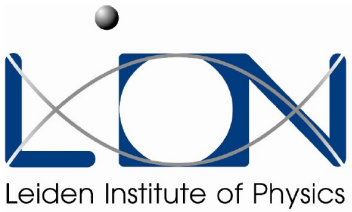
Finite-time Thermodynamic Optimization: Thermodynamic Geometry

陈劲夫|集智俱乐部@非平衡统计物理读书会, 2025.3.20



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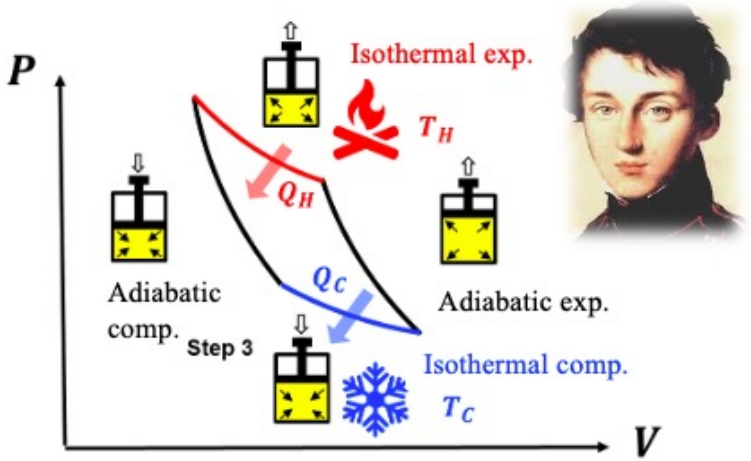


Outline

- Background on finite-time thermodynamics: Acta Phys. Sin., 72, 230501 (2023)
- History developments
  - Macroscopic thermodynamic geometry: Phys. Rev. A 20, 1608 (1979)
  - Modern interpretation with fisher information metric: Phys. Rev. Lett. 99, 100602 (2007)
  - Extension to nonequilibrium: Phys. Rev. Lett. 51, 1127 (1983); Phys. Rev. Lett. 108, 190602 (2012)
- $1/\tau$-scaling of irreversibility: Phys. Rev. Lett. 125, 210601 (2020)
- Extrapolating thermodynamic length: Phys. Rev. E 104, 034117 (2020)
- Thermodynamic consistency: constraint on equation of motion: arXiv:2502.20118

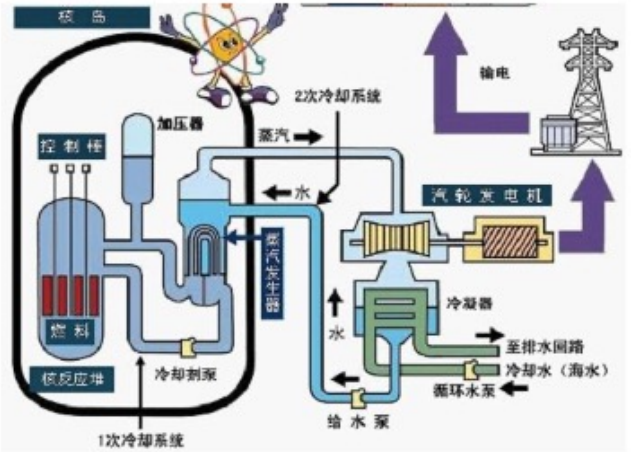
Gap between theory and practice

Ideal Carnot cycle



$$\eta_C = 1 - T_C/T_H$$

Practical need



Cycle time $t \to \infty \quad P = W/t \to 0$

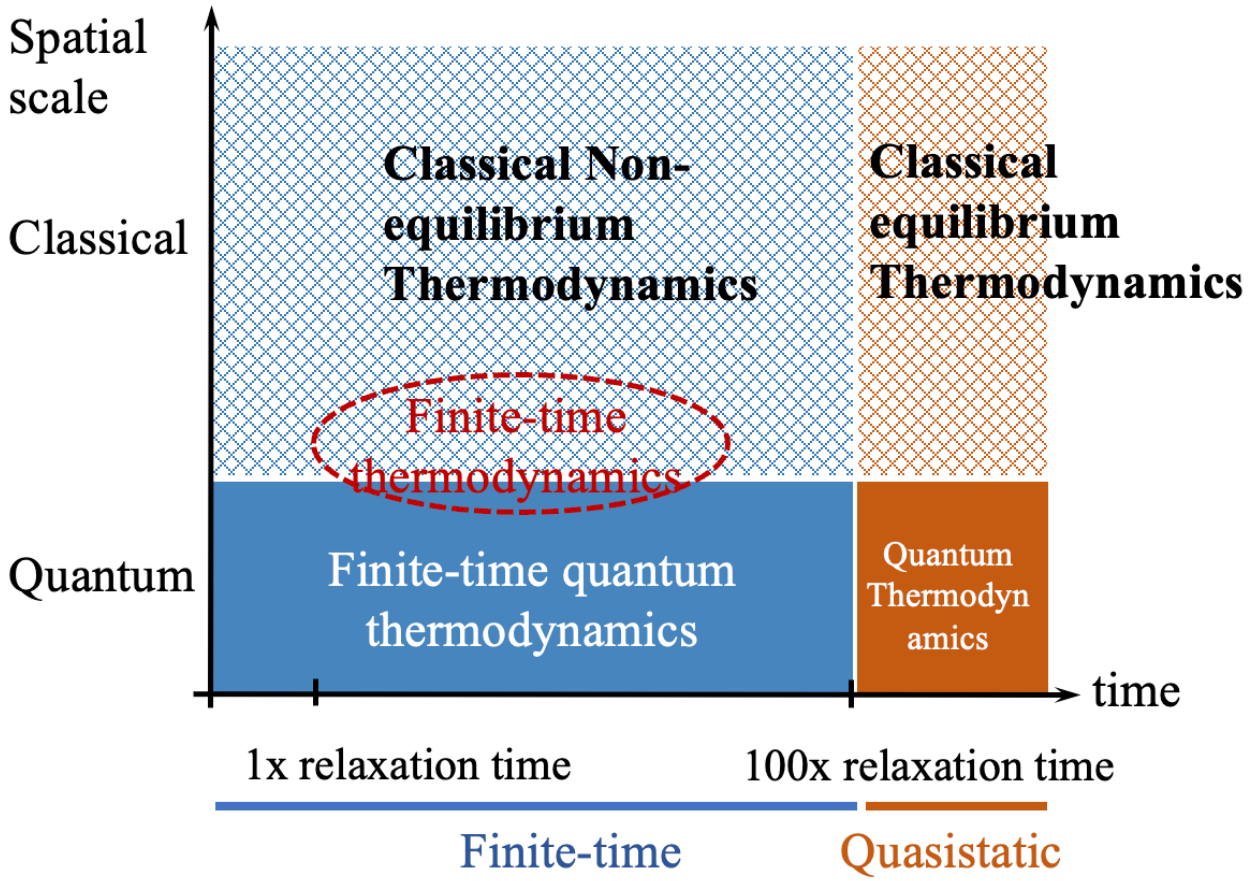
Cycle with zero power.

