中国高能核物理网络论坛
HIGH ENERGY NUCLEAR PHYSICS IN CHINA

Mesoscopic Statistical Thermodynamics : From Classical to Quantum and Relativistic

Haitao Quan (全海涛)

July 3rd 2025

School of Physics, Peking University

outline

- Classical Thermodynamics

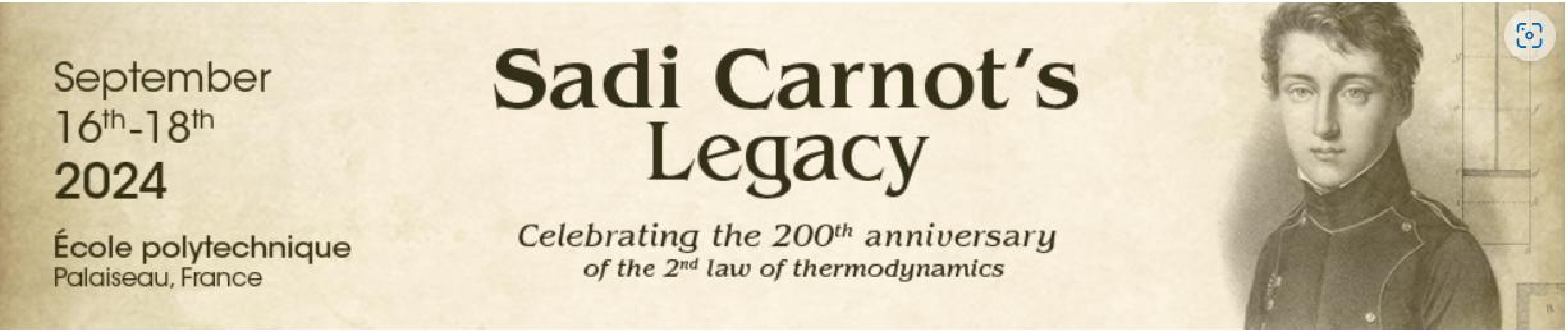
- Stochastic Thermodynamics and Fluctuation Theorems

- Stochastic Thermodynamics and Quantum Thermodynamics

- Stochastic Thermodynamics and Finite-Time Thermodynamics

- Stochastic Thermodynamics and and Special Relativity

- Summary



FR EN

Connexion

NAVIGATION

- Accueil
- **Programme & orateurs**
- Schedule
- Session poster
- Gala event
- Comité scientifique
- Sponsors
- Mon inscription
- Accès & logisitique

PROGRAMME & ORATEURS

Presentations are intended to bring together the thermodynamics community at large. They will give a pedagogical introduction and overview of diverse aspects of the field. As a silverline, each talk will start from the second law: how is it expressed and used in this context?

Presentation will be 40' long. A round table will be held at the end of each session for general discussion and perspectives.

Long breaks for lunch and coffee will allow further exchanges. Posters will be presented during these breaks to support discussions.

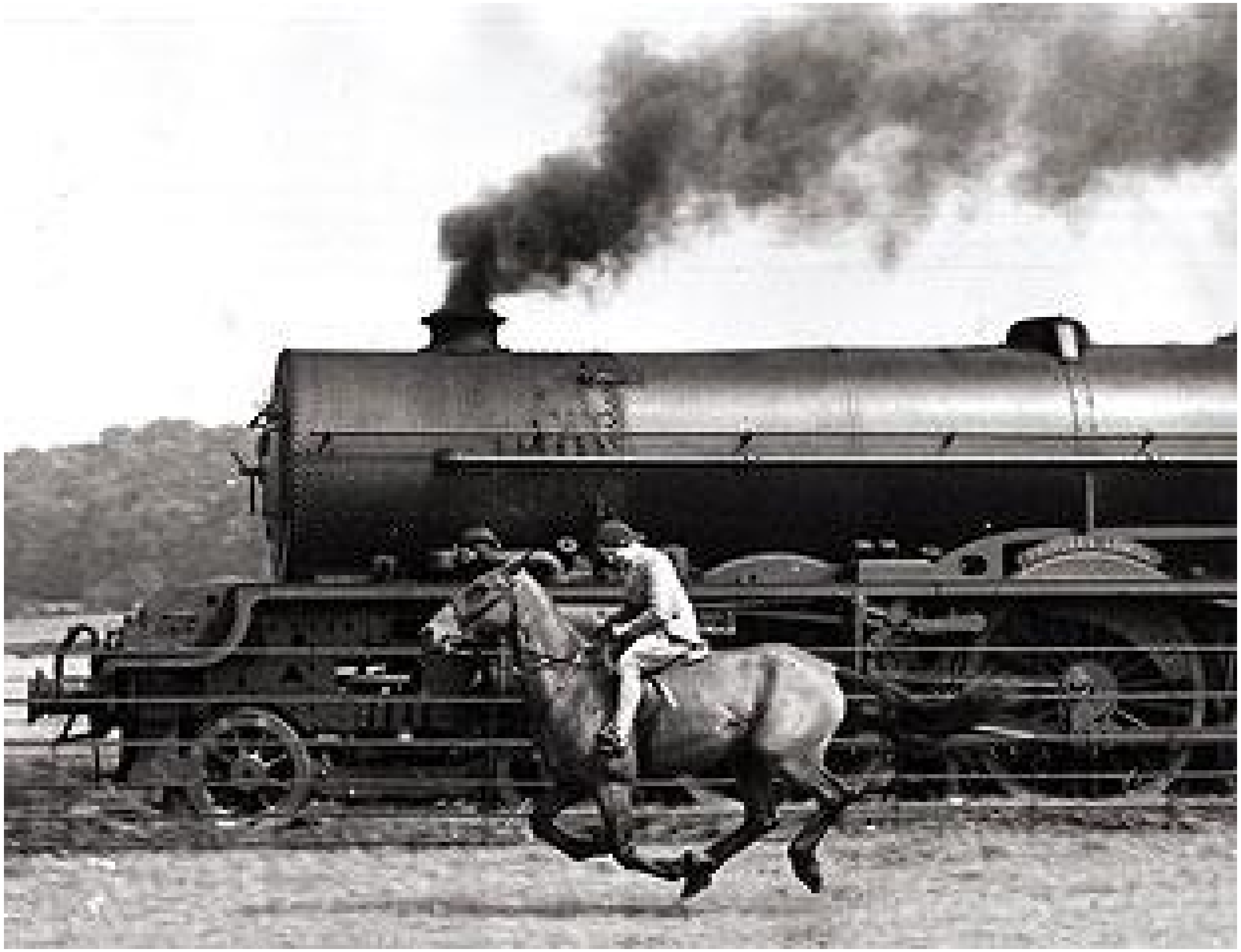
Program overview & confirmed speakers

Session: Introduction

- History: "Reflexions sur la puissance motrice du feu", Sadi Carnot, 1824
    - *Raffaele Pisano (HOPAST at IEMN, Departement of Physics, University of Lille-CNRS, France)*
- Physics: The many faces of entropy
    - *Christophe Goupil (Université Paris Cité, LIED, France)*

[Sadi Carnot's Legacy - Celebrating 200 years of thermodynamics - Sciencesconf.org]()

Classical thermodynamics



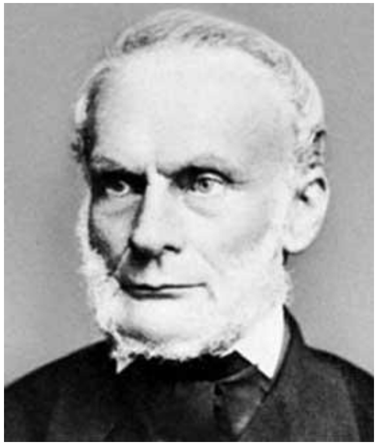
Thermodynamics is a phenomenological theory
Not relevant to quantum or classical,
Not relevant to relativistic or non-relativistic

Background and motivation

Thermodynamics of the 19th century

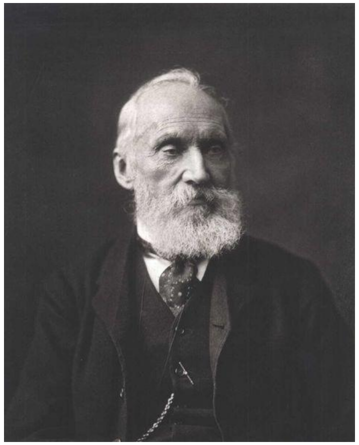
Large system: many degrees of freedom,
many particles,
average values,
vanishingly small fluctuation,
near equilibrium process,

Sadi Carnot



Rdolf Clausius

James Joule



William Thomson

- Perspective

1820 $\simeq$ 1850	classical thermodynamics	$dW = dU + dQ$ $dS \geq 0$
$\simeq$ 1900	eq stat phys	$p_i = \exp[-(E_i - F)/k_B T]$
1930 $\simeq$ 1960	non-eq: linear response	Onsager Green-Kubo, FDT
$\geq$ 1993	non-eq: beyond linear response stochastic thermodynamics	Fluctuation theorem Jarzynski relation

