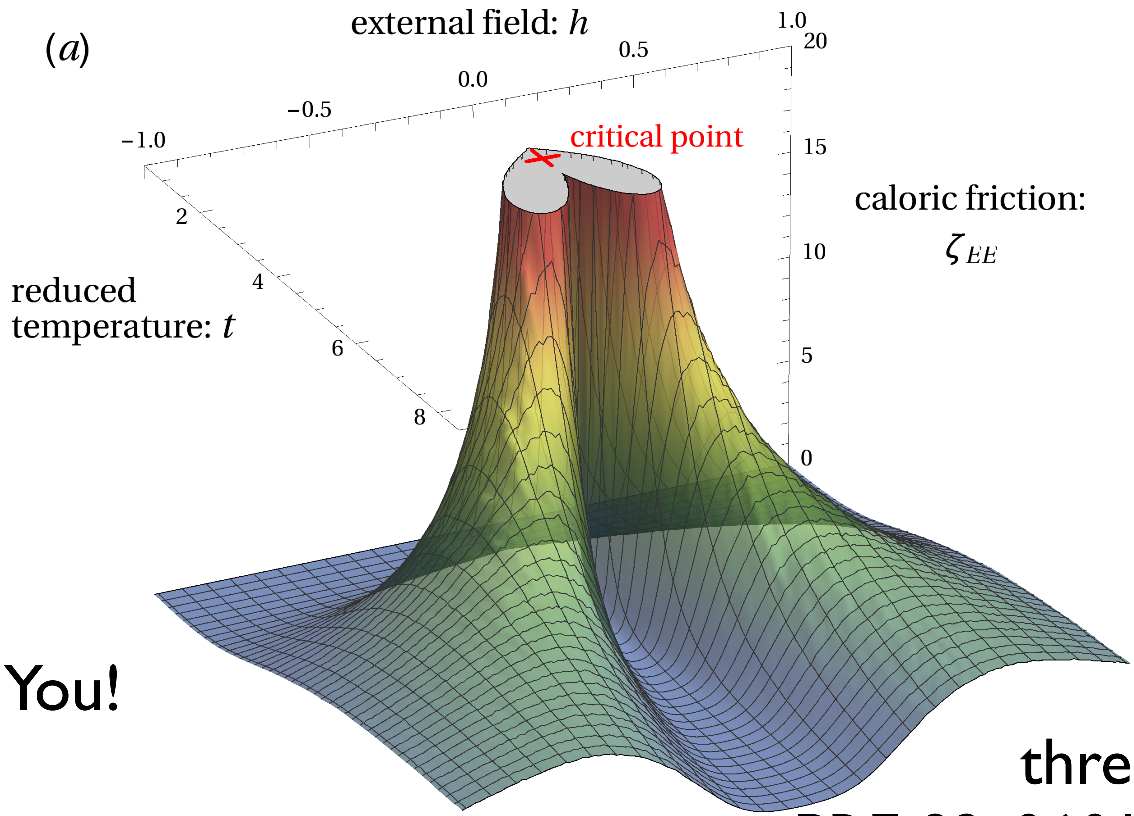
Optimal Thermodynamic Control and the Riemannian Geometry of Ising magnets

Gavin Crooks
Lawrence Berkeley National Lab



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PRE 92, 060102(R) (2015)

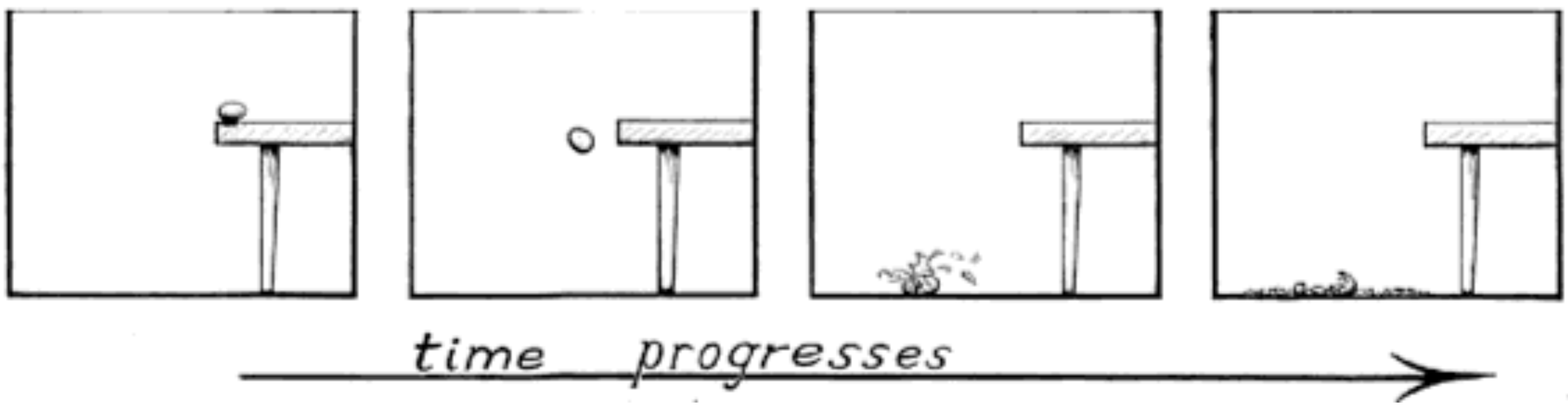
The 2nd Law of Thermodynamics

Clausius inequality (1865)

Entropy

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

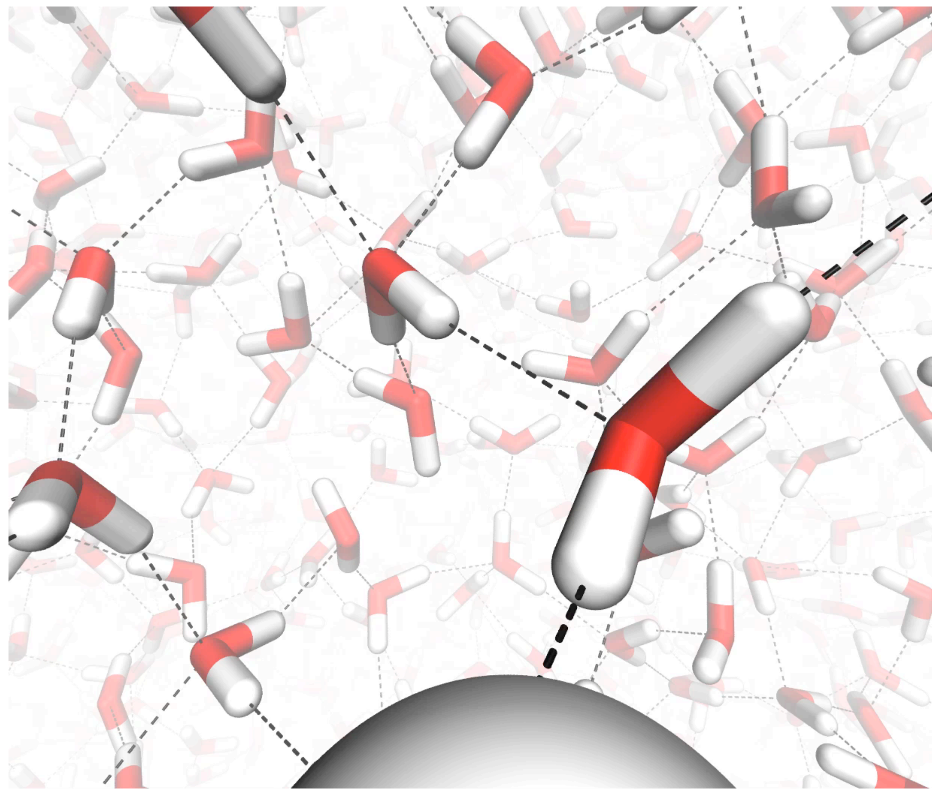
Entropy increases as time progresses



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

Thermodynamic Equilibrium



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

Entropy and Disorder

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

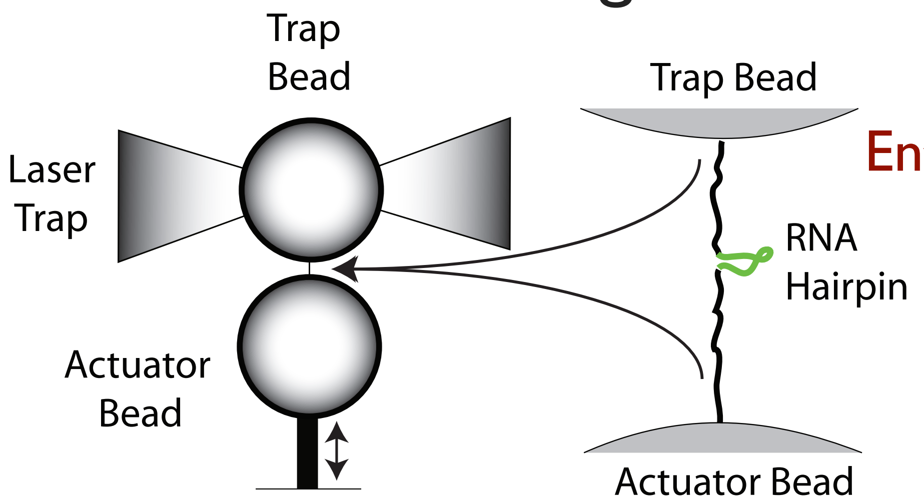
1 natural unit of entropy
equivalent to
1 kT of thermal energy

