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On optimal protocols in stochastic thermodynamics

Anomalous transport: From Billiards to Nanosystems
Sperlonga, September 20-24 2010

joint work (in progress) with
Paolo Muratore-Ginanneschi, U of Helsinki
Carlos Mejía-Monasterio, U of Helsinki & Madrid

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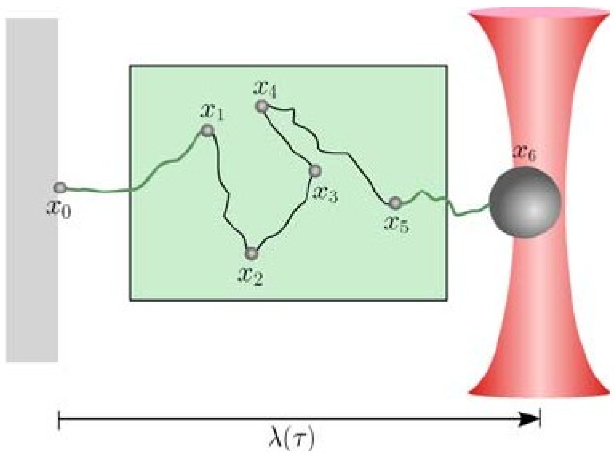
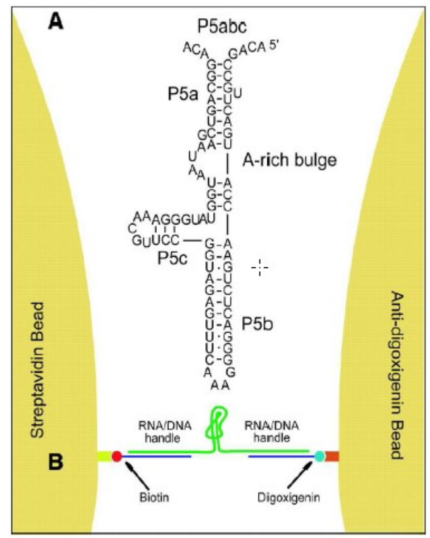
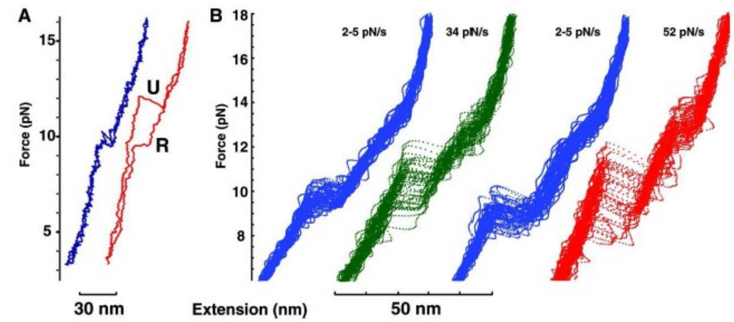
Thermodynamics of small systems





(a)



(b)

Xu Zhou, 2008 Nature blogs   J. Liphardt et. al., Science 296, 1832, 2002

Contributions by Jarzynski, Crooks, Bustamante, Ritort, Peliti, Imparato, Seifert, Rondoni, Vulpiani, Puglisi, Kurchan, Gawedzki, Lebowitz, *and many others*

PHYSICAL REVIEW E VOLUME 56, NUMBER 5 NOVEMBER 1997

Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach

C. Jarzynski*
Theoretical Astrophysics, T-6, MS B288, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 18 June 1997)

In has recently been shown that the Helmholtz free-energy difference between two equilibrium configurations of a system may be obtained from an ensemble of *finite-time* (nonequilibrium) measurements of the work performed in switching an external parameter of the system. Here this result is established, as an identity, within the master equation formalism. Examples are discussed and numerical illustrations provided. [S1063-651X(97)10710-3]

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

"The free energy landscape between two equilibrium states is well related to the irreversible work required to drive the system from one state to the other"

Why optimization & optimal protocols?