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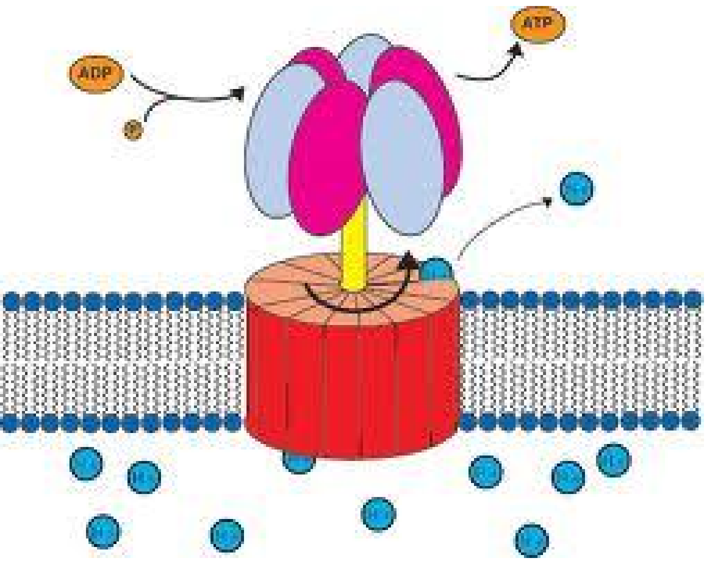
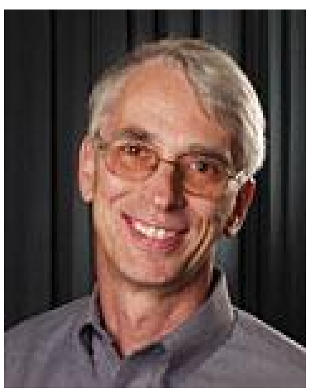
Thermodynamics of the 21th century



Mark Haw, Physics World, **20**, No 11, 25, 2007.

Small system: few degrees of freedom,
single particles,
ample fluctuations,
quantum effects,
non-equilibrium process,

Magnetic domains in ferromagnets: less than 300nm
Quantum dots: less than 100nm
Biological molecular machines: range from 2 to 100nm



Denis Evans

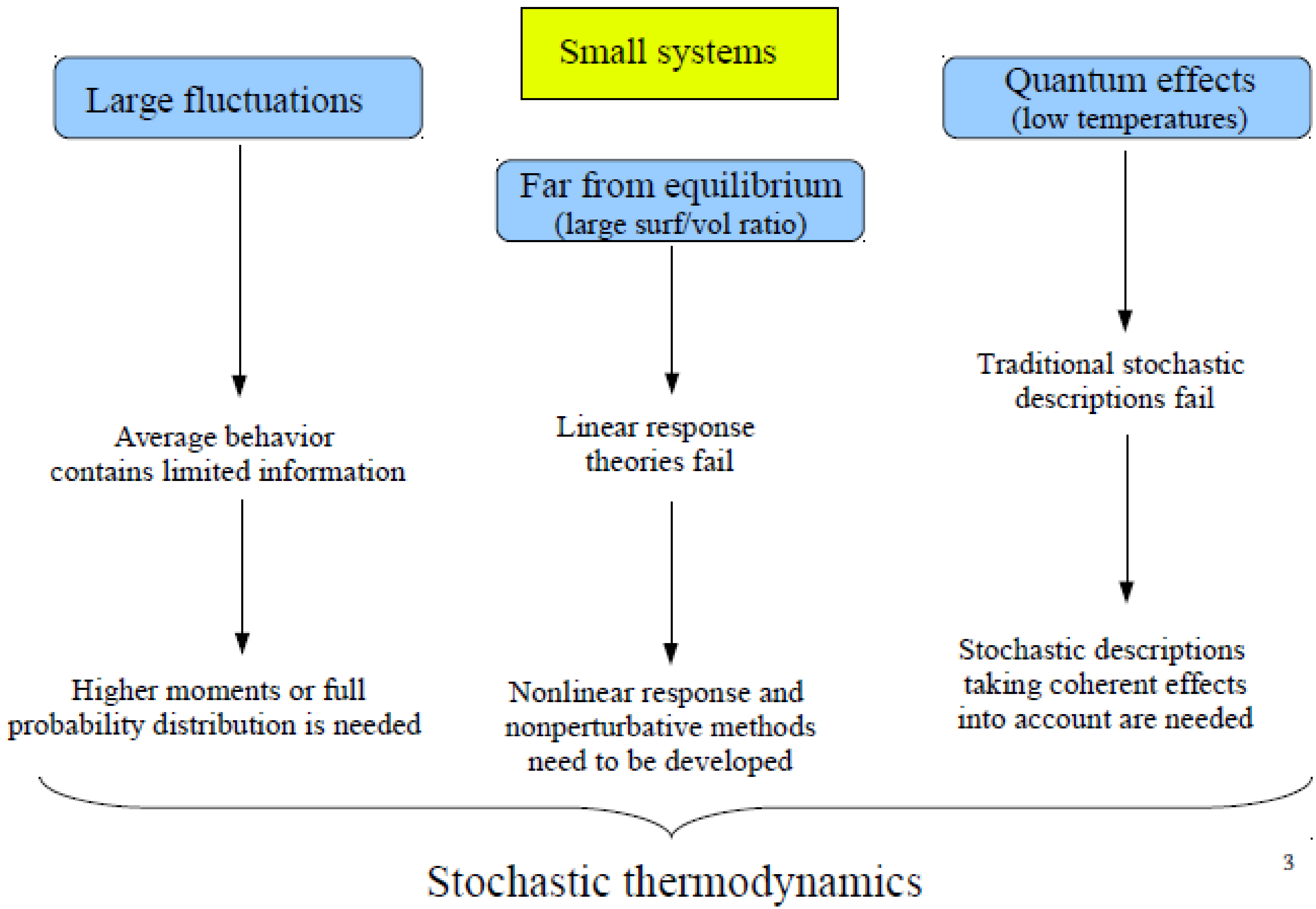
Christopher Jarzynski

Gavin Crooks

Ken Sekimoto

Udo Seifert

Challenges when dealing with small systems



Key point: introduction of the equation of motion

Microscopic work and heat along trajectories

Textbook definition of work:

$$\delta W = \int F(L)\, dL$$

Modern definition of work:

$$\delta W = \int \frac{\partial H_\lambda(\Gamma)}{\partial \lambda} \dot{\lambda}\, dt \qquad \delta Q = \int \frac{\partial H_\lambda(\Gamma)}{\partial \Gamma} \dot{\Gamma}\, dt \qquad \Gamma = (x, y)$$

The first law along trajectories:

$$dU = \delta Q + \delta W = H_{\lambda_1}(\Gamma_1) - H_{\lambda_0}(\Gamma_0)$$

Reproducing the textbook first law: $\langle dU \rangle = \langle \delta Q \rangle + \langle \delta W \rangle$

K. Sekimoto, Stochastic Energetics, Springer, (2010)

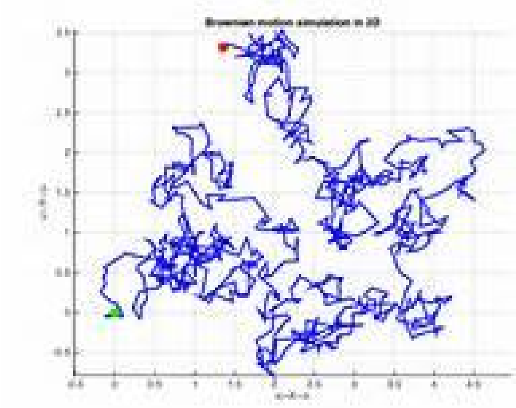
Basic notions of stochastic thermodynamics

Work, heat and Entropy as functionals of a trajectory

Work: $$dw = \frac{\partial H_\lambda(x(t))}{\partial \lambda} \dot{\lambda} dt$$

Heat: $$dq = \frac{\partial H_\lambda(x(t))}{\partial x} \dot{x} dt$$

C. Jarzynski, Phys. Rev. Lett 78, 2690 (1997)
K. Sekimoto, J. Phys. Soc. Jap. 66, 1234 (1997)



For overdamped Langevin Dynamics

$$\dot{x} = \mu F(x,\lambda) + \zeta = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta,$$

$$\langle \zeta(\tau)\zeta(\tau')\rangle = 2D\delta(\tau - \tau')$$

Heat: $$dq = (1/\mu)(\dot{x} - \zeta)dx$$

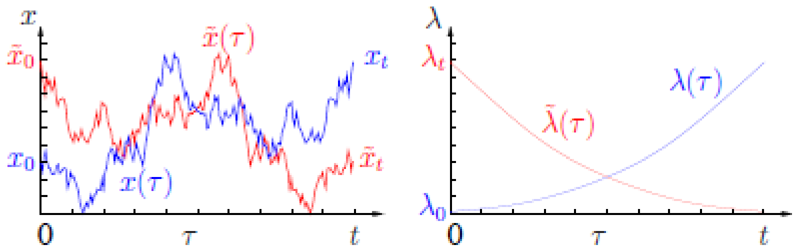
Work: $$dw = f dx + \partial_\lambda V(x,\lambda) d\lambda$$

