Kinetic model for the finite-time thermodynamics of small heat engines

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Outline of the talk

1. Irreversible Heat Engines
2. Coarse Graining - Modelling of small systems
3. Efficiency at maximum power

Molecular model of a piston (Simulations)
Heat Engines: general considerations

System

\[ E(t) \]

Ext.

\[ \dot{Q}(t) \]

Control

\[ \lambda(t) \]

\[ \dot{W}(t) \]

Total time of the cycle

\[ \tau \]

\[ T_o(t) \]
Heat Engines: general considerations

System
\[ E(t) \]
Ext.
\[ \dot{Q}(t) \]
Control
\[ \lambda(t) \]
\[ \dot{W}(t) \]

\[ T_0(t) \]

\[ \tau \] Total time of the cycle

Desiderata

- Predict the dependence of the integrated fluxes \( W \) and \( Q \) on \( \tau \);
- Take into account fluctuations (e.g. predict \( P(W) \));
Beyond standard thermodynamics: two possible approaches

**Stochastic Thermodynamics**
- $N = 1$ particle (*Langevin equation*)
- External time-dependent potential
- Interaction with a reservoir (thermal noise)

![Diagram of a particle with forces and temperatures](image)
Beyond standard thermodynamics: two possible approaches

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**Macroscopic Fluct. Theory**
- $N \gg 1$ particles
- Hydrodynamical description:
  - density field $\rho(x, t)$,
  - velocity field $u(x, t)$,
  - current field $j(x, t)$.
- Thermodynamics $\Leftrightarrow$ external fields and special boundary conditions (*thermostats*).
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A paradigmatic small system

A system composed of $N \sim \mathcal{O}(10^2)$ degrees of freedom

Is it possible to extract mechanical work from this system with a cyclical protocol?
Heat Engine: the Ericsson cycle
Heat Engine: the Ericsson cycle

In each segment:

\[ W = \int dt \frac{\partial \mathcal{H}}{\partial t} = \int dt \dot{F} X(t) \]

\[ Q = \Delta \mathcal{H} - W \]
Results of MD simulations

[L.Cerino, A. Puglisi and A. Vulpiani, PRE E 91, 032128 (2015)]

Thermodynamics forces:

\[
\delta = \frac{T_H - T_C}{T_H + T_C} = 0.08
\]

\[
\epsilon = \frac{F_H - F_L}{F_H + F_L} = 0.1
\]
Coarse-graining: can we understand this behavior?

**Step 1**
Identify the relevant (slow-varying) variables of the system.
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  Derive a set of coupled Langevin equations for these variables;
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Identify the relevant (slow-varying) variables of the system.

► **Step 2**
Derive a set of coupled Langevin equations for these variables;

► **Step 3**
Use stochastic thermodynamics to derive an explicit expression for thermodyn. quantities ($W, Q, \eta \ldots$) and associated fluctuations.
Model with 3 Macroscopic Variables

A coarse grained description is possible in terms of:

- \( X \) piston position
- \( V \) piston velocity
- \( T \) gas kin. energy per particle

\[
y = (X - X_{eq}(t), V, T - T_{eq}(t))
\]

Linear time-dependent Langevin eqn.

\[
\dot{y} = A(t) \cdot y + B(t) \cdot \xi \leftarrow \text{white noise}
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- $A$ is determined via kinetic theory considerations (collisions gas ↔ piston and gas ↔ thermostat).
- $B$ is determined a fortiori to restore detailed balance with equilibrium distribution.
Comparison with MD simulations

- Av. values: Good qualitative agreement (sign inversion, maximum...)
- Fluctuations: Approx. Gaussian behaviour and same stdev.
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- Av. values: Good qualitative agreement (sign inversion, maximum...)
- Fluctuations: Approx. Gaussian behaviour and same stdev.
- Discrepancies: Effect of gas inhomogeneities and non-linear effects.
An even simpler model...

We can pass from 3 variables → 2 variables by simply fixing $T(t) = T_0(t)$

$$\frac{dX}{dt} = V$$

$$\frac{dV}{dt} = -k(t)(X - X_0(t)) - \gamma(t)V + \sqrt{\frac{2\gamma k_B T_0(t)}{M}} \xi$$

$$k(t) = \frac{F(t)^2(m + M)}{M^2 Nk_B T_0(t)} \quad \gamma(t) = \frac{2F(t)}{M} \sqrt{\frac{2m}{\pi k_B T_0(t)}}$$

$$X_0(t) = (N + 1) \frac{k_B T_0(t)}{F(t)}$$
An even simpler model...

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\[
\begin{align*}
\frac{dX}{dt} &= V \\
\frac{dV}{dt} &= -k(t)(X - X_0(t)) - \gamma(t)V + \sqrt{\frac{2\gamma k_B T_0(t)}{M}} \xi 
\end{align*}
\]

▶ An important remark

The energy of the system is “imported” from the molecular model: \( E(t) = \frac{1}{2} NT(t) + F(t)X(t) + \frac{1}{2} MV^2 \).

**In principle** \( E(t) \) is different from the potential \( U(t) = \frac{1}{2} (MV^2 + k(t)(X - X_0)^2) \).
...to obtain analytic formulas!