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

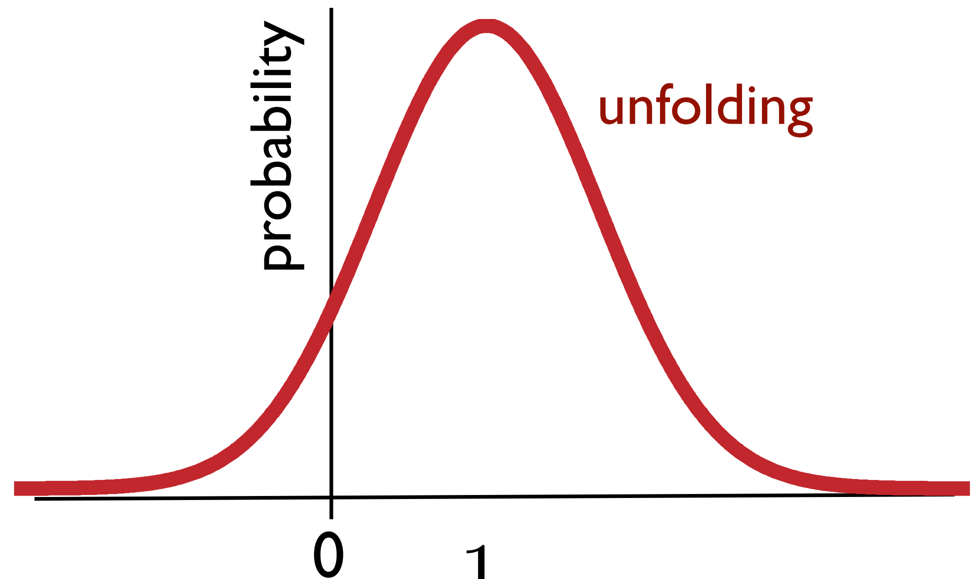
1 kT = 25 meV
= 2.5 kJ/mol
= 4 zeptojoules

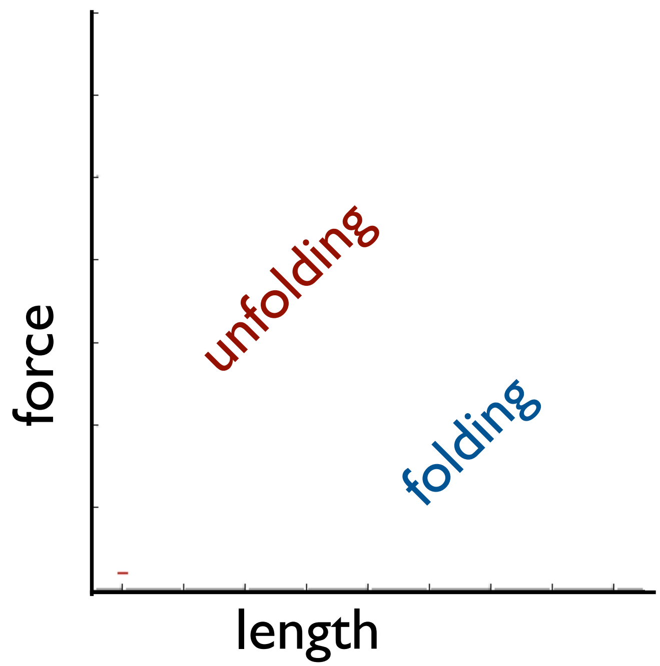
average kinetic energy = 1.5 kT

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)

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

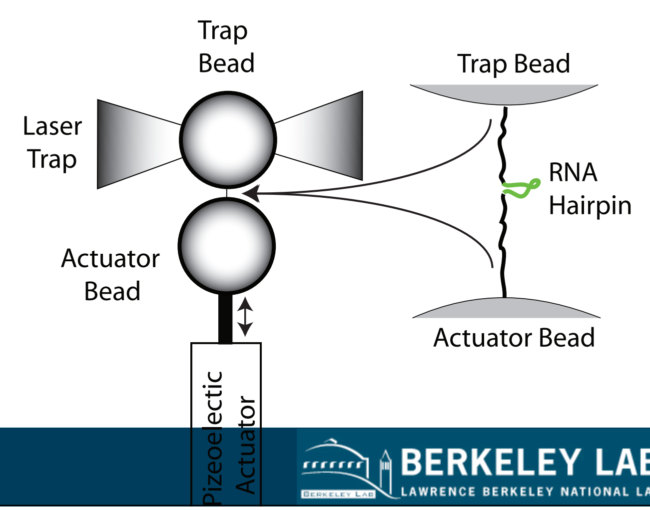
equality only for
reversible process

Jarzynski identity
(1997)

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

equality far-from-equilibrium

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



Fluctuation Theorems:

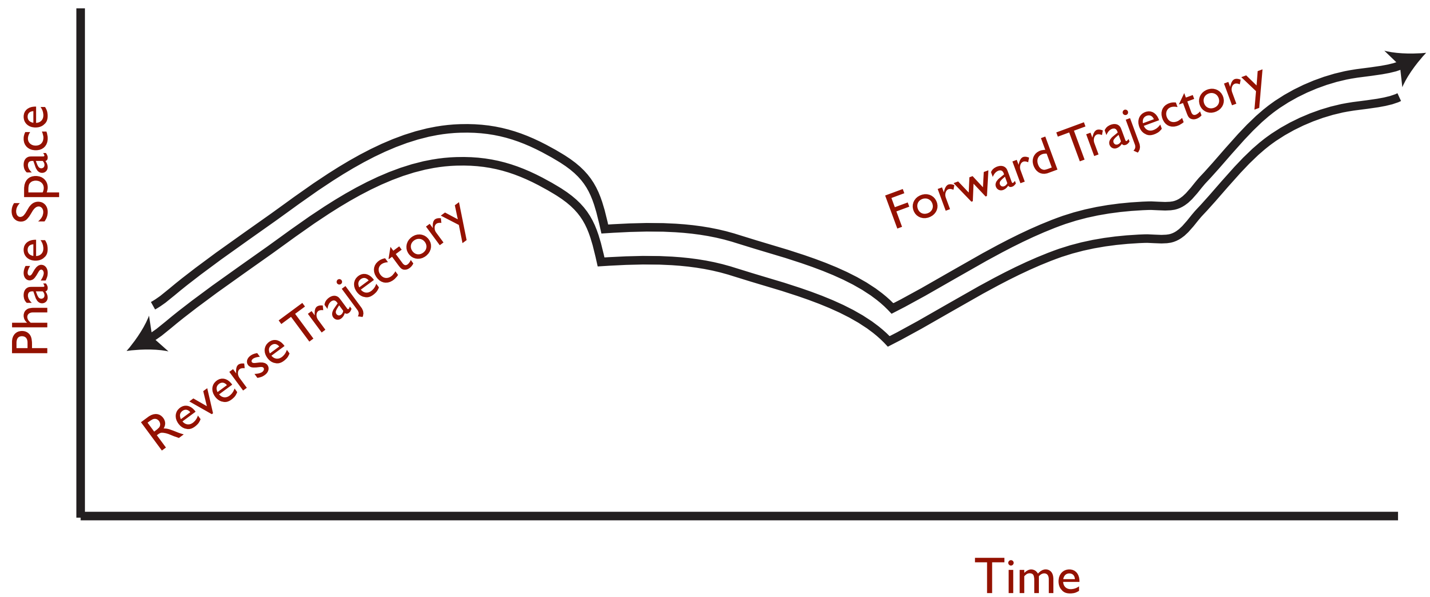
Dissipation (entropy increase) breaks time-reversal symmetry

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

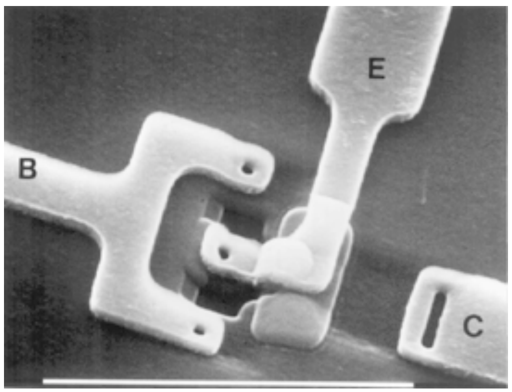
Work

Free Energy Change

Inverse Temperature



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

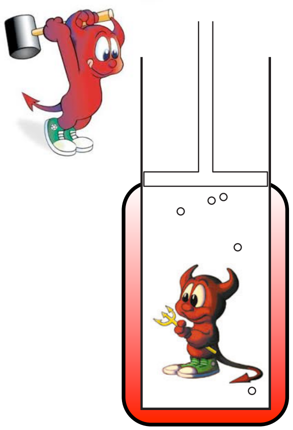


ATP synthase

Free Energy ATP = 20 kT
= 0.5 eV

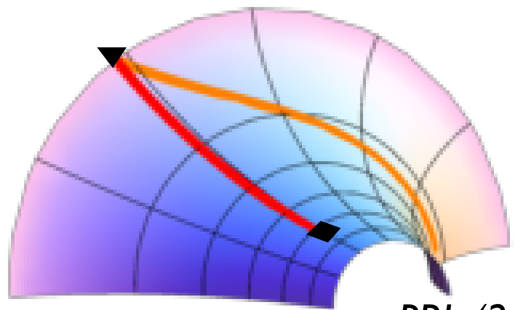
Recent Projects

Coupled Systems & the Thermodynamics of prediction



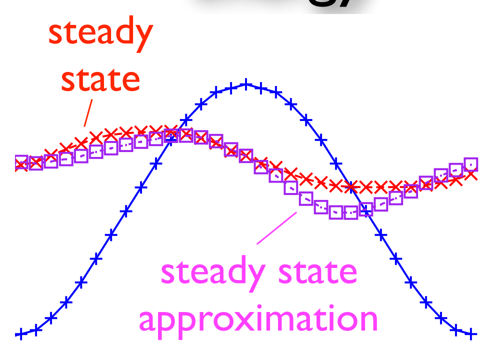
PRL (2012)