Increase the power output:
Obtain more energy per unit of time

Finite-time thermodynamics:
Effect of finite-time dynamics on thermodynamics

New “Phase” Diagram

Dynamics:
equations of motion



Thermodynamics:
equilibrium ensembles

Key question: integrate time into thermodynamics

H.-T. Quan, H. Dong, C. P. Sun, Acta Phys. Sin., 72, 230501 (2023).

《物理学报》创刊 90 周年

运动方程
Equation of motion
+
(非平衡)热力学
(Nonequilibrium)
thermodynamics

介观统计热力学理论与实验*

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(2023 年 10 月 7 日收到; 2023 年 11 月 6 日收到修改稿)

对于只有有限自由度的介观小系统, 传统的热力学定律是否成立? 温度、熵、做功、传热、等温过程、Carnot 循环这些概念还是否有效? 是否需要对原来适用于宏观系统的传统热力学理论进行修改或扩充、以适用于这样的小系统? 在过去近 20 年里, 我们深入研究了在介观小系统和量子系统中热力学基本概念的推广 (例如什么是量子等温过程) 以及基本热力学定律的适用性问题. 研究表明, 在系综平均意义上热力学定律仍然适用于小系统; 考虑了 Maxwell 妖的信息擦除功耗后, 热力学第二定律不会被违反; "小系统"的统计热力学具有一些新的特性, 由于系统和环境之间的耦合不可忽略, 有限系统的平衡态分布偏离正则系综, 这可以描述诸如黑洞等小系统的辐射关联及其信息丢失现象; 在任意远离平衡的情况下, 热力学量的涨落变得十分显著, 并且热力学量的分布函数满足一些严格成立的恒等式. 这些恒等式定义了所谓的涨落定理, 由此通过测量非平衡过程的物理量 (如功分布) 可以获得平衡过程的物理量相对值 (如自由能差等). 此外, 尽管量子属性和信息论的考虑为统计热力学带来一些有别于经典和传统的特性, 有助于理解 Gibbs 佯谬和 Maxwell 妖等基本问题, 但需要指出的是, 量子热机和信息辅助热机的效率并没有超越经典热机. 随着在小系统中引入运动方程, 热力学和力学之间的联系变得更加紧密, 能够从第一性原理出发研究非平衡过程的能量耗散和热机的功率、效率优化及其最优调控微分几何化等问题. 在对具体热循环过程熵产生问题的研究中, 对得到的功率-效率约束关系进行了系统性的实验检验.

Macroscopic thermodynamic geometry

PHYSICAL REVIEW A VOLUME 20, NUMBER 4 OCTOBER 1979

Thermodynamics: A Riemannian geometric model

George Ruppeiner
Department of Physics, Duke University, Durham, North Carolina 27706
(Received 22 January 1979)

By including the theory of fluctuations in the axioms of thermodynamics it is shown that thermodynamic systems can be represented by Riemannian manifolds. Of special interest is the curvature of these manifolds which, for pure fluids, is associated with effective interparticle interaction strength by means of a general thermodynamic "interaction hypothesis." This interpretation of curvature appears to be consistent with hyperscaling and two-scale-factor universality. The Riemannian geometric model is a new attempt to extract information from the axioms of thermodynamics.

Equilibrium states + Riemannian manifold

G. Ruppeiner, Phys. Rev. A 20, 1608 (1979)

Macroscopic thermodynamic geometry

- **Thermodynamic geometry**: Curvature R ➡ Interaction, Critical behavior

- The key idea is to treat the **thermodynamic state space** as a **Riemannian manifold**, with the metric tensor derived from the second derivative of entropy:

$$g_{\mu\nu} = -\frac{\partial^2 S}{\partial X^\mu \partial X^\nu}$$

- S: entropy, X^μ extensive thermodynamic variables (energy, volume, particle number)
- The negative sign ensures positive-definite.

G. Ruppeiner, Phys. Rev. A 20, 1608 (1979)

Macroscopic thermodynamic geometry

- Negative curvature $R < 0 \rightarrow$ **Attractive interactions** (e.g., van der Waals gas, ideal Bose gas).
- Positive curvature $R > 0 \rightarrow$ **Repulsive interactions** (e.g., ideal Fermi gas).
- Divergent curvature $R \rightarrow \infty \rightarrow$ **Critical phenomena** (phase transition points, e.g., BEC).