Jarzynski estimator unbiased for exponentiated Free energy diff.

$$< e^{-\beta W} >_S \equiv \tfrac{1}{S} \sum_{i=1}^{S} e^{-\beta W^{(i)}} \qquad E\left[< e^{-\beta W} >_S\right] = \tfrac{1}{S} \sum_{i=1}^{S} E\left[e^{-\beta W^{(i)}}\right] = e^{-\beta \Delta F}$$

But has a statistic error, scaling with sample number S

$$E\left[\frac{1}{S} \sum_{i=1}^{S} (e^{-\beta W^i} - e^{-\beta \Delta F})^2\right] = (E\left[e^{-2\beta W}\right] - e^{-2\beta \Delta F})/S \quad \textbf{(protocol dep.)}$$

NB: Jarzynski estimator is biased for the Free energy difference

$$< W >_S \equiv \tfrac{1}{S} \sum_{i=1}^{S} W^{(i)} \qquad E\left[< W >_S\right] = E\left[W\right] \geq \Delta F$$

Other motivation(s) for optimization

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If you admit for single small systems (the example will follow)

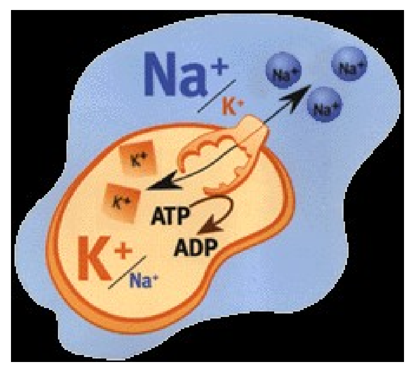
$$\delta W = dU + \delta Q \qquad \Rightarrow \qquad <\delta W> = <dU> + <\delta Q>$$

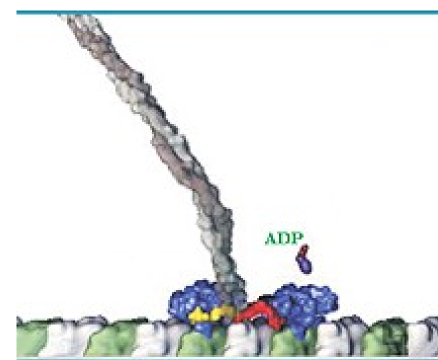
and if the initial and final states are known $\delta W = \Delta F + W_{diss}$

then the expected dissipated work is $<W_{diss}> = <\delta Q> + T\Delta S$

Minimizing expected dissipated work is maximizing efficiency of the small system

Molecular machines have quite high efficiency: Kinesin – 60%
Ion pump on membrane – 70%





Xu Zhou, 2008 Nature blogs

Which optimization tasks? What to optimize? Which constraints?

What to optimize: some expectation value over the paths

$$E[W] \qquad Var[W] \qquad E\left[e^{-2\beta W}\right] \qquad E[Q]$$

Which constraints

Class I: given initial and final states

For instance, equilibrium at the same T but different potentials. Connected to Schrödinger ”Über die Umkehrung des Naturgesetze”, *Sitzung der Preuss. Akad. Wissen. Berlin* **144** (1931); and to Guerra & Morato (1983); Dai Pra (1991)

Class II: given initial state and final control

Schmiedl & Seifert, *Phys. Rev. Lett.* **98** (2007); Gomez-Marin, Schiedl & Seifert, *J. Chem. Phys.* **129** (2008); Then & Engel, *Phys Rev* **E77** (2008).

What is stochastic thermodynamics?

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$$\dot{\xi}_t = -\frac{1}{\tau}\partial_\xi V(\xi_t,\lambda_t) + \sqrt{2/\tau\beta}\,\dot{\omega}_t$$ **(Langevin Equation)**

$$V(\xi_t; t < t_i) = U(\xi_t)$$ **(no control before initial time)**

$$V(\xi_t; t > t_f) = \tilde{U}(\xi_t)$$ **(no control after final time)**

$$\dot{\xi}_t \cdot (-\partial_\xi V) = \tau\dot{\xi}_t \cdot (\dot{\xi}_t - \sqrt{2/\tau\beta}\,\dot{\omega}_t)$$ **(Stratonovich)**

$$W = \int_{t_i}^{t_f} \dot{\lambda}_t \cdot \partial_\lambda V(\xi_t,\lambda_t) \qquad Q = \int_{t_i}^{t_f} \tau\dot{\xi}_t \cdot (\dot{\xi}_t - \sqrt{2/\tau\beta}\,\dot{\omega}_t)$$

$$W - Q = \tilde{U}(\xi_f) - U(\xi_i) = \Delta U$$

Sekimoto *Progr. Theor. Phys.* **180** (1998); Seifert *PRL* **95** (2005)

