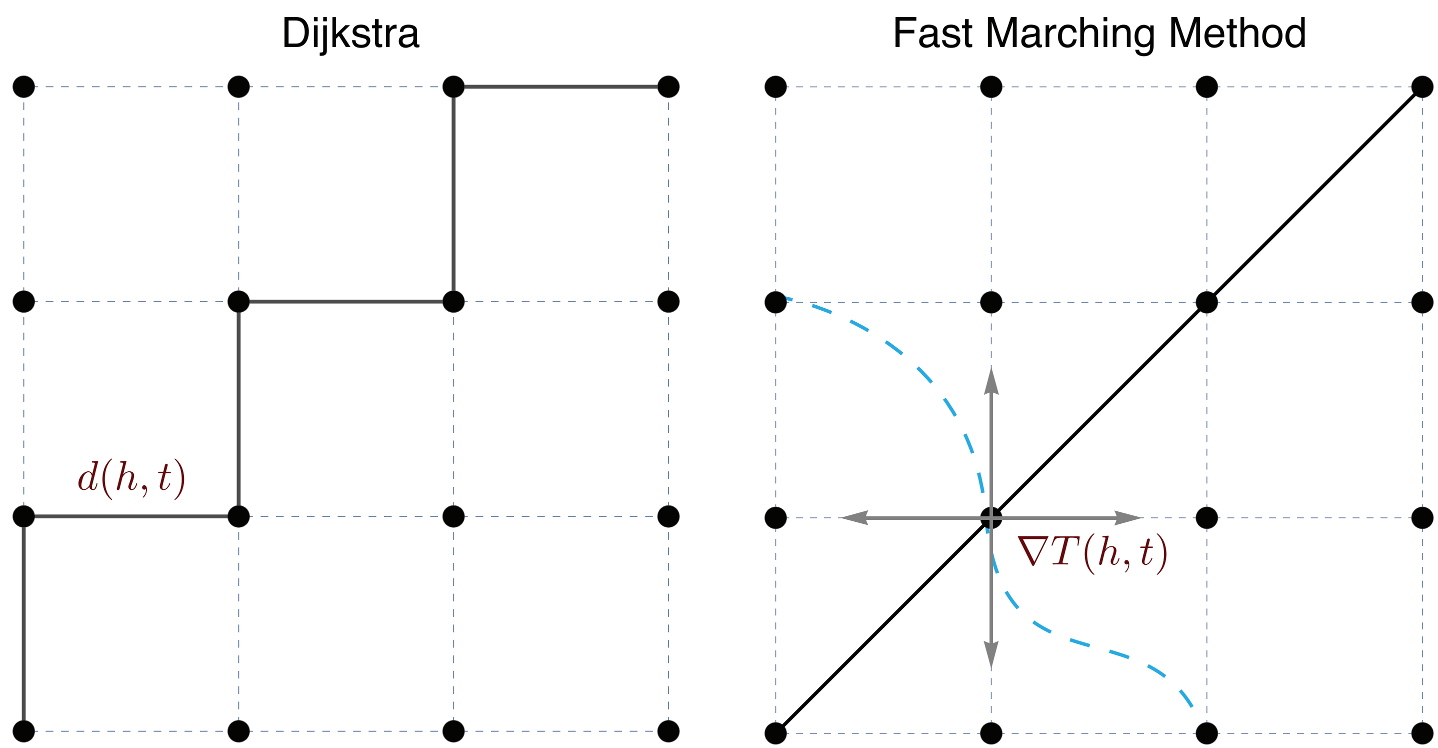
