Thermodynamic anomaly in overdamped systems with time-dependent temperature

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Main Result

We quantitatively show that the overdamped approximation fails when thermodynamic quantities such as the total entropy production and heat transfer rate are considered, in the presence of time-varying temperature.

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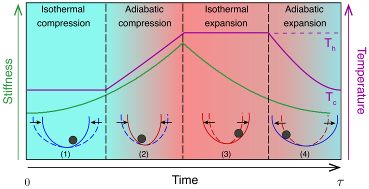
- Effect on efficiency calculations.
- Experimental implications.

Brownian Heat Engines

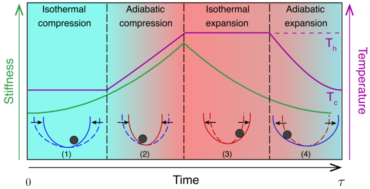


Martínez, Roldán, Dinis, Petrov, Parrondo, Rica

Nature Physics 12 67–70, 2016

Temperature and Potential profiles for Brownian Carnot Engine

Brownian Heat Engines



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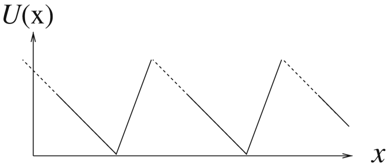


Büttiker, Z. Phys. B 68 161, 1987

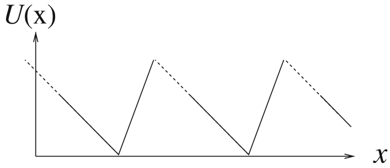
Landauer, J. Stat. Phys. 53 233, 1998

Potential energy $U(x)$ of Büttiker and Landauer ratchet. The temperature $T(x)$ takes the value T_h on the thick solid line and T_c on the dashed line

Ratchet Engine

- Matsuo and Sasa showed that the system approaches Carnot efficiency in the overdamping limit during a quasistatic process. Physica A 276, 2000

- Hondou and Sekimoto showed the unattainability of Carnot efficiency in the Brownian heat engine. PRE 62 6021, 2000



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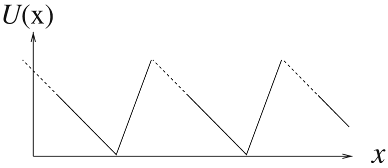

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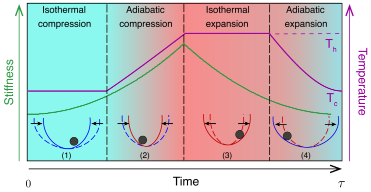
- The overdamped approximation fails in the presence of temperature gradients.

Celani, Bo, Eichhorn, Aurell PRL 109 260603, 2012

- The average rate of entropy production, in the limit of vanishing inertia, is

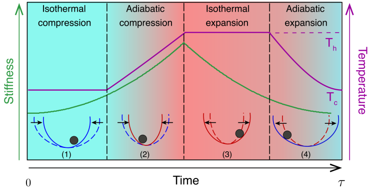
$$\frac{d}{dt}\langle S_{tot}\rangle = \frac{d}{dt}\left\langle S_{tot}^{(over)}\right\rangle + \frac{5}{6}\left\langle \frac{T}{\gamma}\left(\frac{\nabla T}{T}\right)^2\right\rangle \longrightarrow \text{entropic anomaly} \qquad (1)$$

Time-periodic Engines



Temperature and Potential profiles for Brownian Carnot Engine

Time-periodic Engines



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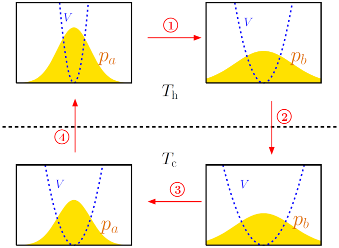


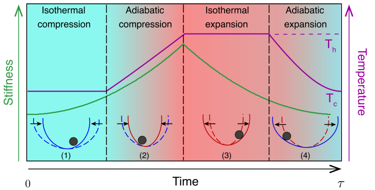
Stochastic heat engine operating between heat baths at temperature T_h and T_c.

- Additional heat flux: $Q_{kin} = (T_h - T_c)/2$.
- Heat Leakage is found in specific models.

Schmiedl, Seifert EPL 81 20003, 2008

Arold, Dechant, Lutz PRE 97 022131,2018
SA, Dutta, PRE 106 064116, 2022

Time-periodic Engines



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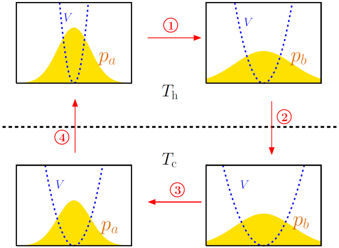

Stochastic heat engine operating between heat baths at temperature T_h and T_c.