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Class I: minimizing expected released heat with given initial and final states

$$\Pr(\xi_i \in [x_i, x_i + dx_i]) = \mu_i(dx_i) \quad \Pr(\xi_f \in [x_f, x_f + dx_f]) = \mu_f(dx_f)$$

Re-writing Q with the Ito convention gives, in expectation:

$$E\left[Q \mid \mu_i, \mu_f\right] = \int_{t_i}^{t_f} \frac{dt}{\tau} (<|b|^2 - T\partial_\xi \cdot b>) \qquad b = -\partial_\xi V(\xi_t, \lambda_t)$$

b **(for short) is the stochastic control of the Langevin equation**

$$\dot{\xi}_t = \frac{1}{\tau} b + \sqrt{2/\tau\beta}\,\dot{\omega}_t$$

which gives a forward Fokker-Planck equation for the density

$$\partial_t m + \frac{1}{\tau} \partial_x (bm) = \frac{1}{\beta\tau} \partial_x^2 m \qquad m(x, t_i) dx = \mu_i(dx)$$

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Class I: minimizing expected released heat with given initial and final states

Density evolution, forward Fokker-Planck

t_i → t_f

$\mu_i(dx_i)$ **Optimal control, Bellman equation** $\mu_f(dx_f)$

$$-\partial_t S = \frac{(|b|^2 + T\partial \cdot b)}{\tau} + \frac{(b\cdot\partial)S}{\tau} + \frac{1}{\tau\beta}\partial^2 S$$

t, x

$\mu_f(dx_f)$

$t - dt, y$

$$\bar{S}(t) = \int m(x,t) S(x,t;\mu_f)\,dx$$

$$E[Q \mid \mu_i, \mu_f] = \bar{S}(t_i)$$

$$b^* = \partial R - \partial S \quad R = T \log m$$

Problem: b^* depends both on the forward and the backward proceses

Class I: minimizing expected released heat with given initial and final states

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$$R = T \log m \qquad \partial_t m + \partial_x [\frac{\partial_x (R-S)}{2\tau} m] = \frac{1}{\beta\tau}\partial_x^2 m$$

$$[\partial_t + \frac{\partial_x (R-S)}{2\tau}\partial_x + \frac{1}{\tau\beta}\partial_x^2]S = -\frac{|\partial_x (R-S)|^2}{4\tau} - \frac{1}{2\beta\tau}\partial_x^2 (R-S)$$

$$\psi = -\frac{1}{2\tau}(S+R)$$

$$v = \partial_x \psi$$

$$\partial_t v + (v\cdot\partial)v = 0$$

$$\partial_t m + \partial\cdot(vm) = 0$$

Burgers' equation and mass transport by Burgers' field

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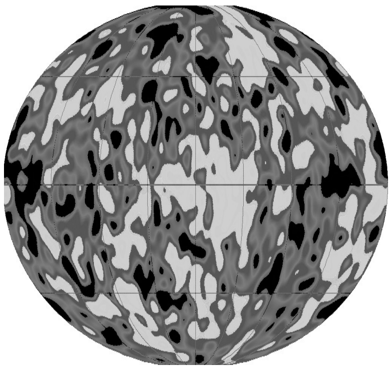
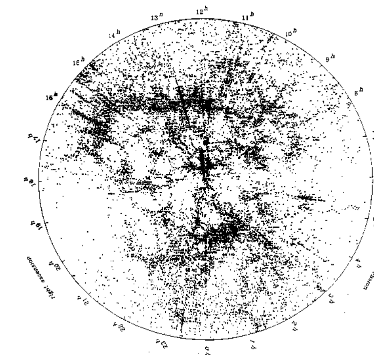
Burgers' equation with initial and final densities is a problem we know well