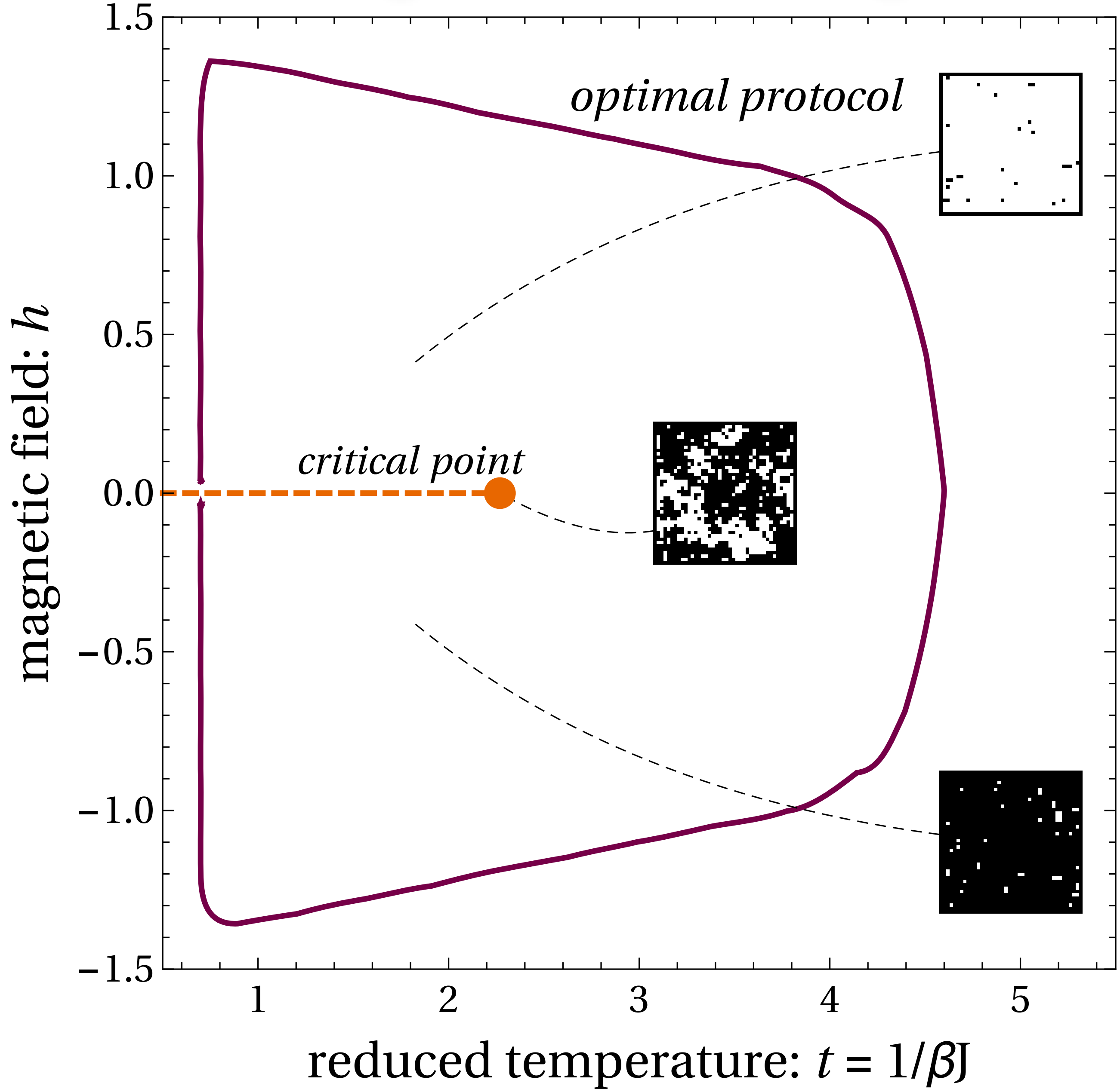