Geometry of thermodynamic control



PRL (2012)
PRE (2012)
PRE (2015)

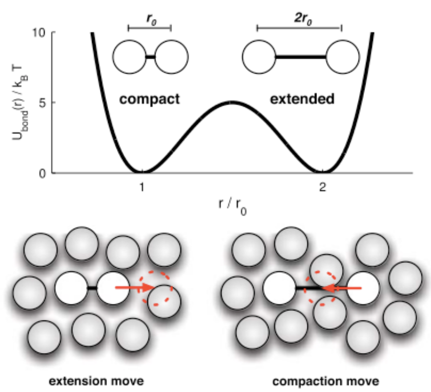
Measurement of nonequilibrium free energy



PRL (2012)

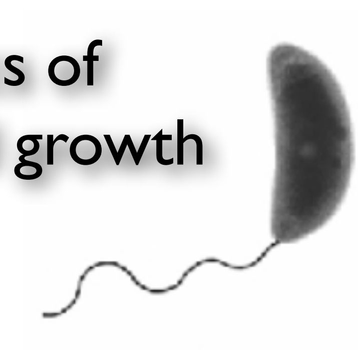
Nonequilibrium simulation

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

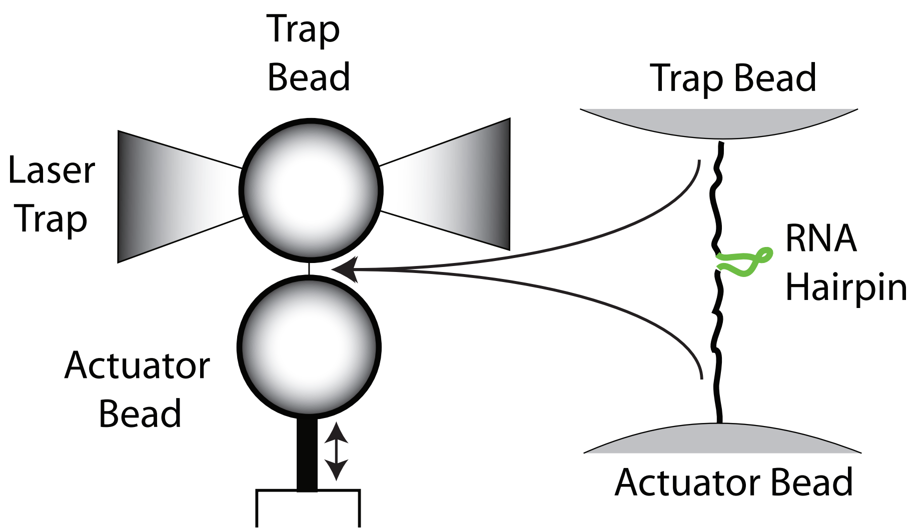


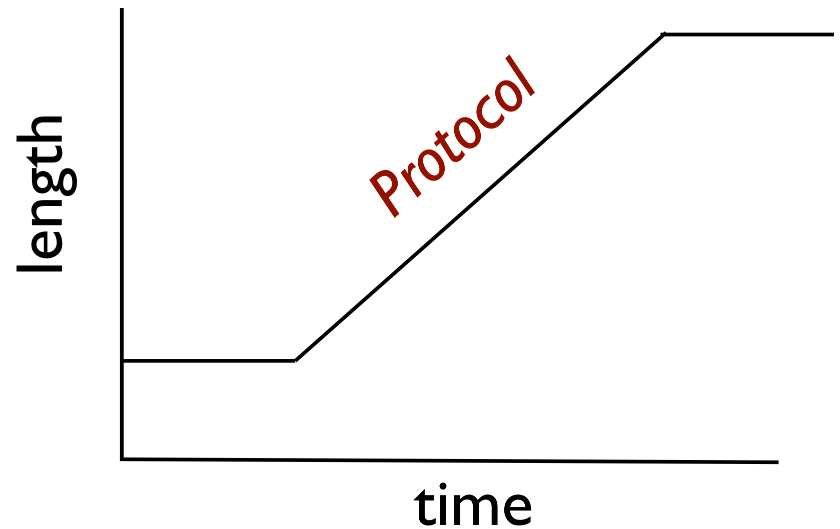
Dynamics of bacterial cell growth

PNAS (2014)
PRL (2014)



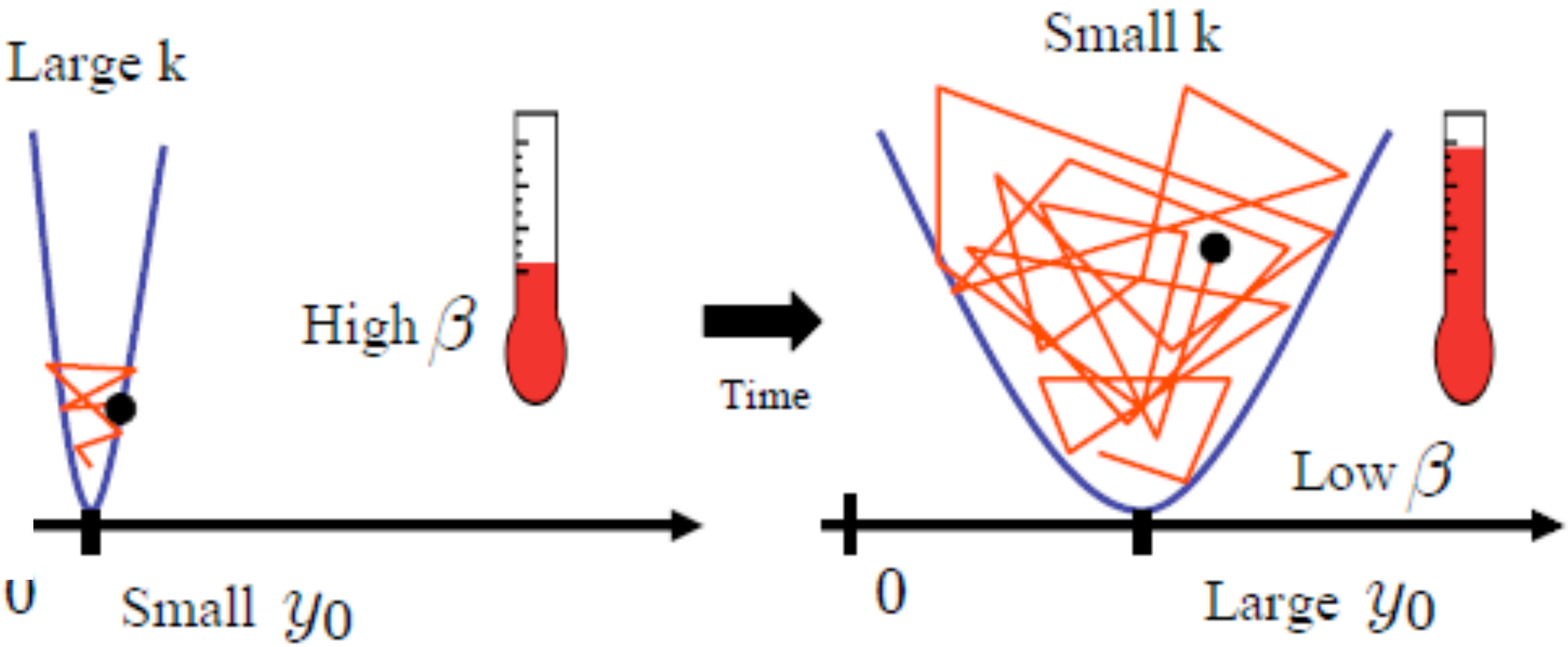
Optimal thermodynamic control of molecular scale systems





Which finite-time experimental protocols minimize dissipation?

