Fluctuations in small heat engines

— from quasi-static to finite-time regimes

Ito, Xu, Jiang, Roldán, Martínez, Rica, GW, arXiv:1910.08096
GW & Minami, Phys. Rev. Res. **4**, L012008 (2022)
Xu & GW, Phys. Rev. Res. **4**, L032017 (2022)

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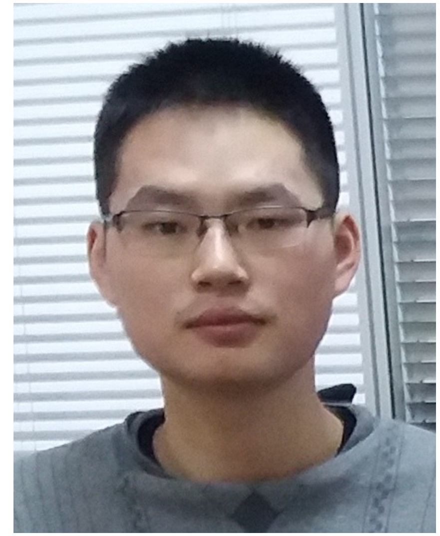

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Ito, Xu, Jiang, Roldán, Martínez, Rica, GW, arXiv:1910.08096
GW & Minami, Phys. Rev. Res. **4**, L012008 (2022)
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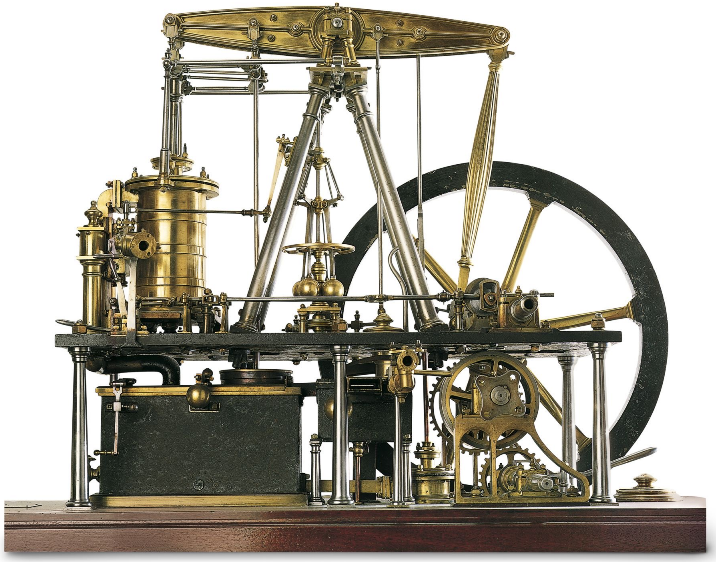
Downsizing the heat engines

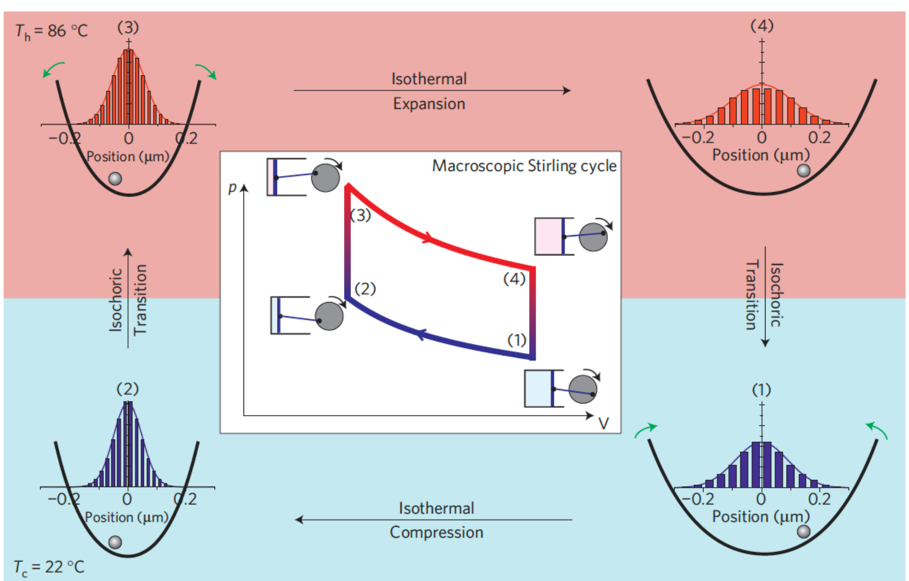


Technological developments allow us to downsize the heat engines.

A small system as a working substance.

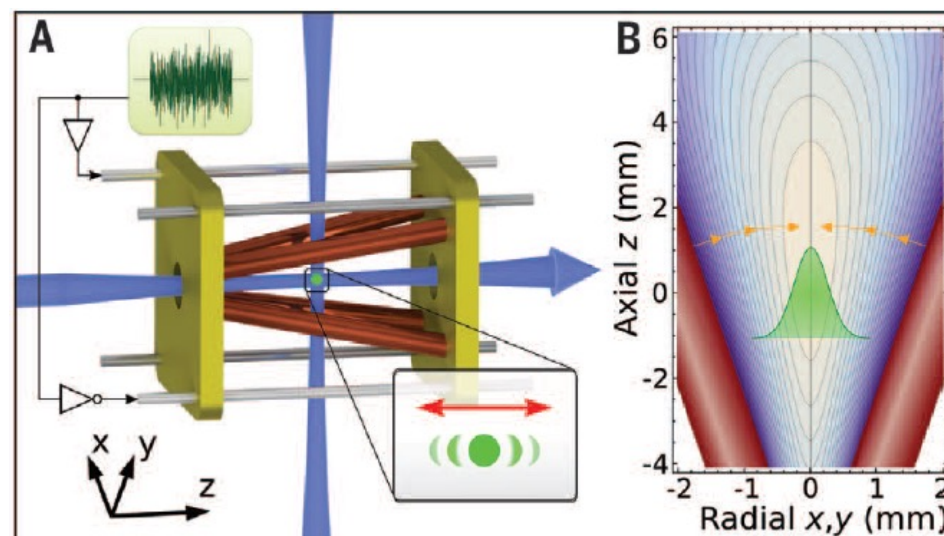
"small" : Number of DOF is small.

A colloidal particle in a trap



Blickle & Bechinger, Nat. Phys. **8**, 143 (2012)

An ion in a trap



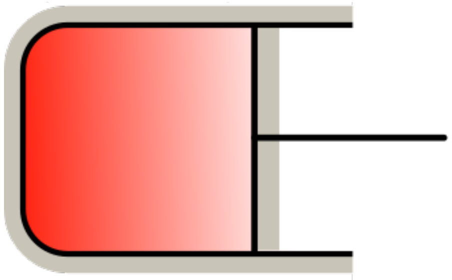
Roßnagel *et al.*, Science **352**, 325 (2016)

Thermodynamic quantities in macroscopic vs microscopic sys.

Thermodynamic quantities (e.g., E, W, Q, etc.)

Conventional thermodynamics

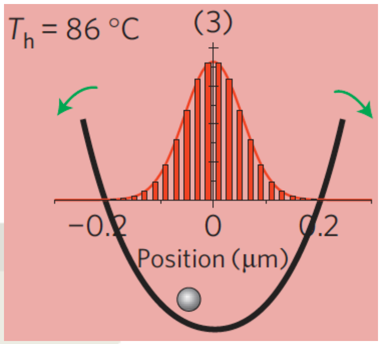
Same value for all the realizations (deterministic)



Always same amount of W for the same protocol.

Thermodynamics of small systems

Their value is different for each realization (stochastic)



Every time, different amount of W even for the same protocol.

Thermodyn. quantities are random variables!

Thermodynamic cycles of small systems

In small sys., E, P, W, Q, etc. are random variables.

→ Even if the control parameters return to the initial value, these random variables do not return to the initial value.

However, statistical properties should return to the initial state.

Thermodynamic cycle of small sys.:

- Control parameters λ_μ (such as λ, T) must be cyclic.

$$\lambda_\mu(t+\tau) = \lambda_\mu(t)$$

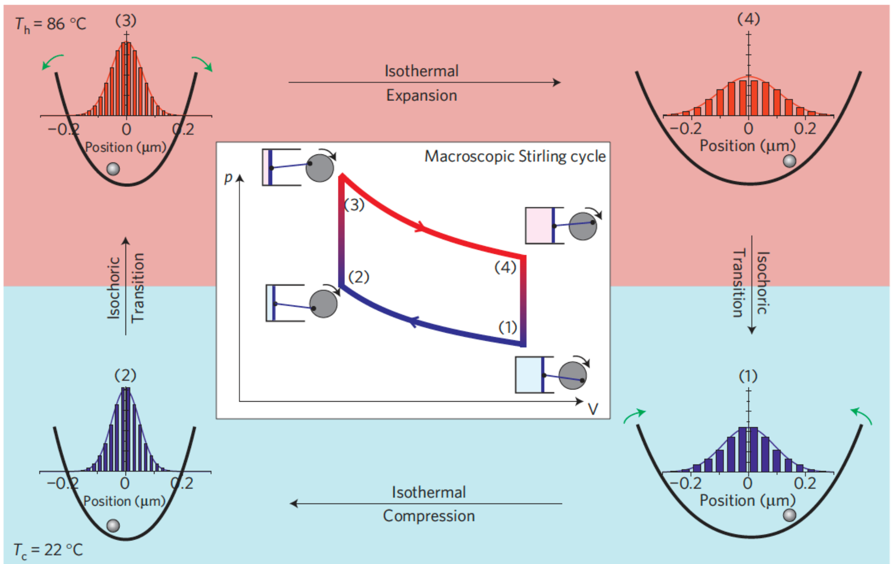
- Phase-space distribution function $p(\Gamma, t)$ must be cyclic.

$$p(\Gamma, t+\tau) = p(\Gamma, t)$$

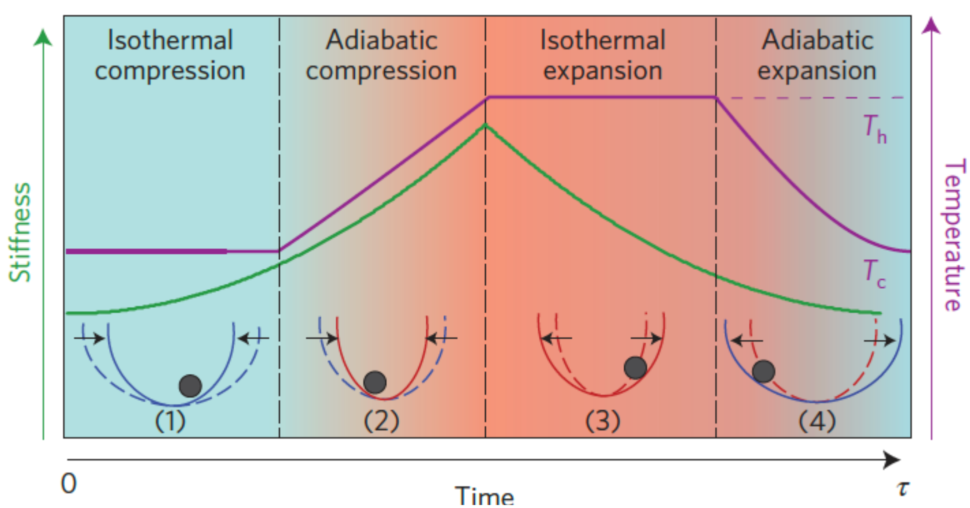
τ: cycle period

Experimental platforms

- <u>Brownian particles</u>

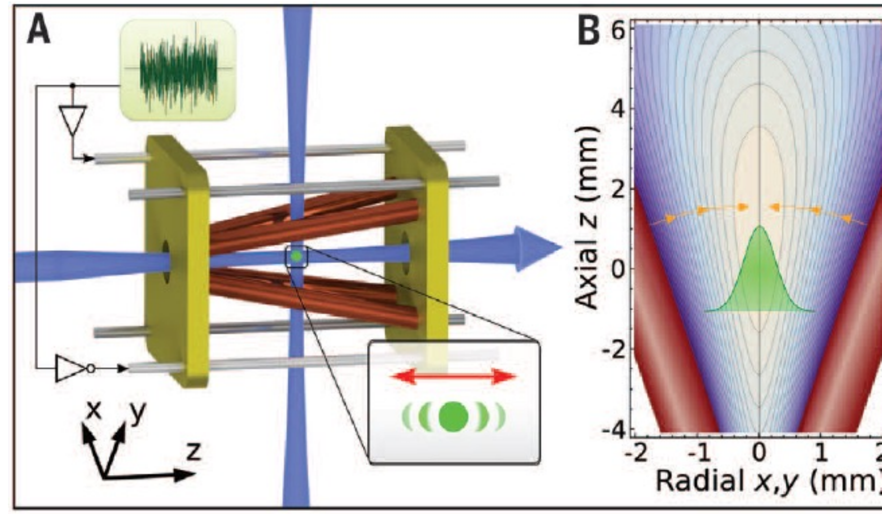


Blickle & Bechinger, Nat. Phys. **8**, 143 (2012)



