Efficient Heat Engines are Powerless

a fundamental tradeoff relation in thermodynamics proved in 2016

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prerequisites

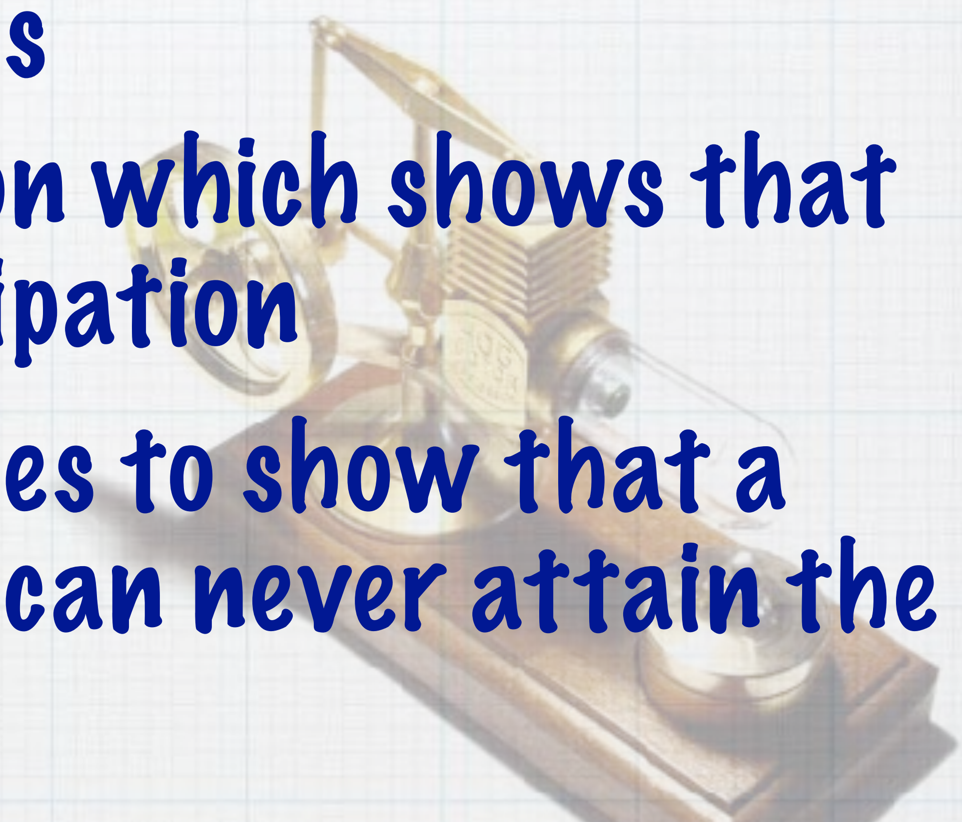
part 1: some idea about college thermodynamics

part 2: some knowledge about statistical mechanics and stochastic processes

about part 2

- ☑ an application of techniques of non equilibrium statistical mechanics to the fundamental problem in thermodynamics about power and efficiency of heat engines

- ☑ **Here we shall**
  - treat general Markov processes
  - prove a general tradeoff relation which shows that nonzero heat current implies dissipation
  - apply the relation to heat engines to show that a heat engine with non-zero power can never attain the Carnot efficiency