With a simpler protocol

\[
T_{o}(t) = T_0 \left[ 1 + \delta \sin \left( \frac{2\pi t}{\tau} \right) \right]
\]

\[
F(t) = F_0 \left[ 1 + \epsilon \cos \left( \frac{2\pi t}{\tau} \right) \right]
\]

An analytic expression for \( P(W) \) (in the engine regime for small \( \epsilon \) and \( \delta \)): Gaussian!
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An analytic expression for \( P(W) \) (in the engine regime for small \( \epsilon \) and \( \delta \)): Gaussian!
Linear regime and Onsager-coefficients

- Total entropy production

\[ \Delta S = - \int_{0}^{\tau} \frac{\langle \dot{E}(t) - \dot{W}(t) \rangle}{T(t)} dt \]
Linear regime and Onsager-coefficients

- Total entropy production

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\Delta S = - \int_0^\tau \frac{\langle \dot{E}(t) - \dot{W}(t) \rangle}{T(t)} \, dt = J_1 \epsilon + J_2 \delta
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Linear regime and Onsager-coefficients

Total entropy production

\[ \Delta S = - \int_{0}^{\tau} \left\langle \dot{E}(t) - \dot{W}(t) \right\rangle \frac{1}{T(t)} dt = J_1 \epsilon + J_2 \delta \]

Physical interpretation (Brandner, Saito and Seifert arXiv preprint (2015)):

\[ J_1 = - \frac{W}{\epsilon T_C} \]
\[ J_2 = \frac{T_C + T_H}{T_C T_H} \int_{0}^{\tau} \gamma(t) \dot{Q}(t) dt \]

where \( \gamma(t) \) is a smoothing function. E.g. with two thermostats \( \gamma(t) = 1 \) if \( T = T_H \) and \( \gamma(t) = 0 \) if \( T = T_C \).
Onsager coefficients in the 2V Model

\[ \Delta S = J_1 \epsilon + J_2 \delta \]

- In the linear regime:

\[
\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \epsilon \\ \delta \end{pmatrix}
\]

\[ \Delta S \rightarrow 0 \text{ for } \tau \rightarrow \infty \]
Onsager coefficients in the 2V Model

\[ \Delta S = J_1 \epsilon + J_2 \delta \]

- In the linear regime: 2V

\[
\begin{pmatrix}
J_1 \\
J_2
\end{pmatrix}
= A \left( \frac{2\pi}{\tau} \right)
\begin{pmatrix}
\sin \phi \left( \frac{2\pi}{\tau} \right) & - \cos \phi \left( \frac{2\pi}{\tau} \right) \\
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The Onsager coefficients have the right symmetries (derived from time-reversal);

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- \( \Delta S \to 0 \) for \( \tau \to \infty \).
Onsager Coeff. in the molecular model

$J_1$ vs $\delta$ ($\tau=30$)
$J_2$ vs $\varepsilon$ ($\tau=30$)
$J_1$ vs $\delta$ ($\tau=100$)
$J_2$ vs $\varepsilon$ ($\tau=100$)
$J_1$ vs $\delta$ ($\tau=1000$)
$J_2$ vs $\varepsilon$ ($\tau=1000$)
$J_1$ vs $\delta$ ($\tau=4000$)
$J_2$ vs $\varepsilon$ ($\tau=4000$)

$\tau$

$L_{12}$
Efficiency at maximum power

- Efficiency:

\[ \eta = - \frac{W}{Q_{in}} \leq \eta_C = 1 - \frac{T_C}{T_H} \approx 2\delta \]

where \( \delta = \frac{T_H - T_C}{T_H + T_C} \).
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- \( \ldots \) but when \( \tau = \infty \), the output power vanishes! \( \Rightarrow \)
- \( \tilde{\eta} = \text{Efficiency at max. power}: \)
Efficiency at maximum power

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- \( \ldots \) but when \( \tau = \infty \), the output power vanishes! \( \Rightarrow \)

- \( \tilde{\eta} = \) Efficiency at max. power: \( \ldots \) but maximum with respect to which parameter????
Efficiency at maximum power: General
Results in the Linear Regime

- Max. with respect to $\epsilon \propto \Delta F$ (Van Den Broeck, Phys. Rev. Lett. (2005)):

- Violated outside the linear regime (Schmiedl and Seifert, EuroPhys. Lett. (2008)).

What about the time $\tau$ of the cycle?
Efficiency at maximum power: General Results in the Linear Regime

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1. Symmetry of Onsager coefficients: $L_{12} = L_{21}$
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$$\tilde{\eta} \leq \eta_{CA} = 1 - \sqrt{\frac{T_C}{T_H}} \approx \frac{\eta_c}{2}$$

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- What about the time $\tau$ of the cycle?
Efficiency at $\tau$-maximum power

Power: $w = -\frac{W}{\tau} = -\epsilon \frac{T_0 J_1}{\tau}$

Efficiency: $\eta = -\frac{2\epsilon J_1}{J_2} \to 2\delta \; \tau \to \infty$
Efficiency at $\tau$-maximum power

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Efficiency: $\eta = -\frac{2\epsilon J_1}{J_2} \rightarrow 2\delta \quad \tau \rightarrow \infty$

Efficiency at maximum $w$ with respect to $\tau$ at different values of $\epsilon$
Efficiency at $\tau$-maximum power

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Efficiency: $\eta = -\frac{2\epsilon J_1}{J_2} \rightarrow 2\delta \quad \tau \rightarrow \infty$

Efficiency at maximum $w$ with respect to $\tau$ at different values of $\epsilon$
- Rich phenomenology (due to $N \neq 1$);
- Fluctuating thermodynamic quantities (due to $N \neq \infty$);
- Non trivial Langevin description (e.g. impossible to define energy from the Lang. Eq.).

A good insight into the thermodynamics of small systems!
Thank you for the attention!