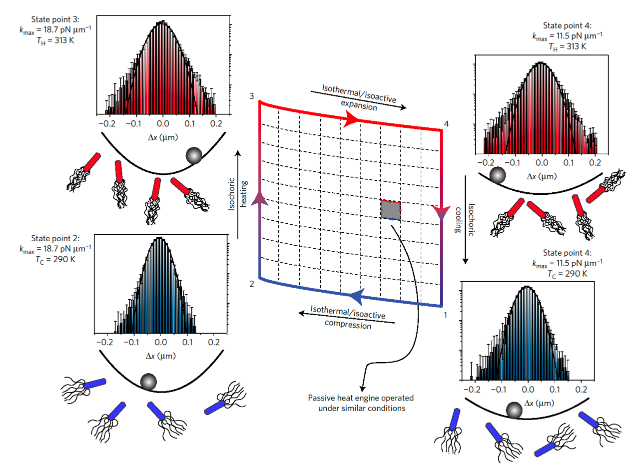
Martínez *et al*., Nat. Phys. **12**, 67 (2016)

- <u>Trapped ions</u>



Roßnagel *et al*., Science **352**, 325 (2016)

- <u>Colloids in an active bath</u>



Krishnamurthy *et al*.,
Nat. Phys. **12**, 1134 (2016)

Microscopic heat engines: Grand motivation

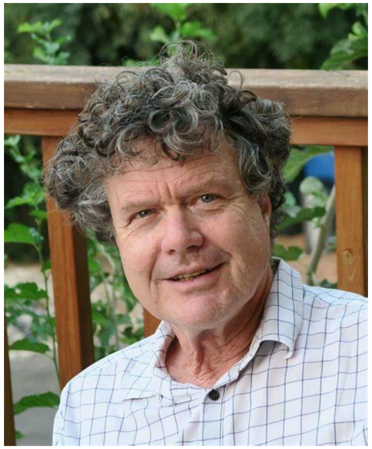
Grand motivation of microscopic heat engines

1. Practical side

Miniaturization of refrigerators

Study on microscopic heat engines would open a way to miniaturize refrigerators.

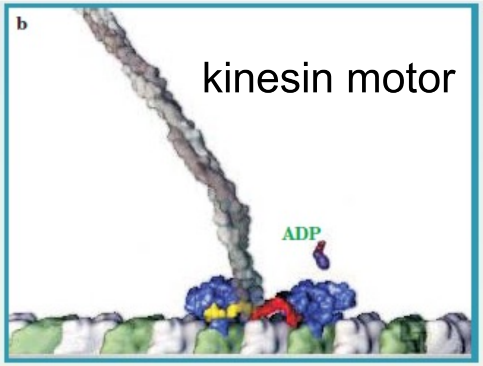
(Ronnie Kosloff @ KIAS Workshop on Quantum Information and Thermodynamics, Nov. 2019)



Ronnie Kosloff

Microscopic thermal machines are ubiquitous

e.g., biological molecular motors



Bustamante *et al.*, Phys. Today **58**, 43 (2005)

Microscopic heat engines: Grand motivation

2. Fundamental side

Understanding of thermodynamics of small systems.

Main agenda:

- How small can systems go for thermodynamics to be applicable?
- Is the formulation of thermodynamics possible for microscopic systems (classical and quantum)?
- What is microscopic origin of the laws of thermodynamics?

Christopher Jarzynski

how (and to what extent, and in what forms) the laws of thermodynamics apply to microscopic systems

Jarzynski, Eur. Phys. J. B **64**, 331 (2008)

Fluctuations in small heat engines

Small systems (number of DOF is small)

➡ Fluctuations are non-negligible.

Characterization of the performance **beyond mean values** is important for small heat engines.

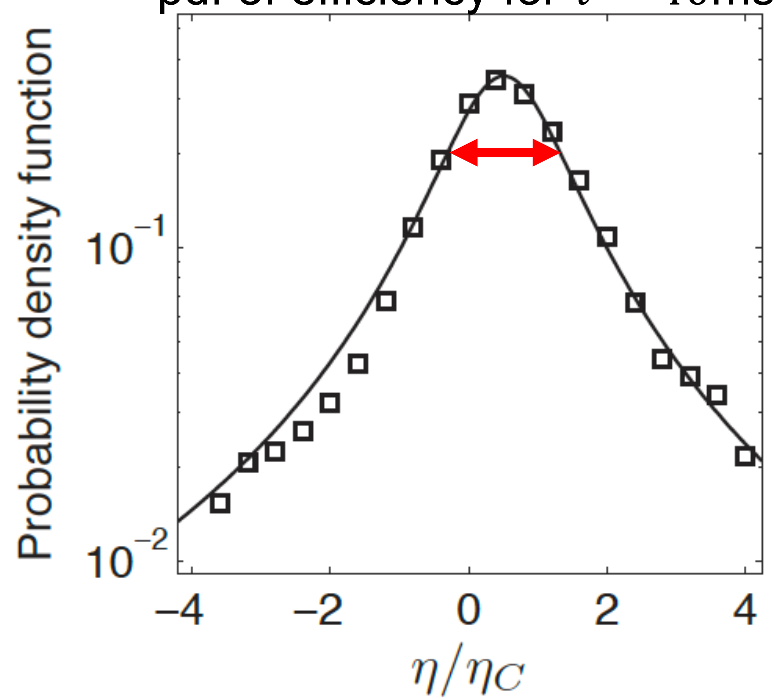
Conventional measures of the performance:

efficiency : $\eta \equiv \frac{\langle W \rangle}{\langle Q_h \rangle}$ power : $P \equiv \frac{\langle W \rangle}{\tau}$

$\langle \cdots \rangle$: ensemble avr.

Fluctuations in small heat engines

Performance of the engine largely fluctuates btwn. realizations!



τ: cycle period

Martínez *et al*., Nat. Phys. **12**, 67 (2016)

Variance of efficiency is ~1 and
pdf of efficiency spreads even to the negative side.

Fluctuations in small heat engines

From quasi-static to finite-time regime

1. Quasi-static limit $(\dot{\lambda} \to 0)$ "Almost still"

$$\lambda/\dot{\lambda} \to \infty \quad \text{(at least } \lambda/\dot{\lambda} \gg \tau_{corr}) \quad \Rightarrow \quad p(\Gamma, t) \cong p_{eq}(\Gamma; \lambda(t))$$

2. Linear response regime "Very slow"

$\lambda/\dot{\lambda} \gg \tau_{corr}$ but $\lambda/\dot{\lambda}$ is finite.

$$\Rightarrow \quad p(\Gamma, t) \cong p_{eq}\big(\Gamma; \lambda(t)\big) + \delta p(\Gamma, t) \quad \text{with} \quad \delta p(\Gamma, t) \propto \dot{\lambda}(t)$$

3. Beyond linear response regime "Fast"

$$\lambda/\dot{\lambda} \lesssim \tau_{corr}$$

From quasi-static to finite-time regime

1. Quasi-static limit $(\dot{\lambda} \to 0)$

Ito, Xu, *et al.*, arXiv:1910.08096 (2019)

Universal relation btwn. fluctuations of work & heat

$$\eta^{(n)} \equiv \frac{\langle (\Delta W)^n \rangle}{\langle (\Delta Q_h)^n \rangle} = \left(1 - \frac{T_c}{T_h}\right)^n = \eta_C^n$$

2. Linear response regime

GW & Minami, PRR **4**, L012008 (2022)

Theory of finite-time thermodynamics of fluctuations.

Brownian Carnot cycle allows us to minimize the mean and fluctuation of the dissipation simultaneously.

3. Beyond linear response regime $\left(\lambda/\dot{\lambda} \lesssim \tau_{corr}\right)$

Xu & GW, PRR **4**, L032017 (2022)

Stabilization of the performance by the intercycle correlation.

From quasi-static to finite-time regime

1. Quasi-static limit $(\dot{\lambda} \to 0)$ "Almost still"

$$\lambda/\dot{\lambda} \to \infty \quad \text{(at least } \lambda/\dot{\lambda} \gg \tau_{corr}\text{)} \quad \Rightarrow \quad p(\Gamma, t) \cong p_{eq}(\Gamma; \lambda(t))$$

2. Linear response regime "Very slow"

$\lambda/\dot{\lambda} \gg \tau_{corr}$ but $\lambda/\dot{\lambda}$ is finite.

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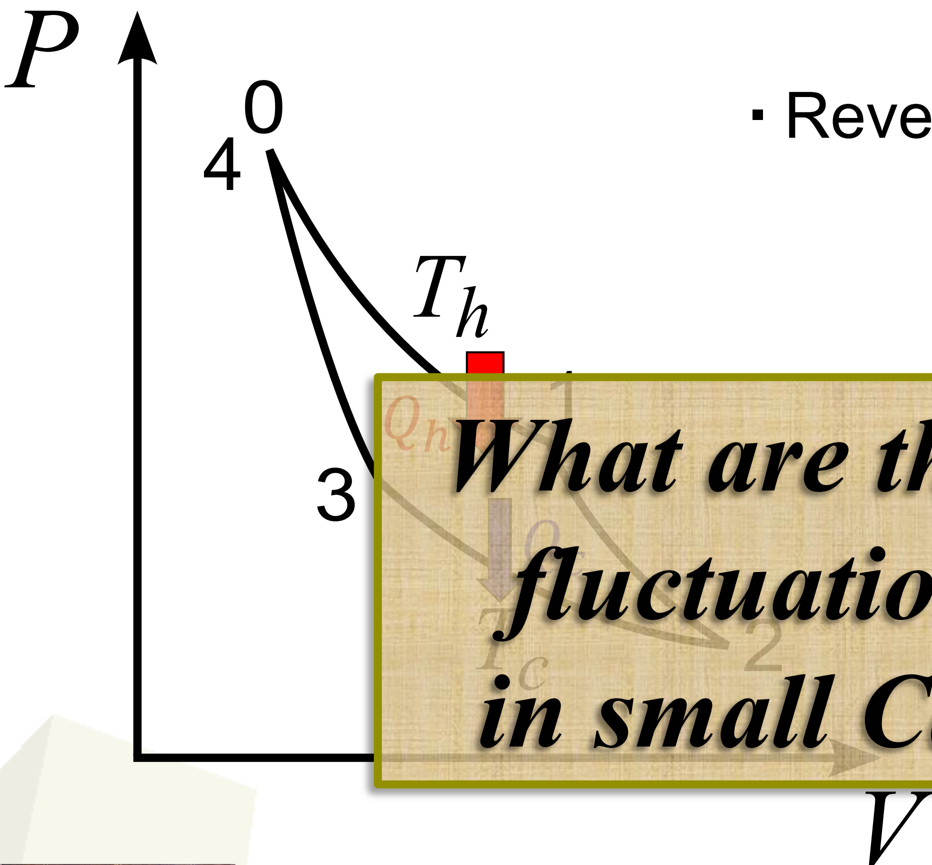
3. Beyond linear response regime "Fast"

$$\lambda/\dot{\lambda} \lesssim \tau_{corr}$$



- Reversible cycle consisting of

  - 2 quasi-static isothermal strokes: 0→1 2→3
  - 2 quasi-static adiabatic strokes: 1→2 3→4

What are the properties of fluctuations of W & Q in small Carnot engines.

