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

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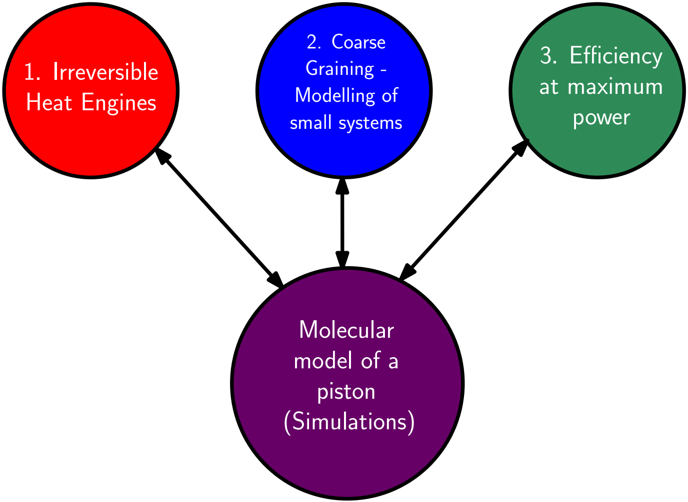
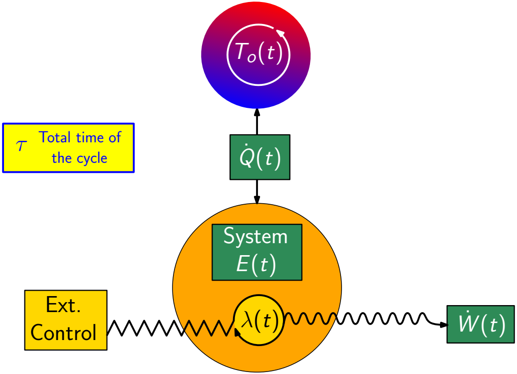
Outline of the talk



Heat Engines: general considerations



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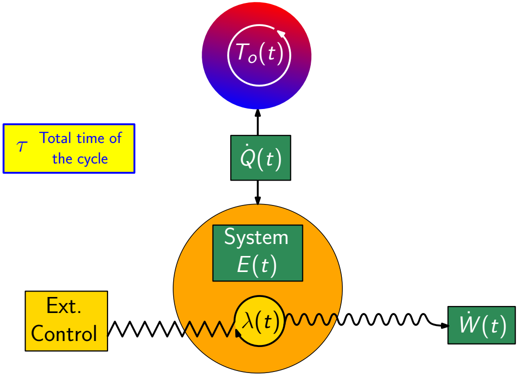


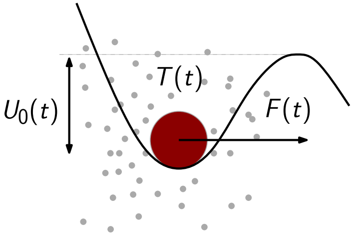
Desiderata

- Predict the dependence of the integrated fluxes W and Q on τ;
- 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)



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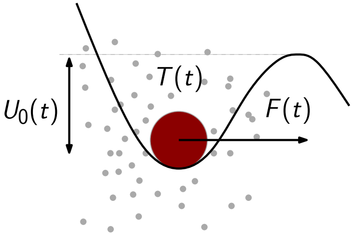

Macroscopic Fluct. Theory

- $N \gg 1$ particles
- Hydrodynamical description:
  - density field $\rho(\mathbf{x}, t)$,
  - velocity field $u(\mathbf{x}, t)$,
  - current field $j(\mathbf{x}, \mathbf{t})$.
- Thermodynamics $\Leftrightarrow$ external fields and special boundary conditions (*thermostats*).

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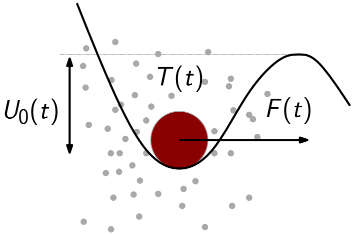

...in the middle?

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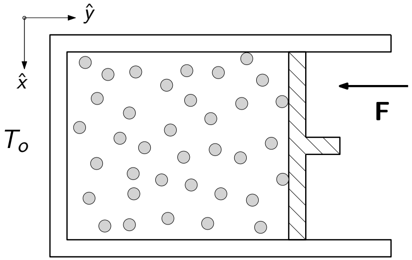
A paradigmatic small system

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



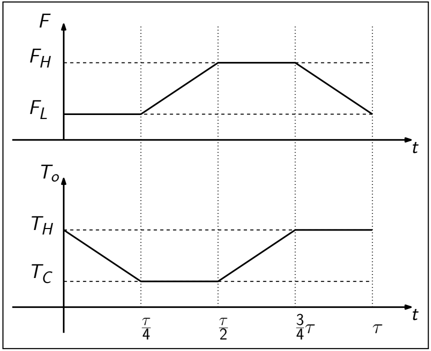
$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{P^2}{2M} + FY$$

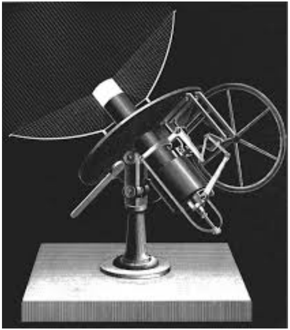
(+ elastic collision between particles and piston)

(+ thermal wall on the left side at temperature T_o)

Is it possible to extract mechanical work from this system with a cyclical protocol?