Ken Sekimoto, Stochastic Energetics (2010)

- Path integral representation
  - "Boltzmann factor for a whole trajectory"

$$p[\zeta(\tau)] \sim \exp\ [-\int_0^t d\tau\ \zeta^2(\tau)/4D]$$

$$p[x(\tau)|x_0] \sim \exp\ [-\int_0^t d\tau\ (\dot{x}-\mu F)^2/4D]$$



Lars Onsager

  - "time reversal" $\tilde{x}(\tau) \equiv x(t-\tau)$ and $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$
  - Ratio of forward to reversed path

$$\frac{p[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} = \frac{\exp\ [-\int_0^t d\tau\ (\dot{x}-\mu F)^2/4D]}{\exp\ [-\int_0^t d\tau\ (\dot{\tilde{x}}-\mu \tilde{F})^2/4D]}$$

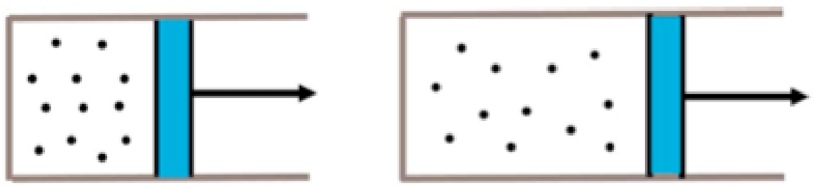
$$= \exp\ \beta\int_0^t d\tau\ \dot{x}F = \exp\ \beta q[x(\tau)] = \exp \Delta s_m$$

L. Onsager, S. Machlup, Phys. Rev. 91, 1505 (1953).

Timeline of the second law

- Maximum Work Principle (1876)

$$\langle W \rangle \geq \Delta F$$



- Fluctuation-Dissipation relation (1950)

$$\langle W \rangle - \Delta F = \frac{1}{2}\beta\sigma_W^2$$

- Jarzynski equality (1997)

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

$$\Downarrow \quad \langle e^{x} \rangle \geq e^{\langle x \rangle}$$

$$\langle W \rangle \geq \Delta F$$

- Hummer-Szabo relation (2001)

$$\left\langle \delta(\tilde{\Gamma} - \Gamma_\tau) e^{-\beta W} \right\rangle = \frac{e^{-\beta U_\tau(\tilde{\Gamma})}}{Z_0}$$

- Crooks Fluctuation Theorem (1998)

$$\frac{P_R(-W)}{P_F(W)} = e^{-\beta(W-\Delta F)}$$

- Differential Fluctuation Theorem (2008)

$$P_F(W, \Gamma_0 \to \Gamma_\tau) e^{-\beta(W-\Delta F)} = P_R(-W, \Gamma_\tau^* \to \Gamma_0^*)$$

Time reversed: $\overline{\lambda}_t = \lambda_{\tau - t}$

Hatano-Sasa relation

Generalization when initial condition is in a non-equilibrium steady state (NESS)

Work like functional $Y_t = \int_0^t d\tau \dot{\lambda} \frac{\partial \phi}{\partial \lambda}(x_\tau, \lambda_\tau)$ where $\phi(x, \lambda) = -\ln P_{stat}(x, \lambda)$

- Average over non-equilibrium trajectories leads to steady-state behavior

$$\langle e^{-Y_t} \rangle = 1$$

T. Hatano and S. Sasa, (2001)

Now $\langle Y_t \rangle \geq 0$ where the equality holds for a quasi-stationary process

Evans-Searles and Gallavotti-Cohen relation

1. <u>Transient fluctuation theorem of Evans-Searles</u>

- The system is initially at equilibrium and evolves towards a NESS

$$\frac{P_\tau(\Delta S)}{P_\tau(-\Delta S)} = e^{\Delta S/k_B}$$

Evans DJ, Searles DJ, (1994)

- NESS can be created from multiple reservoirs or from time-symmetric driving
- Also holds separetely for parts of entropy production under conditions

2. <u>Fluctuation theorem of Gallavotti-Cohen</u>

- The asymptotic distribution of entropy production rate $\sigma = \Delta S/\tau$ in a NESS

$$\lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{P_\tau(\sigma)}{P_\tau(-\sigma)} = \frac{\sigma}{k_B T}$$

Gallavotti G., Cohen EGD, (1995)

- Implies relations for distribution of currents in a NESS

Physics Reports 510 (2012) 1–86

Contents lists available at SciVerse ScienceDirect

Physics Reports

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Stochastic theory of nonequilibrium steady states and its applications. Part I

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非平衡态统计物理的随机数学理论

Physics Reports 510 (2012) 87–118

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Stochastic theory of nonequilibrium steady states. Part II: Applications in chemical biophysics

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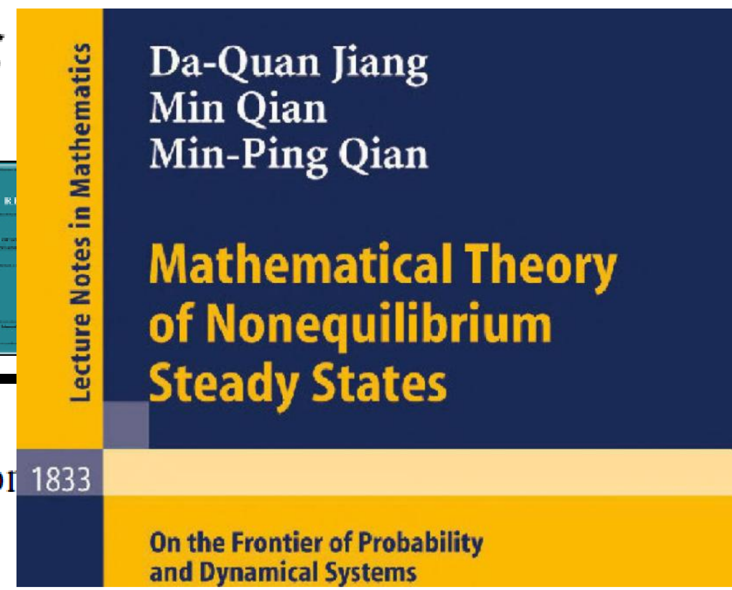
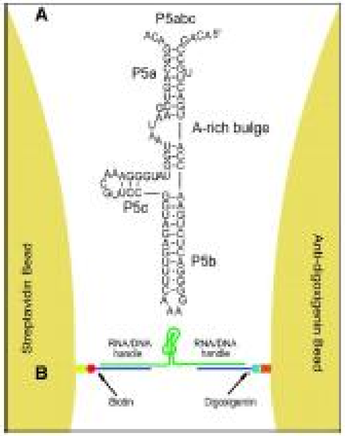
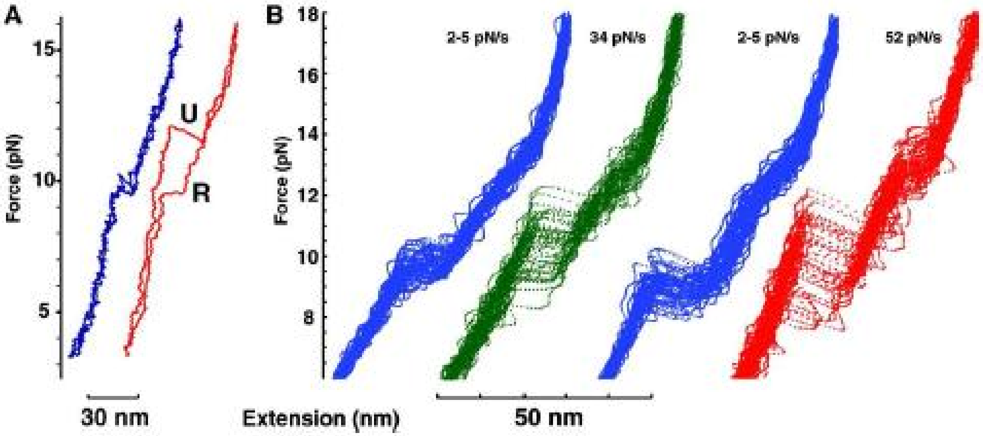


Experimental test of Jarzynski's equality

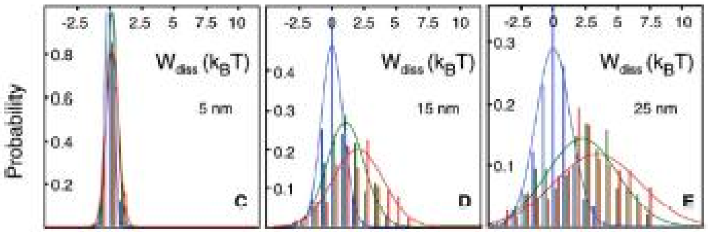
- Nano-world Experiment: Stretching RNA

  [Liphardt et al, Science **296** 1832, 2002.]