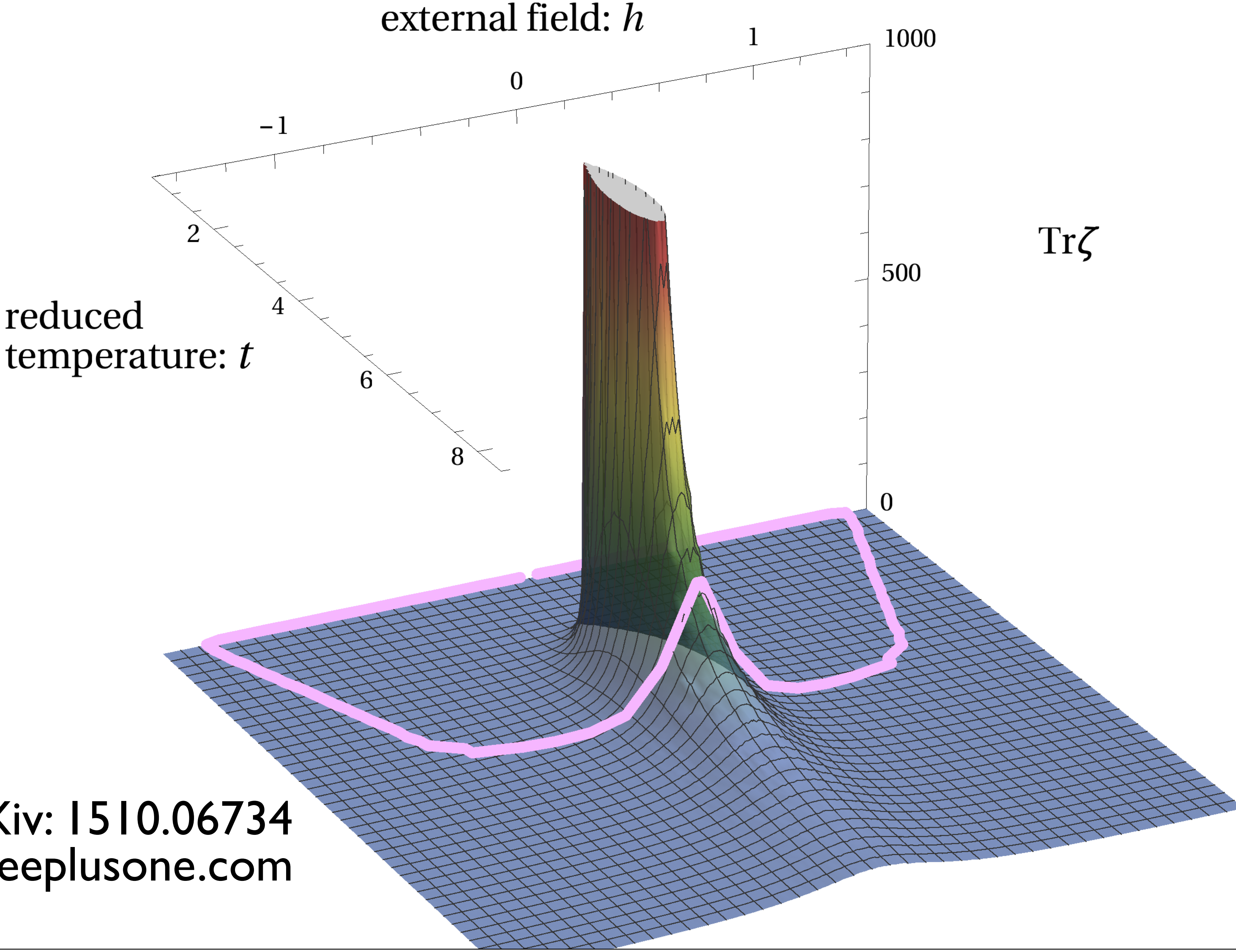
$$\frac{T - T_{\mathrm{C}}}{T_{\mathrm{C}}}$$