- Gives maximum possible efficiency: $\eta \equiv \frac{\langle W \rangle}{\langle Q_h \rangle} = 1 - \frac{T_c}{T_h}$

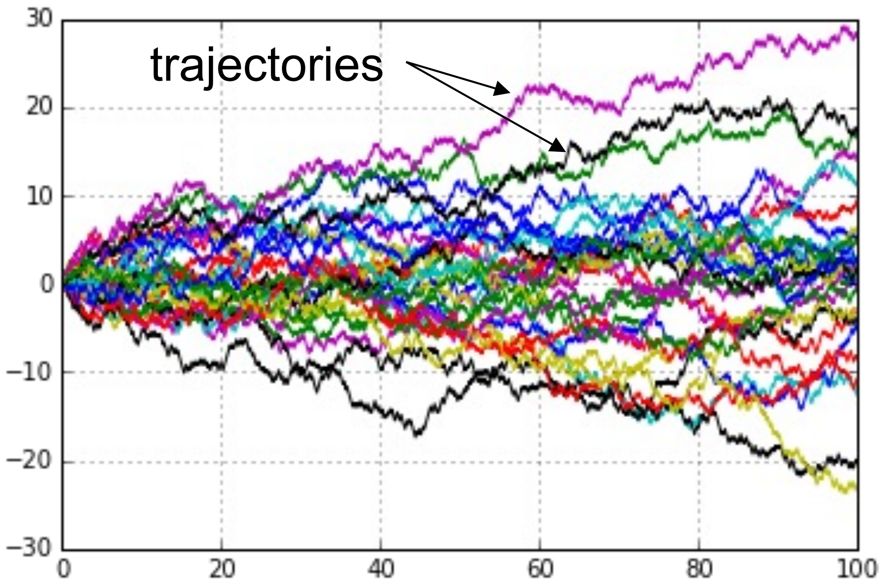
$$\eta_C \equiv 1 - \frac{T_c}{T_h}$$ (Carnot efficiency)

- Plays a key role in thermodynamics.

Sadi Carnot (1796-1832)

Deterministic work in quasistatic isothermal processes

Trajectories of a Brownian particle



Random force from the heat bath

→ Work in an isothermal process is stochastic.

$$W[\gamma] \neq \langle W \rangle$$

Work along a trajectory γ:

$$W[\gamma] \equiv -\int_{t_{\mathrm{init}}}^{t_{\mathrm{fin}}} dt\, \underline{\frac{d\lambda}{dt}\frac{\partial H_\lambda[\gamma]}{\partial \lambda}}$$

power

However, fluctuation of work becomes negligible for quasi-static isothermal processes.

・The system thoroughly takes all the possible microstates at each instant value of λ.

Law of large numbers → $W[\gamma_1] = W[\gamma_2] = \cdots = \langle W \rangle$

Sekimoto, *Stochastic energetics* (Springer, 2010)

On equilibration in adiabatic systems

- Thermodynamics for macroscopic systems

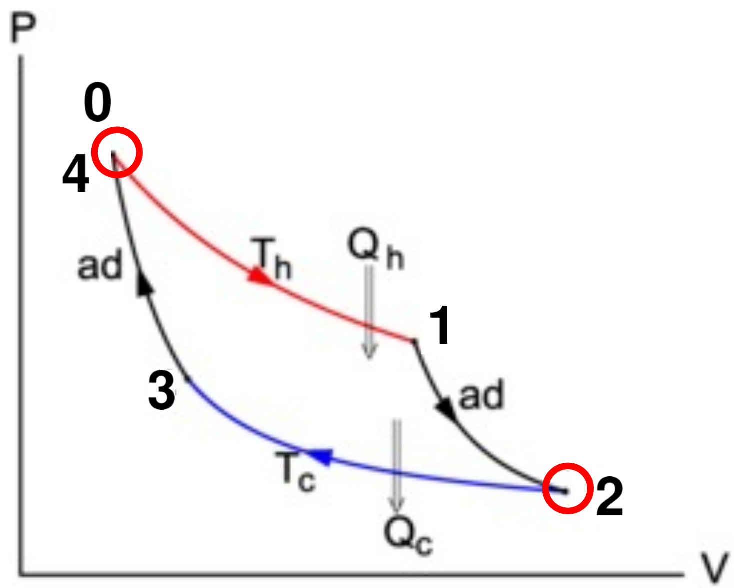
After a sufficiently long time, adiabatic systems will be in an equilibrium state at some temperature.

- Thermodynamics for small systems

Adiabatic systems might never relax into an equilibrium state.

After an adiabatic process, even if it is quasi-static,
the final state is different from canonical state in general.

Quasi-static adiabatic process in small systems



1^-: canonical st. for λ_1 & T_h

1^+: a microst. chosen from canonical distribution for λ_1 & T_h

↓ q.s. adiabatic evolution

2^-: a microst. adiabatically evolved from the one at 1+

2^+: canonical st. for λ_2 & T_c

} Different distribution in general.

- To be reversible, the final st. of q.s. adiabatic strokes should follow the canonical distribution of the subsequent q.s. isothermal stroke.

➡ Otherwise, irreversible heat flow occurs at points 2 and 4.

Working substance considered

Condition for "adiabatic reversibility":

For adiabat from (λ_1, T_1) & $\lambda_1 \to \lambda_2$

Final state of the quasi-static adiabatic stroke is consistent with the Canonical ensemble for H_{λ_2} at some temp. T_2.

$$\Leftrightarrow \quad \frac{E_1}{T_1} = \frac{E_2}{T_2} \quad \text{up to a constant.}$$

Sato, Sekimoto, Hondou & Takagi, PRE **66**, 016119 (2002)

Our working substance:

Such T_2 can be found for any λ_1, λ_2 & T_1.

i.e., Carnot cycle can be formed for an arbitrary choice of T_h & T_c, and arbitrary λ at starting points of quasi-static adiabatic strokes.

Example: Working substance with the number of st. $I_\lambda(E) = f(\lambda)E^\alpha$

A single particle trapped in
- 1D HO pot. $I_{\omega^{-1}} = 2\pi\omega^{-1}E$
- 1D box pot. $I_d = \sqrt{8m}\, d\, E^{1/2}$

Universal relation & bound of fluctuations

Fluctuations in microscopic Carnot engines

- Universal relation btwn. fluctuations of work and heat

$$\eta^{(n)} \equiv \frac{\langle (\Delta W)^n \rangle}{\langle (\Delta Q_h)^n \rangle} = \left(1 - \frac{T_c}{T_h}\right)^n = \eta_C^n$$

central moment $\langle (\Delta X)^n \rangle \equiv \langle (X - \langle X \rangle)^n \rangle$

$\eta^{(n)}$ depends only on the temperature ratio T_c/T_h.

- $\eta^{(2)}$ of the Carnot cycle is **maximum** among quasi-static cycles.

$$\eta^{(2)} \equiv \frac{\langle \Delta W^2 \rangle}{\langle \Delta Q_h^2 \rangle} \leq \eta_{\mathrm{C}}^{(2)} \quad \text{with} \quad \eta_{\mathrm{C}}^{(2)} = \left(1 - \frac{T_c}{T_h}\right)^2$$

Ito, Xu, Jiang, Roldán, Martínez, Rica, GW, arXiv:1910.08096

[see also Saryal *et al*., PRL **127**, 190603 (2021) (quantum steady-st. engine).]

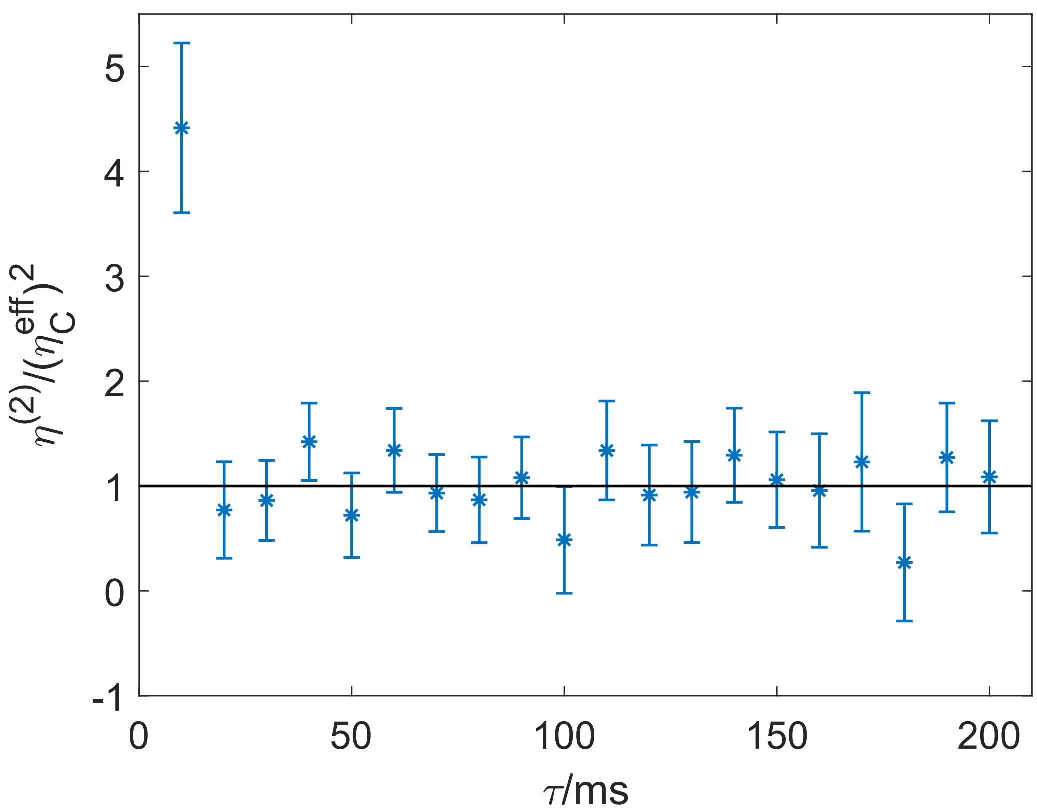
Experimental verification

Correspondence relation btwn. work variance of the true adiabatic stroke & heat variance of the isentropic stroke in the Brownian engine:

$$\left\langle \left(\Delta W_i^{\mathrm{true}}\right)^2 \right\rangle = \left\langle \left(\Delta Q_i^{\mathrm{Brow}}\right)^2 \right\rangle - 2k_B^2 T_h T_c$$

➡ Evaluate $\eta^{(2)}$ using exp. data of the Brownian Carnot engine.

Exp.: Martínez *et al.*, Nat. Phys. **12**, 67 (2016)



Consistent with the exp. data even in the non-quasistatic regime!

Application of our results

$$\eta^{(2)} \equiv \frac{\langle \Delta W^2 \rangle}{\langle \Delta Q_h^2 \rangle} \leq \eta_{\mathrm{C}}^{(2)}$$

$$\eta_{\mathrm{C}}^{(2)} = \left(1 - \frac{T_c}{T_h}\right)^2$$

New guiding principle
in optimizing fluctuations
in small heat engines

$$\sqrt{\langle \Delta W^2 \rangle} \leq \eta_C \sqrt{\langle \Delta Q_h^2 \rangle}$$

To reduce fluctuation of the work output, fluctuation of heat input from the hot heat bath should be reduced.

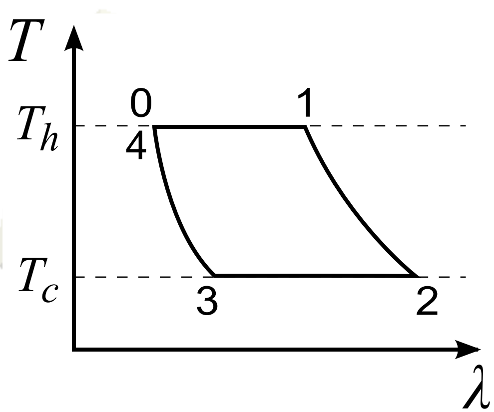
Application of our results

$$\sqrt{\langle \Delta W^2 \rangle} \le \eta_C \sqrt{\langle \Delta Q_h^2 \rangle}$$

To reduce fluctuation of the work output, fluctuation of heat input from the hot heat bath should be reduced.