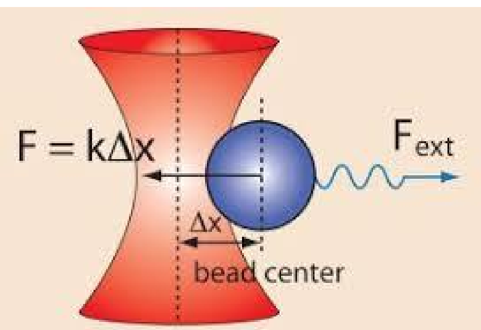
– distributions of $W_{\rm diss}$:



The Nobel Prize in Physics 2018

Arthur Ashkin
"Optical tweezer"

Key application:
Study of Stochastic thermodynamics



Ill. Niklas Elmehed. © Nobel Media

Arthur Ashkin

Prize share: 1/2

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Gérard Mourou

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Ill. Niklas Elmehed. © Nobel Media

Donna Strickland

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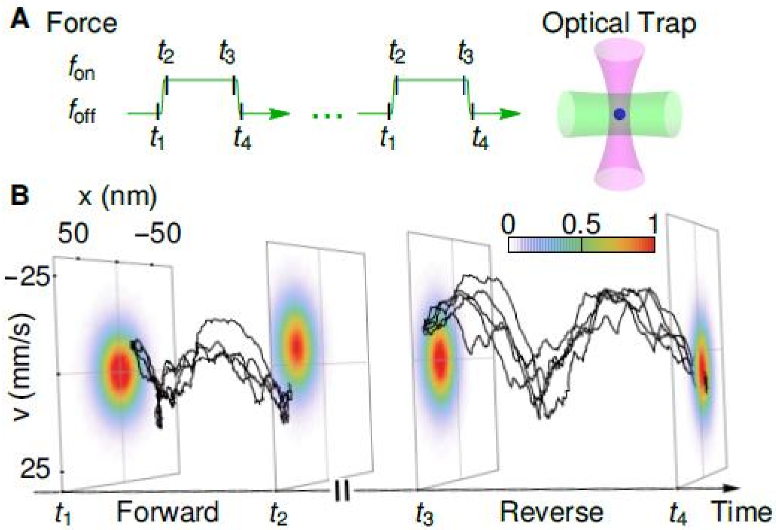
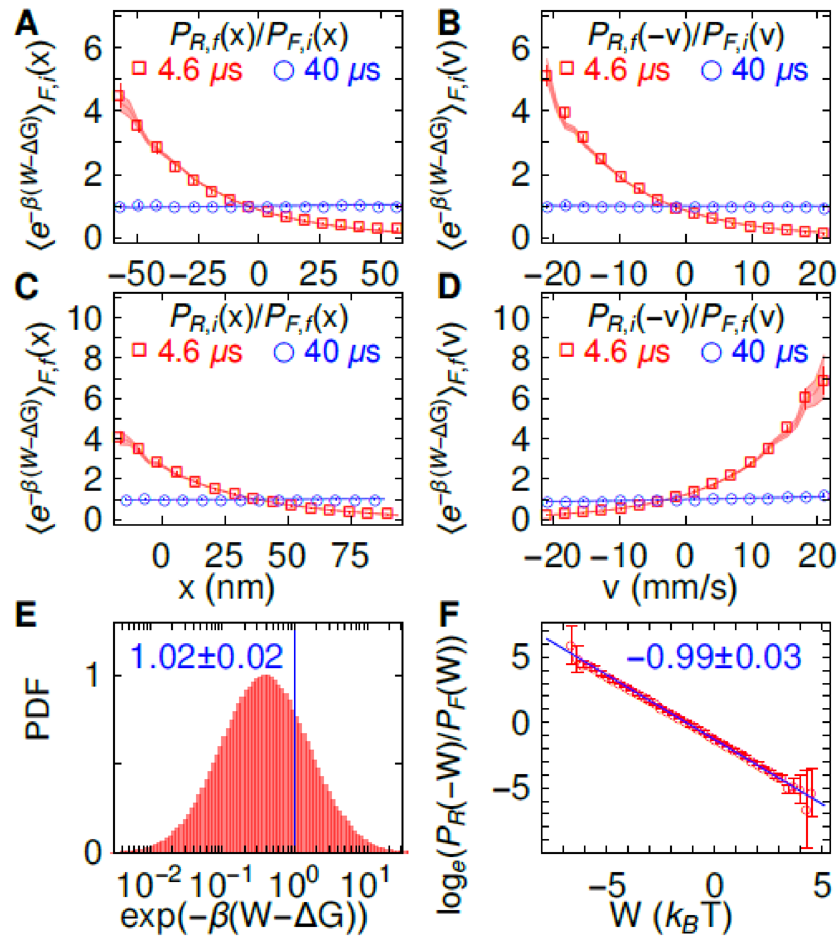
RNA molecules under mechanical force [36]. Force-extension curves for an RNA molecule were subsequently used for the first experimental test [37] of Jarzynski's equality in stochastic thermodynamics, which relates nonequilibrium work distributions to equilibrium free energy differences [38].





Physics

Synopsis: Fluctuation Theorems Tested with a Levitating Bead

February 22, 2018

*T. M. Hoang, ..., **HTQ**., and T. Li, Phys. Rev. Lett. 120, 080602 (2018)*

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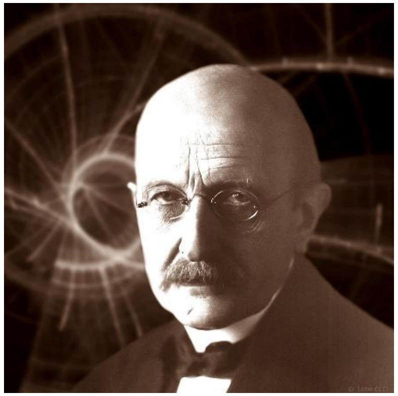
Quantum Heat Engines and Quantum Thermodynamics

The concept of “quantum” originated from Boltzmann’s hypothesis of discrete energy unit in 1872 and 1877



Planck proposed the energy quantization when he studied the blackbody radiation. Hence quantum mechanics and thermodynamics has been interweaved

Within the framework of quantum mechanics, some thermodynamic concepts can be understood in a transparent way. For example, what is work, heat and what is isothermal process.

Work and heat in discrete energy system

Hamiltonian

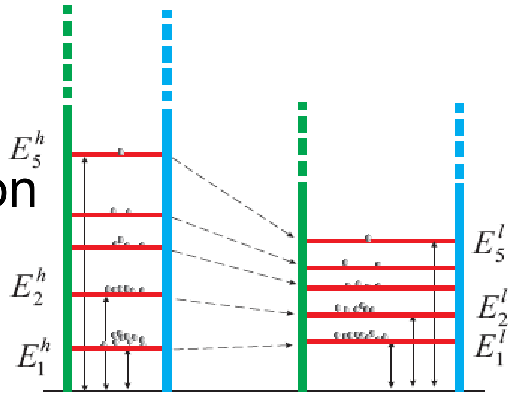
$$H = \sum_n E_n |n\rangle\langle n|$$

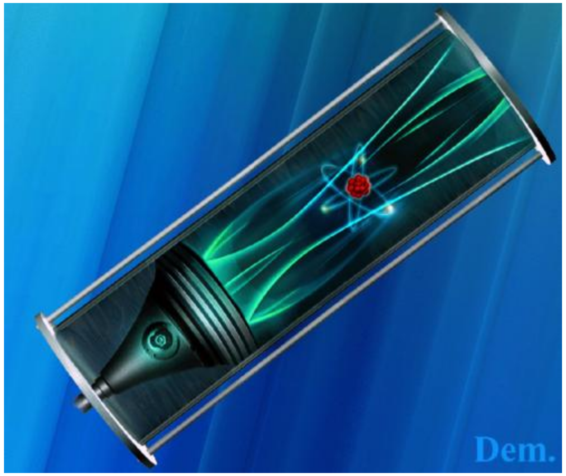
Probability distribution

$$\rho = \sum_n P_n |n\rangle\langle n|$$

Internal energy

$$U = \langle H \rangle = \sum_n P_n E_n,$$





***HTQ**, Yu-xi Liu, C. P. Sun F. Nori, Phys. Rev. E 76, 031105 (2007)*

For small systems, the second law are still valid on the ensemble level.