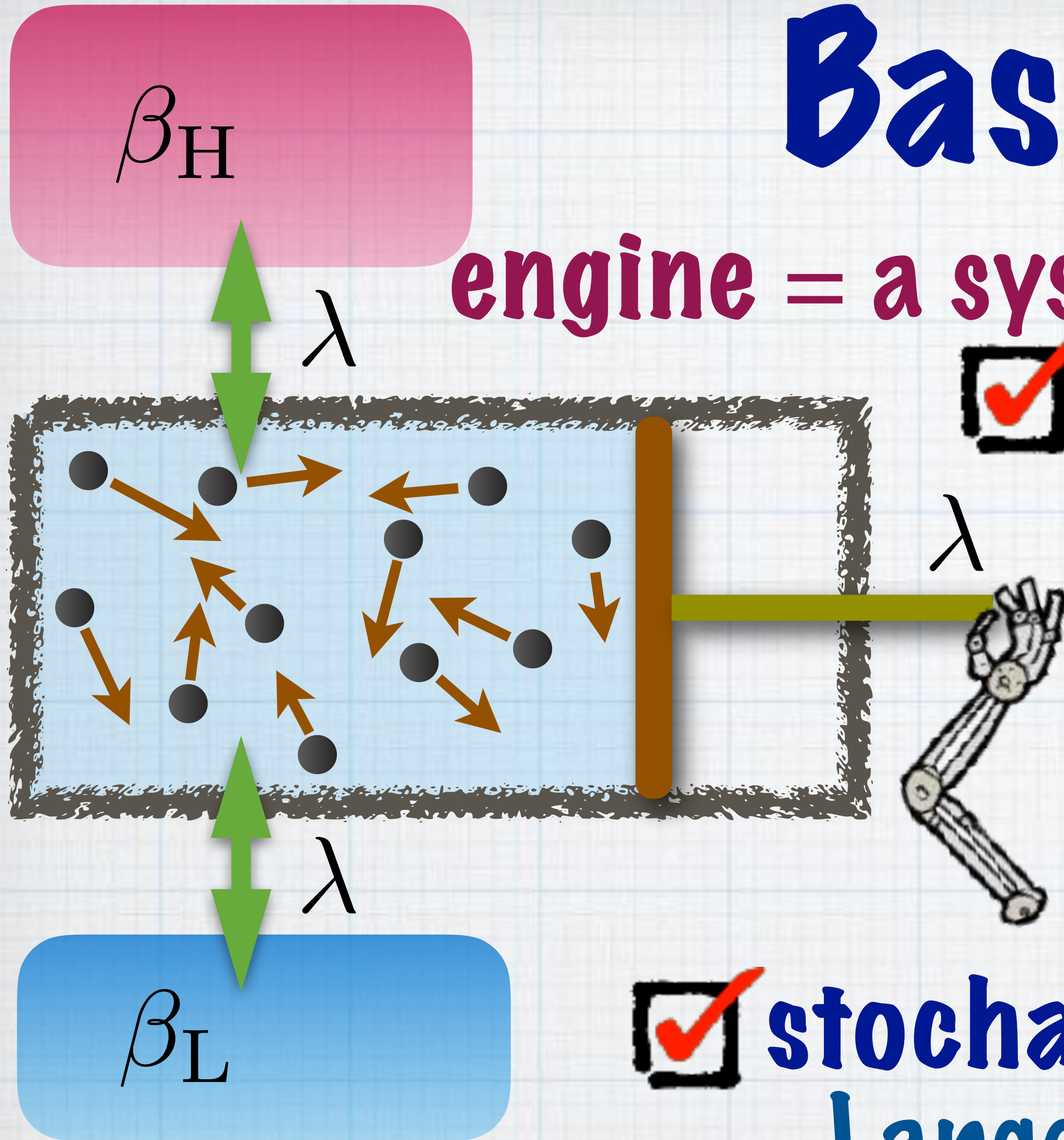


Model Stirling engine. By Richard Wheeler (Zephyris) 2007

Stochastic Thermodynamics

microscopic model of thermodynamic systems

Basic setting



engine = a system of N classical particles

☑ **deterministic dynamics**

Newton equation with arbitrary force and interactions

conserves energy and phase space volume (when λ is fixed)

☑ **stochastic dynamics**

Langevin type noise which describes the effect of two (or more) heat baths

λ parameter (a set of parameters) which controls the external forces, the interactions, and the couplings to the heat baths

λ is varied (by an external agent) according to a fixed protocol

Deterministic dynamics

engine = a system of N classical particles

state of the system $X = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{v}_1, \ldots, \boldsymbol{v}_N) \in \mathbb{R}^{6N}$

☑ **deterministic dynamics with fixed λ**

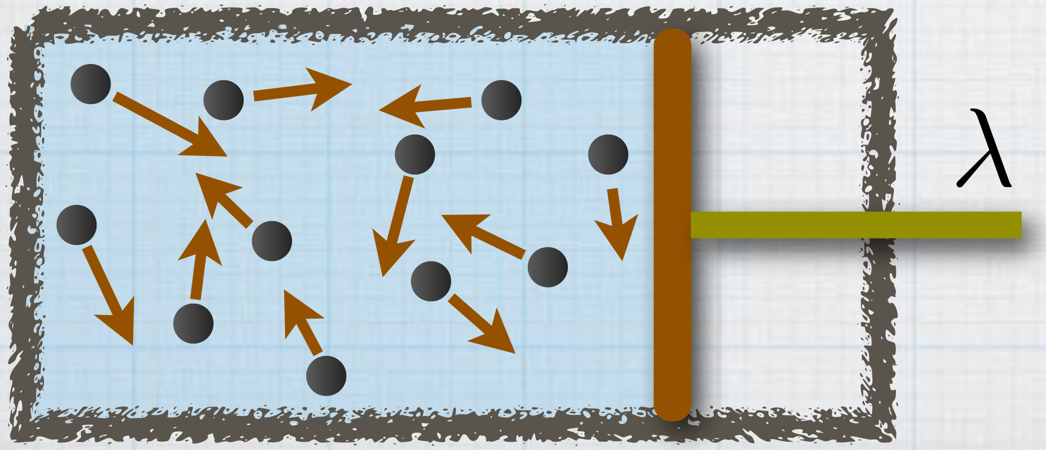
Newton equation with arbitrary force and interactions which conserves total energy

$$m_i \frac{d}{dt}\boldsymbol{v}_i(t) = \boldsymbol{F}_i^\lambda(X(t)) \qquad \frac{d}{dt}\boldsymbol{r}_i(t) = \boldsymbol{v}_i(t)$$

$$i = 1, \ldots, N$$

$E^\lambda(X)$ energy of X at parameter λ

$$\frac{d}{dt}E^\lambda(X(t)) = 0$$



Stochastic dynamics

state of the system $X = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{v}_1, \ldots, \boldsymbol{v}_N) \in \mathbb{R}^{6N}$