Example: Carnot cycle $\langle W \rangle = \eta_C \langle Q_h \rangle$ $\sqrt{\langle \Delta W^2 \rangle} = \eta_C \sqrt{\langle \Delta Q_h^2 \rangle}$

We can reduce $\langle \Delta W^2 \rangle$ with keeping $\langle W \rangle$ fixed.



e.g., by using a box pot. instead of HO one

Working substance with $I_\lambda(E) = f(\lambda)E^\alpha$ (I_λ: phase-space vol.)

$$\langle Q_h \rangle = k_B T_h \ln \frac{f(\lambda_1)}{f(\lambda_0)}$$ Depends only on λ.

$$\langle \Delta Q_h^2 \rangle = \langle \Delta E_0^2 \rangle + \langle \Delta E_1^2 \rangle = 2(k_B T_h)^2 \alpha$$ Depends only on α.

box pot.: $\alpha = 1/2$

HO pot.: $\alpha = 1$

From quasi-static to finite-time regime

1. Quasi-static limit $(\dot{\lambda} \to 0)$ "Almost still"

$$\lambda/\dot{\lambda} \to \infty \quad \text{(at least } \lambda/\dot{\lambda} \gg \tau_{corr}) \;\Rightarrow\; p(\Gamma, t) \cong p_{eq}(\Gamma; \lambda(t))$$

2. Linear response regime "Very slow"

$\lambda/\dot{\lambda} \gg \tau_{corr}$ but $\lambda/\dot{\lambda}$ is finite.

$\Rightarrow$ $p(\Gamma, t) \cong p_{eq}\big(\Gamma; \lambda(t)\big) + \delta p(\Gamma, t)$ with $\delta p(\Gamma, t) \propto \dot{\lambda}(t)$

3. Beyond linear response regime "Fast"

$$\lambda/\dot{\lambda} \lesssim \tau_{corr}$$

Finite-time operations of small heat engines

- **Small sys. (small DOFs)**: Fluctuation is non-negligible!
- **Finite-time operations**: Dissipation is non-negligible!

Linear response regime: $\lambda/\dot{\lambda}$ is finite but $\lambda/\dot{\lambda} \gg \tau_{corr}$

➡ Key quantity: **Fluctuation of dissipation**

Guiding principle to suppress both the mean & fluctuation of dissipation is highly desirable.

Finite-time thermodynamics of fluctuations in small sys.

GW & Minami, Phys. Rev. Res. **4**, L012008 (2022)

Dissipated availability A: Quantity characterizing dissipation.

Salamon & Berry, PRL **51**, 1127 (1983)

Brandner & Saito, PRL **124**, 040602 (2020)

$$A \equiv (\text{thermal energy input}) - (\text{work output}) = U - W$$

thermal energy input $U \equiv \oint_C T dS$

work output $W \equiv \oint_C P dV$

$U = Q$ (heat input) for quasi-static cycles, but $U \neq Q$ in general.

(∵ Temp. of the sys. is not necessary equal to T.)

Impact of A on efficiency and its fluctuation

Efficiency $\epsilon \equiv \frac{\langle W \rangle}{\langle U \rangle} \approx 1 - \frac{\langle A \rangle}{\mathcal{W}}$

$\mathcal{W}$: quasi-static work, deterministic ($\mathcal{W} = \langle \mathcal{W} \rangle$)

Stochastic efficiency $\mathcal{E} \equiv \frac{W}{U} \approx 1 - \frac{A}{\mathcal{W}}$

$\Rightarrow \langle \Delta \mathcal{E}^2 \rangle \approx \frac{\langle \Delta A^2 \rangle}{\mathcal{W}^2}$

Simultaneous reduction of $\langle A \rangle$ & $\langle \Delta A^2 \rangle$ is desirable!

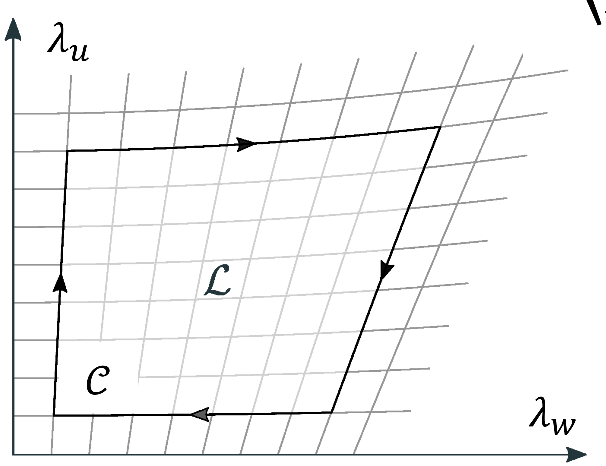
Dissipation in terms of metric tensor

$\langle A \rangle$ can be written by $g_{\mu\nu}$ and can also be related to the length defined by this $g_{\mu\nu}$.

Parameters (displacements) : $\lambda_\mu \equiv (\lambda_w, \lambda_u) = (V, T)$

Conjugate forces : $X_\mu \equiv (X_w, X_u) = (P, S)$

$$\langle A \rangle = -\int_0^\tau dt \, \langle X_\mu \rangle \, \dot{\lambda}_\mu$$



linear approx.: $\langle X_\mu \rangle \cong \langle X_\mu \rangle_{\mathrm{eq}} + R_{\mu\nu} \, \dot{\lambda}_\nu$

response coeff.

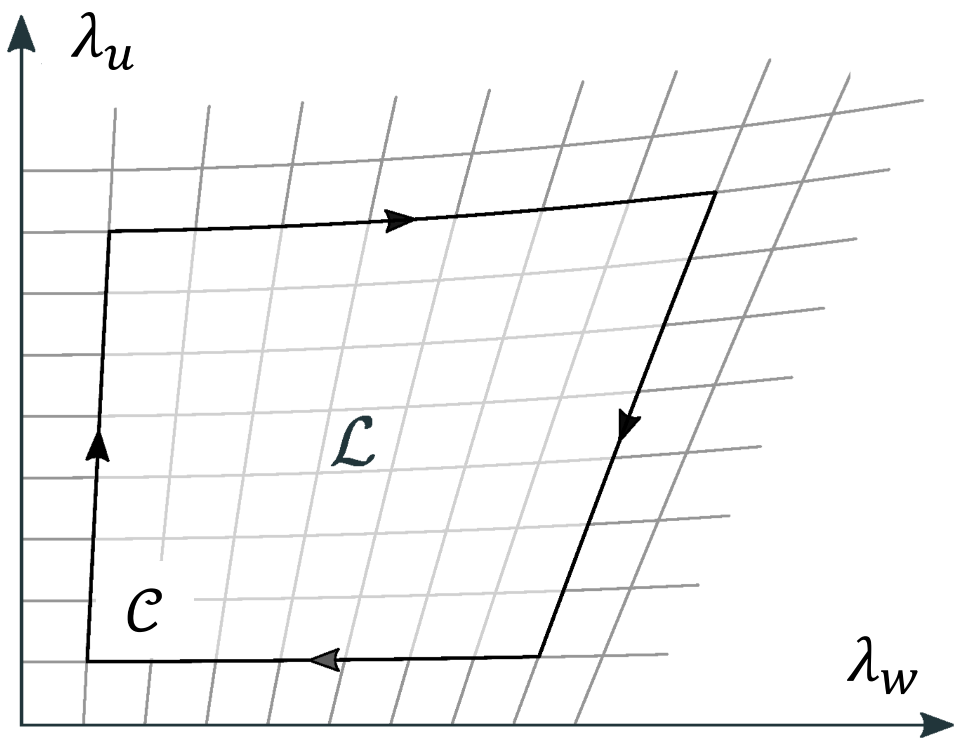
$$= \int_0^\tau dt \, g^{(1)}_{\mu\nu} \, \dot{\lambda}_\mu \, \dot{\lambda}_\nu$$

with $g^{(1)}_{\mu\nu} \equiv -(R_{\mu\nu} + R_{\nu\mu})/2$

Geometric interpretation of dissipated availability

Mean dissipation $\langle A \rangle$ is lower bounded by the "length" of the path in the control parameter space.

Salamon & Berry, PRL **51**, 1127 (1983)
Brandner & Saito, PRL **124**, 040602 (2020)



$$\langle A \rangle \geq \left(\mathcal{L}^{(1)}\right)^2 / \tau$$

thermodyn. length:

$$\mathcal{L}^{(1)} = \oint_{\mathcal{C}} \sqrt{g^{(1)}_{\mu\nu} d\lambda_\mu d\lambda_\nu}$$

Once the path is given, $\mathcal{L}^{(1)}$ is fixed.
(geometric quantity)

Even if the path is given, $\langle A \rangle$ depends on how to traverse the path.

Time scale matters

To describe the fluctuation of work, information of the time scale of the system is necessary.

$$W = -\int_{t_i}^{t_f} dt\, \dot{\lambda}(t) \frac{\partial H(t)}{\partial \lambda}$$

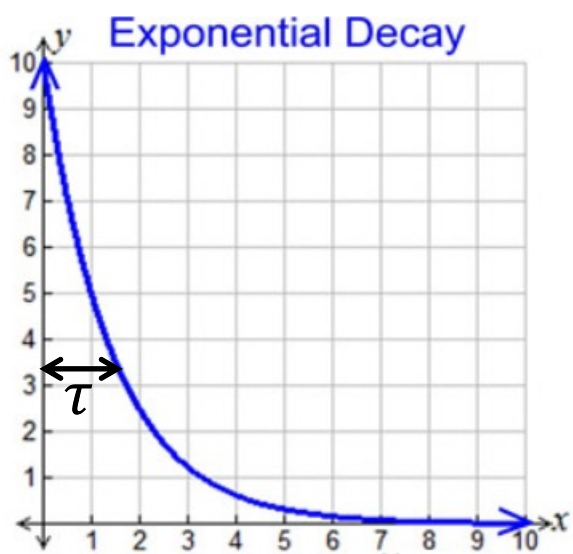
2nd moment:

$$\langle W^2 \rangle = \int_{t_i}^{t_f} dt \int_{t_i}^{t_f} dt'\, \dot{\lambda}(t)\, \dot{\lambda}(t') \left\langle \frac{\partial H(t)}{\partial \lambda} \frac{\partial H(t')}{\partial \lambda} \right\rangle$$

$\left\langle \frac{\partial H(t)}{\partial \lambda} \frac{\partial H(t')}{\partial \lambda} \right\rangle$: two-time correlation function

Introducing time scale in thermodynamics

Correlations in the sys. under thermal environment often show exponential decay asymptotically.



In coarse-grained timescale, exp with decay time τ can be approximated by a half-delta function with strength 2τ:

$$e^{-t/\tau} \;\to\; 2\tau\,\delta(t) \quad [t \geq 0]$$

$$\left\langle \Delta X_\mu(t)\,\Delta X_\nu(t')\right\rangle \cong 2\left\langle \Delta X_\mu(t)\,\Delta X_\nu(t)\right\rangle \tau_{\mu\nu}(t)\,\delta(t-t')$$

$\tau_{\mu\nu}$: correlation time

Minimal prescription to introduce time scale through $\tau_{\mu\nu}$.

Fluctuation of dissipated availability

$$\langle \Delta X_\mu(t)\, \Delta X_\nu(t') \rangle \cong 2 \,\langle \Delta X_\mu(t)\, \Delta X_\nu(t) \rangle\, \tau_{\mu\nu}(t)\, \delta(t - t')$$

$$\Rightarrow \quad \langle \Delta A^2 \rangle = \int_0^\tau dt\, g^{(2)}_{\mu\nu}\, \dot{\lambda}_\mu\, \dot{\lambda}_\nu$$

with $g^{(2)}_{\mu\nu}(t) \equiv 2\, \tau_{\mu\nu}(t)\, \langle \Delta X_\mu(t)\, \Delta X_\nu(t) \rangle$

Similarly to $\langle A \rangle$, we obtain:

$$\langle \Delta A^2 \rangle \geq {(\mathcal{L}^{(2)})^2}/{\tau}$$

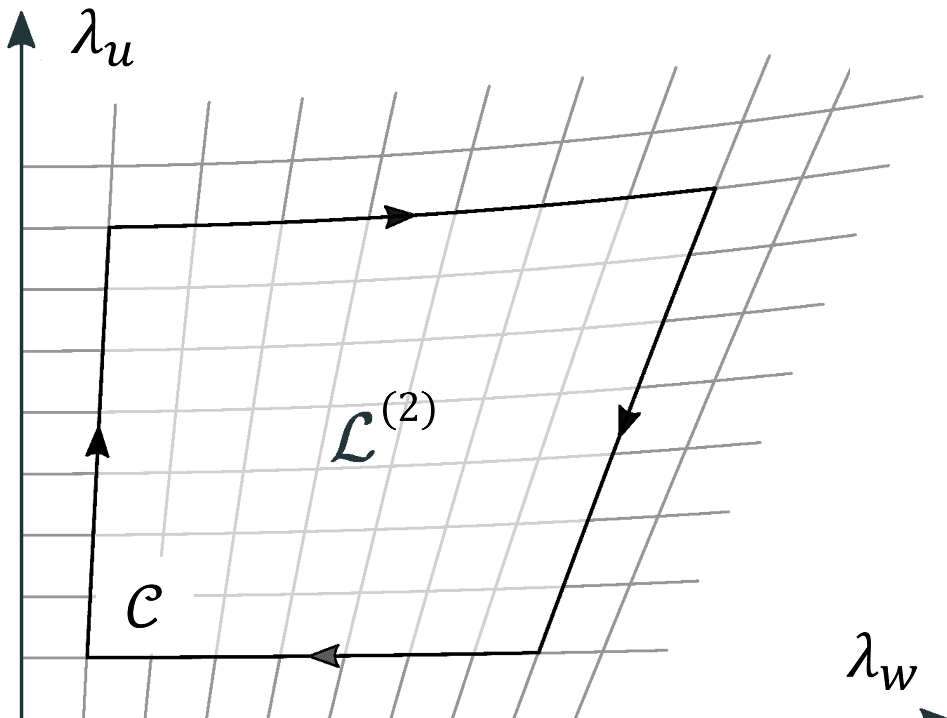
$$\mathcal{L}^{(2)} \equiv \int_0^\tau dt \sqrt{g^{(2)}_{\mu\nu}\, \dot{\lambda}_\mu\, \dot{\lambda}_\nu} = \oint_C \sqrt{g^{(2)}_{\mu\nu}\, d\lambda_\mu d\lambda_\nu}$$

Equality holds if and only if $g^{(2)}_{\mu\nu}\, \dot{\lambda}_\mu\, \dot{\lambda}_\nu = const.$

Geometric interpretation of dissipated availability

Fluctuation $\langle \Delta A^2 \rangle$ is also lower bounded by another length of the path in the control parameter space.