Work and heat in discrete energy system

First law of Thermodynamics

$$dU = \delta Q + \delta W = \sum_n TdS + Y_n dy_n .$$

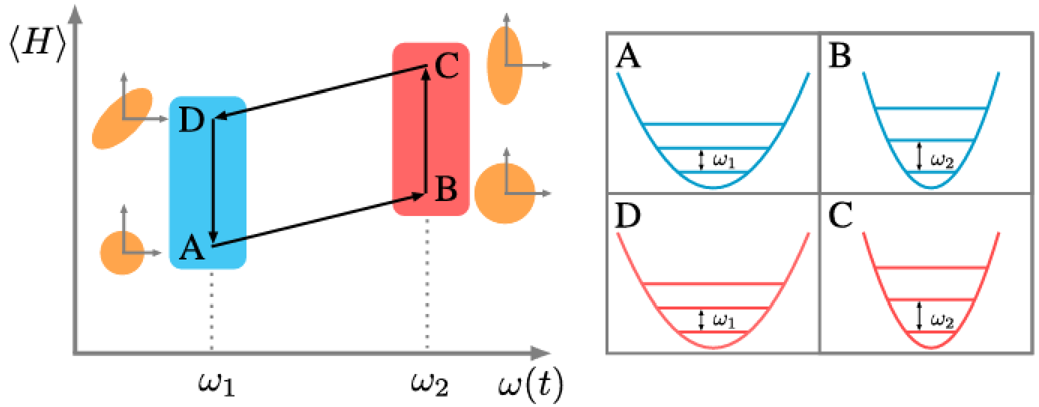
Heat: $\delta Q = \sum_n E_n \, dP_n .$ Work: $\delta W = \sum_n P_n \, dE_n .$

Pressure: $P = \dfrac{\delta W}{dL} = \sum_n P_n \dfrac{dE_n}{dL} .$ Entropy: $S = \sum_n P_n \ln P_n .$

Quantum version of the first law: $dU = \sum_n \left[E_n \, dP_n + P_n \, dE_n \right]$

***HTQ**, Yu-xi Liu, C. P. Sun F. Nori, Phys. Rev. E 76, 031105 (2007)*

Quantum Otto Cycle

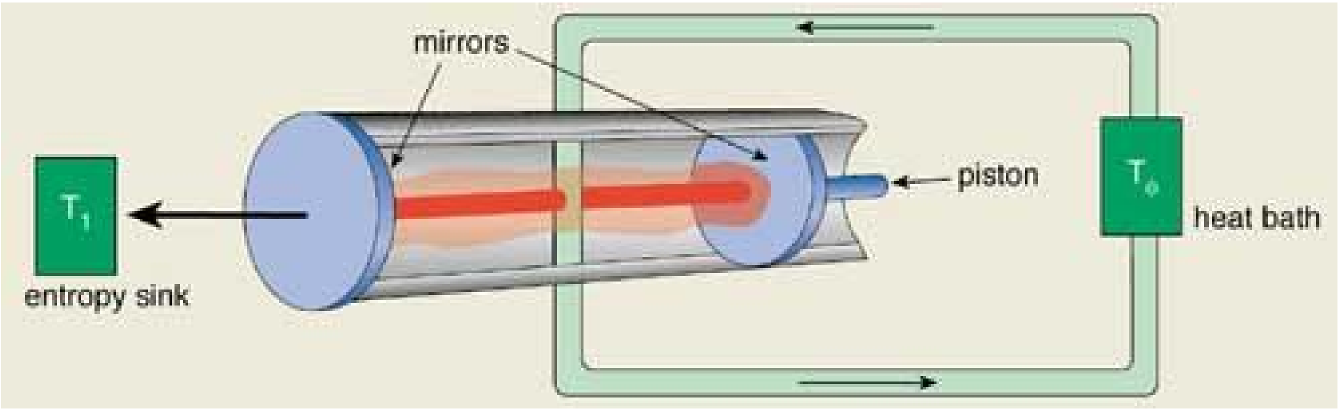


Efficiency $\eta = 1 - \frac{\omega_1}{\omega_2}$ Positive-Work condition $T_1 > 1 - \frac{\omega_2}{\omega_1} T_2$

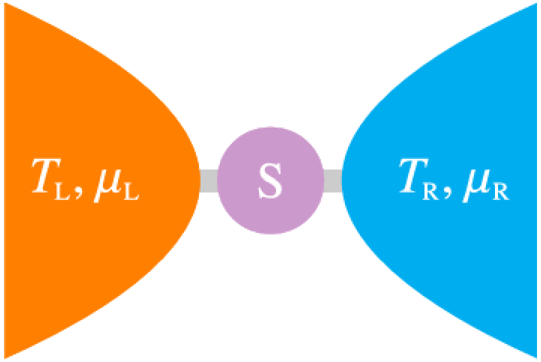
***HTQ**, Yu-xi Liu, C. P. Sun F. Nori, Phys. Rev. E 76, 031105 (2007)*

Quantum Heat Engines

Photon-
Carnot
engine



Thermoelectric
effect



Recent Review on about Quantum Heat Engines

AVS Quantum Science REVIEW scitation.org/journal/aqs

Quantum thermodynamic devices: From theoretical proposals to experimental reality

Cite as: AVS Quantum Sci. **4**, 027101 (2022); doi: 10.1116/5.0083192
Submitted: 22 December 2021 · Accepted: 22 March 2022 ·
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Nathan M. Myers,[1,2,a)] Obinna Abah,[3,b)] and Sebastian Deffner[1,4,c)]

Physics Reports 1087 (2024) 1–71

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Quantum engines and refrigerators

Check for updates

Loris Maria Cangemi[1], Chitrak Bhadra[1], Amikam Levy[*]

Department of Chemistry, Institute of Nanotechnology and Advanced Materials, Center for Quantum Entanglement Science and Technology, Bar-Ilan University, Ramat-Gan, 52900, Israel

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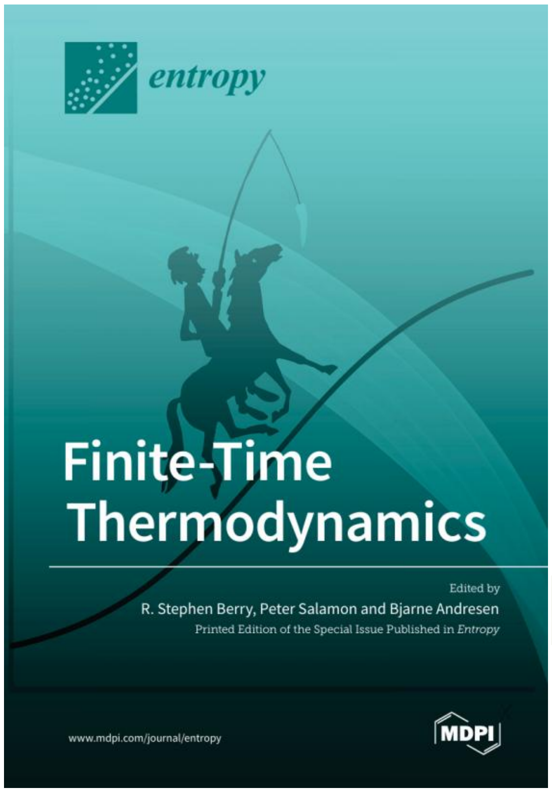
Finite-Time thermodynamics and Curzon-Ahlborn Heat Engine



Thermodynamics in finite time

Asking how well systems can perform if they are to deliver power, not just energy, leads to investigations both in abstract, fundamental thermodynamics and in almost-applicable physics, such as determining the optimal motion of a piston.

Bjarne Andresen, Peter Salamon and R. Stephen Berry

62 PHYSICS TODAY / SEPTEMBER 1984 0031-9228 / 84 / 0900 62-09 / $01.00

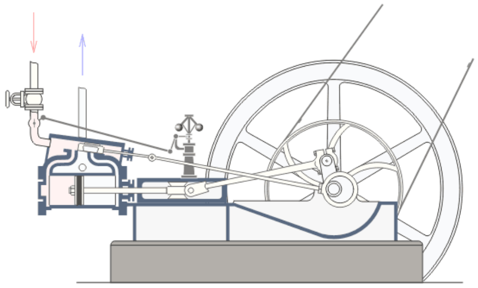
Actually we are interested in the maximum-power cycle. One question is what is the efficiency corresponding to the maximum power. This is the starting point of finite-time thermodynamics since about fifty years ago.

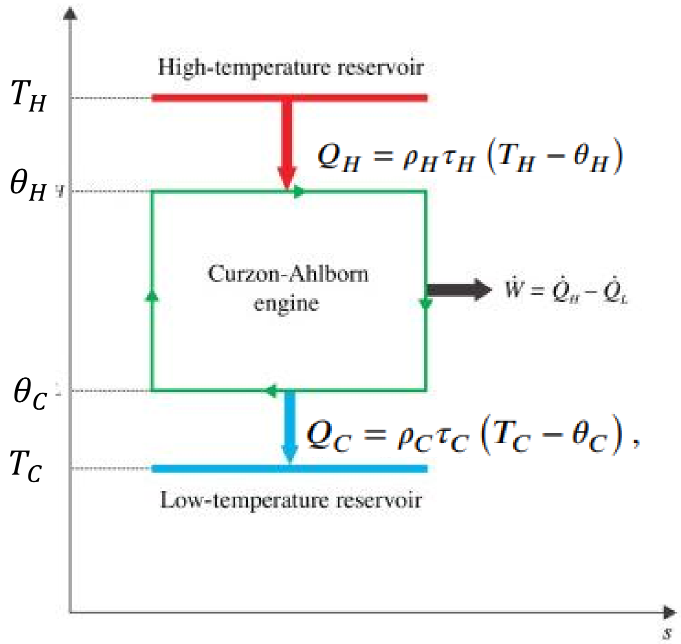
What about finite-time heat engines with finite power output?