$\mathcal{P}_t(X)$ probability density to find the system in X at t

☑ **Kramers equation with fixed λ and single bath**

$$\frac{\partial}{\partial t}\mathcal{P}_t(X) = \hat{\mathcal{L}}_{\mathrm{det}}\mathcal{P}_t(X) + \hat{\mathcal{L}}_{\mathrm{bath}}\mathcal{P}_t(X)$$

corresponds to the Newton equation ←

$$\hat{\mathcal{L}}^{\lambda}_{\mathrm{det}} = \sum_{i=1}^{N}\left\{-\boldsymbol{v}_i \cdot \frac{\partial}{\partial \boldsymbol{r}_i} - \frac{1}{m_i}\frac{\partial}{\partial \boldsymbol{v}_i} \cdot \boldsymbol{F}^{\lambda}_i(X)\right\}$$

random motion from the bath ←

$$\hat{\mathcal{L}}_{\mathrm{bath}} = \sum_{i=1}^{N}\frac{\gamma(\boldsymbol{r}_i)}{m_i}\left\{\frac{\partial}{\partial \boldsymbol{v}_i} \cdot \boldsymbol{v}_i + \frac{1}{\beta m}\frac{\partial^2}{\partial {\boldsymbol{v}_i}^2}\right\}$$

$$\lim_{t\uparrow\infty}\mathcal{P}_t(X) = \frac{\exp\left[-\beta E^{\lambda}(X)\right]}{Z(\beta)}$$

equilibrium distribution at β

The whole equation

the parameter is varied according to a fixed protocol $\lambda(t)$

$\lambda(t) = \lambda(t+\tau)$ for any t with a fixed period τ

Kramers equation (continuous master equation)

$\mathcal{P}_t(X)$ probability density to find the system in X at t

$$\frac{\partial}{\partial t}\mathcal{P}_t(X) = \hat{\mathcal{L}}_{\rm det}^{\lambda(t)}\mathcal{P}_t(X) + \sum_{B=\mathrm{H},\mathrm{L}} \hat{\mathcal{L}}_B^{\lambda(t)}\mathcal{P}_t(X)$$

corresponds to the Newton equation ←

$$\hat{\mathcal{L}}_{\rm det}^{\lambda} = \sum_{i=1}^{N}\left\{-\boldsymbol{v}_i\cdot\frac{\partial}{\partial\boldsymbol{r}_i} - \frac{1}{m_i}\frac{\partial}{\partial\boldsymbol{v}_i}\cdot\boldsymbol{F}_i^{\lambda}(X)\right\}$$

brings the system to equilibrium at β_B ←

$$\hat{\mathcal{L}}_B^{\lambda} = \sum_{i=1}^{N}\frac{\gamma_B(\lambda,\boldsymbol{r}_i)}{m_i}\left\{\frac{\partial}{\partial\boldsymbol{v}_i}\cdot\boldsymbol{v}_i + \frac{1}{\beta_B m_i}\frac{\partial^2}{\partial{\boldsymbol{v}_i}^2}\right\}$$

state of the system $X = (\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;\boldsymbol{v}_1,\ldots,\boldsymbol{v}_N)$