$$a, t_i \longleftrightarrow x, t_f$$

$$\det\left(\frac{\partial x}{\partial a}\right) = \frac{m_f(x)}{m_i(a)}$$



$$v_0(a, t_i) = \partial_a \psi_0(a) \qquad a(x) = \arg\max\left[\psi_o(a) - \frac{(x-a)^2}{2\Delta t}\right]$$

$$v(x, t_f) = v_0(a, t_i) = \frac{x - a(x)}{\Delta t}$$

Valid as long as there are no shocks in the field

Monge-Ampère-Kantorovich Reconstruction of the early Universe

Frisch et al *Nature* (2002), **417** 260; Brenier et al *MNRAS* (2003), **346** 501

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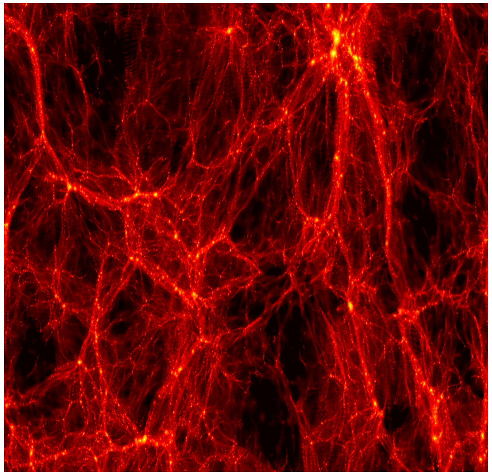
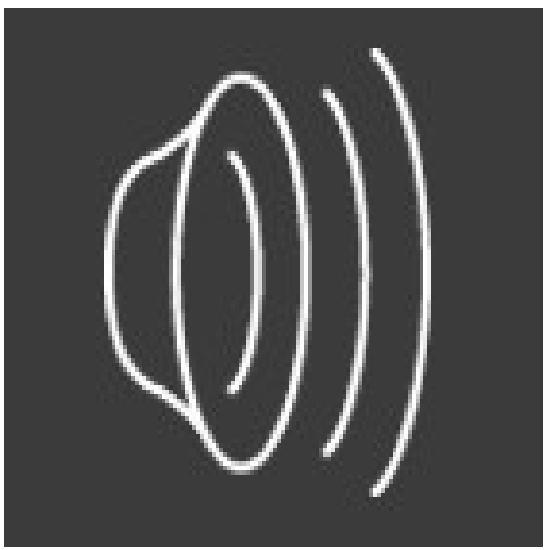
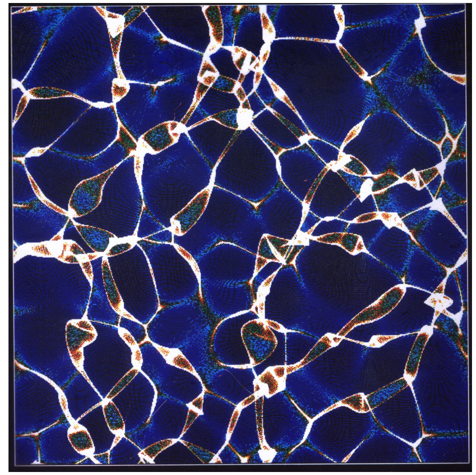
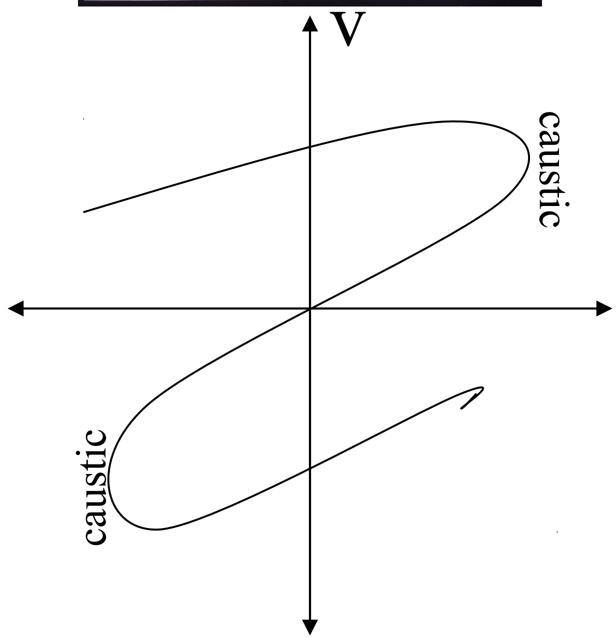
« True » equations of early Universe