Minimum Dissipation Protocol (Geodesics)



 Gavin E. Crooks

Minimum Dissipation Protocol (Geodesics)



arXiv: 1510.06734
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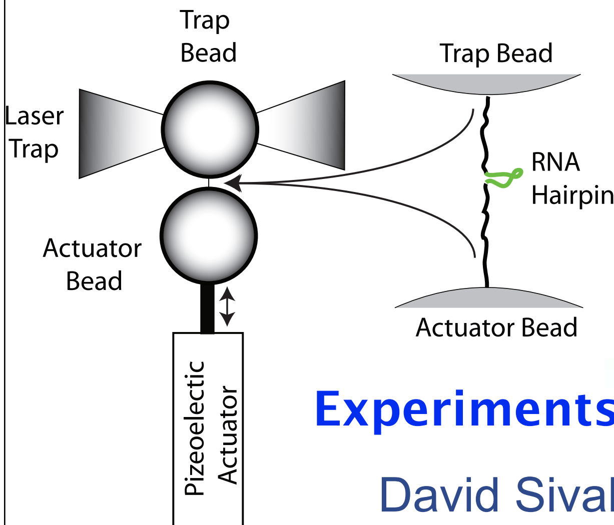
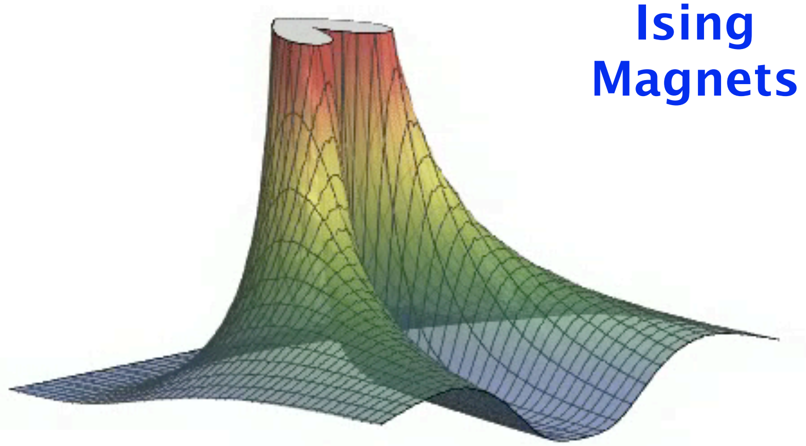
Frontiers of geometric thermodynamics



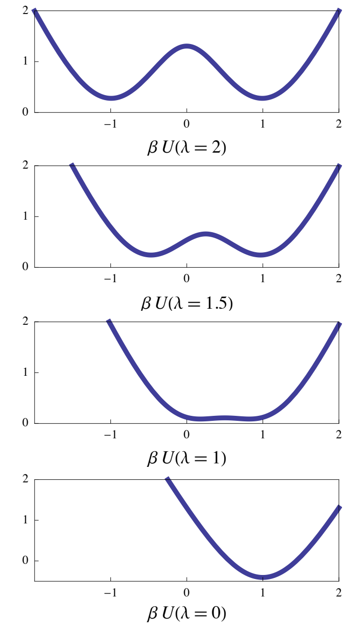
Experiments

David Sivak



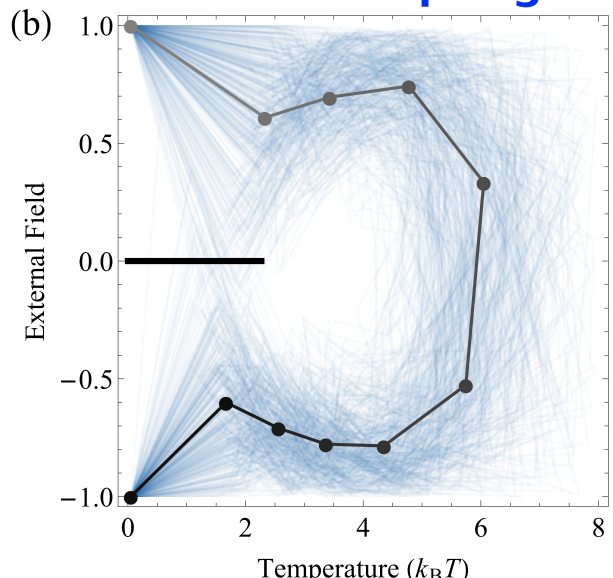
Ising Magnets

Optimal Control



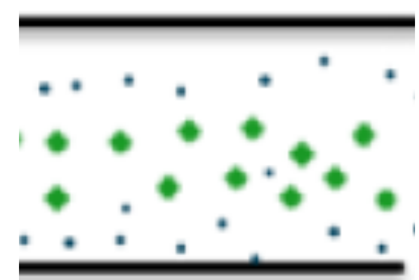
Patrick R. Zulkowski, Michael R. DeWeese

Protocol Sampling



Todd Gingrich, Grant Rotskoff, Phill Geissler

Coordinate Dependent Diffusion



Alexander Berezhkovskii, Attila Szabo

Steady states

$$\xi_{\mu\nu} = -\sum_{i,j} \pi_j \frac{\partial \ln \pi_i}{\partial \lambda_\nu} R^{+}_{ij} \frac{\partial \ln \pi_j}{\partial \lambda_\mu}.$$

Dibyendu Mandal, Chris Jarzynski