Heat and work

energy expectation value $E(t) = \int dX\, E^{\lambda(t)}(X)\, \mathcal{P}_t(X)$

flow of work … **flow of heat**

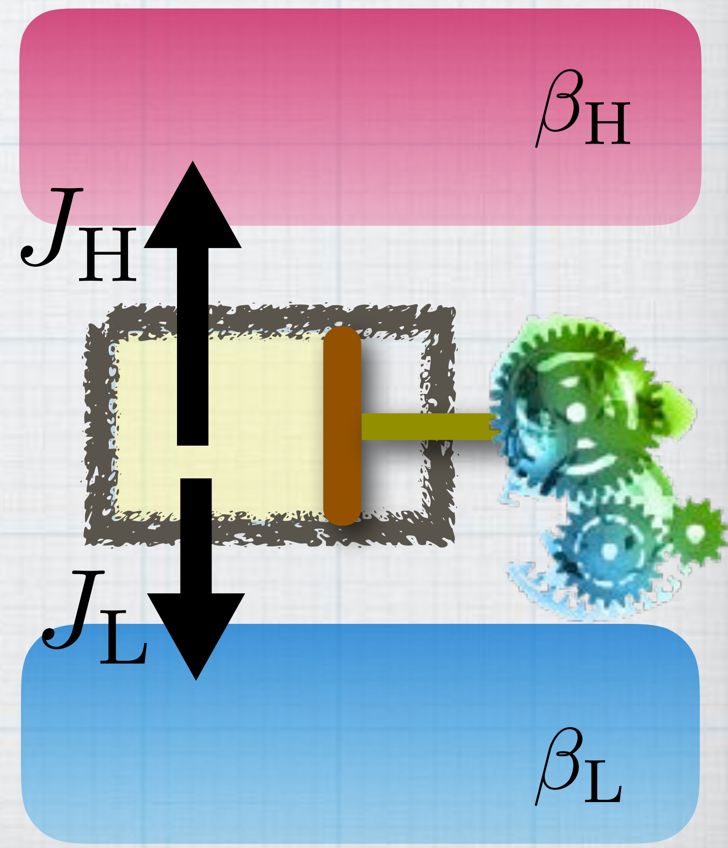
$$\frac{d}{dt}E(t) = \int dX\, \dot{\lambda}(t) \left(\frac{dE^{\lambda}(X)}{d\lambda} \right)_{\lambda=\lambda(t)} \mathcal{P}_t(X) + \int dX\, E^{\lambda(t)}(X)\, \frac{\partial}{\partial t}\mathcal{P}_t(X)$$

$$\int dX\, E^{\lambda(t)}(X)\, \frac{\partial}{\partial t}\mathcal{P}_t(X) = -\{J_{\mathrm{H}}(t) + J_{\mathrm{L}}(t)\}$$

heat currents from the system to the baths

$$J_B(t) = -\int dX\, E^{\lambda(t)}(X) (\hat{\mathcal{L}}_B^{\lambda(t)} \mathcal{P}_t)(X)$$

$$B = \mathrm{H}, \mathrm{L}$$



$$\frac{\partial}{\partial t}\mathcal{P}_t(X) = \hat{\mathcal{L}}_{\mathrm{det}}^{\lambda(t)} \mathcal{P}_t(X) + \sum_{B=\mathrm{H,L}} \hat{\mathcal{L}}_B^{\lambda(t)} \mathcal{P}_t(X)$$

Main results

Entropy production rate

$\mathcal{P}_t(X)$ probability density to find the system in X at t

$J_{\mathrm{B}}(t)$ heat current to bath $\mathrm{B} = \mathrm{H}, \mathrm{L}$ at t

total entropy production rate

$$\sigma(t) = \frac{d}{dt} H(\mathcal{P}_t) + \beta_{\mathrm{H}} J_{\mathrm{H}}(t) + \beta_{\mathrm{L}} J_{\mathrm{L}}(t)$$

change in the Shannon entropy of the system (microscopic)

$$H(\mathcal{P}) = -\int dX\, \mathcal{P}(X) \log \mathcal{P}(X)$$

entropy production rates in the baths (phenomenological)

$$\Delta S = \frac{\Delta Q}{T} = \beta \Delta Q$$

Main tradeoff inequality

$J_{\mathrm{B}}(t)$ heat current to bath $\mathrm{B}=\mathrm{H},\mathrm{L}$ at t

total entropy production rate

$$\sigma(t)=\frac{d}{dt}H(\mathcal{P}_t)+\beta_{\mathrm{H}}J_{\mathrm{H}}(t)+\beta_{\mathrm{L}}J_{\mathrm{L}}(t)$$

improved Shiraishi-Saito bound

$$|J_{\mathrm{H}}(t)|+|J_{\mathrm{L}}(t)|\le\sqrt{\Theta(t)\,\sigma(t)}$$ for any t

$$\hat{\mathcal{L}}_B^{\lambda}=\sum_{i=1}^{N}\frac{\gamma_B(\lambda,\boldsymbol{r}_i)}{m_i}\Bigl\{\frac{\partial}{\partial\boldsymbol{v}_i}\cdot\boldsymbol{v}_i+\frac{1}{\beta_B m_i}\frac{\partial^2}{\partial{\boldsymbol{v}_i}^2}\Bigr\}$$

close to equilibrium

$$\Theta(t)=\sum_{i=1}^{N}\sum_{B=\mathrm{L},\mathrm{H}}\frac{1}{\beta_B}\bigl\langle\gamma_B(\lambda(t),\boldsymbol{r}_i)\,|\boldsymbol{v}_i|^2\bigr\rangle_t\simeq\kappa$$