Exact minimum dissipation protocols



Control trap position: Schmiedl & Seifert PRL (2007)

Geometry of thermodynamic control

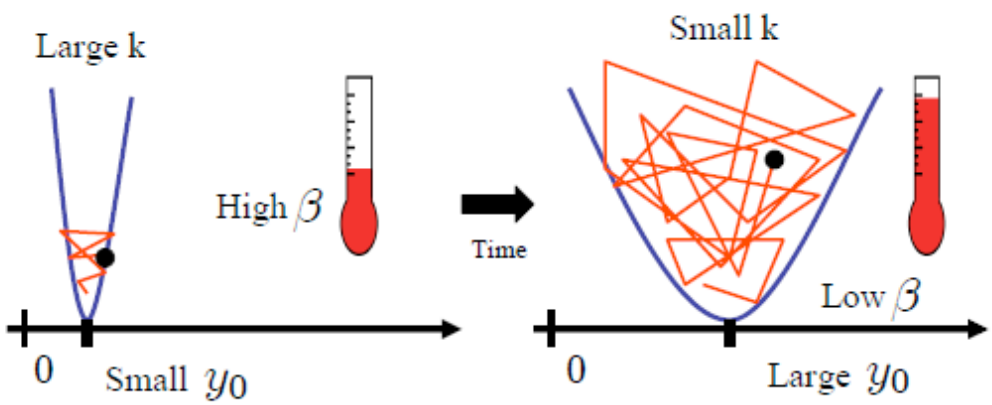
- Finite time thermodynamics with linear response friction tensor
- Riemannian metric, minimum dissipation paths are *geodesics*

Prof. David Sivak
(Simon Fraser U.)

nonequilibrium excess power imposed by protocol Λ

linear response friction tensor

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



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

Combine linear response and thermodynamic geometry

free energy — *inverse temperature*

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

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

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

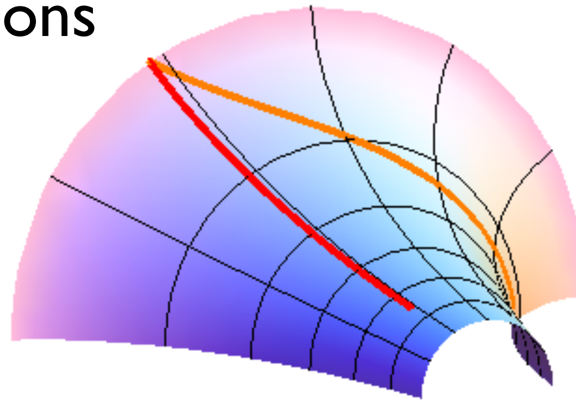
imposed by protocol Λ

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)



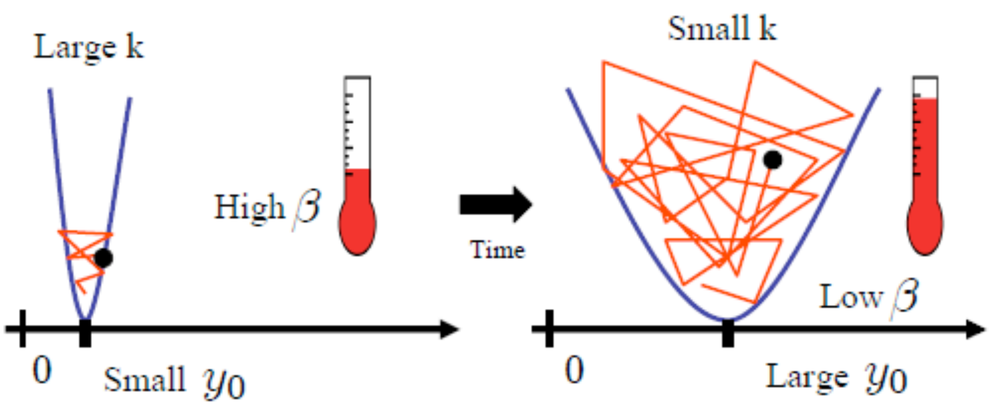
Thermodynamic Geometry of a Harmonic Trap

- 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

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



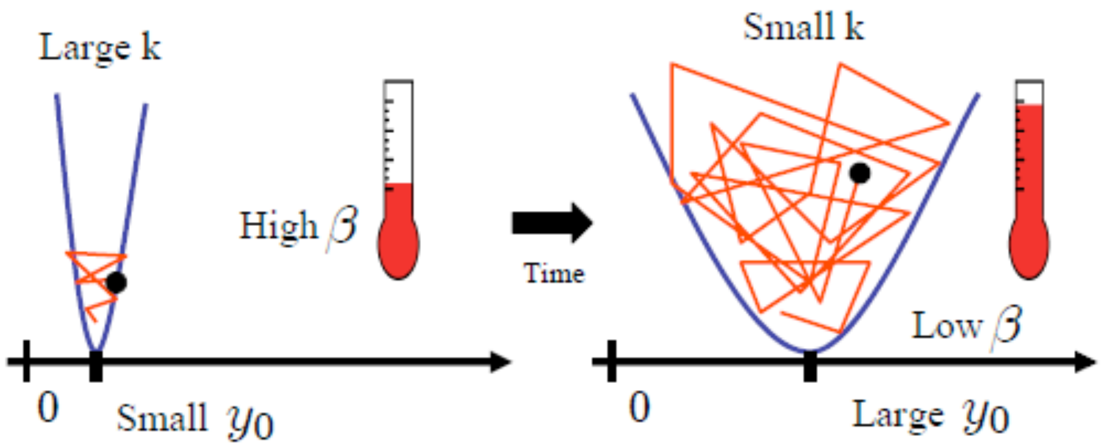
Sivak & Crooks, *Phys. Rev. Lett.*, 2012
Zulkowski, Sivak, Crooks & DeWeese *Phys. Rev. E* 2012