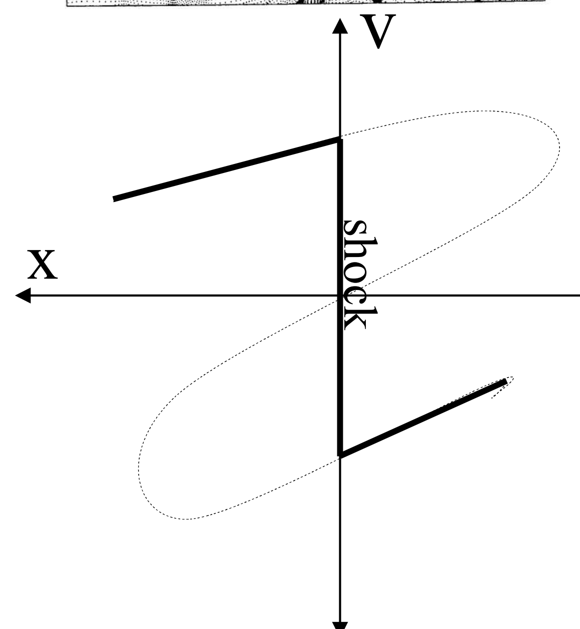


« Zeldovich » approximation





« Burgers » equation and mass transport



Courtesy Sobolevskii & Mohayaee

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MAK-reconstruction applied to optimal protocols in stochastic thermodynamics

One can now express released heat from initial to final state as

$$< Q^* >_i^f = \tau \Delta t < v_0^2 >_i + TS_i - TS_f$$

In relaxation, no work is done: $< Q >_f^{rel} =< \tilde{U} >_f - < \tilde{U} >_{rel}$

So using the equivalence $< W >=< U > + < Q >$

We have also $< W^* >_i^{rel} = \tau \Delta t < v_0^2 >_i + F_f - F_i$

Since $F_f - F_i =< \tilde{U}(a + v_0 \Delta t) - U(a) - T \log(1 + \Delta t \partial_a v_0) >_i$

It should also be possible to optimize over final state *f* (Class II)

Comparison with Seifert’s examples

T. Schield & U. Seifert ”Optimal Finite-time processes in stochastic thermodynamics”, *Phys Rev Lett* **98** (2007): 108301

We have not worked this out yet.....

(that’s why this is work in progress...)

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Some other problems can be solved this way also (but not easily)

Mimimizing the statistical error of the Jarzynski estimator

$$E\left[e^{-2\beta W}\right]$$

Can be turned into a non-linear transport problem

$$\partial_t m + \frac{2}{\tau}\partial_x \cdot [(\partial_x \log\phi)m] = 0$$

$$\partial_t \phi - \frac{2}{\tau}\partial_x \cdot [(\partial_x \log m)\phi] = 0$$

Which is a bit more difficult than mass transport by Burgers' eq.

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Conclusions and open problems

Work out the mixed backward-forward equations for other problems in stochastic thermodynamics.

Are there other examples that are as solvable as Burgers' eq.?

Compare to Seifert's state-independent protocols for the harmonic trap (shame on us, we have not done so as yet).

What do shocks and caustics in the optimal control problem mean for stochastic thermodynamics?

Does any of this generalize to other systems *e.g.* jump processes?

Thanks to

Collaborators on the project

Paolo Muratore-Ginanneschi

Carlos Mejía-Monasteiro

For posing and framing the problem

Udo Seifert

For contributing slides

Xu Zhou (through Nature blogs)

Andrei Sobolevskii & Roya Mohayaee

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