heat conductivity

$J\simeq\kappa\Delta\beta$

average with respect to $\mathcal{P}_t$

Main tradeoff inequality and its use

improved Shiraishi-Saito bound

$$|J_{\mathrm{H}}(t)| + |J_{\mathrm{L}}(t)| \le \sqrt{\Theta(t)\,\sigma(t)}$$

"current" always induces "dissipation" (measured by $\sigma(t)$)

nonzero power

↓

nonzero current

↓

nonzero dissipation

↓

the maximum efficiency cannot be attained

Main tradeoff inequality and its use

improved Shiraishi-Saito bound

$$|J_{\rm H}(t)|+|J_{\rm L}(t)|\le\sqrt{\Theta(t)\,\sigma(t)}$$

"current" always induces "dissipation" (measured by $\sigma(t)$)

integrate over a period $t\in[0,\tau]$

$$\int_0^\tau dt\{|J_{\rm H}(t)|+|J_{\rm L}(t)|\}\le\int_0^\tau dt\sqrt{\Theta(t)\,\sigma(t)}$$

Schwarz inequality →

$$\le\Bigl(\int_0^\tau dt\,\Theta(t)\Bigr)^{1/2}\Bigl(\int_0^\tau dt\,\sigma(t)\Bigr)^{1/2}$$

we can assume the periodicity $\mathcal{P}_0=\mathcal{P}_\tau$

$$\int_0^\tau dt\,\sigma(t)=H(\mathcal{P}_\tau)-H(\mathcal{P}_0)+\int_0^\tau dt\{\beta_{\rm H}J_{\rm H}(t)+\beta_{\rm L}J_{\rm L}(t)\}$$

$H(\mathcal{P}_\tau)-H(\mathcal{P}_0)$ = 0

Shannon entropy disappears from the theory

$$\sigma(t)=\frac{d}{dt}H(\mathcal{P}_t)+\beta_{\rm H}J_{\rm H}(t)+\beta_{\rm L}J_{\rm L}(t)$$

Main tradeoff inequality and its use

$$\int_0^\tau dt\{|J_\mathrm{H}(t)|+|J_\mathrm{L}(t)|\}\le\Bigl(\int_0^\tau dt\,\Theta(t)\Bigr)^{1/2}\Bigl(\int_0^\tau dt\,\sigma(t)\Bigr)^{1/2}$$

$$\int_0^\tau dt\,\sigma(t)=\int_0^\tau dt\{\beta_\mathrm{H}J_\mathrm{H}(t)+\beta_\mathrm{L}J_\mathrm{L}(t)\}$$

$$\Bigl(\int_0^\tau dt\{|J_\mathrm{H}(t)|+|J_\mathrm{L}(t)|\}\Bigr)^2\le\tau\,\bar{\Theta}\int_0^\tau dt\{\beta_\mathrm{H}J_\mathrm{H}(t)+\beta_\mathrm{L}J_\mathrm{L}(t)\}$$

inequality between observable quantities $J_\mathrm{H}(t)$, $J_\mathrm{L}(t)$

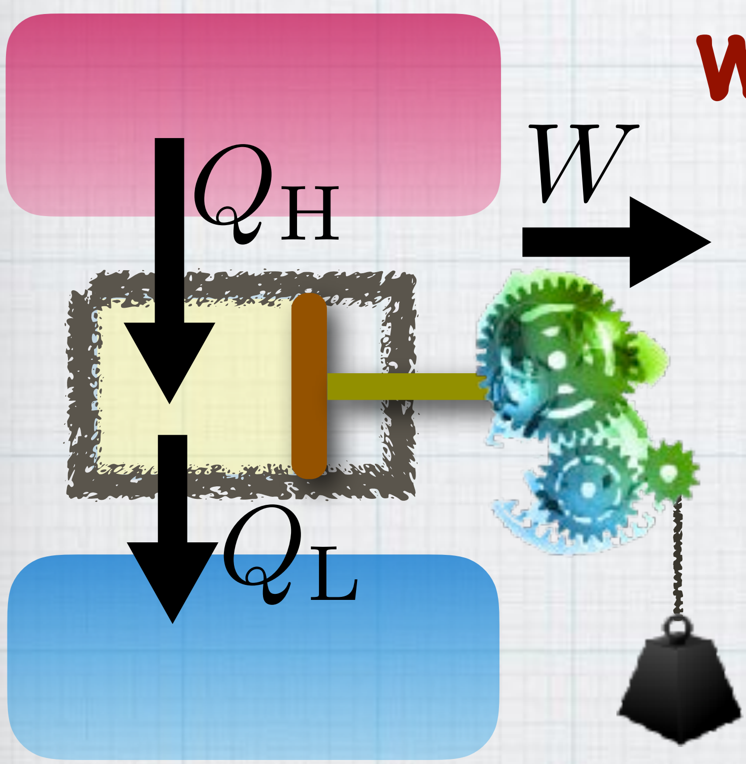
$$\bar{\Theta}=\frac{1}{\tau}\int_0^\tau dt\,\Theta(t)$$

$$\Theta(t)=\sum_{i=1}^{N}\sum_{B=\mathrm{L,H}}\frac{1}{\beta_B}\bigl\langle\gamma_B(\lambda(t),\boldsymbol{r}_i)\,|\boldsymbol{v}_i|^2\bigr\rangle_t$$