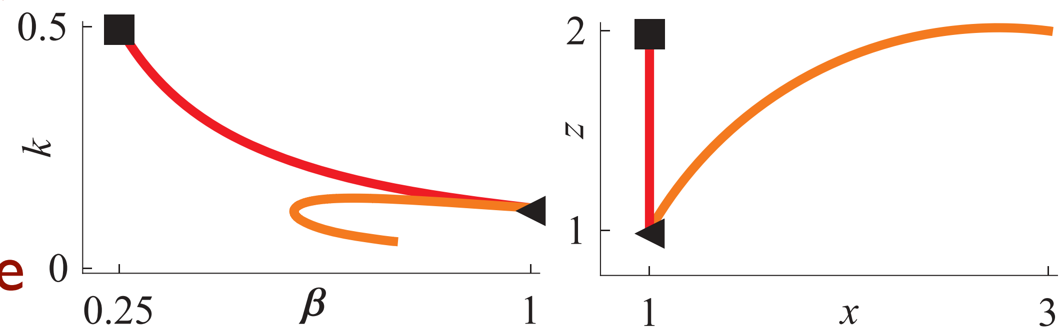
David Sivak

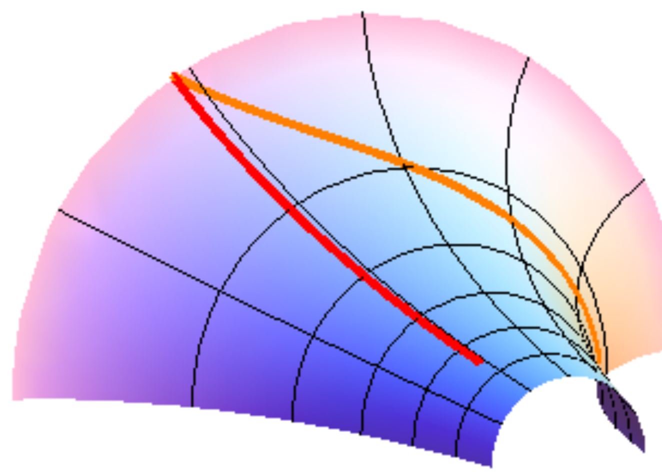
Michael DeWeese

Patrick Zulkowski

Thermodynamic Geometry of a Harmonic Trap





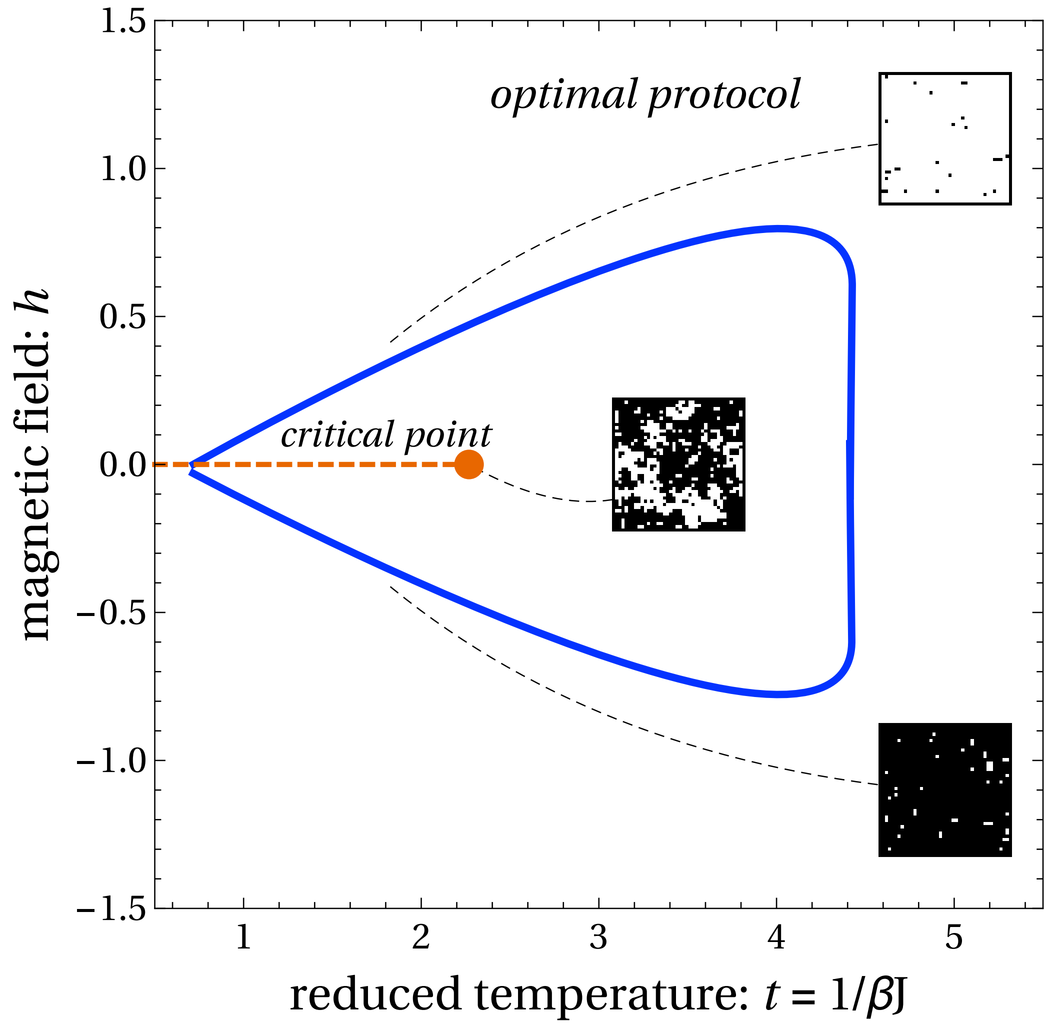


Hyperbolic geometry

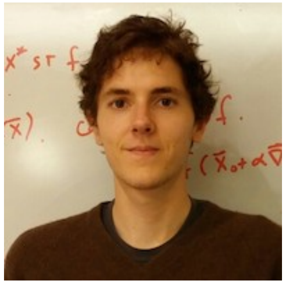
Zulkowski, Sivak, Crooks & DeWeese *Phys. Rev. E* 2012