Metric
$$g_{\mu\nu} = -\frac{\partial^2 S}{\partial X^\mu \partial X^\nu},$$

Christoffel symbols
$$\Gamma^\lambda_{\mu\nu} = \frac{1}{2} g^{\lambda\sigma} \left(\partial_\mu g_{\nu\sigma} + \partial_\nu g_{\mu\sigma} - \partial_\sigma g_{\mu\nu} \right),$$

Riemann curvature tensor
$$R^\lambda_{\mu\nu\rho} = \partial_\nu \Gamma^\lambda_{\mu\rho} - \partial_\rho \Gamma^\lambda_{\mu\nu} + \Gamma^\sigma_{\mu\rho} \Gamma^\lambda_{\sigma\nu} - \Gamma^\sigma_{\mu\nu} \Gamma^\lambda_{\sigma\rho},$$

Ricci curvature tensor
$$R_{\mu\nu} = R^\lambda_{\mu\lambda\nu},$$

Scalar curvature
$$R = g^{\mu\nu} R_{\mu\nu},$$

G. Ruppeiner, Rev. Mod. Phys. 67, 605 (1995).

Modern interpretation

PRL 99, 100602 (2007) PHYSICAL REVIEW LETTERS week ending 7 SEPTEMBER 2007

Measuring Thermodynamic Length

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(Received 4 June 2007; revised manuscript received 17 July 2007; published 7 September 2007)

Thermodynamic length is a metric distance between equilibrium thermodynamic states. Among other interesting properties, this metric asymptotically bounds the dissipation induced by a finite time transformation of a thermodynamic system. It is also connected to the Jensen-Shannon divergence, Fisher information, and Rao's entropy differential metric. Therefore, thermodynamic length is of central interest in understanding matter out of equilibrium. In this Letter, we will consider how to define thermodynamic length for a small system described by equilibrium statistical mechanics and how to measure thermodynamic length within a computer simulation. Surprisingly, Bennett's classic acceptance ratio method for measuring free energy differences also measures thermodynamic length.

DOI: 10.1103/PhysRevLett.99.100602 PACS numbers: 05.70.Ln, 05.40.−a

Thermodynamic length: Statistical distance
Riemannian metric: Fisher information matrix

Gavin E. Crooks, Phys. Rev. Lett. 99, 100602 (2007)

Modern interpretation

- Gibbs ensemble

$$p(x|\lambda) = \frac{1}{Z} e^{-\beta H(x,\lambda)} = \frac{1}{Z} e^{-\lambda^i(t) X_i(x)}.$$

- Partition function Z, free energy F, free entropy ψ (Massieu potential), entropy S

$$\ln Z = -\beta F = \psi = S - \lambda^i \langle X_i \rangle$$

Gavin E. Crooks, Phys. Rev. Lett. 99, 100602 (2007)

Modern interpretation

- First derivatives of the free entropy: first moments of the collective variables

$$\frac{\partial \psi}{\partial \lambda^i} = -\langle X_i \rangle$$

- Second derivatives: covariance metric

$$g_{ij} = \frac{\partial^2 \psi}{\partial \lambda^i \partial \lambda^j} = -\frac{\partial \langle X_i \rangle}{\partial \lambda^j} = \langle (X_i - \langle X_i \rangle)(X_j - \langle X_j \rangle) \rangle .$$

- Classical Fisher information matrix

$$\begin{aligned} g_{ij}(\lambda) &= \sum_x p(x) \frac{\partial \ln p(x)}{\partial \lambda^i} \frac{\partial \ln p(x)}{\partial \lambda^j} \\ &= \sum_x p(x) \left(X_i + \frac{\partial \psi}{\partial \lambda^i} \right) \left(X_j + \frac{\partial \psi}{\partial \lambda^j} \right) \\ &= \langle (X_i - \langle X_i \rangle)(X_j - \langle X_j \rangle) \rangle . \end{aligned}$$

Modern interpretation

- Thermodynamic length:

$$\mathcal{L} = \int_0^\tau \sqrt{\frac{d\lambda^i}{dt} g_{ij} \frac{d\lambda^j}{dt}} dt$$

- Thermodynamic divergence of the path

$$\mathcal{J} = \tau \int_0^\tau \frac{d\lambda^i}{dt} g_{ij} \frac{d\lambda^j}{dt} dt.$$

- The length and the divergence satisfies

$$\mathcal{J} \geq \mathcal{L}^2,$$

- Physical meaning of the divergence?

Modern interpretation

Originally, Weinhold [1] defined the thermodynamic length $\mathcal{L}$ using the second derivatives of the internal energy $U(S, V, N)$ with respect to the extensive variables as a metric tensor, and by Ruppeiner [2] using the corresponding derivatives of the entropy, $S(U, V, N)$. Using intensive variable derivatives of the free energy was first discussed by Schlögl [5,10,11]. For macroscopic thermodynamic systems these different definitions of the metric are essentially equivalent [4,5], analogously to the macroscopic equivalence of ensembles. However, in small systems these metrics are in general different and the Weinhold and Ruppeiner metrics may not exist, since the second derivatives of the entropy and entropy are not guaranteed to be positive. The definition adopted in this Letter [Eq. (4)], essentially that of Schlögl, does not require the thermodynamic limit.

Gavin E. Crooks, Phys. Rev. Lett. 99, 100602 (2007)

Extension to nonequilibrium

VOLUME 51, NUMBER 13 PHYSICAL REVIEW LETTERS 26 SEPTEMBER 1983

Thermodynamic Length and Dissipated Availability

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Department of Mathematical Sciences, San Diego State University, San Diego, California 92182

and

R. Stephen Berry
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(Received 10 January 1983)

New expressions for the availability dissipated in a finite-time endoreversible process are found by use of Weinhold's metric on equilibrium states of a thermodynamic system. In particular, the dissipated availability is given by the square of the length of the corresponding curve, times a mean relaxation time, divided by the total time of the process. The results extend to local thermodynamic equilibrium if instead of length one uses distance (length of the shortest curve) between initial and final states.