Power and efficiency

$$\left(\int_0^\tau dt\{|J_\mathrm{H}(t)|+|J_\mathrm{L}(t)|\}\right)^2 \le \tau\,\bar{\Theta}\int_0^\tau dt\{\beta_\mathrm{H}J_\mathrm{H}(t)+\beta_\mathrm{L}J_\mathrm{L}(t)\}$$

we get an inequality between Q_H and Q_L



$$(Q_\mathrm{H}+Q_\mathrm{L})^2 \le \tau\,\bar{\Theta}\,(-\beta_\mathrm{H}Q_\mathrm{H}+\beta_\mathrm{L}Q_\mathrm{L})$$

$$W = Q_\mathrm{H} - Q_\mathrm{L}$$

$$\eta = W/Q_\mathrm{H}$$

$$Q_\mathrm{H} = -\int_0^\tau dt\,J_\mathrm{H}(t)$$

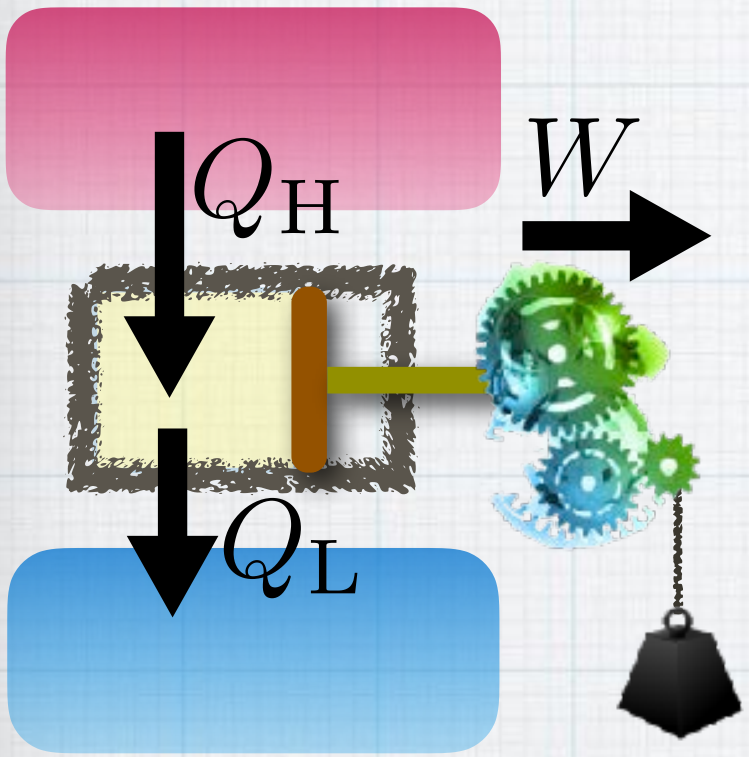
$$Q_\mathrm{L} = \int_0^\tau dt\,J_\mathrm{L}(t)$$