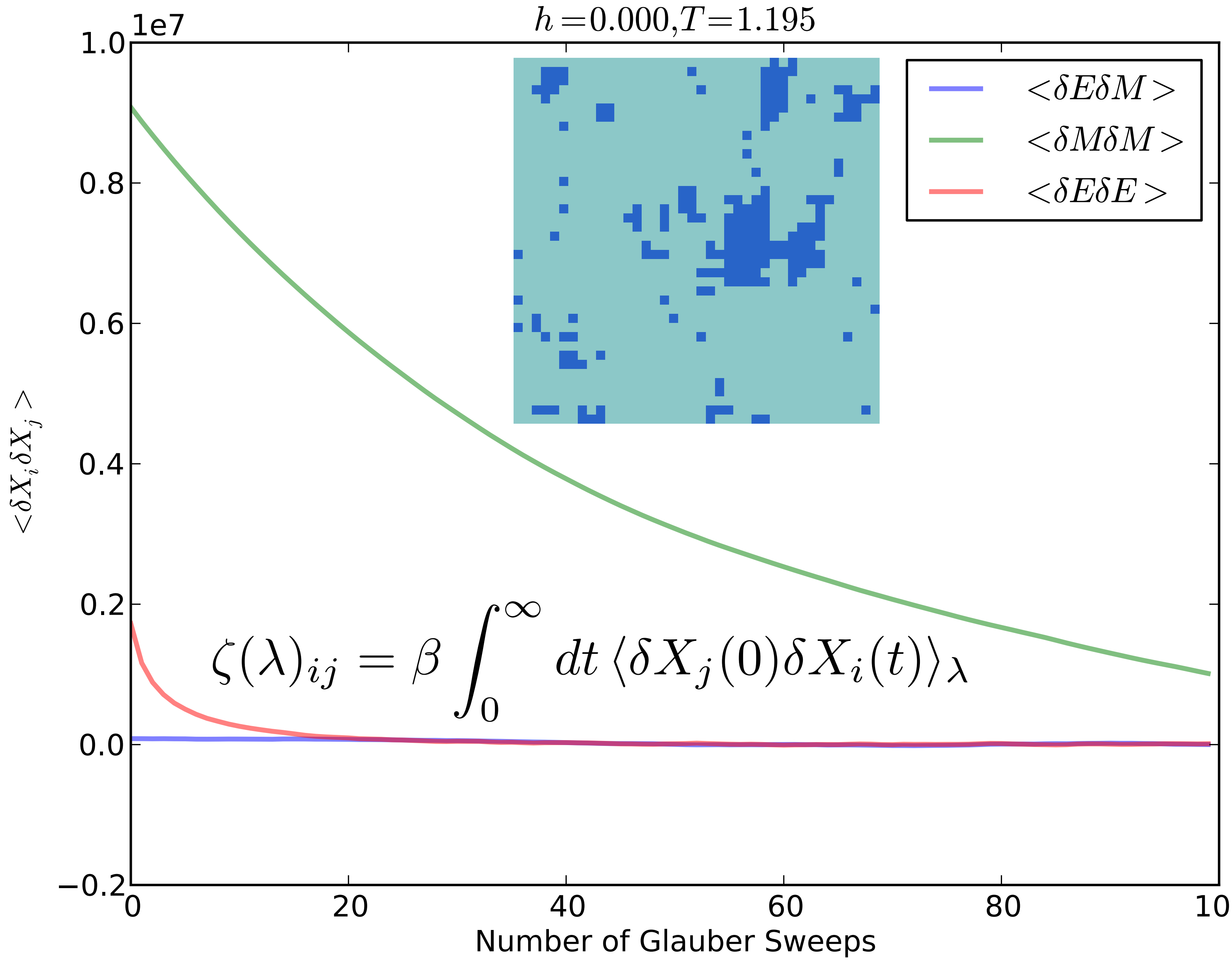
The Ising Model

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



Grant Rotskoff





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

Energy-Energy

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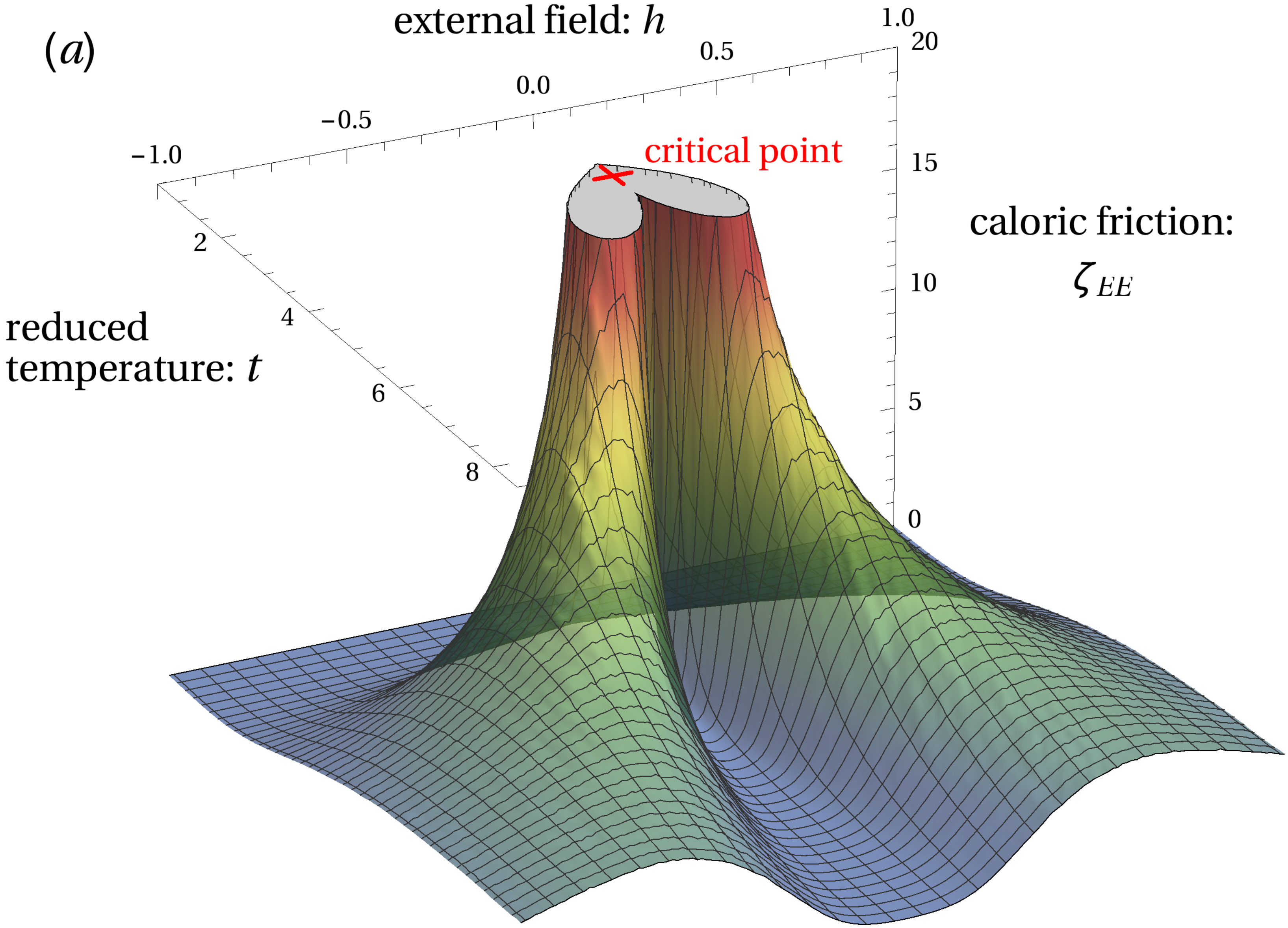
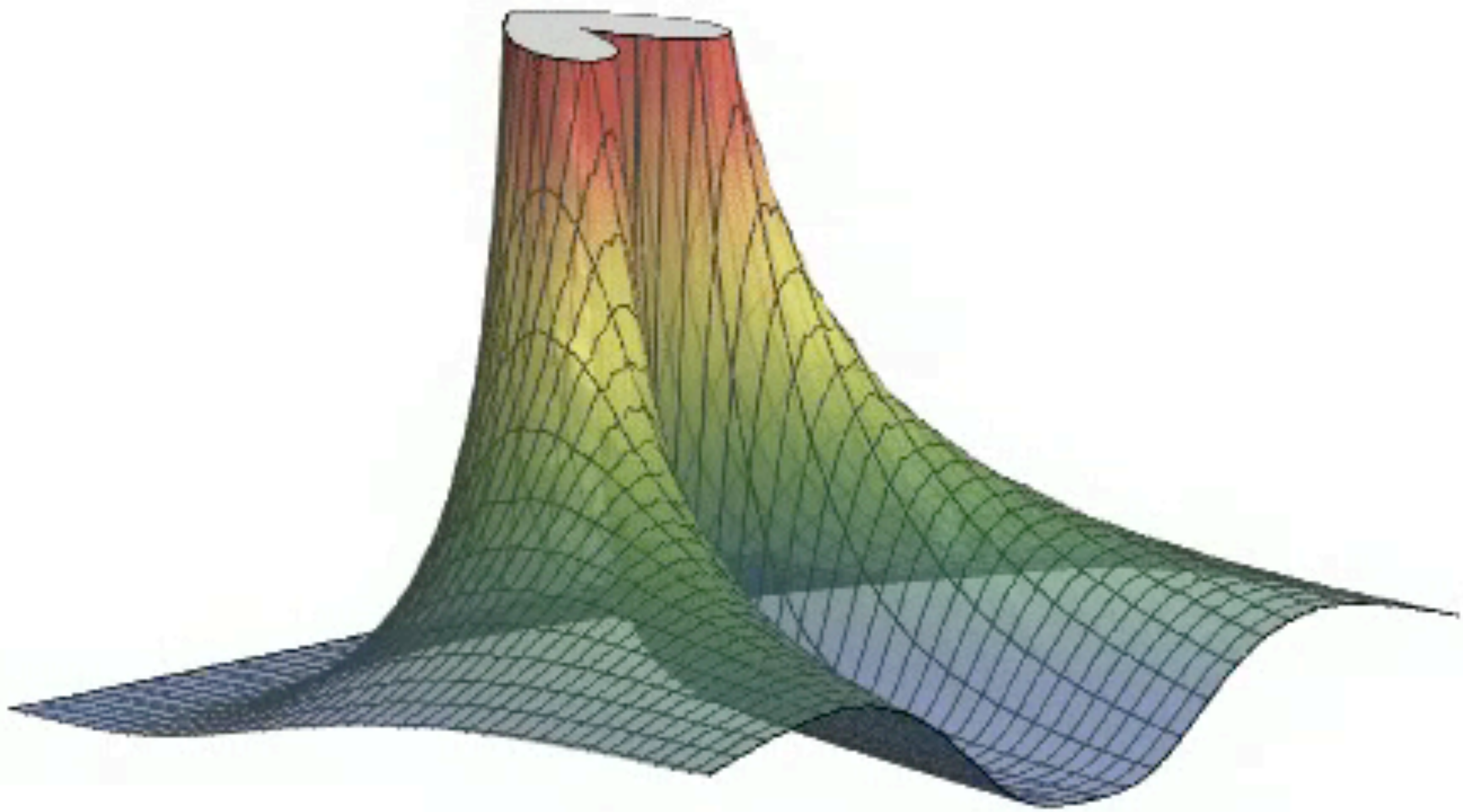
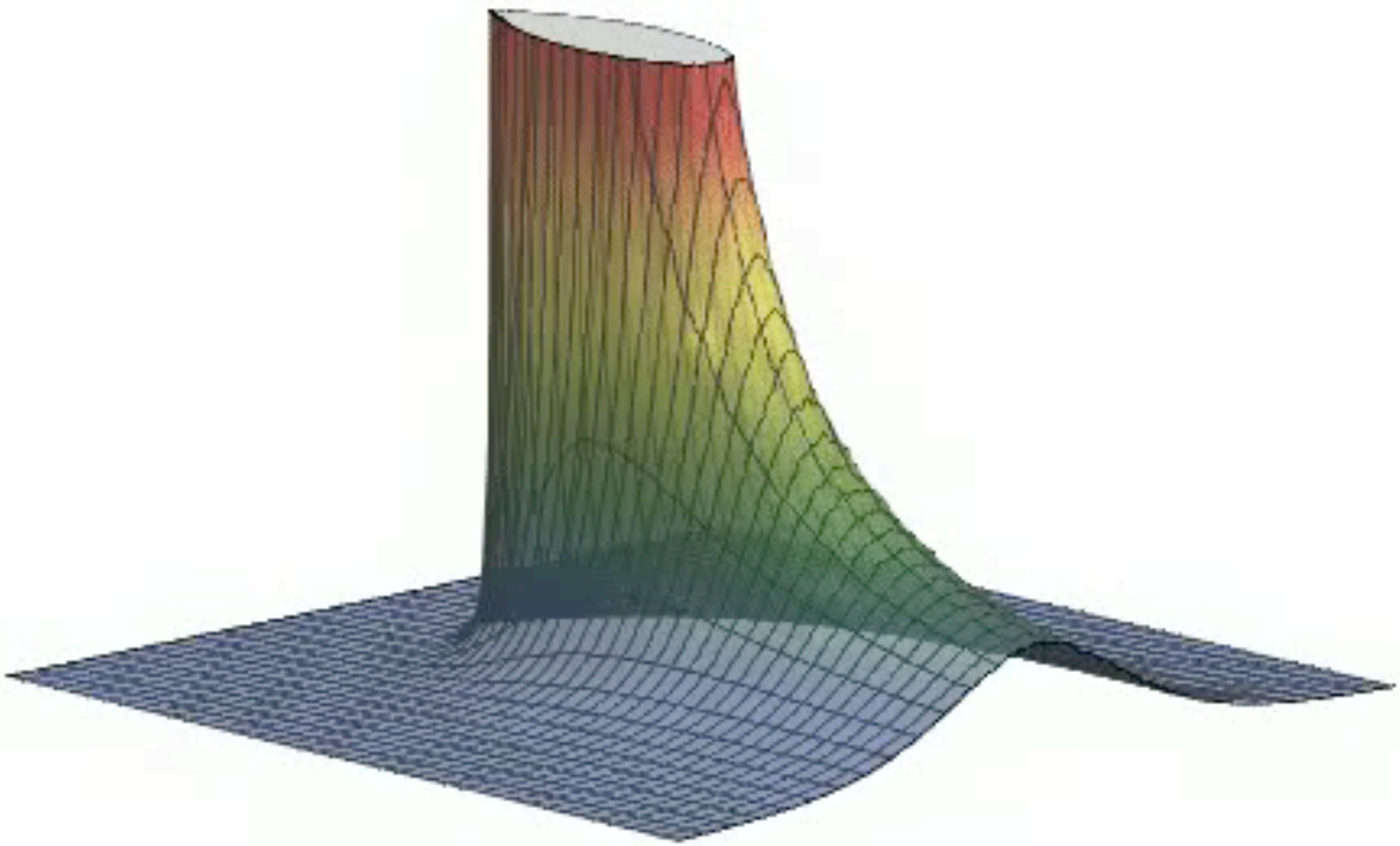