PACS numbers: 05.70.-a

Peter Salamon, R. Stephen Berry, Phys. Rev. Lett. **51**, 1127 (1983)

Extension to nonequilibrium

- With fixed T, define the metric from the internal energy

$$\eta_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j}$$

Weinhold's approach

- They define the thermodynamic length as

$$L = \int_0^{\xi^{\max}} \left(\frac{dX^t}{d\xi}\eta\frac{dX}{d\xi}\right)^{1/2} d\xi.$$

F. Weinhold, J. Chem. Phys. 63, 2479–2483 (1975)
Peter Salamon, R. Stephen Berry, Phys. Rev. Lett. 51, 1127 (1983)

Extension to nonequilibrium

- The dissipated availability or the excess work is

$$\Delta A_u = \int_0^\tau \sum_i [Y_i^e(t) - Y_i(t)] \frac{dX_i}{dt} dt$$

$$= \ldots$$

$$= \int_0^\tau \frac{dX^t}{dt} \eta \frac{dX}{dt} \epsilon dt$$

$$= \bar{\epsilon} \int_0^\tau \frac{dX^t}{dt} \eta \frac{dX}{dt} dt$$

$$\geq \bar{\epsilon} L^2 / \tau$$

Y: associated intensity
Y^e: equilibrium value
ϵ: lag time
τ: duration of the process

$1/\tau$ scaling of irreversibility

$$\int_0^\tau \dot{X}^t \eta \dot{X} dt \geq \left[\int_0^\tau \left(\dot{X}^t \eta \dot{X} \right)^{1/2} dt \right]^{2/\tau} = L^2/\tau$$

Peter Salamon, R. Stephen Berry, Phys. Rev. Lett. **51**, 1127 (1983)

Example in stochastic thermodynamics

PRL **108,** 190602 (2012) PHYSICAL REVIEW LETTERS week ending 11 MAY 2012

Thermodynamic Metrics and Optimal Paths

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(Received 19 January 2012; published 8 May 2012)

A fundamental problem in modern thermodynamics is how a molecular-scale machine performs useful work, while operating away from thermal equilibrium without excessive dissipation. To this end, we derive a friction tensor that induces a Riemannian manifold on the space of thermodynamic states. Within the linear-response regime, this metric structure controls the dissipation of finite-time transformations, and bestows optimal protocols with many useful properties. We discuss the connection to the existing thermodynamic length formalism, and demonstrate the utility of this metric by solving for optimal control parameter protocols in a simple nonequilibrium model.

DOI: 10.1103/PhysRevLett.108.190602 PACS numbers: 05.70.Ln, 02.40.Ky, 02.60.Cb, 05.40.−a

Example in stochastic thermodynamics

- Stochastic work and heat

$$\mathcal{P} \equiv \frac{d\langle W\rangle_{\Lambda}}{dt} \equiv -\frac{d\boldsymbol{\lambda}^{T}}{dt}\cdot\langle \mathbf{X}\rangle_{\Lambda}.$$

$$\frac{d\langle \mathcal{Q}\rangle_{\Lambda}}{dt} \equiv \left\langle \frac{dx^{T}}{dt}\frac{\partial E}{\partial x}\right\rangle_{\Lambda},$$

- Excess work

$$\mathcal{P}_{\mathrm{ex}}(t_0) = -\left[\frac{d\boldsymbol{\lambda}^{T}}{dt}\right]_{t_0}\cdot\langle \Delta\mathbf{X}(t_0)\rangle_{\Lambda},$$

Derivation from the equilibrium

$$\Delta\mathbf{X}(t_0) \equiv \mathbf{X}(t_0) - \langle \mathbf{X}\rangle_{\boldsymbol{\lambda}(t_0)}$$

- Slow driving: linear response theory

$$\langle \Delta\mathbf{X}(t_0)\rangle_{\Lambda} \simeq \int_{-\infty}^{t_0} dt'\boldsymbol{\chi}(t_0 - t')\cdot[\boldsymbol{\lambda}(t') - \boldsymbol{\lambda}(t_0)],$$

$$\chi_{ij}(t) \equiv \beta d\Sigma_{ij}^{(\boldsymbol{\lambda}(t_0))}(t)/dt$$

$$\Sigma_{ij}^{(\boldsymbol{\lambda}(t_0))}(t) \equiv \langle \delta X_j(0)\delta X_i(t)\rangle_{\boldsymbol{\lambda}(t_0)}$$

David A. Sivak and Gavin E. Crooks, Phys. Rev. Lett. **108**, 190602 (2012)

Example in stochastic thermodynamics

When the control parameter velocities change on time scales slower than the relaxation time of the system's force fluctuations, we can keep only the constant term, yielding

$$\mathcal{P}_{\mathrm{ex}}(t_0) = \left[\frac{d\boldsymbol{\lambda}^T}{dt}\right]_{t_0} \cdot \beta \int_0^\infty dt'' \boldsymbol{\Sigma}^{(\boldsymbol{\lambda}(t_0))}(t'') \cdot \left[\frac{d\boldsymbol{\lambda}}{dt}\right]_{t_0}. \quad (11)$$

- The key result:

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

$$\zeta_{ij}(\boldsymbol{\lambda}(t_0)) = \beta \int_0^\infty dt'' \Sigma_{ij}^{(\boldsymbol{\lambda}(t_0))}(t''),$$

$$= \beta \int_0^\infty dt'' \langle \delta X_j(0) \delta X_i(t'') \rangle_{\boldsymbol{\lambda}(t_0)}.$$

$\zeta(\boldsymbol{\lambda})$: Friction tensor

$$\mathcal{L} = \int_0^{\Delta t} dt \sqrt{\mathcal{P}_{\mathrm{ex}}(t)}$$

$$\mathcal{J} = \Delta t \int_0^{\Delta t} dt \mathcal{P}_{\mathrm{ex}}(t)$$

$$W_{\mathrm{ex}} \geq \mathcal{L}^2 / \Delta t$$

- This metric characterizes the excess work!