One important property is the EMP (efficiency at maximum power). The EMP of endoreversible heat engine is

Curzon-Ahlborn efficiency

$$\eta_{CA} = 1 - \sqrt{\frac{T_C}{T_H}}$$



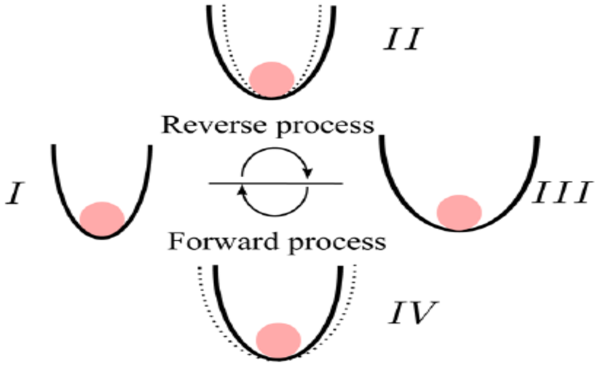


F. L. Curzon and B. Ahlborn, Am. J. Phys 43, 22 (1975).

Citation number: 2960

Application of stochastic thermodynamics: Heat engine based on a single atom

QUICK STUDY



A single-atom heat engine

Eric Lutz

The power of an engine scales with the number of particles

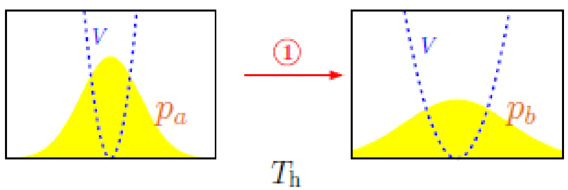
that make up its working fluid,

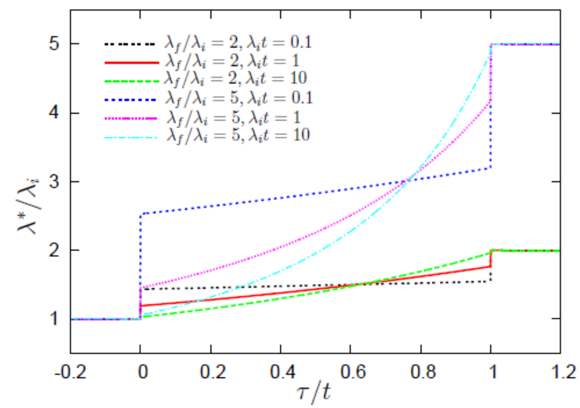
a generalization that has proven true down to a single atom.

66 PHYSICS TODAY | MAY 2020

How to achieve the maximum work output in an isothermal process for a fixed period of time?

What work protocol will lead to the maximum work output? optimization



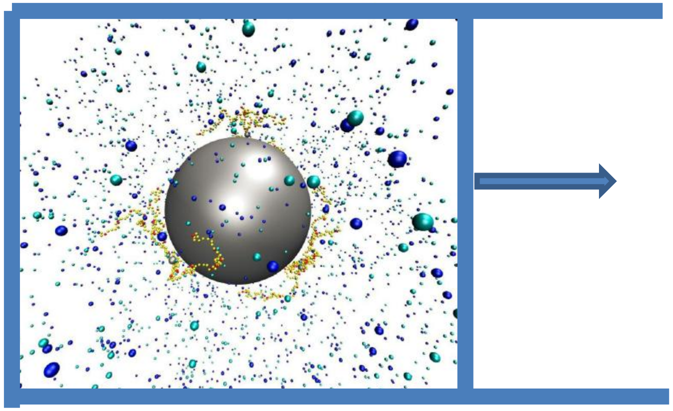


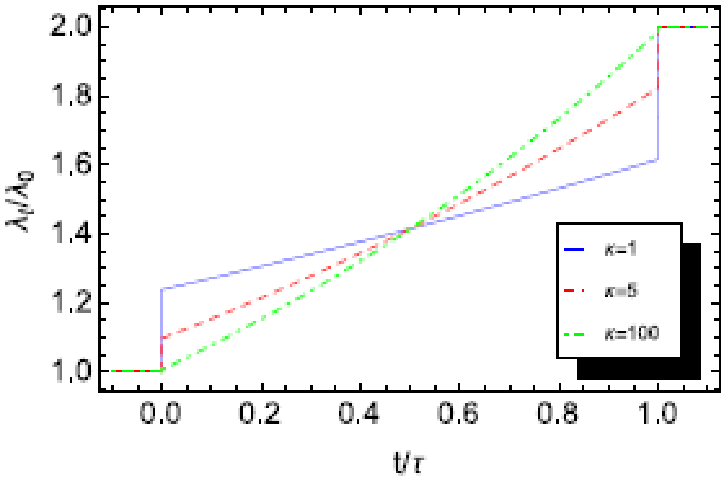
A harmonic oscillator with a varying stiffness

T. Schmiedl and U. Seifert, Phys. Rev. Lett., 98, 108301 (2007)

How to achieve the maximum work output in an isothermal process for a fixed period of time?

What work protocol will lead to the maximum work output? optimization



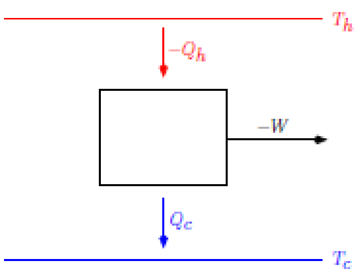


Optimal protocol for the piston system: $\lambda_t = \lambda_0 2^{t/\tau}$

*Zongping Gong, Yueheng Lan, and **HTQ**, Phys. Rev. Lett, 117, 180603 (2016)*

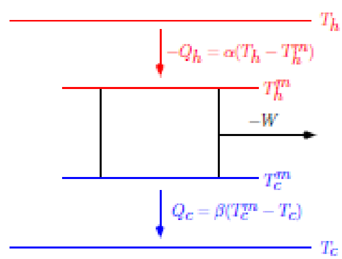
Efficiency at the maximum power of a Carnot cycle

– Carnot (1824)



– $\eta_c \equiv 1 - T_c/T_h$
but zero power

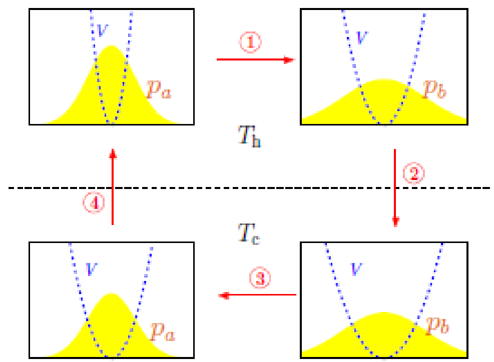
– Curzon-Ahlborn (1975)



– efficiency at maximum power
$\eta_{ca} \equiv 1 - \sqrt{T_c/T_h}$
– recent claims for universality(?)
– what about fluctuations?

Brownian heat engine at maximal power

[T. Schmiedl and U.S., EPL **81**, 20003, (2008)]

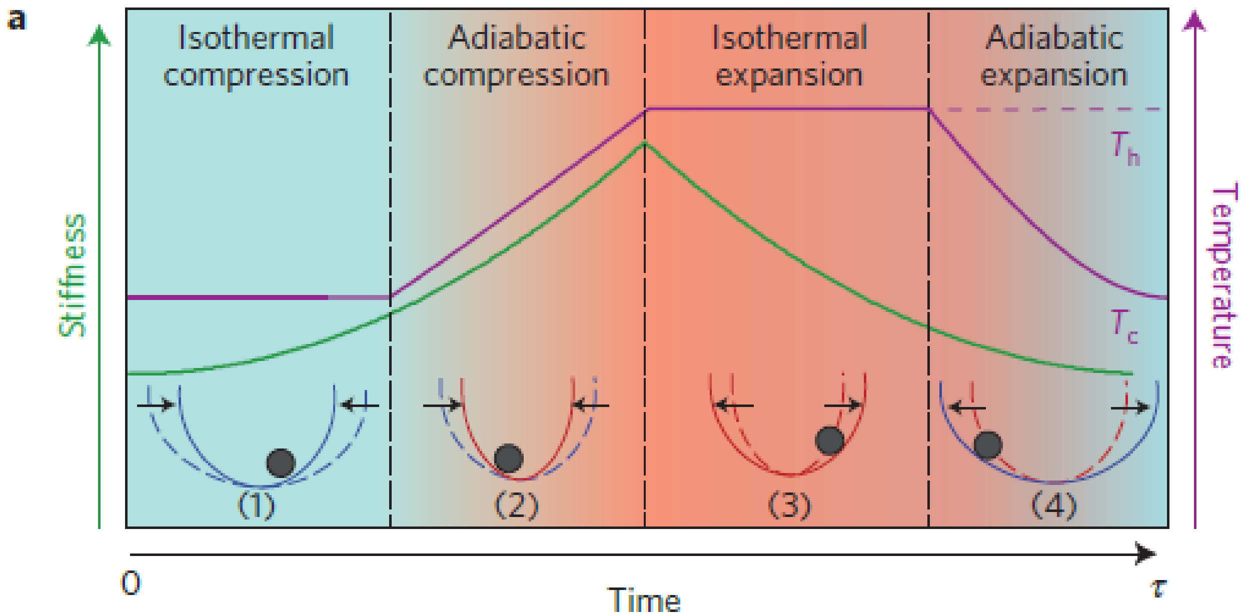


– Curzon-Ahlborn neither universal nor a bound

T. Schmiedl and U. Seifert, Europhys. Lett., 81, 20003 (2008)

Realizing Carnot heat engine with a single Brownian particle in a potential

Carnot cycle based on a single Brownian particle in an externally controlled potential



V. Blickle and C. Bechinger, Nat. Phys. 8, 143 (2011).
I. A. Martínez, É. Roldán, L. Dinis, D. Petrov, J. M. R. Parrondo, and R. A. Rica, Nat. Phys. 12, 67 (2015).