Heat Engine: the Ericsson cycle





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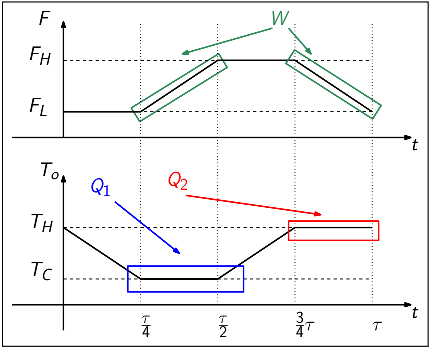
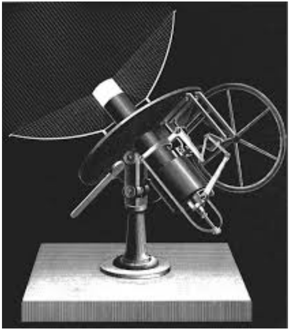




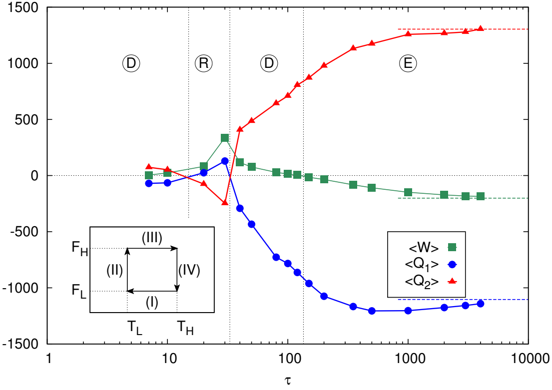
In each segment:

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

$$Q = \Delta \mathcal{H} - W$$

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**
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- **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

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

Linear time-dependent Langevin eqn.

$$\dot{\mathbf{y}} = \mathbf{A}(\mathbf{t}) \cdot \mathbf{y} + \mathbf{B}(\mathbf{t}) \cdot \boldsymbol{\xi} \leftarrow \text{white noise}$$

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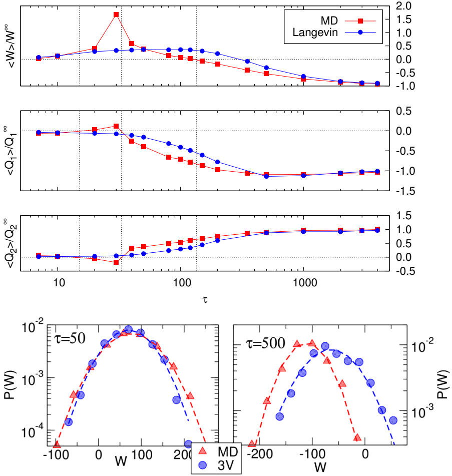
- **B** is determined a *fortiori* to restore detailed balance with equilibrium distribution.

Comparison with MD simulations



- Av. values: Good qualitative agreement (sign inversion, maximum...)
- Fluctuations: Approx. Gaussian behaviour and same stdev.

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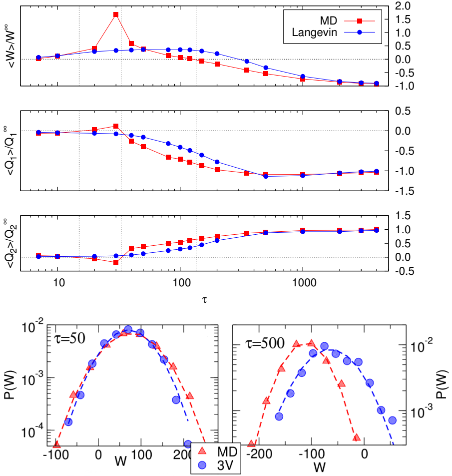

- Av. values: Good qualitative agreement (sign inversion, maximum...)
- Fluctuations: Approx. Gaussian behaviour and same stdev.
- Discrepancies: Effect of gas inhomogeneities and non-linear effects.

An even simpler model...

We can pass from 3 variables $\rightarrow$ 2 variables by simply fixing $T(t) = T_o(t)$

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

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

$$k(t) = \frac{F(t)^2(m+M)}{M^2 N k_B T_o(t)} \qquad \gamma(t) = \frac{2F(t)}{M}\sqrt{\frac{2m}{\pi k_B T_o(t)}}$$

$$X_0(t) = (N+1)\frac{k_B T_o(t)}{F(t)}$$

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- **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 $U(t) = \frac{1}{2}\left(MV^2 + k(t)(X - X_0)^2\right)$.

...to obtain analytic formulas!