$1/\tau$-scaling of irreversibility

- For finite-time thermodynamic processes, the irreversibility is characterized by irreversible entropy production

$$\Sigma = \Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{bath}} \geq 0,$$

- or the excess work

$$W_{\mathrm{ex}} = W - \Delta F.$$

- For dissipative processes without phase transition, the irreversibility satisfies

$$W_{\mathrm{ex}} \propto 1/\tau$$

Irreversibility in isothermal processes

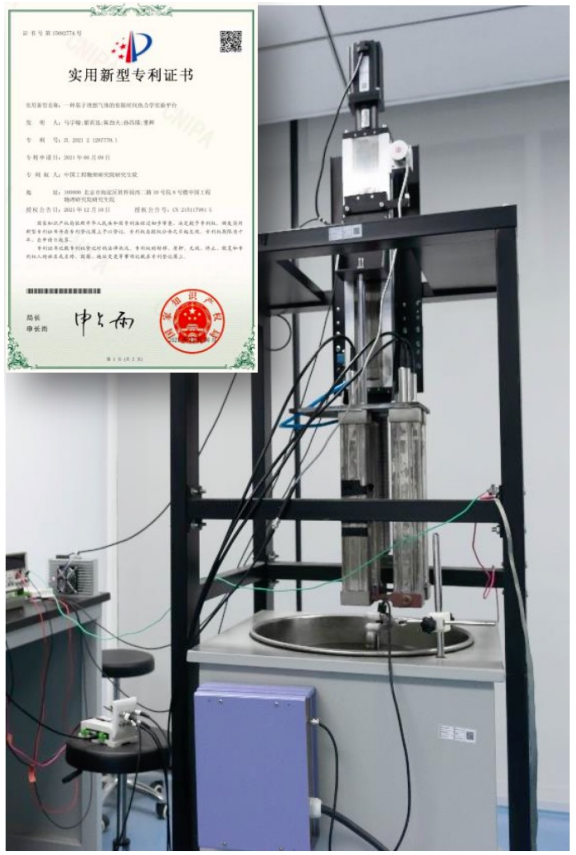
	Heat	Work
Quasi-static	$\Delta S = Q_h/T_h$	$W = \Delta F$
Finite-time (textbook)	$\Delta S \geq Q_h/T_h$	$W \geq \Delta F$
Finite-time (slow driving)	$Q_h = Q_h^{(r)} - \frac{M_h}{\tau_h}$	$W(\tau) = \Delta F + \mathcal{C}/\tau_h$

$1/\tau$-scaling in slow-driving regime

- Finite-time thermodynamics
  - P. Salamon, A. Nitzan, B. Andresen, and R. S. Berry, Phys. Rev. A 21, 2115 (1980)
  - T. Schmiedl and U. Seifert, Europhys. Lett. 81, 20003 (2008)
  - M. Esposito, R. Kawai, K. Lindenberg, and C. V. den Broeck, Phys. Rev. Lett. 105, 150603 (2010)
- Stochastic thermodynamics
  - Z. Gong, Y. Lan, and H. T. Quan, Phys. Rev. Lett. 117, 180603 (2016)
  - G. Li, H. T. Quan, and Z. C. Tu, Phys. Rev. E 96, 012144 (2017)
- Thermodynamics length

  $W_{\mathrm{ex}} \propto 1/\tau$
  - D. A. Sivak and G. E. Crooks, Phys. Rev. Lett. 108, 190602 (2012)
- Quantum thermodynamics
  - V. Cavina, A. Mari, and V. Giovannetti, Phys. Rev. Lett. 119, 050601 (2017)
  - Y. H. Ma, D. Xu, H. Dong, and C. P. Sun, Phys. Rev. E 98, 042112 (2018)

Experimental Test



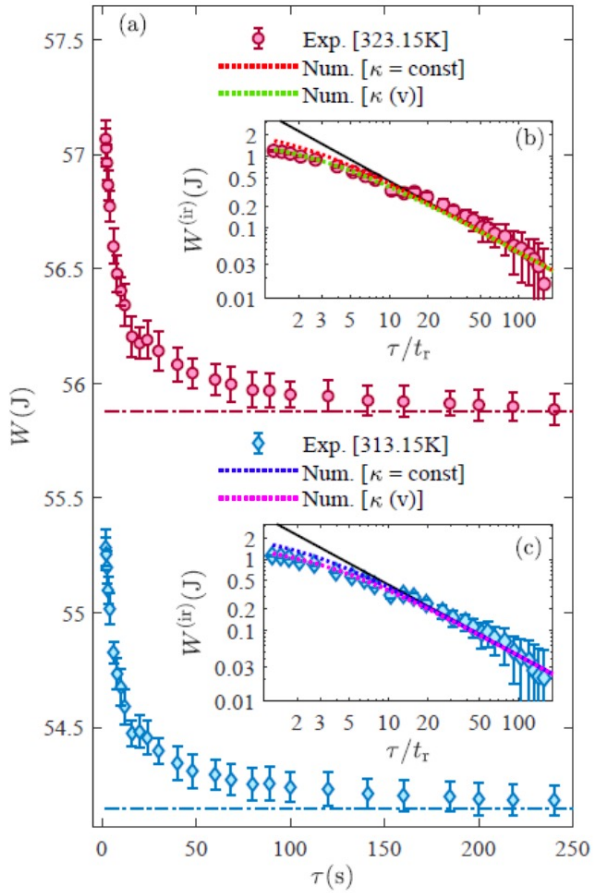
Internal energy Heat exchange Work

$$C_V \frac{dT_\mathrm{s}}{dt} = -\kappa(T_\mathrm{s} - T_\mathrm{e}) - \frac{nRT_\mathrm{s}}{V}\frac{dV}{dt}$$