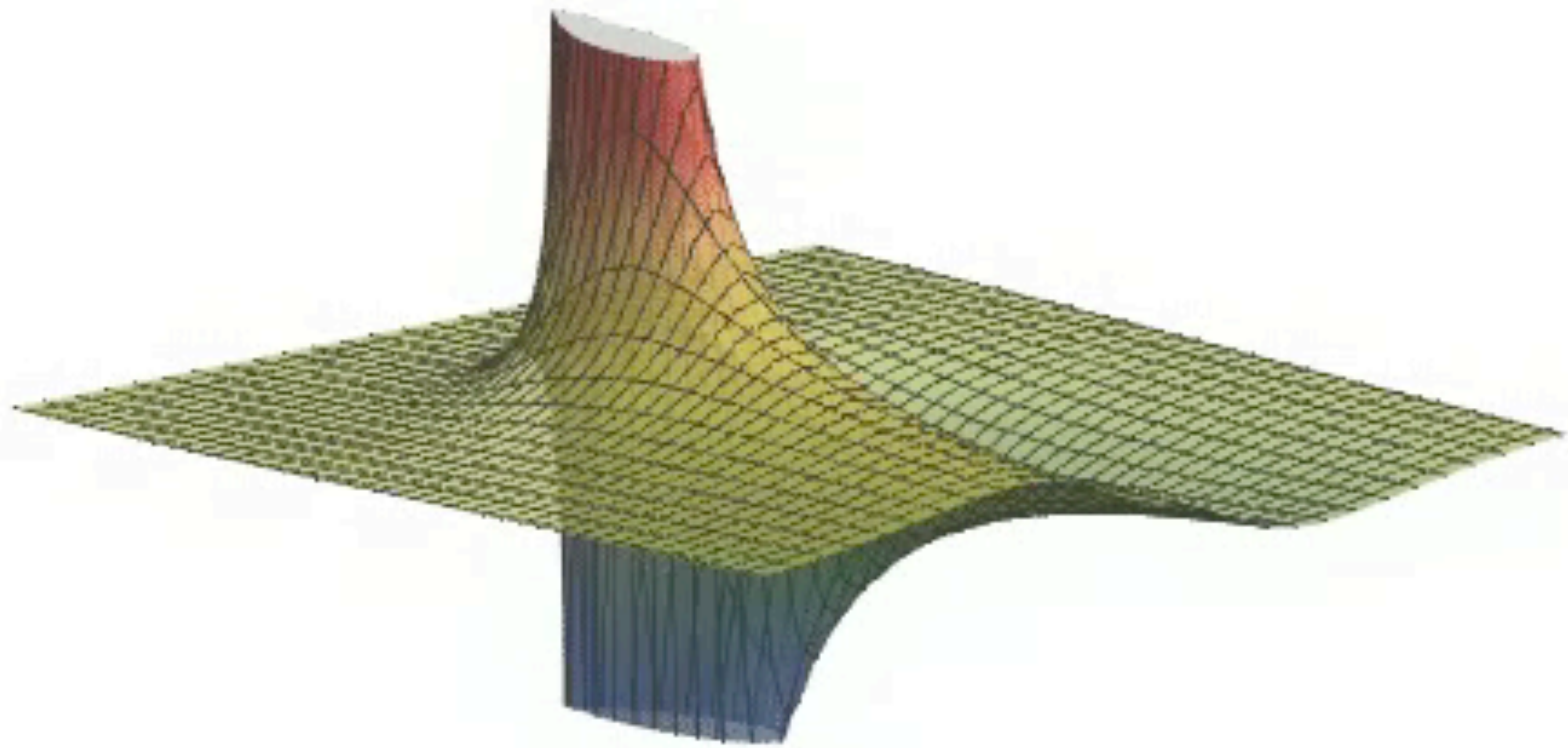
Energy-Energy



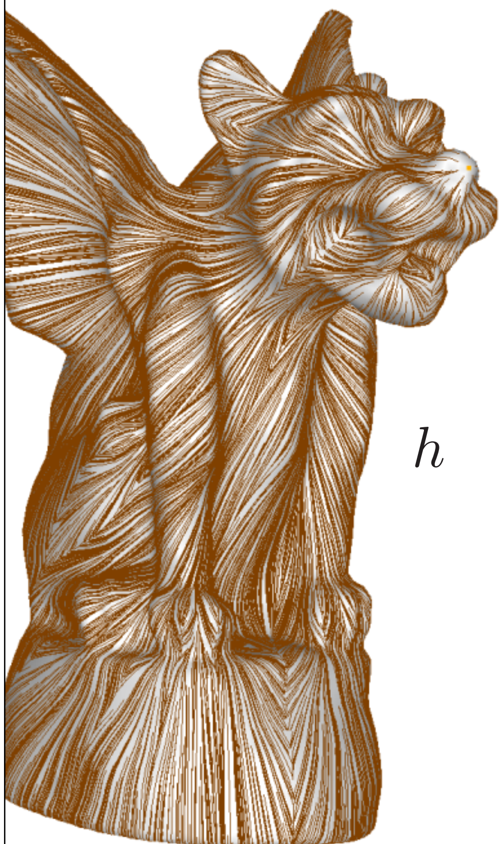
Magnetization-Magnetization



Energy - Magnetization



Fast Marching for Finding Geodesics on a Mesh.