With a simpler protocol

$$
\begin{aligned}
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]
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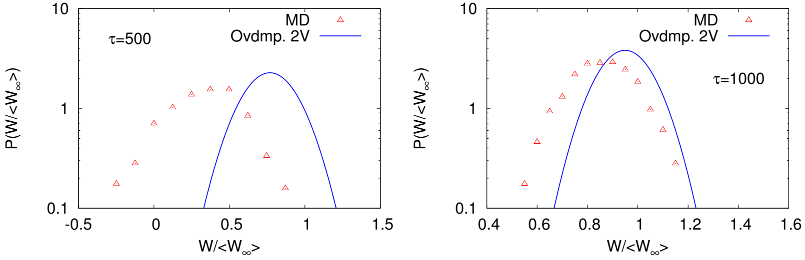

Linear regime and Onsager-coefficients

- Total entropy production

$$\Delta S = -\int_0^{\tau} \frac{\left\langle \dot{E}(t) - \dot{W}(t) \right\rangle}{T(t)} dt$$

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- 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:

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

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$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = A\left(\frac{2\pi}{\tau}\right) \begin{pmatrix} \sin\phi\left(\frac{2\pi}{\tau}\right) & -\cos\phi\left(\frac{2\pi}{\tau}\right) \\ \cos\phi\left(\frac{2\pi}{\tau}\right) & \sin\phi\left(\frac{2\pi}{\tau}\right) \end{pmatrix} \begin{pmatrix} \epsilon \\ \delta \end{pmatrix}$$

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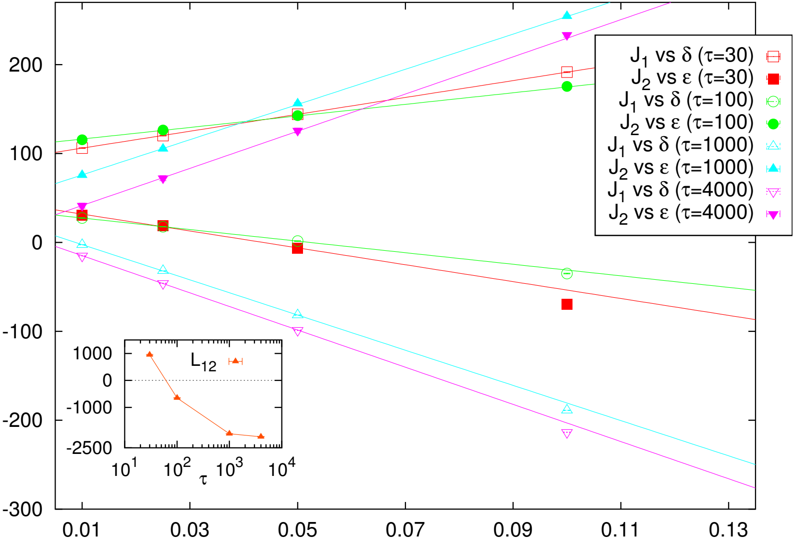
- $\Delta S \to 0$ for $\tau \to \infty$.

Onsager Coeff. in the molecular model



Efficiency at maximum power

- Efficiency:

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- $\tilde{\eta} =$ Efficiency at max. power: ...but maximum with respect to which parameter????

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

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- Violated outside the linear regime (Schmiedl and Seifert, EuroPhys. Lett. (2008))
- What about the time τ of the cycle?

Efficiency at τ-maximum power

$$\begin{aligned} \text{Power: } w &= -\frac{W}{\tau} = -\epsilon\frac{T_0 J_1}{\tau} \\ \text{Efficiency: } \eta &= -\frac{2\epsilon J_1}{J_2} \to 2\delta \;\; \tau \to \infty \end{aligned}$$

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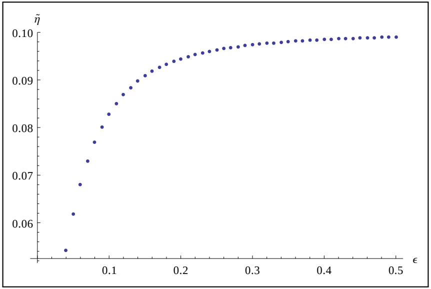

Efficiency at maximum w with respect to τ at different values of ϵ

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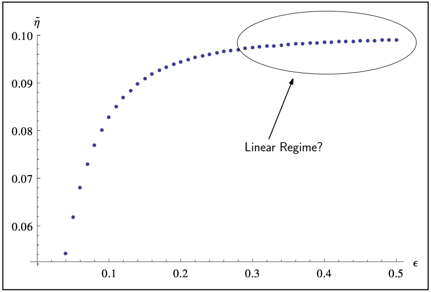

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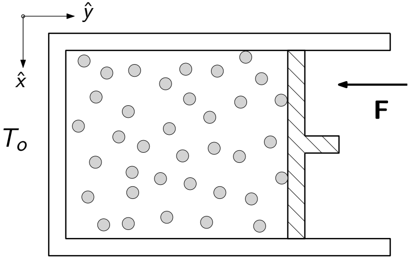
Summarizing...



- 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!