$$W = -\int_0^\tau p(t)\frac{dV}{dt}dt$$

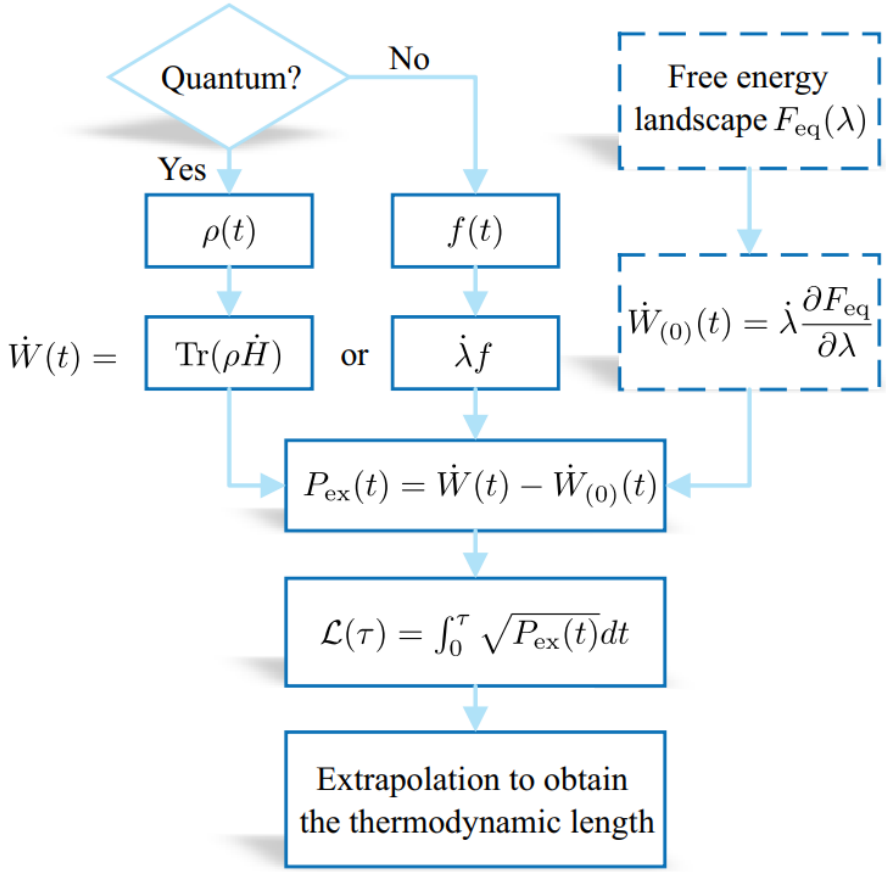
T_s Temperature of system

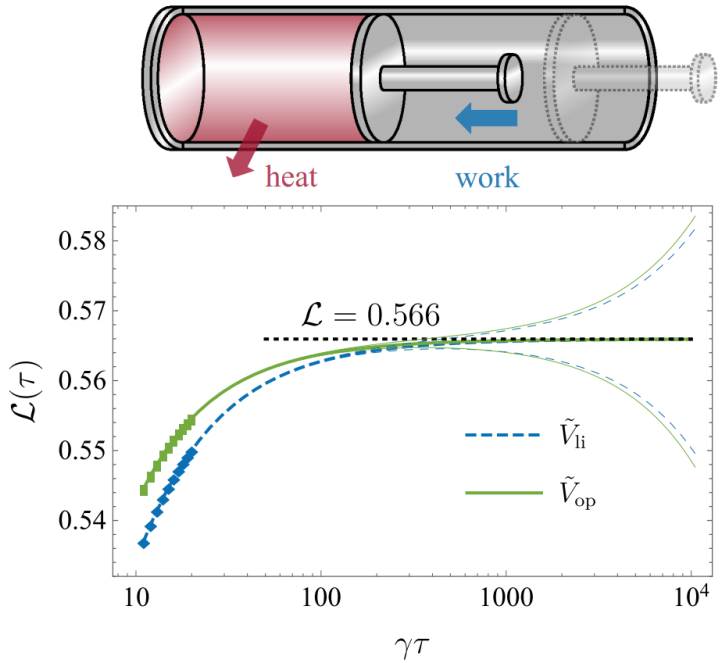
T_e Temperature of heat bath



Y. H. Ma, R. X. Zhai, JFC, C. P. Sun, and H. Dong, Phys. Rev. Lett. 125, 210601 (2020)

How to measure thermodynamic length?





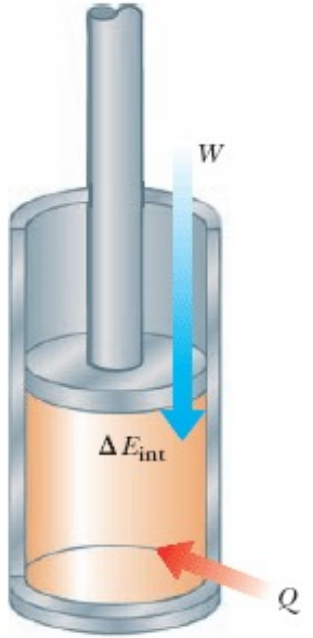
Error scales with operation time

$$W(\tau)_{\rm min} = \Delta F + \frac{\mathcal{L}^2}{\tau}$$

JFC, C. P. Sun, H. Dong, Phys. Rev. E 104, 034117 (2020)

Start with ideal gas compression

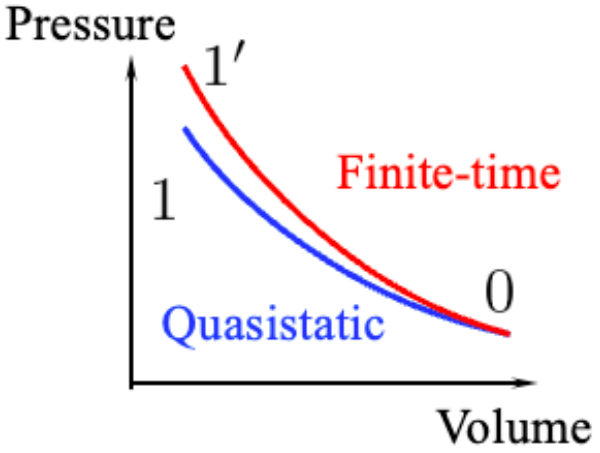
$$C_V \frac{dT_\mathrm{s}}{dt} = -\kappa(T_\mathrm{s} - T_\mathrm{e}) - \frac{nRT_\mathrm{s}}{V}\frac{dV}{dt} \qquad \frac{nR}{\gamma C_V}\frac{\dot{V}}{V} \ll 1$$



$$W(\tau) = -\int_0^\tau \frac{nRT_\mathrm{s}}{V}\dot{V}dt$$

$$\approx \underbrace{-\int_0^\tau \frac{nRT_\mathrm{b}}{V}\dot{V}dt}_{\Delta F} + \underbrace{\int_0^\tau \frac{(nR)^2 T_\mathrm{b}}{\kappa C_V}\left(\frac{\dot{V}}{V}\right)^2 dt}_{W_\mathrm{ex}}$$

$$\geq \frac{1}{\tau}\left[\int_0^\tau \underbrace{\sqrt{\frac{(nR)^2 T_\mathrm{b}}{\kappa C_V}\left(\frac{\dot{V}}{V}\right)^2}}_{\mathcal{L}} dt\right]^2$$