GW & Minami, PRR **4**, L012008 (2022)



$$\langle \Delta A^2 \rangle \geq \left(\mathcal{L}^{(2)}\right)^2 / \tau$$

thermodyn. length for 2nd moment:

$$\mathcal{L}^{(2)} = \oint_C \sqrt{g^{(2)}_{\mu\nu}\, d\lambda_\mu d\lambda_\nu}$$

$$g^{(2)}_{\mu\nu}(t) \equiv 2\tau_{\mu\nu}(t) \left\langle \Delta X_\mu(t)\, \Delta X_\nu(t) \right\rangle$$

correlation time

Relation between $g_{\mu\nu}^{(1)}$ and $g_{\mu\nu}^{(2)}$

- Linear-response regime: $\lambda/\dot{\lambda} \gg \tau_{corr}$
- Coarse-grained timescale Δt: $\lambda/\dot{\lambda} \gg \Delta t \gg \tau_{corr}$

⇒ Relation between the metrics for $\langle A \rangle$ and $\langle \Delta A^2 \rangle$.

$$g_{\mu\nu}^{(2)}(t) \cong 2k_B T(t)\, g_{\mu\nu}^{(1)}(t)$$

(analogous to the fluct-dissip. relation)

Application to the Brownian Carnot cycle

Carnot engine with an overdamped Brownian particle in a harmonic oscillator potential.

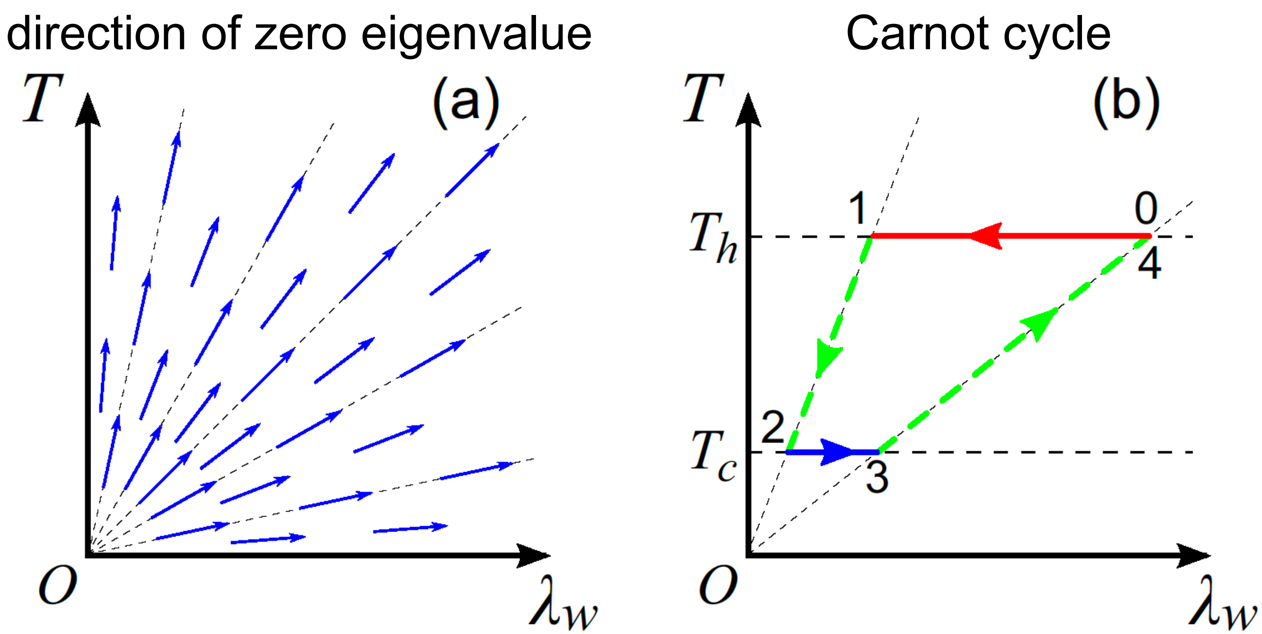
$$H\big(q,\lambda_w(t)\big) = V(q) = \frac{\lambda_w}{2} q^2$$

Metric for $\langle \Delta A^2 \rangle$: $g_{\mu\nu}^{(2)}(t) \equiv 2\,\tau_{\mu\nu}(t)\,\big\langle \Delta X_\mu(t)\,\Delta X_\nu(t) \big\rangle_{\mathrm{eq}}$

$$g_{\mu\nu}^{(2)} = \frac{\gamma}{2\lambda_w}\begin{bmatrix} (k_B T/\lambda_w)^2 & -k_B T/\lambda_w \\ -k_B T/\lambda_w & 1 \end{bmatrix}$$

Singular metric with zero eigenvalue.

Simultaneous optimization of $\langle A \rangle$ & $\langle \Delta A^2 \rangle$



Isentrope is along the path of the zero eigenvalue.

➡ $\langle A \rangle, \langle \Delta A^2 \rangle, \mathcal{L}^{(i)} = 0$ for the isentropic strokes

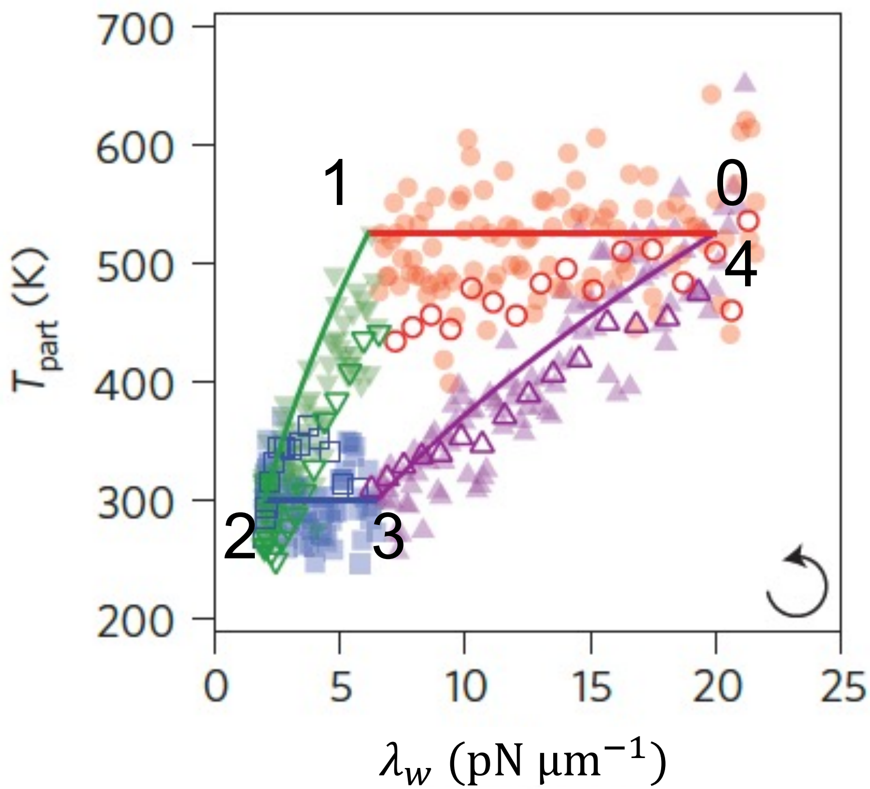
Only isothermal strokes should be optimized.

$g_{\mu\nu}^{(1)} \neq g_{\mu\nu}^{(2)}$, but they differ just by a constant factor $(2k_B T)$ in isothermal strokes.

➡ **Simultaneous minimization of $\langle A \rangle$ & $\langle \Delta A^2 \rangle$ is possible!**

Optimization for current experiment

Martínez *et al*., Nat. Phys. **12**, 67 (2016)

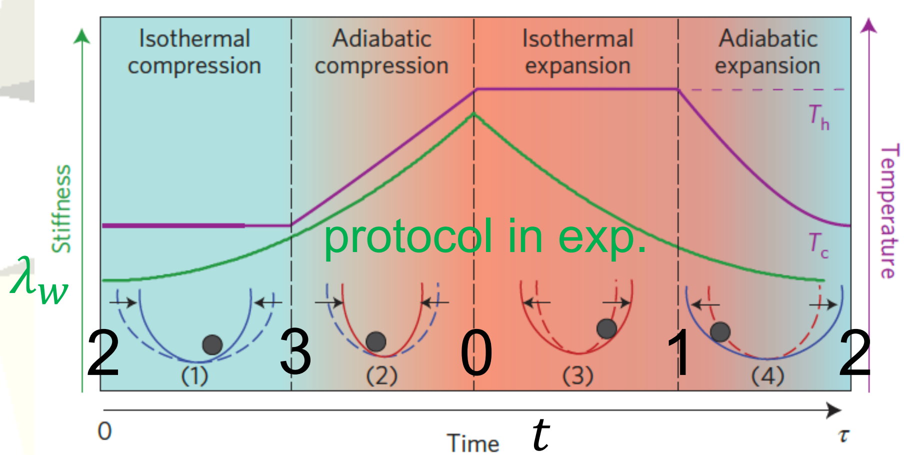


$T_c = 300\text{K}$ $\qquad \tau = 200\text{ms}$

$T_h = 525\text{K}$ $\qquad \gamma = 8.4\ \text{pN}\mu\text{m}^{-1}\ \text{ms}$

$t_1 = 0.26\tau, t_2 = 0.5\tau, t_3 = 0.75\tau$

$\lambda_{w,0} = 20.0, \lambda_{w,1} = 6.2, \lambda_{w,3} = 2.0\ \text{pN}\ \mu\text{m}^{-1}$



<u>Optimal protocol vs protocol in exp.</u>

$$\frac{\langle A_{opt}\rangle}{\langle A_{exp}\rangle} = 0.65 \qquad \frac{\langle \Delta A^2_{opt}\rangle}{\langle \Delta A^2_{exp}\rangle} = 0.70$$

Improvement by 30-35%.

Extension for multiple time scales

GW, Xu, Minami, in prep.