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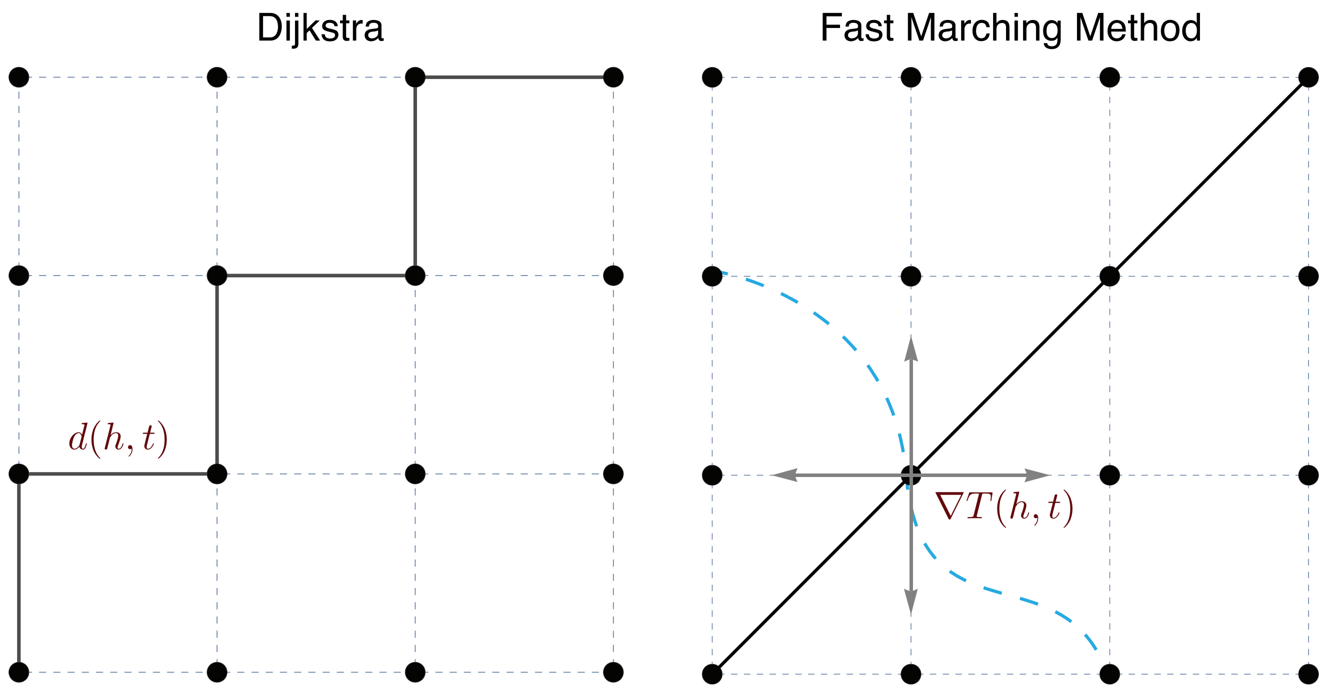
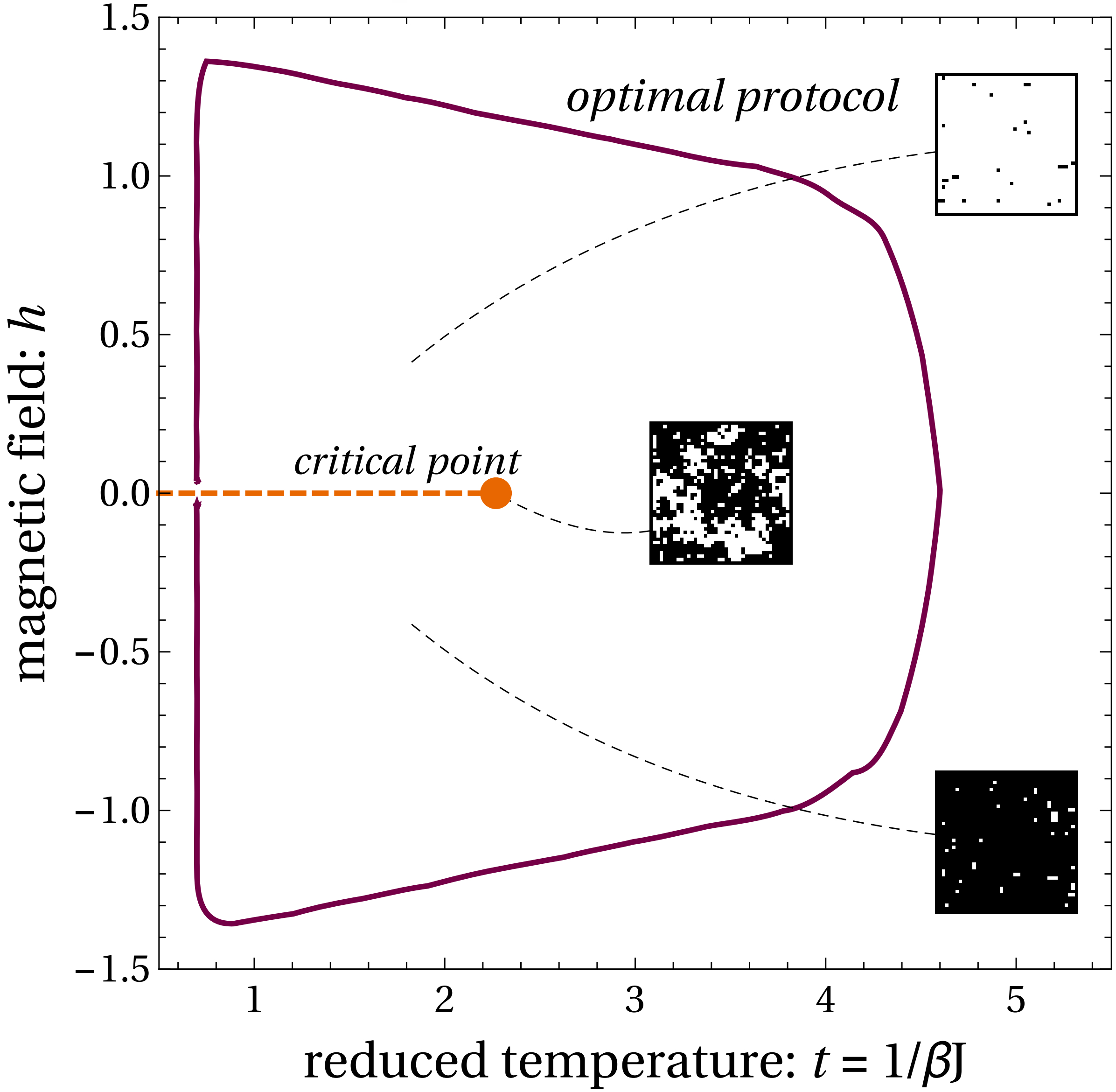
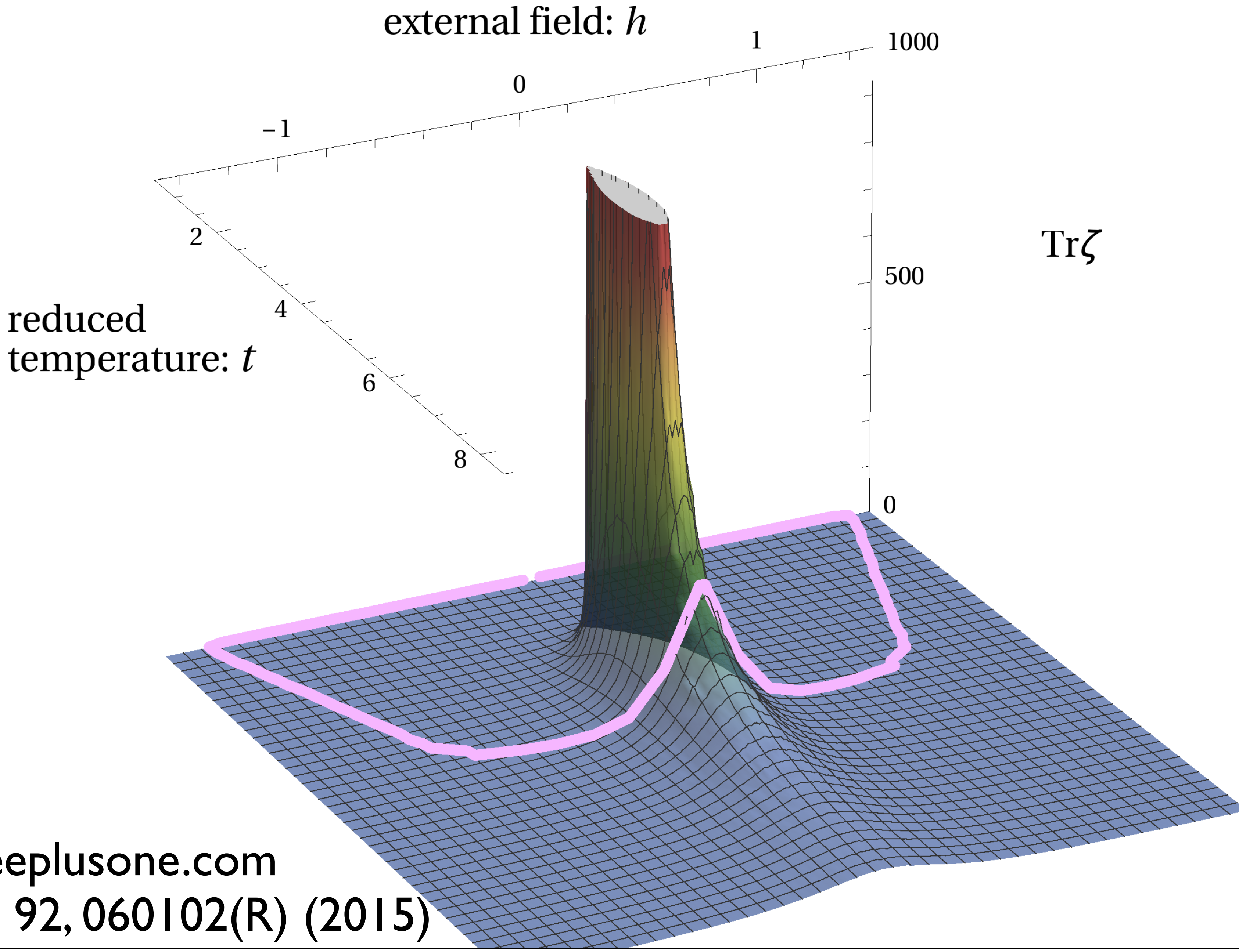


$$\frac{T - T_{\mathrm{C}}}{T_{\mathrm{C}}}$$

Minimum Dissipation Protocol (Geodesics)



Minimum Dissipation Protocol (Geodesics)



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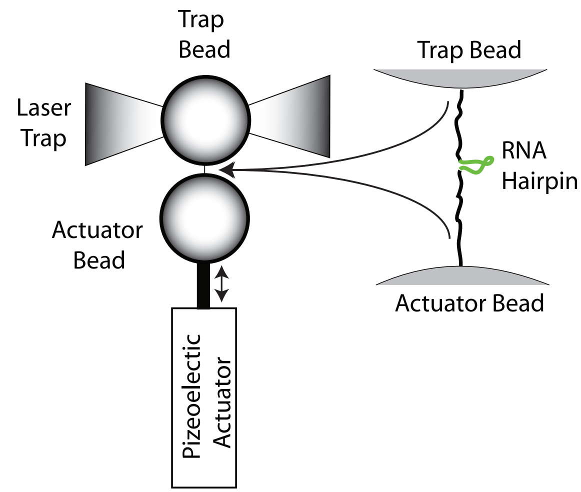
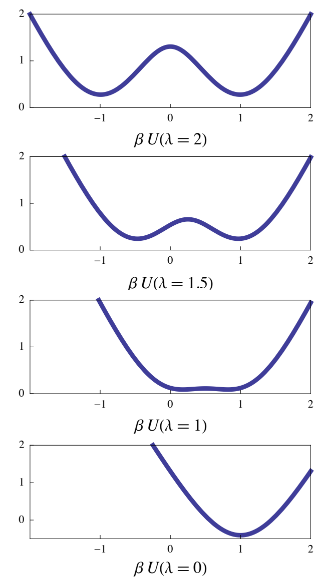
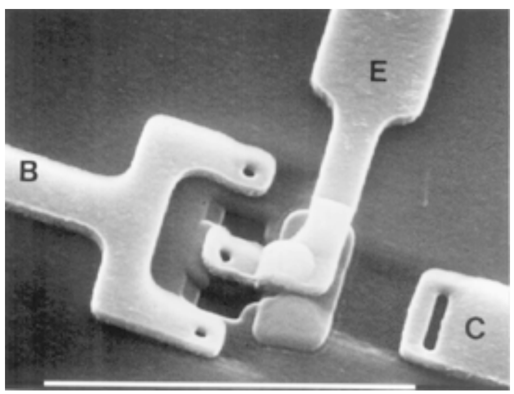
Frontiers of thermodynamic control



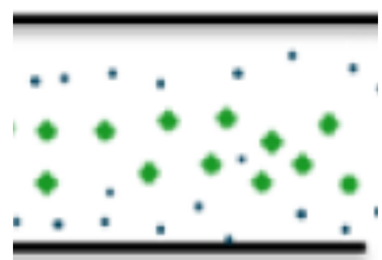
Experiments



Optimal Control



Minimum dissipation computation



Domain scale simulation