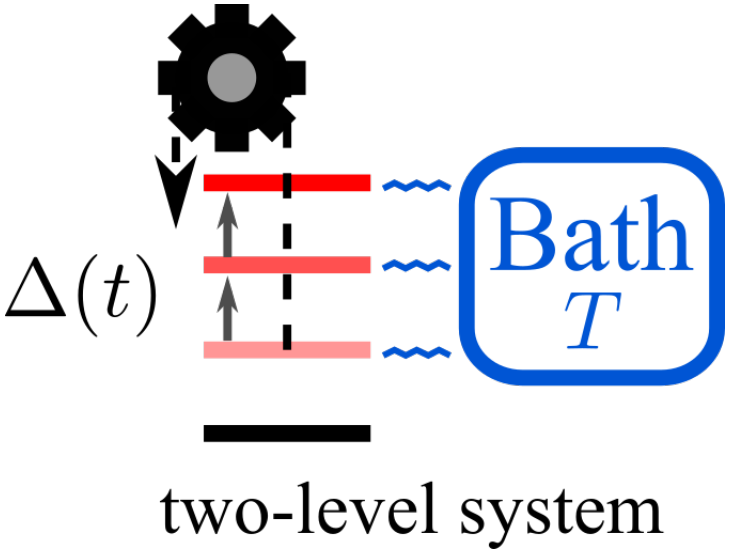
Example in open systems

- Time-local master equation

$$\dot{\rho} = \mathscr{L}_{\lambda(t)}\rho,$$

- The unique steady state

$$\rho_{\rm eq}(t) = \frac{e^{-\beta_b H(t)}}{Z(t)}, \qquad \mathscr{L}_{\lambda(t)}\rho_{\rm eq} = 0$$



- Work and heat

$$W = \int_0^\tau \dot{\lambda}\mathrm{tr}(\rho(t)\frac{\partial H}{\partial \lambda})dt, \qquad Q = \int_0^\tau \mathrm{tr}(\frac{\partial \rho}{\partial t}H)dt$$

- Excess work

$$W_{\rm ex} = \int_0^\tau \dot{\lambda}\mathrm{tr}[(\rho(t) - \rho_{\rm eq}(t))\frac{\partial H}{\partial \lambda}]dt > 0$$

JFC, C. P. Sun, H. Dong, Phys. Rev. E 104, 034117 (2020)

Perturbation expansion

- Rewrite

$$\dot{\rho} = \mathscr{L}_{\lambda(t)}(\rho - \rho_{\mathrm{eq}}(t))$$

- We use the pseudo-inverse

$$\rho = \rho_{\mathrm{eq}}(t) + \mathscr{L}^{-1}_{\lambda(t)}\dot{\rho}$$

- Which gives the perturbative solution

$$\rho(t) = \sum_{n=0}^{\infty} \left(\mathscr{L}^{-1}_{\lambda(t)} \frac{d}{dt} \right)^n \rho_{\mathrm{eq}}(t).$$

- Excess work

$$P_{\mathrm{ex}}(t) = \mathrm{Tr}\left\{ \frac{\partial \tilde{H}(s)}{\partial s} \sum_{n=1}^{\infty} \frac{1}{\tau^{n+1}} \left(\mathscr{L}^{-1}_{\tilde{\lambda}(s)} \frac{\partial}{\partial s} \right)^n [\tilde{\rho}_{\mathrm{eq}}(s)] \right\},$$

Pseudo-inverse

$$\mathscr{L} = \begin{pmatrix} 0 & & & & \\ & 2 & & & \\ & & 3 & & \\ & & & 4 & \\ & & & & \dots \end{pmatrix},$$

$$\mathscr{L}^{-1} = \begin{pmatrix} 0 & & & & \\ & \frac{1}{2} & & & \\ & & \frac{1}{3} & & \\ & & & \frac{1}{4} & \\ & & & & \dots \end{pmatrix}$$

Extrapolating thermodynamic length

- In the following, we try to measure the thermodynamic length in finite-time processes

$$\mathcal{L}(\tau) = \int_0^\tau \sqrt{P_{\mathrm{ex}}(t)}\, dt.$$

- τ cannot be too large since $P_{\mathrm{ex}} \propto 1/\tau^2$ leads to measurement errors.
- Extrapolating strategy:

$$\mathcal{L}(\tau) = a_0 + \sum_{j=1}^{N} \frac{a_j}{\tau^j}$$

- Measure $\mathcal{L}(\tau)$ with different protocols $\tilde{\lambda}(s)$ and duration τ.

Thermodynamically consistency

- First law:

Ensemble average

$$\Delta U = W + Q$$



Trajectory

$$\Delta u = w + q$$

- Second law: Fluctuation theorems $\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta F}$ A single heat bath



Principle of maximum work $W_{\mathrm{ex}} = W - \Delta F > 0,$ $g_{ij} > 0$

- Equation of motion should be consistent with thermodynamic laws.

Thermodynamically consistency

- Classical stochastic thermodynamics: Markovian jump processes

$$\dot{p} = L_{\lambda(t)} p$$

- Detailed balance condition (heat exchange with the heat bath)

$$L_{ij} p_j^{\mathrm{eq}} = L_{ji} p_i^{\mathrm{eq}}.$$

- The first and second laws can be extended to the trajectories of Markov jump processes and classical Brownian motion.
- Can we formulate a similar framework for quantum systems?

Quantum stochastic thermodynamics

- We consider the Lindblad master equations for open quantum systems.
  - Dissipators should satisfy quantum detailed balance condition (see Fagnola, F., Umanità, Commun. Math. Phys. 298, 523–547 (2010)).
  - Quantum work and heat are not observables: Quasiprobabilities

- Consequently, the first law holds on the ensemble average.
- The fluctuation theorems hold.
- The state during a quasistatic isothermal process is in equilibrium $\rho_\beta \propto e^{-\beta H}$.
- The thermodynamic length works for optimizing slow processes works.