- **General heat Anomaly?**
- **Entropy Anomaly?**

Underdamped Langevin model

- The underdamped Langevin equation is given by

$$m\ddot{X}_t = f(X_t, \lambda(t)) - \gamma \dot{X}_t + \eta_t \ . \tag{2}$$

- The thermal noise η_t is a random variable following a Gaussian probability characterized by a zero mean and a two-time correlation function given by

$$\langle \eta_t \eta_{t'} \rangle = 2\gamma T(t)\delta(t - t') \ . \tag{3}$$

- Using Karmer-Moyal expansion, we obtain the Fokker-Planck (FP) equation given by

$$\frac{\partial}{\partial t} P_{\mathrm{ud}}(x, v, t) = \mathcal{L}_{\mathrm{FP}}(x, v; g(t)) P_{\mathrm{ud}}(x, v, t) \ , \tag{4}$$

  where g denotes all the parameters, including γ, T and force parameters λ, and the FP operator $\mathcal{L}$ is defined as

$$\mathcal{L}_{\mathrm{FP}} := -\frac{\partial}{\partial x} v - \frac{1}{m} \frac{\partial}{\partial v} \left(-\gamma v - f(x, \lambda)\right) + \frac{\gamma T(t)}{m^2} \frac{\partial^2}{\partial v^2} \ . \tag{5}$$

Thermodynamics of the Underdamped Langevin model

- The rate of average heat exchanged for the underdamped system is given by

$$\left.\frac{\langle đQ\rangle}{dt}\right|_{\text{ud}} = -\langle \gamma v^2\rangle_{\text{ud}} + \langle v \circ \eta\rangle_{\text{ud}} = \int_{x,v} m\ v\ J^{\text{irr}}_{\text{ud}}(x,v,t)\ . \tag{6}$$

- $J^{\text{irr}}_{\text{ud}}(x,v,t)$ is the irreversible probability current defined on the phase space variables as

$$J^{\text{irr}}_{\text{ud}}(x,v,t) \equiv \left(\frac{\gamma v}{m} - \frac{\gamma T(t)}{m^2}\right) P_{\text{ud}}(x,v,t)\ . \tag{7}$$

- The total entropy production rate by the system is given by

$$\left.\frac{d}{dt}\langle S_{\text{tot}}\rangle\right|_{\text{ud}} = \int_{x,v} \frac{m}{\gamma T(t)} \left(\frac{(J^{\text{irr}}_{\text{ud}})^2}{P_{\text{ud}}}\right)\ . \tag{8}$$

Overdamped Langevin equation

- In the large viscous regime, the system follows the overdamped Langevin equation

$$\cancel{m\ddot{X}_t}^{\,0} = f(X_t, \lambda(t)) - \gamma \dot{X}_t + \eta_t \ . \tag{9}$$

- The heat exchanged in for this process is given by

$$\left.\frac{\langle đQ \rangle}{dt}\right|_{\mathrm{od}} = \int_x (-f(x, \lambda)) J_{\mathrm{od}}(x, t) \ , \tag{10}$$

where J_{od} is the probability current defined as

$$J_{\mathrm{od}}(x, t) = \frac{1}{\gamma} \left(f(x, t) P_{\mathrm{od}} - T(t) \frac{\partial}{\partial x} P_{\mathrm{od}} \right) \ . \tag{11}$$

- The total entropy production rate for the overdamped system is given by

$$\left.\frac{d}{dt} \langle S_{\mathrm{tot}} \rangle\right|_{\mathrm{od}} = \int_x \frac{\gamma}{T(t)} \left(\frac{J_{\mathrm{od}}^2}{P_{\mathrm{od}}} \right) \ . \tag{12}$$

Methodology

- We use the Brinkman's hierarchy method. Physica 22 29, 1956
- We expand the underdamped distribution as

$$P_{\mathrm{ud}}(x, v, t) = \sum_{n=0}^{\infty} c_n(x, t)\psi_n(v, t), \qquad \psi_n = \frac{1}{\sqrt{2^n n!}}\psi_0 H_n\left(\sqrt{\frac{m}{2T}}v\right) \ . \tag{13}$$

- In the large viscosity limit,

$$c_n \sim O(\gamma^{\lfloor -n/2 \rfloor}) \tag{14}$$

- c_0 has a physical meaning. In large viscosity limit

$$c_0 = P_{\mathrm{od}}(x, t) \ . \tag{15}$$

Thermodynamic anomaly

- Heat anomaly is found to be

$$\boxed{\left.\frac{\langle đQ\rangle}{dt}\right|_{\text{ud}} = \underbrace{\frac{\dot{T}}{2}}_{O(1)} + \underbrace{\left.\frac{\langle đQ\rangle}{dt}\right|_{\text{od}} - \frac{m\ddot{T}}{4\gamma}}_{O(\gamma^{-1})}} \tag{16}$$