Two-point function of ΔX_μ & ΔX_ν:

$$\left\langle \Delta X_\mu(t)\, \Delta X_\nu(t') \right\rangle = 2 \left\langle \Delta X_\mu(t)\, \Delta X_\nu(t) \right\rangle \sum_i C_{\mu\nu}^{(i)} \exp\left(-|t - t'| / \tau_{\mu\nu}^{(i)} \right)$$

$\tau_{\mu\nu}^{(i)}$ can be complex in general

$$\left\langle \Delta X_\mu(t)\, \Delta X_\nu(t') \right\rangle \cong 2 \left\langle \Delta X_\mu(t)\, \Delta X_\nu(t) \right\rangle \overline{\tau}_{\mu\nu}(t)\, \delta(t - t')$$

with $$\overline{\tau}_{\mu\nu} \equiv \sum_i C_{\mu\nu}^{(i)}\, \tau_{\mu\nu}^{(i)}$$

From quasi-static to finite-time regime

1. Quasi-static limit $(\dot{\lambda} \to 0)$ "Almost still"

$\lambda/_{\dot{\lambda}} \to \infty$ (at least $\lambda/_{\dot{\lambda}} \gg \tau_{corr}$) ⇨ $p(\Gamma, t) \cong p_{eq}(\Gamma; \lambda(t))$

2. Linear response regime "Very slow"

$\lambda/_{\dot{\lambda}} \gg \tau_{corr}$ but $\lambda/_{\dot{\lambda}}$ is finite.

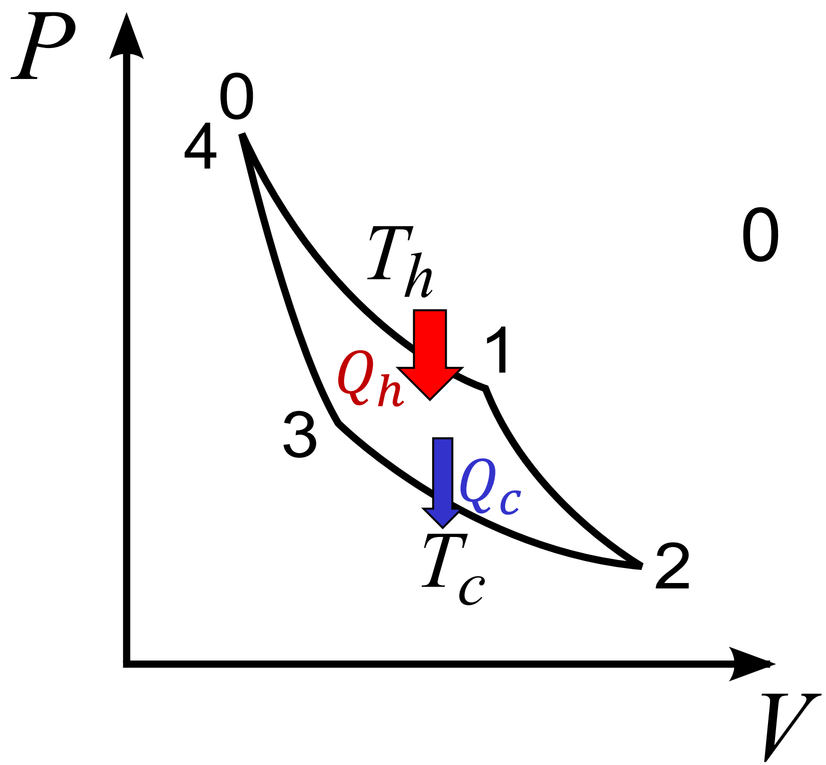
⇨ $p(\Gamma, t) \cong p_{eq}\big(\Gamma; \lambda(t)\big) + \delta p(\Gamma, t)$ with $\delta p(\Gamma, t) \propto \dot{\lambda}(t)$

3. Beyond linear response regime "Fast"

$\lambda/_{\dot{\lambda}} \lesssim \tau_{corr}$

In textbooks of thermodynamics, we consider a single-cycle operation to evaluate the performance of an engine…

Carnot cycle



0 (start) → 4 (end)

Single cycle or multiple cycles?

<u>Question</u>

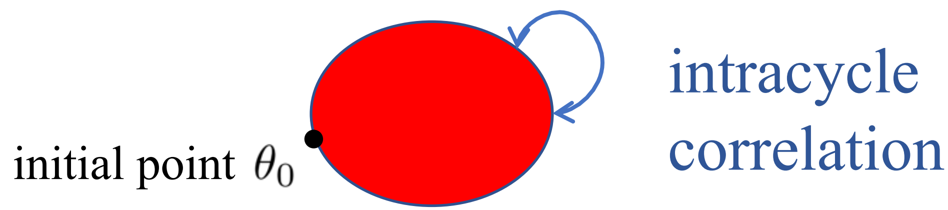
Is analysis based on a single-cycle operation sufficient for practical situations?

- No, for cycles with finite period.

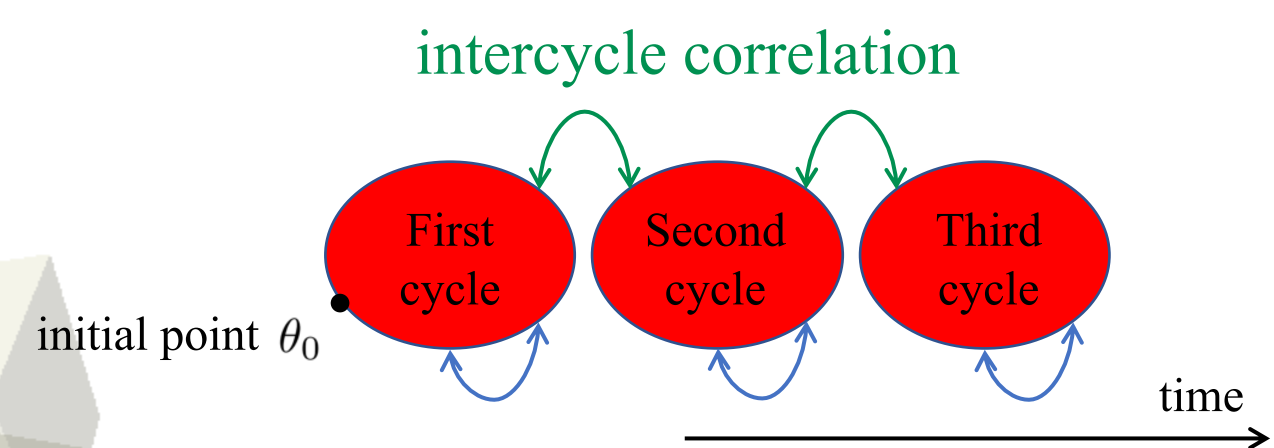
There is intercycle correlation (influence over different cycles) unlike quasi-static case.

Fluctuations in multiple cycles

Quasistatic limit — period $\gg$ correlation time



Finite-time regime — period ~ correlation time



Motivation: Make use of intercycle correlation to reduce fluctuations

Xu & GW, PRR **4**, L032017 (2022)

Uncertainty of work

Effect $\mathcal{C}_{\theta_0}^{(n)}$ of intercycle correlation: $\mathrm{Var}[W_{\theta_0}^{(n)}] = n\,\mathrm{Var}[W_{\theta_0}^{(1)}] + \mathscr{C}_{\theta_0}^{(n)}$

Uncertainty of work for n-cycle operation (θ_0: start point)

$$\Delta_{\theta_0}^{(n)} \equiv n \frac{\mathrm{Var}\left[W_{\theta_0}^{(n)}\right]}{\left\langle W_{\theta_0}^{(n)} \right\rangle^2}$$

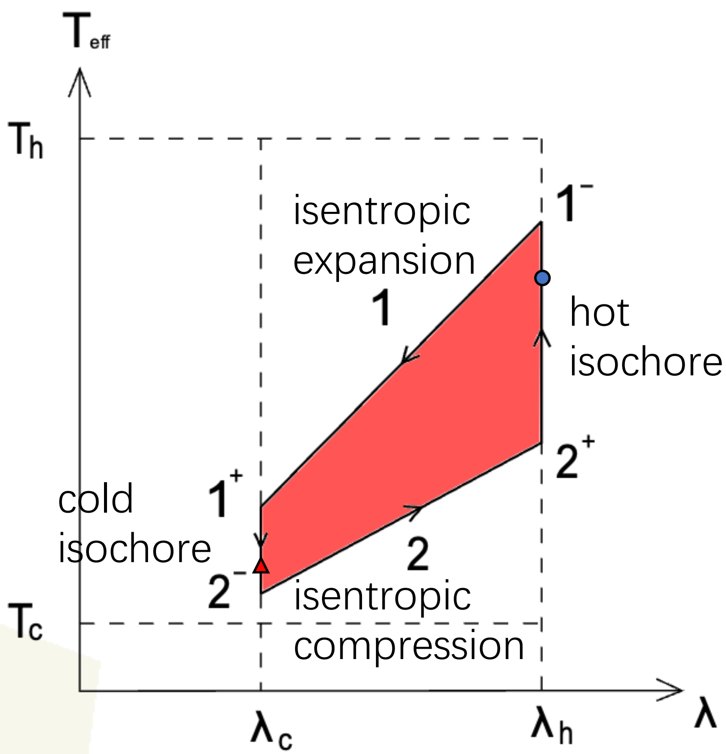
$W_{\theta_0}^{(n)}$: work through n-cycle operation starting from θ_0

Scaled by the factor of n since $\mathrm{Var}\left[W_{\theta_0}^{(n)}\right] / \left\langle W_{\theta_0}^{(n)} \right\rangle^2 \sim 1/n$ for $n \gg 1$.

Goal: Find a protocol giving $\Delta^{\infty}\ [\equiv \lim_{n\to\infty} \Delta_{\theta_0}^{(n)}] < \Delta_{\theta_0}^{(1)}$

(i.e., $\mathcal{C}_{\theta_0}^{(n)} < 0$) for any θ_0.

Example: Otto engine with an overdamped Brownian particle



$$H(q, \lambda(t)) = V(q) = \frac{\lambda}{2} q^2$$

T. Schmiedl and U. Seifert, EPL **81**, 20003 (2008)

2 isochoric strokes & 2 isentropic strokes

<u>Isentropic strokes:</u>

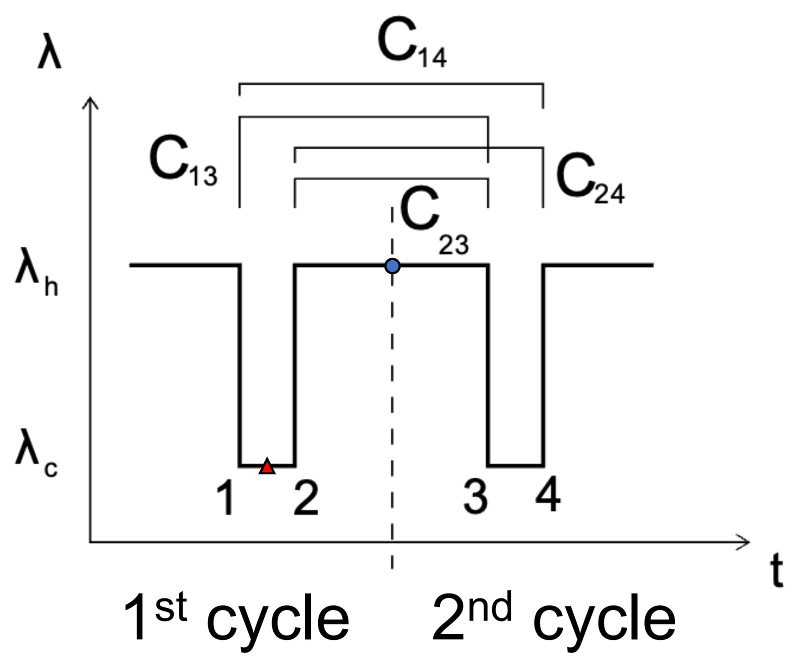
Quench T & λ simultaneously to keep the Shannon entropy $\langle S \rangle$ unchanged.

$$\langle S \rangle \equiv -k_B \langle \ln p \rangle$$

Stability induced by intercycle correlation

Fluctuation of the performance can be reduced by the intercycle correlation!