Jin-Fu Chen, arXiv:2502.20118

Thermodynamics of open quantum systems

$$\mathscr{L}_{\lambda(t)}[\rho] = -i[H,\rho] + \mathscr{D}[\rho]$$

$$\mathscr{D}[\cdot] = \frac{\kappa}{2}(-i[K,\cdot] + A\cdot A^\dagger - \frac{1}{2}\{A^\dagger A,\cdot\})$$

Details see arXiv:2411.03420

Effective parametrization

$$\dot{\Gamma} = \mathcal{H}(\Gamma) + \mathcal{D}(\Gamma)$$

Work: $$\frac{\partial H}{\partial t} = \sum_{ij} \dot{\lambda}_i \Theta_{ij} O_j$$

$$W = \int_0^\tau \dot{\lambda}^T \Theta \Gamma dt$$

Observables: $$\Gamma_j = \mathrm{tr}(\rho O_j)$$

Jin-Fu Chen, arXiv:2502.20118

Metric: linear response

- In the slow driving, the approximate linear equation is

$$\dot{\Gamma} = L_{\lambda(t)}(\Gamma - \Gamma^{\mathrm{eq}}) \qquad L_\lambda = \left.\frac{\partial \mathcal{L}_\lambda(\Gamma)}{\partial \Gamma}\right|_{\Gamma=\Gamma^{\mathrm{eq}}}$$

- The linear response:

$$\Gamma \approx \Gamma^{\mathrm{eq}} + L^{-1}_{\lambda(t)}\dot{\Gamma}^{\mathrm{eq}} = \Gamma^{\mathrm{eq}} + L^{-1}_{\lambda(t)}\Xi\dot{\lambda}$$

- The excess work and the thermodynamic length follow

$$g_\lambda = [\Theta L_\lambda^{-1}\Xi + (\Theta L_\lambda^{-1}\Xi)^T]/2$$

$$\dot{W}^{\mathrm{ex}} \approx \dot{\lambda}^T \Theta L^{-1}_{\lambda(t)}\Xi\dot{\lambda}$$

$$\mathfrak{L} = \int_{\mathcal{P}} \sqrt{d\lambda^T g_\lambda d\lambda},$$

Θ Linear response of control parameter

L_λ Near equilibrium relaxation

Ξ Change of equilibrium state

Application to quantum Brownian motion

- This framework is applied to quantum Brownian motion with the modified Lindblad master equation

$$\dot{\rho} = \mathscr{L}_\omega[\rho] = -i[H,\rho] + \mathscr{D}[\rho]$$
$$H = p^2/(2m) + m\omega^2 x^2/2$$
$$\mathscr{D}[\cdot] = \frac{\kappa}{2}(-i[K,\cdot] + A\cdot A^\dagger - \frac{1}{2}\{A^\dagger A,\cdot\})$$

- The dissipator is constructed as

$$K = \frac{1}{2\cosh(\beta\omega/2)}(xp+px),$$
$$A = \sqrt{m\omega\coth\left(\frac{\beta\omega}{4}\right)}x + i\sqrt{\frac{\tanh(\beta\omega/4)}{m\omega}}p.$$

Application to quantum Brownian motion

TABLE I. The optimal protocol for quantum Brownian motion in different limits.

		$\kappa/\omega \to 0$	$\kappa/\omega \to \infty$
High temperature	$\beta\omega \to 0$	$\omega_0(\omega_\tau/\omega_0)^s$	$\omega_0/[(\omega_0/\omega_\tau - 1)s + 1]$
Low temperature	$\beta\omega \to \infty$	$\omega_0/[1 + (\sqrt{\omega_0/\omega_\tau} - 1)s]^2$	$\omega_0[1 + (\sqrt{\omega_\tau/\omega_0} - 1)s]^2$
		Underdamped limit	Overdamped limit

Rescaled time: $s = t/\tau$

Summary

- Thermodynamic length

$$W \geq \Delta F \quad \Rightarrow \quad W - \Delta F \geq \frac{\mathcal{L}^2}{\tau}$$

Finite-time thermodynamics	JFC, CP Sun, H Dong, Phys. Rev. E 104, 034117 (2020) JFC†, RX Zhai†, CP Sun, H Dong, PRX Energy 2 (3), 033003 (2023)
Classical stochastic thermodynamics	YH Ma, JFC, CP Sun, H Dong, Phys. Rev. E 106, 034112 (2022)
Shortcut strategies:	G Li, JFC, CP Sun, H Dong, Phys. Rev. Lett. 128, 230603 (2022) JFC, Phys. Rev. E 106, 054108 (2022)
Quantum stochastic thermodynamics	JFC, arXiv:2502.20118

Summary

- Thermodynamically consistent framework

$$\Delta U = W + \sum_{\nu} Q_{\nu}, \qquad \left\langle e^{-\beta_S w + \sum_{\nu}(\beta_{\nu} - \beta_S) q_{\nu}} \right\rangle = e^{-\beta_S \Delta F_S}.$$

Joint fluctuation theorems of work and heat — JFC, HT Quan, Phys. Rev. E 107, 024135 (2023)

Optimal control theory — YH Chen, JFC, Z Fei, HT Quan, Phys. Rev. E 106, 024105 (2022)
JFC, HT Quan, Phys. Rev. E 110, L042105 (2024)

Finite-time scalings of phase transitions — YX Wu, JFC, HT Quan, arXiv:2401.15592

Quasiprobabilities in quantum thermodynamics — JH Pei, JFC, HT Quan, Phys. Rev. E 108, 054109 (2023)

Relativistic thermodynamics — JH Pei, JFC, HT Quan, arXiv:2312.17621

Quantum many-body systems — JFC, K. S. Rai, P. Emonts, D. Farina, M. Płodzień, P. Grzybowski, M. Lewenstein, J. Tura, arXiv:2411.03420

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