Realizing Curzon-Ahlborn heat engine with a single Brownian particle in a potential

Working substance: single Brownian particle in an external potential. Work is done when tuning the potential

$$E = m\dot{x}^2/2 + U(x,t)$$

$$\mathcal{U}(x,t) = k(t)x^{2n}/(2n)$$

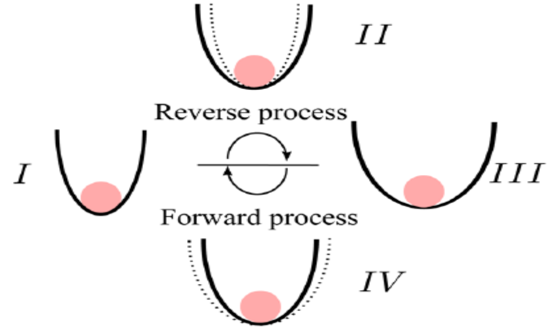
$$\ddot{x} + \gamma_i \dot{x} + 2nk(t)x^{2n-1} = \frac{1}{m}\xi(t)$$

In the underdamped limit, the period of the Brownian particle satisfies

$$\tau \ll \gamma_i^{-1},$$

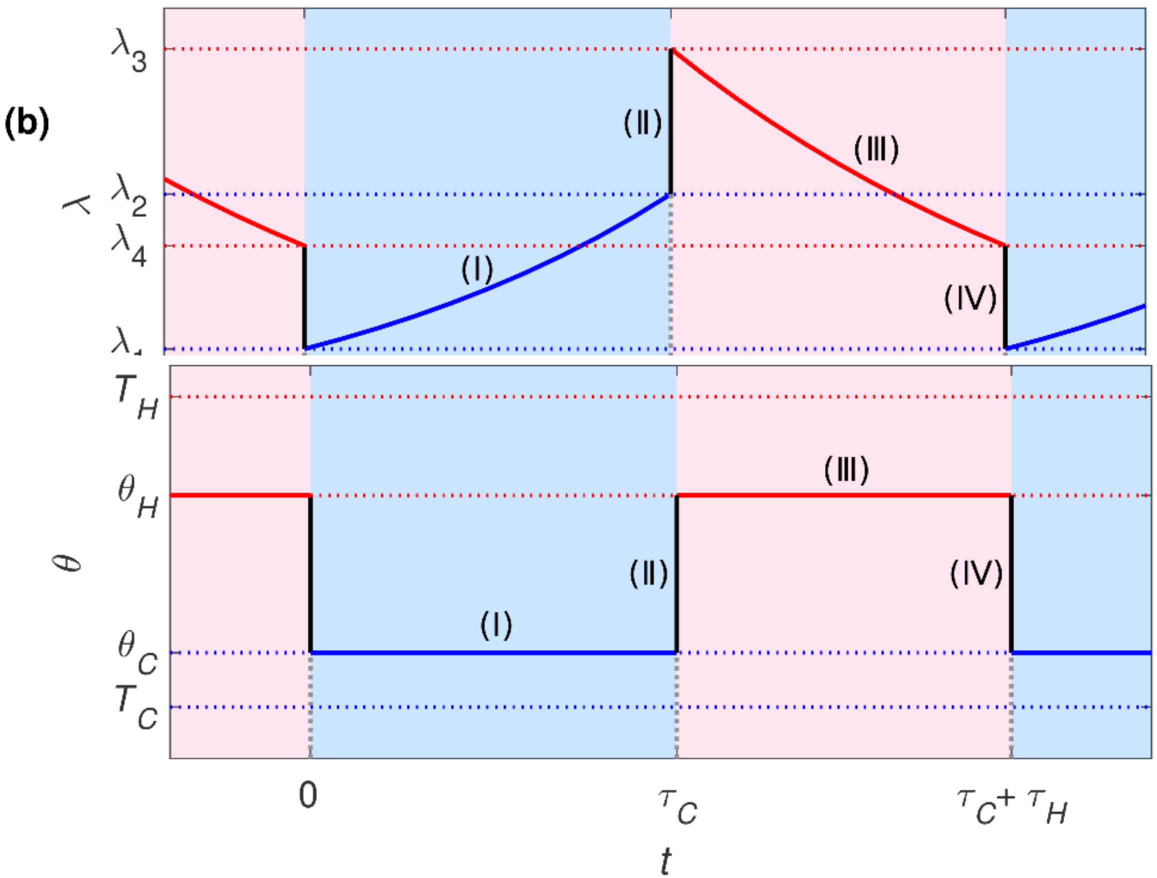
The work parameter is tuned slowly

$$\tau \ll k/\dot{k}.$$



D. S. P. Salazar and S. A. Lira, J. Phys. A: Math. Theor. 49, 465001 (2016).
D. S. Salazar and S. A. Lira, Phys. Rev. E 99, 062119 (2019).

Realizing Curzon-Ahlborn heat engine with a single Brownian particle in a potential



Work parameter in a cycle

$$\lambda(t) = \lambda_1(\lambda_2/\lambda_1)^{t/\tau_C}$$

$$\lambda(t) = \lambda_3(\lambda_4/\lambda_3)^{(t-\tau_C)/\tau_H}$$

Effective temperature of the system in a cycle

$$\theta_C = \frac{\tau_C\Gamma_C}{\tau_C\Gamma_C - \ln r}T_C.$$

$$\theta_H = \frac{\tau_H\Gamma_H}{\tau_H\Gamma_H + \ln r}T_H,$$

A. Dechant, N. Kisel, and E. Lutz, Europhys. Lett. 119, 500003 (2017).

*Y. H. Chen, Jinfu Chen, Zhaoyu Fei, **HTQ**, PRE, 106, 024105 (2022)*

outline

- Classical Thermodynamics
- Stochastic Thermodynamics and Fluctuation Theorems
- Stochastic Thermodynamics and Quantum Thermodynamics
- Stochastic Thermodynamics and Finite-Time Thermodynamics
- Stochastic Thermodynamics and and Special Relativity
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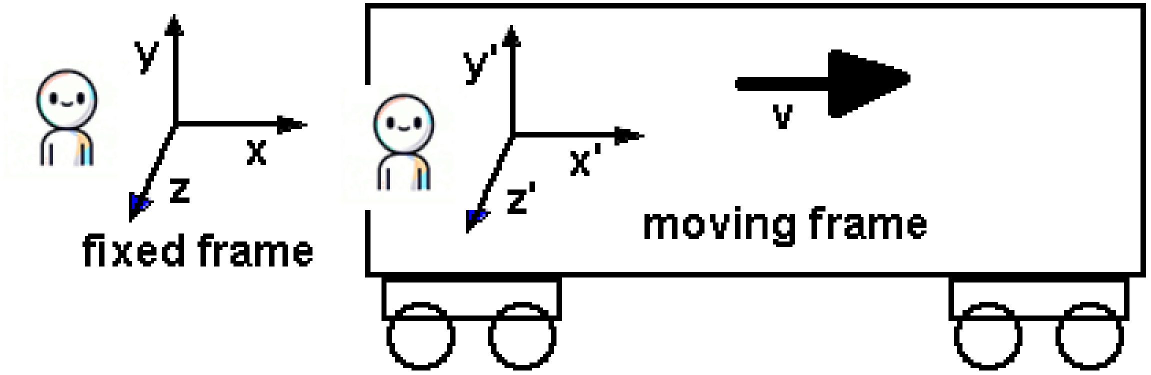
A fundamental requirement: Covariance of physical laws

- Newton's equation is invariant under Galileo transformation (1687)
- Maxwell's equations are invariant under Lorentz transformation (1904)



Coordinates do not exist *a priori* in nature, but are only artifices used in describing nature, and hence should play no role in the formulation of fundamental physical laws.----Wikipedia article "general covariance"