Xu & GW, PRR **4**, L032017 (2022)



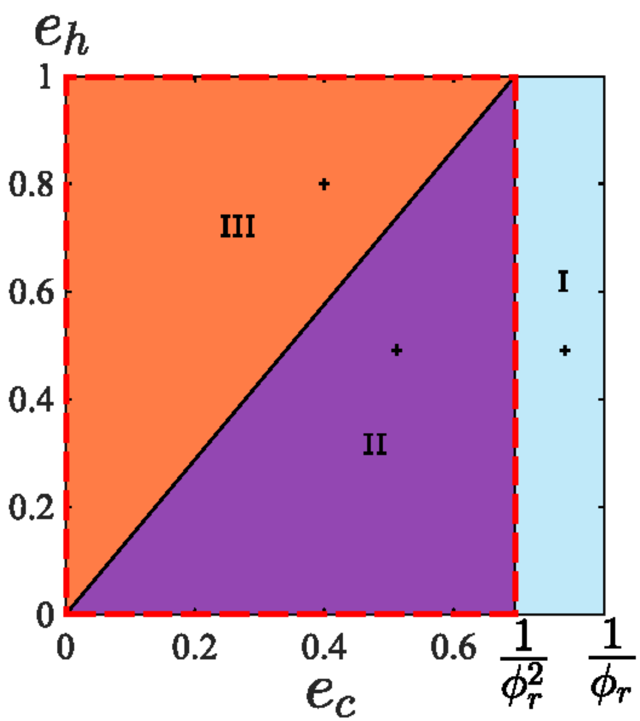
Example: $n = 2$ cycles

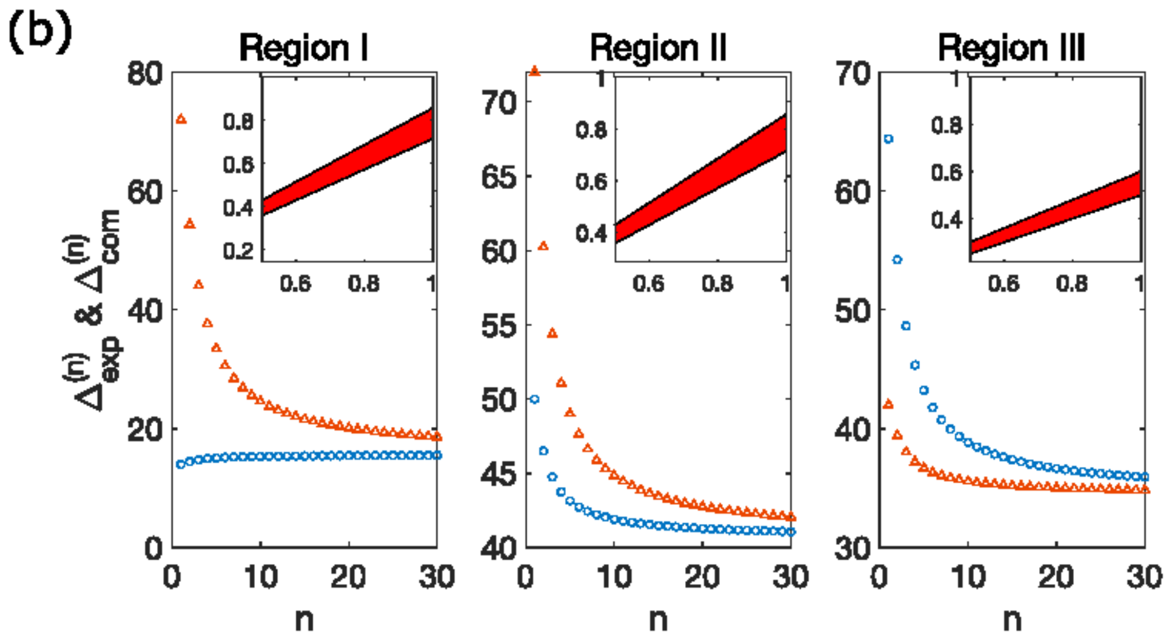
Intercycle correlation btwn. compression & expansion: $C_{23} < 0$ and dominant.

Optimize the protocol to make the net correlation negative:

$$\mathcal{C}_{\theta_0}^{(2)} = C_{23} + C_{14} + C_{13} + C_{14} < 0$$

Reduction of uncertainty by intercycle correlation





$e_i \equiv e^{-2\mu\lambda_i\tau_i}$ (incompleteness of equilibration)

$\phi_r \equiv \phi_{11}/\phi_{22}$ $\quad \phi_{ij} \equiv \langle x(t_i)\, x(t_j) \rangle$

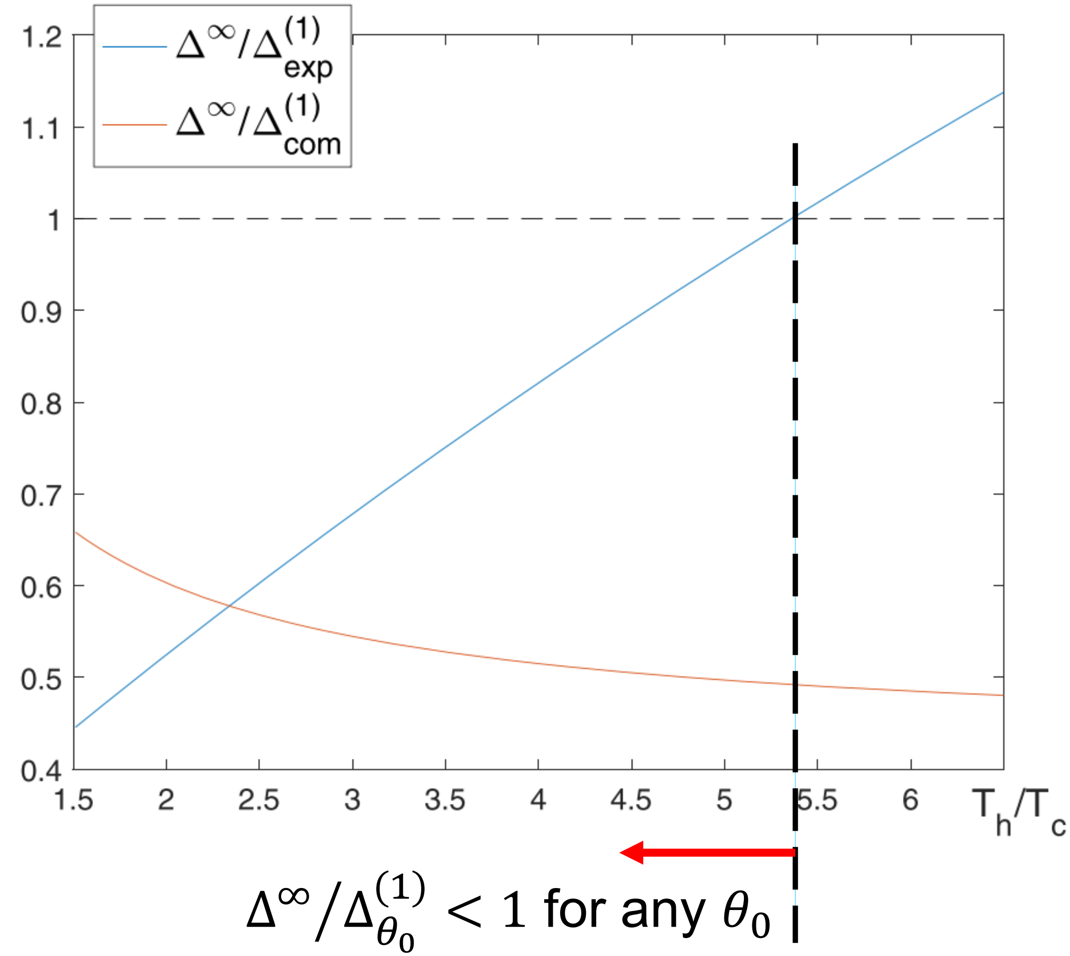
$\Delta^{(\infty)} < \Delta_{\theta_0}^{(1)}$ in Regions II & III.

Uncertainty is reduced by the intercycle correlation!

Xu & GW, PRR **4**, L032017 (2022)

Experimental feasibility

$T_c = 300$ K
$\mu = 0.119\ \mu\text{m}\cdot\text{pN}^{-1}\cdot\text{ms}^{-1}$
$\lambda_c = 1.6\ \text{pN}\cdot\mu\text{m}^{-1}$
$\lambda_h = 2.4\ \text{pN}\cdot\mu\text{m}^{-1}$
$\tau_c = 0.7$ ms
$\tau_h = 0.3$ ms



Stability induced by intercycle correlation can be realized for parameters comparable to current exp.!

Summary

1. Quasi-static limit $(\dot{\lambda} \to 0)$

Ito, Xu, *et al.*, arXiv:1910.08096 (2019)

Universal relation btwn. fluctuations of work & heat

$$\eta^{(n)} \equiv \frac{\langle (\Delta W)^n \rangle}{\langle (\Delta Q_h)^n \rangle} = \left(1 - \frac{T_c}{T_h}\right)^n = \eta_C^n$$

Universal bound on $\eta^{(2)}$

2. Linear response regime

GW & Minami, PRR **4**, L012008 (2022)

Geometric formalism of finite-time thermodynamics of fluctuation.

Simultaneous minimization of $\langle A \rangle$ & $\langle \Delta A^2 \rangle$ is possible for Brownian Carnot cycle!

3. Beyond linear response regime $\left({}^{\lambda}/_{\dot{\lambda}} \lesssim \tau_{corr}\right)$

Xu & GW, PRR **4**, L032017 (2022)

Stabilization of the performance by the intercycle correlation.

Future prospects

1. TUR for cyclic heat engines (with Xu & Saito)

Also Vu & Hasegawa, PRRes (2020); Cangemi *et al*., PRB (2020); Koyuk & Seifert, PRL (2020); Miller *et al*., PRL (2021); etc.

Geometric bound on fluctuation.

Please see today's poster by Guohua Xu for details.

2. Finite-time thermodynamics of fluctuation for quantum sys.

Also Miller *et al*., PRL (2019); etc.

Formalism applicable to both overdamped & underdamped regimes

Condition for reversibility

Condition for reversibility:

Canonical ensemble for H_{λ_2} at some temp. T_2 is consistent with the final state of the quasi-static adiabatic stroke.

$\Longleftrightarrow \quad \dfrac{E_1}{T_1} = \dfrac{E_2}{T_2}$ up to a constant.

Sato, Sekimoto, Hondou & Takagi, PRE **66**, 016119 (2002)

(Proof)

$$P^{\mathrm{eq}}_{\beta_1,\lambda_1}(E_1)\,dE_1 = \frac{e^{-\beta_1 E_1}}{Z_{\beta_1,\lambda_1}} g_{\lambda_1}(E_1)\,dE_1$$

DOS: $g_\lambda(E) \equiv \dfrac{\partial I_\lambda(E)}{\partial E}$

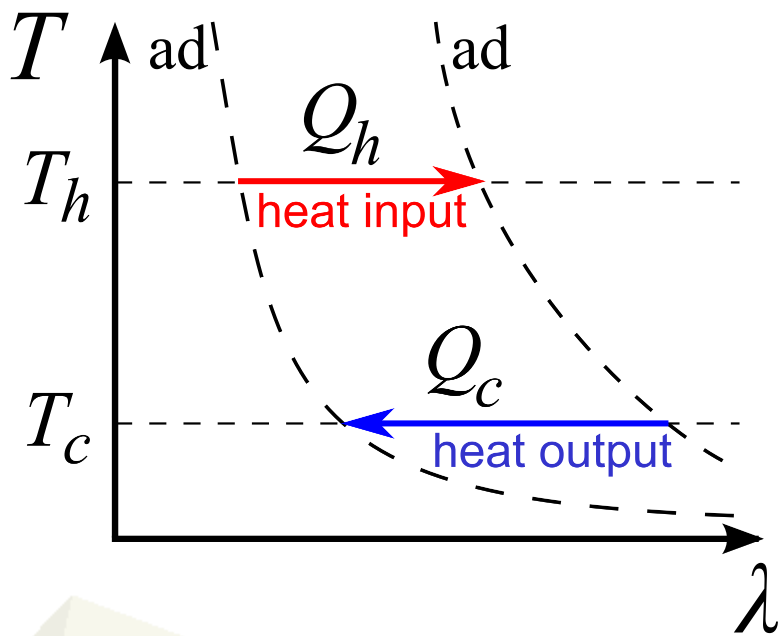
Adiabatic theorem: $I_{\lambda_1}(E_1) = I_{\lambda_2}(E_2) \Rightarrow g_{\lambda_1}(E_1)\,dE_1 = g_{\lambda_2}(E_2)\,dE_2$

Probability conservation: $P^{\mathrm{eq}}_{\beta_1,\lambda_1}(E_1)\,dE_1 = P_{\lambda_2}(E_2)\,dE_2$

$$\therefore P_{\lambda_2}(E_2)\,dE_2 = P^{\mathrm{eq}}_{\beta_1,\lambda_1}(E_1)\,dE_1 = \frac{e^{-\beta_1 E_1}}{Z_{\beta_1,\lambda_1}} g_{\lambda_2}(E_2)\,dE_2$$

This is supposed to agree with $P^{\mathrm{eq}}_{\beta_2,\lambda_2}(E_2)\,dE_2 = \dfrac{e^{-\beta_2 E_2}}{Z_{\beta_2,\lambda_2}} g_{\lambda_2}(E_2)\,dE_2$ at some T_2.