$$\frac{W}{\tau} \le \bar{\Theta}\beta_\mathrm{L}\,\eta(\eta_\mathrm{C}-\eta)$$

$Q_\mathrm{H}, Q_\mathrm{L} > 0$

rigorous and quantitative tradeoff relation between power and efficiency

Power and efficiency



$$\frac{W}{\tau} \le \bar{\Theta}\beta_{\rm L}\,\eta(\eta_{\rm C}-\eta)$$

work $W = Q_{\rm H} - Q_{\rm L}$

power W/τ

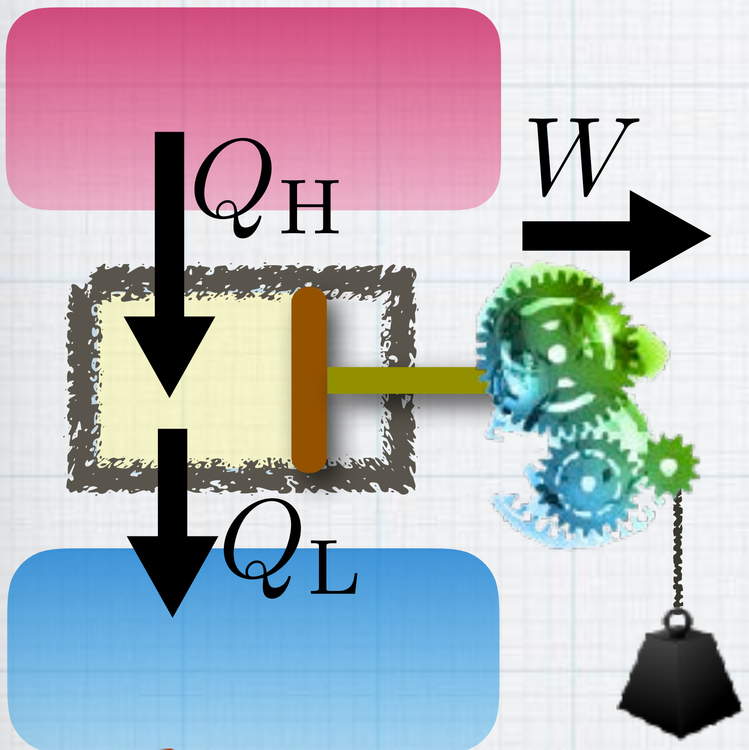
efficiency $\eta = W/Q_{\rm H}$

$W/\tau \to 0$ **as** $\eta \uparrow \eta_{\rm C}$

a heat engine with non-zero power can never attain the Carnot efficiency

- ☑ applies to any heat engine that can be described by classical mechanics (with or without time-reversal symmetry) and Markov process
- ☑ state of the engine can be arbitrarily far from equilibrium

Power and efficiency



$$\frac{W}{\tau} \le \bar{\Theta} \beta_\mathrm{L}\, \eta(\eta_\mathrm{C} - \eta)$$

the key quantity $\bar{\Theta} = \frac{1}{\tau}\int_0^\tau dt\, \Theta(t)$

- ☑ not a universal constant, but is always finite
- ☑ proportional to the size of the system (the bound is meaningful in thermodynamic limit)
- ☑ approaches the heat conductivity κ in the limit of equilibrium dynamics

$$J \simeq \kappa \Delta\beta$$

$$\hat{\mathcal{L}}_B^\lambda = \sum_{i=1}^{N} \frac{\gamma_B(\lambda, \boldsymbol{r}_i)}{m_i} \left\{ \frac{\partial}{\partial \boldsymbol{v}_i} \cdot \boldsymbol{v}_i + \frac{1}{\beta_B m_i} \frac{\partial^2}{\partial {\boldsymbol{v}_i}^2} \right\}$$

$$\Theta(t) = \sum_{i=1}^{N} \sum_{B=\mathrm{L,H}} \frac{1}{\beta_B} \left\langle \gamma_B(\lambda(t), \boldsymbol{r}_i)\, |\boldsymbol{v}_i|^2 \right\rangle_t$$

Derivation
some essence

Proof of the improved Shiraishi-Saito bound in the simplest setting

Markov jump process

$|J(t)| \le \sqrt{\Theta(t)\,\sigma(t)}$

finite discrete state space $\mathcal{S} \ni x, y, \ldots$

λ parameter(s) of the model

E_x^λ energy of state x with λ

R_{xy}^λ transition rate for stochastic dynamics which satisfies the detailed balance condition for single β

$$R_{xy}^\lambda \ge 0 \ (x \ne y) \qquad \sum_x R_{xy}^\lambda = 0$$

$$R_{xy}^\lambda e^{-\beta E_y^\lambda} = R_{yx}^\lambda e^{-\beta E_x^\lambda}$$ for any x, y

no time-reversal!

the parameter changes according to a fixed protocol $\lambda(t)$

$p_x(t)$ probability to find the system in x at t

master equation $\dot{p}_x(t) = \sum_y R_{xy}^{\lambda(t)} p_y(t)$

Lower bound for $\sigma(t)$

entropy production rate

$$J(t) = -\sum_{x,y} E_x^{\lambda(t)} R_{xy}^{\lambda(t)} p_y(t)$$

$$\sigma(t) = \frac{d}{dt}\{-\sum_x p_x(t)\log p_x(t)\} + \beta J(t)$$

$$= \sum_{x\neq y} R_{xy}^{\lambda(t)} p_y(t) \log \frac{R_{xy}^{\lambda(t)} p_y(t)}{R_{yx}^{\lambda(t)} p_x(t)}$$

standard expression

$$= \frac{1}{2}\sum_{x\neq y}\{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)\} \log \frac{R_{xy}^{\lambda(t)} p_y(t)}{R_{yx}^{\lambda(t)} p_x(t)}$$

$$\geq \sum_{x\neq y} \frac{\{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)\}^2}{R_{xy}^{\lambda(t)} p_y(t) + R_{yx}^{\lambda(t)} p_x(t)}$$

$$R_{xy}^{\lambda} e^{-\beta E_y^{\lambda}} = R_{yx}^{\lambda} e^{-\beta E_x^{\lambda}}$$