Equilibrium distribution in special relativity

- Relativistic covariant equilibrium distribution (Juttner distribution for a single rest particle system), valid for arbitrary observer

$$\rho_{\mathrm{eq}} \propto \exp(-\beta_\mu P^\mu)$$

4-momentum P^μ

4-vector inverse temperature

$$\beta_\mu = \beta u_\mu$$

4-velocity of the moving system

(rest) inverse temperature $\beta = \sqrt{\beta_\mu \beta^\mu}$

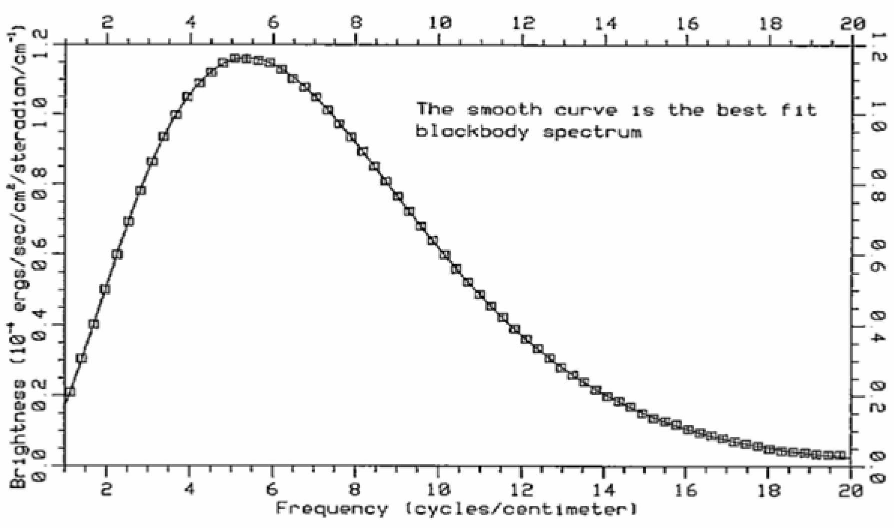
$$u_\mu = \eta_{\mu\nu} \frac{\mathrm{d}x^\nu}{\mathrm{d}\tau}$$

metric $\eta_{\mu\nu} = \mathrm{diag}(1, -1, -1, -1)$

- For rest system, $u^\mu = (1,0,0,0)$, it reduces to $\rho_{\mathrm{eq}} \propto \exp(-\beta H)$

D. van Dantzig, Physica 6, 673 (1939)
N.G. van Kampen, Phys. Rev. 173, 295 (1968)
Z. C. Wu, Europhys.Lett., 88, 20005 (2009)

More on the 4-vector inverse temperature

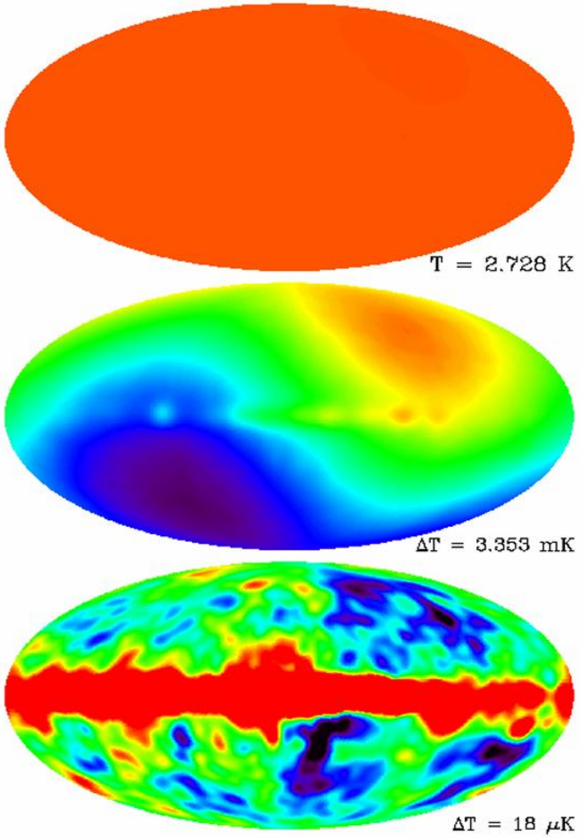


$$exp\{\hbar\omega\gamma(1-\beta cos\theta)/kT_0\} = exp\{\gamma(\epsilon - \mathbf{p}.\mathbf{v})/kT_0\}$$

$$exp\{(\epsilon - \mathbf{p}.\mathbf{v})/kT_0\}.$$

$$exp(p_\mu v^\mu/kT)$$

Kamran Derakhshani, arXiv: 1908.08599



NASA's COBE, 1993

Nobel prize in 2006


John C. Mather, George F. Smoot

for their discovery of the blackbo
dy form and anisotropy of the co
smic microwave background radi
ation

Nobel prize in 2019

James Peebles

for theoretical
discoveries in
physical cosmology

Covariant thermodynamic quantities

Momentum components and energy component are equally important for moving systems

- Covariant generalization of trajectory work and trajectory heat:

$$\Delta P^{\mu}[\omega] = W^{\mu}[\omega] + Q^{\mu}[\omega]$$

- 4-vector work: 4-momentum change due to external driving
- 4-vector heat: 4-momentum change due to energy exchange with the heat bath

N.G. van Kampen, Phys. Rev. 173, 295 (1968)
K. Sekimoto, Stochastic Energetics, Springer, (2010)

Covariant Fluctuation Theorems

- Integral fluctuation theorems (IFTs)

$$\langle \exp(-\beta_\mu W^\mu) \rangle = \exp(-\beta \Delta F)$$ (Lorentz covariant Jarzynski's equality)

$$\left\langle \exp((\beta^s_\mu - \beta_\mu) Q^\mu) \right\rangle = 1$$ (Lorentz covariant heat exchange fluctuation theorem)

- All statements of the second law and FTs should be modified to include momentum components, e.g.

$$\left\langle (\beta^{\mathrm{s}}_\mu - \beta_\mu) Q^\mu \right\rangle \geq 0$$ modified Clausius statement for relaxation process

$$\langle \beta_\mu W^\mu \rangle \geq 0$$ modified Kelvin statement for cyclic driving process

*J. H. Pei, J. F Chen, **HTQ**, Phys. Rev. Lett.* 134, 237102 (2025)
Editor's suggestion

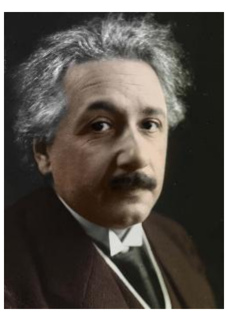
A century-long debate about the temperature transformation in special relativity

Plank, Einstein(1908): $T' = \frac{T}{\gamma}, \gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$

Ott, Arzeliès (1963): $T' = \gamma T$

Landsberg (1966): $T' = T$

van Kampen (1968): $\beta_\mu = \beta u_\mu, \beta = \frac{1}{k_B T}$



Einstein

Planck

Landsberg

van Kampen

A possible solution to the long debate about the temperature transformation in special relativity？

https://journals.aps.org/prl/

EDITORS' SUGGESTION

Promoting Fluctuation Theorems into Covariant Forms

13 JUNE, 2025

The principle of covariance and fluctuation theorems are combined into a coherent framework of relativistic thermodynamics, applicable to moving thermodynamic systems and moving heat baths.

Ji-Hui Pei (裴继辉), Jin-Fu Chen (陈劲夫), and H. T. Quan (全海涛)
Phys. Rev. Lett. **134**, 237102 (2025)

Personal Perspective

- Quasistatic process only
- Microscopic equation of motion

Macroscopic Thermodynamic → Stochastic thermodynamics

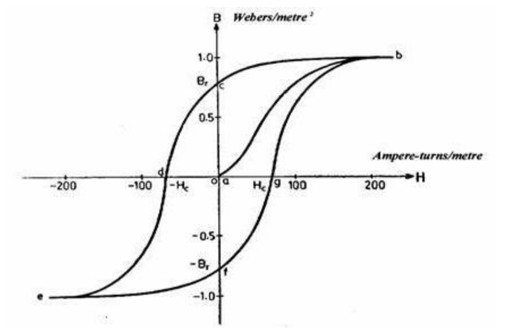
Macroscopic

?

microscopic

- Nonequilibrium many-body system

"More is different"



Initial magnetization curve, *ab*, and hysteresis loop, *bcdefgb*.

outline

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Summary

•On the ensemble averaged level, thermodynamic laws are still valid in small systems, but fluctuation theorems are nonnegligible

•The fluctuations of thermodynamic quantities satisfy strict equalities—fluctuation theorems, and the second law can be derived from these quantities.

•Quantum extension of the stochastic thermodynamics

•Stochastic thermodynamics may have potential applications in finite-time thermodynamics

•Fluctuation theorems are promoted to covariant forms, and shed new light on the theory of relativistic thermodynamics


SPIRIT

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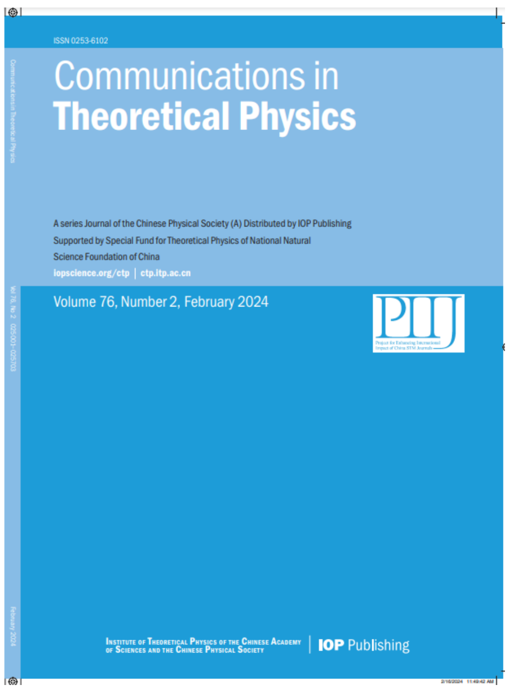

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- 何祚庥院士为第二任主编
- 现任主编为孙昌璞院士

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