For two q.s. isotherms connecting two q.s. adiabats.



In macroscopic thermodynamics

$$\frac{\langle Q_h \rangle}{T_h} = \frac{\langle Q_c \rangle}{T_c}$$

"... this is the center of the universe of thermodynamics." (R. P. Feynman)

In small systems, similar relation holds for *n*th order moment:

$$\frac{\langle (\Delta Q_h)^n \rangle}{T_h^n} = \frac{\langle (\Delta Q_c)^n \rangle}{T_c^n}$$

Ito, Xu, Jiang, Roldán, Martínez, Rica, GW, arXiv:1910.08096

- $\eta^{(2)}$ for the Carnot cycle is **maximum** among quasi-static cycles.

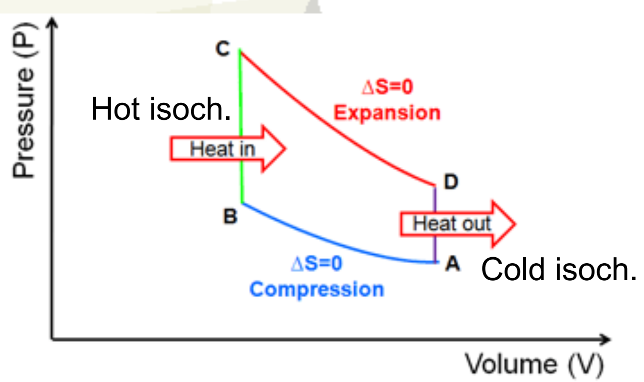
(cycles consisting of q.s. isothermal, q.s. adiabatic, isochoric, or q.s. isobaric strokes)

$$\eta^{(2)} \equiv \frac{\langle \Delta W^2 \rangle}{\langle \Delta Q_h^2 \rangle} \leq \eta_{\mathrm{C}}^{(2)} \quad \text{with} \quad \eta_{\mathrm{C}}^{(2)} = \left(1 - \frac{T_c}{T_h}\right)^2$$

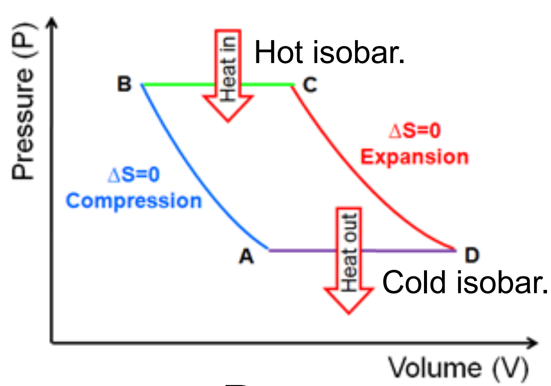
Caveats

1. Working substance satisfying the reversibility condition.
2. Adiabatic expansion (compression) strokes are preceded (followed) by a heat exchange stroke with hot bath.

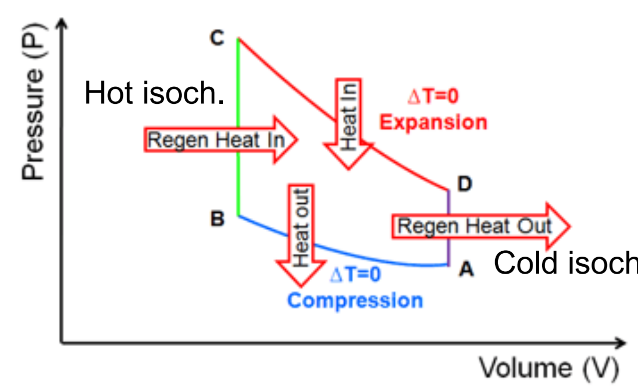
⇐ All the typical cycles satisfy this condition.



Otto



Brayton



Stirling

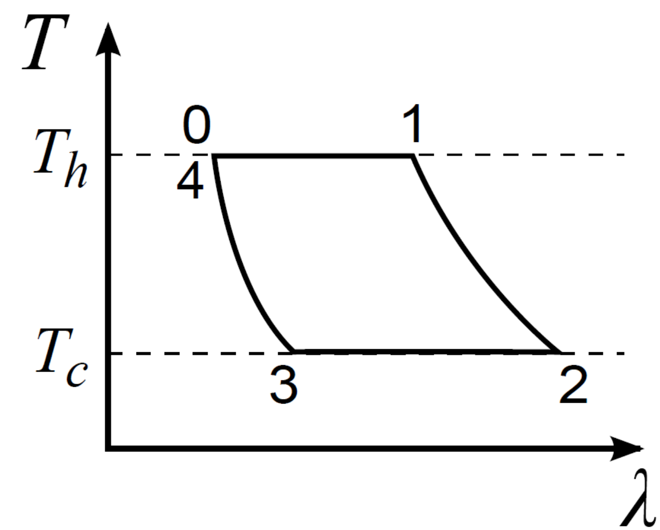
Fluctuation of work through quasistatic isothermal strokes is negligible.

$$\Delta W = W - \langle W \rangle = W_{\mathrm{adiab}} - \langle W_{\mathrm{adiab}} \rangle$$

$$\Delta Q_h \equiv Q_h - \langle Q_h \rangle = (E_1 - \langle E_1 \rangle) - (E_0 - \langle E_0 \rangle) \qquad Q_h = E_1 - E_0 + W_{0\to 1}$$

Adiabatic reversibility condition:

$$\frac{E_{\mathrm{init}}}{T_{\mathrm{init}}} = \frac{E_{\mathrm{fin}}}{T_{\mathrm{fin}}}$$



Work through reversible ad. strokes depends solely on the energy of initial or final state.

$$\Delta W = [1 - (T_c/T_h)][(E_1 - \langle E_1 \rangle) - (E_0 - \langle E_0 \rangle)]$$

$$\eta^{(n)} \equiv \frac{\langle (\Delta W)^n \rangle}{\langle (\Delta Q_h)^n \rangle} = \left(1 - \frac{T_c}{T_h}\right)^n$$

Fluctuations of work output & heat input

Fluctuations of work output & heat input through stroke $i \to i+1$

Process	$\langle \Delta W^2_{i\to i+1} \rangle$	$\langle \Delta Q^2_{i\to i+1} \rangle$
(1) Isothermal	0	$\langle \Delta E_i^2 \rangle + \langle \Delta E_{i+1}^2 \rangle$
(2) Adiabatic	$[1-(T_{i+1}/T_i)]^2 \langle \Delta E_i^2 \rangle$ $= [(T_i/T_{i+1})-1]^2 \langle \Delta E_{i+1}^2 \rangle$	0
(3) Isochoric	0	$\langle \Delta E_i^2 \rangle + \langle \Delta E_{i+1}^2 \rangle$
(4) Isobaric	0	$\langle \Delta E_i^2 \rangle + \langle \Delta E_{i+1}^2 \rangle$

- Only adiabatic strokes have non-zero work fluctuation.
- The other heat exchanging strokes have non-zero heat fluctuation.
- Heat fluct. is given by the variance of the internal energy at end points.

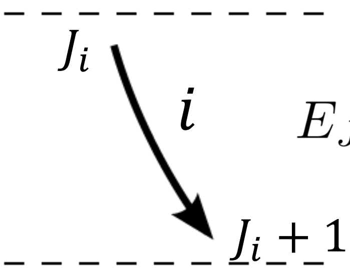
Sketch of the proof

Process	$\langle \Delta W^2_{i\to i+1}\rangle$	$\langle \Delta Q^2_{i\to i+1}\rangle$
(1) Isothermal	0	$\langle \Delta E_i^2\rangle + \langle \Delta E_{i+1}^2\rangle$
(2) Adiabatic	$[1-(T_{i+1}/T_i)]^2 \langle \Delta E_i^2\rangle = [(T_i/T_{i+1})-1]^2 \langle \Delta E_{i+1}^2\rangle$	0
(3) Isochoric	0	$\langle \Delta E_i^2\rangle + \langle \Delta E_{i+1}^2\rangle$
(4) Isobaric	0	$\langle \Delta E_i^2\rangle + \langle \Delta E_{i+1}^2\rangle$

For ith adiabatic expansion stroke: $J_i \to J_i + 1$

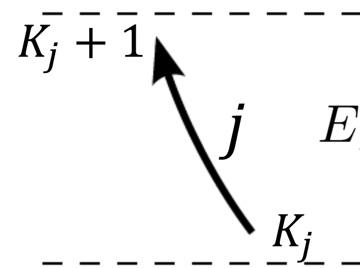
For jth adiabatic compression stroke: $K_j \to K_j + 1$

expansion



$$E_{J_i+1} = (T_{J_i+1}/T_{J_i})E_{J_i}$$

compression



$$E_{K_j} = (T_{K_j}/T_{K_j+1})E_{K_j+1}$$

Only adiabatic strokes contribute to the work fluctuation:

$$\langle \Delta W^2\rangle = \underbrace{\sum_i [1-(T_{J_i+1}/T_{J_i})]^2 \langle \Delta E_{J_i}^2\rangle}_{\text{expansion}} + \underbrace{\sum_j [1-(T_{K_j}/T_{K_j+1})]^2 \langle \Delta E_{K_j+1}^2\rangle}_{\text{compression}}$$

$$\leq [1-(T_c/T_h)]^2 \left(\sum_i \langle \Delta E_{J_i}^2\rangle + \sum_j \langle \Delta E_{K_j+1}^2\rangle\right)$$

In addition to nodes J_i and $K_j + 1$, other nodes might contribute to $\langle \Delta Q_h^2\rangle$:

$$\langle \Delta Q_h^2\rangle \geq \sum_i \langle \Delta E_{J_i}^2\rangle + \sum_j \langle \Delta E_{K_j+1}^2\rangle$$

$$\Rightarrow \quad \boxed{\eta^{(2)} \equiv \frac{\langle \Delta W^2\rangle}{\langle \Delta Q_h^2\rangle} \leq \eta_C^2}$$

Brownian Carnot engine

Carnot engine with an overdamped Brownian particle in a harmonic oscillator potential.

$$H\big(q, \lambda_w(t)\big) = V(q) = \frac{\lambda_w}{2} q^2$$

$$\begin{cases} X_w = P = -\dfrac{\partial H}{\partial \lambda_w} = -\dfrac{q^2}{2} \\ X_u = S = -k_B \ln p^{\mathrm{eq}} = k_B \left(\beta \dfrac{\lambda_w}{2} q^2 + \ln Z \right) \end{cases}$$

Both ΔX_w & $\Delta X_u \propto \Delta(q^2)$

$$\therefore \ \big\langle \Delta X_\mu(t)\, \Delta X_\nu(0) \big\rangle_{\mathrm{eq}} \propto \langle q^2(t)\, q^2(0) \rangle_{\mathrm{eq}} - \langle q^2 \rangle_{\mathrm{eq}}^2$$

$$\tau_{ww} = \tau_{uu} = \tau_{wu}$$

Correlation time and metric

From the solution of the FP eq. for Ornstein-Uhlenbeck process, correlation func. of q^2 reads

$$\langle q^2(t)\, q^2(0)\rangle_{\mathrm{eq}} - \langle q^2\rangle_{\mathrm{eq}}^2 = 2\left(\frac{k_B T}{\lambda_w}\right)^2 \exp\left[-\frac{2\lambda_w t}{\gamma}\right]$$

(γ: friction coeff.)

$$\Rightarrow \quad \tau_{ww} = \tau_{uu} = \tau_{wu} = {}^{\gamma}\!/_{2\lambda_w}$$

Metric for $\langle \Delta A^2\rangle$: $\quad g_{\mu\nu}^{(2)}(t) \equiv 2\,\tau_{\mu\nu}(t)\,\big\langle \Delta X_\mu(t)\,\Delta X_\nu(t)\big\rangle_{\mathrm{eq}}$

$$g_{\mu\nu}^{(2)} = \frac{\gamma}{2\lambda_w}\begin{bmatrix} (k_B T/\lambda_w)^2 & -k_B T/\lambda_w \\ -k_B T/\lambda_w & 1 \end{bmatrix}$$

Singular metric with zero eigenvalue.