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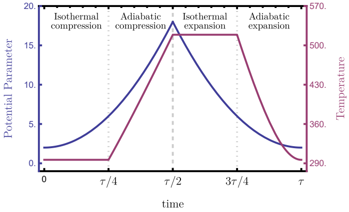
- Origin of the anomaly

$$\boxed{\left.\frac{\langle đQ\rangle}{dt}\right|_{\text{ud}} - \left.\frac{\langle đQ\rangle}{dt}\right|_{\text{od}} = \frac{d}{dt}\langle E_k\rangle} \tag{18}$$

Time-Scales of the problem

- The quantity $T/\dot{T}$ appearing in the entropy anomaly represents an additional time scale associated with the temperature change.
- We have assumed that assumed that $\dot{T}/T \sim O(\gamma^0)$.
- In this case, the positional dynamics are correctly captured by the overdamped Langevin equation.
- For slower temperature variations of $O(\gamma^{-1})$ and beyond, the entropy anomaly appears at higher orders and would not meaningfully alter the overdamped entropy production.
- If the temperature variation is too fast i.e. of $O(\gamma)$, the overdamped approximation cannot even correctly capture the positional dynamics.
- This is because of the breakdown of the relaxation time-scale separation.

Numerical Verification



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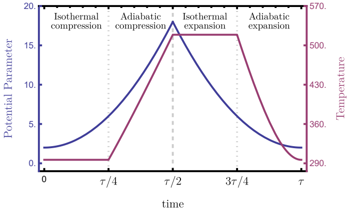
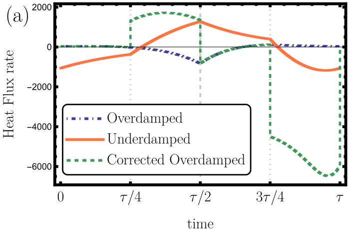
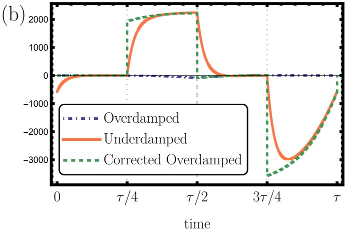
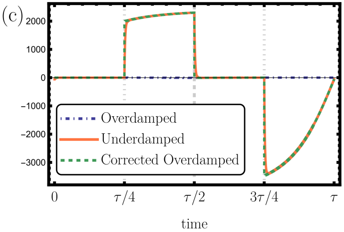




(a) $\gamma = 10$,



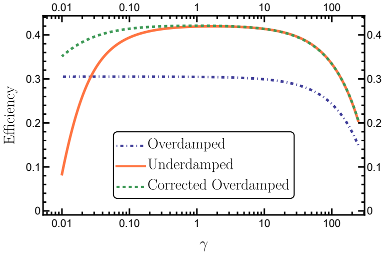
(b) $\gamma = 100$,



(c) $\gamma = 1000$.

Efficiency of an engine

- A direct consequence of the heat anomaly is on the calculation of the efficiency η of the heat engine.



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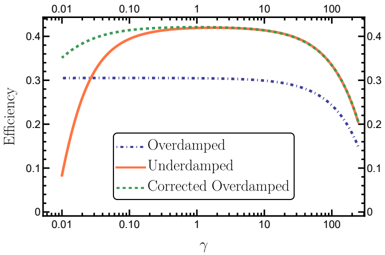
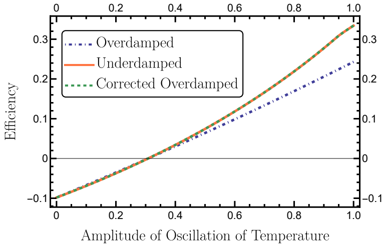


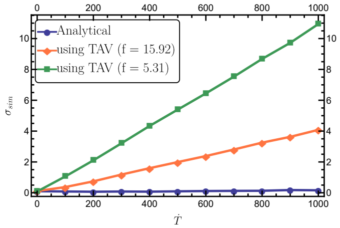


Experimental Implications

- It was already known that the overdamped is inadequate for Langevin systems with time-dependent temperature.
- Therefore, attempts were made to study the full underdamped systems.
- However, keeping track of the kinetic energy is difficult in experiments.
- A TAV-method was introduced by Roldán et. al. in *Applied Physics Letters 104, 2014*.

$$\langle v^2(t)\rangle = L(f)^{-1}\langle \overline{v}_f^2(t)\rangle.$$

- Our methods outperform the TAV method in the measurement of kinetic energy in the overdamped regime.



Mean square error σ_{sim} of predicted $\langle v^2\rangle$ from the simulated result versus the time-derivative of temperature T. The temperature is increased linearly starting from 300K.

Summary

- We found that the overdamped approximation is inadequate to capture the complete thermodynamics for Langevin systems with time-dependent temperature.
- We explicitly calculated the anomaly for the rate of heat transfer and numerically verified for "Carnot Engine".
- We explicitly calculated the entropy anomaly.
- We compared the experimental TAV method with our analytical result.
- For systems with large viscosity and time-varying temperature, the overdamped description can be used for studying their thermodynamics, provided the corresponding anomalies are suitably accounted for.

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Thank you for your attention!