$$(a-b)\log\frac{a}{b} \geq \frac{2(a-b)^2}{a+b}$$

Upper bound for $|J(t)|$

$$J(t) = -\sum_{x,y} E_x^{\lambda(t)} R_{xy}^{\lambda(t)} p_y(t)$$

$$= -\sum_{x,y} E_x^{\lambda(t)} \{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)\}$$

$$= -\frac{1}{2} \sum_{x \neq y} \{E_x^{\lambda(t)} - E_y^{\lambda(t)}\}\{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)\}$$

$$= -\frac{1}{2} \sum_{x \neq y} \{E_x^{\lambda(t)} - E_y^{\lambda(t)}\} \sqrt{R_{xy}^{\lambda(t)} p_y(t) + R_{yx}^{\lambda(t)} p_x(t)} \frac{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)}{\sqrt{R_{xy}^{\lambda(t)} p_y(t) + R_{yx}^{\lambda(t)} p_x(t)}}$$

Schwarz

$$|J(t)| \leq \sqrt{\frac{1}{4} \sum_{x \neq y} \{E_x^{\lambda(t)} - E_y^{\lambda(t)}\}^2 \{R_{xy}^{\lambda(t)} p_y(t) + R_{yx}^{\lambda(t)} p_x(t)\}} \sqrt{\sigma(t)}$$

$$\frac{1}{2} \sum_{x \neq y} \{E_x^{\lambda(t)} - E_y^{\lambda(t)}\}^2 R_{xy}^{\lambda(t)} p_y(t) =: \Theta(t)$$

$$|J(t)| \leq \sqrt{\Theta(t)\, \sigma(t)}$$

$$\sigma(t) \geq \sum_{x \neq y} \frac{\{R_{xy}^{\lambda(t)} p_y(t) - R_{yx}^{\lambda(t)} p_x(t)\}^2}{R_{xy}^{\lambda(t)} p_y(t) + R_{yx}^{\lambda(t)} p_x(t)}$$

Treatment of the full model

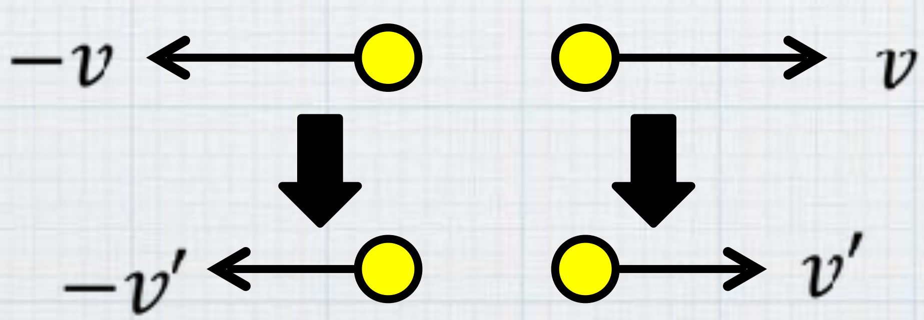
master equation (Kramers equation)

$$\frac{\partial}{\partial t}\mathcal{P}_t(X) = \hat{\mathcal{L}}_{\mathrm{det}}^{\lambda(t)}\mathcal{P}_t(X) + \sum_{B=\mathrm{H,L}} \hat{\mathcal{L}}_B^{\lambda(t)}\mathcal{P}_t(X)$$

never satisfies detailed balance, but does not produce entropy

written as a continuum limit of a discrete model with detailed balance

(this reflects the reflection symmetry of the transition rate)



$$\hat{\mathcal{L}}_B^{\lambda} = \sum_{i=1}^{N} \frac{\gamma_B(\lambda, \boldsymbol{r}_i)}{m_i}\left\{\frac{\partial}{\partial \boldsymbol{v}_i}\cdot \boldsymbol{v}_i + \frac{1}{\beta_B m_i}\frac{\partial^2}{\partial {\boldsymbol{v}_i}^2}\right\}$$

Summary

- ☑ We have proved a tradeoff relation (improved Shiraishi-Saito bound) which shows that a non-vanishing heat current implies dissipation

$$|J_{\mathrm{H}}(t)| + |J_{\mathrm{L}}(t)| \le \sqrt{\Theta(t)\,\sigma(t)}$$

- ☑ The bound, when applied to a heat engine, leads to a tradeoff relation between power and efficiency, which implies that a heat engine with non-zero power can never attain the Carnot efficiency

$$\frac{W}{\tau} \le \bar{\Theta}\beta_{\mathrm{L}}\,\eta(\eta_{\mathrm{C}} - \eta)$$

For further discussion, see
Shiraishi, Saito, and Tasaki 2016, Shiraishi and Saito 2019