Fluctuation relations for manipulated systems

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Introduction
❖ Motivations
❖ Outline
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production

Motivations

- Remarkable, deceptively simple relations obeyed by fluctuation statistics in out-of-equilibrium systems
- Relevant for small systems, where fluctuations are large
- Provide tools for the investigation of equilibrium properties of small systems
- Provide structure to the “thermodynamic” properties of non-equilibrium steady states
- Could be relevant to understand the working of biological system, like biological motors

Outline

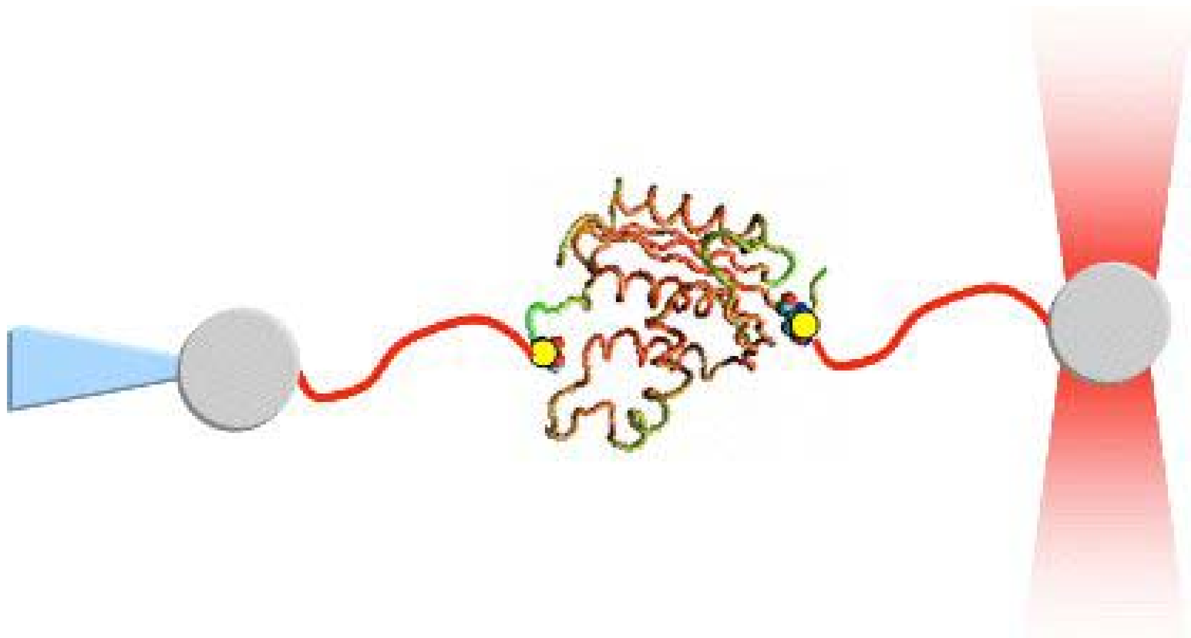
- Fluctuation relations for the work:
  - Jarzynski's relation and its applications
  - Crooks's relation and its consequences
  - Experiments and applications to biomolecules
  - On the estimation of the free energy

Outline

- Fluctuation relations for the work:
  - ✦ Jarzynski's relation and its applications
  - ✦ Crooks's relation and its consequences
  - ✦ Experiments and applications to biomolecules
  - ✦ On the estimation of the free energy
- Fluctuation relations for the entropy:
  - ✦ Entropy production in a single trajectory: Seifert's relation and its consequences
  - ✦ Entropy production in nonequilibrium steady states: The Gallavotti-Cohen relation

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Nanomanipulation



Manipulation of a biopolymer by optical tweezers

Manipulating a system out of equilibrium

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

- A system at equilibrium at inverse temperature β:

$$Z_\mu = \operatorname*{Tr}_x \mathrm{e}^{-\beta H(x,\mu)} = \mathrm{e}^{-\beta F(\mu)}$$

- Manipulation protocol:

$$\boldsymbol{\mu} : \mu = \mu(t); \qquad \mu(0) = \mu_0; \qquad \mu(t_\mathrm{f}) = \mu_\mathrm{f}$$

- Fluctuating work:

$$\mathcal{W}[\boldsymbol{x}, \boldsymbol{\mu}] = \int_0^{t_\mathrm{f}} \mathrm{d}t\; \dot{\mu}(t)\; \frac{\partial H}{\partial \mu}\bigg|_{x(t),\mu(t)}$$

Manipulating a system out of equilibrium

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

- A system at equilibrium at inverse temperature β:

$$Z_\mu = \mathop{\mathrm{Tr}}_x \mathrm{e}^{-\beta H(x,\mu)} = \mathrm{e}^{-\beta F(\mu)}$$

- Manipulation protocol:

$$\boldsymbol{\mu} : \mu = \mu(t); \qquad \mu(0) = \mu_0; \qquad \mu(t_\mathrm{f}) = \mu_\mathrm{f}$$

- Fluctuating work:

$$\begin{aligned} \mathcal{W}[\boldsymbol{x}, \boldsymbol{\mu}] &= \int_0^{t_\mathrm{f}} \mathrm{d}t\ \dot{\mu}(t)\ \frac{\partial H}{\partial \mu}\bigg|_{x(t),\mu(t)} \\ \langle \mathcal{W} \rangle &\geq F(\mu_\mathrm{f}) - F(\mu_0) \end{aligned}$$

Jarzynski's relation (1997)

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

What does nonequilibrium tell us of equilibrium?

$$\boxed{\left\langle \mathrm{e}^{-\beta \mathcal{W}} \right\rangle = \mathrm{e}^{-\beta(F(\mu_{\mathrm{f}})-F(\mu_0))}}$$

Average over all realizations of the system history $\boldsymbol{x}(t)$:

$$\langle \cdots \rangle = \mathop{\mathrm{Tr}}_{\boldsymbol{x}} \mathcal{P}[\boldsymbol{x}] \cdots$$

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

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Average over all realizations of the system history $\boldsymbol{x}(t)$:

$$\langle\cdots\rangle = \mathop{\mathrm{Tr}}_{\boldsymbol{x}} \mathcal{P}[\boldsymbol{x}]\,\cdots$$

Assumptions:

- Evolution equation for $P(x,t)$: $\quad \partial_t P = -\widehat{\mathcal{H}}_{\mu(t)} P$
- Equilibrium distribution: $\widehat{\mathcal{H}}_{\mu} P^{\mathrm{eq}} = 0$

$$P^{\mathrm{eq}}(x,\mu) = \frac{\mathrm{e}^{-\beta H(x,\mu)}}{Z_\mu}$$

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

A simple proof

$$\psi(x,t) = \int \mathcal{D}\boldsymbol{x}\, \delta(x(t)-x)\, \mathrm{e}^{-\beta \mathcal{W}[\boldsymbol{x}]}\, \mathcal{P}[\boldsymbol{x}]$$

Evolution equation:

$$\frac{\partial \psi}{\partial t} = -\widehat{\mathcal{H}}_{\mu(t)}\, \psi - \beta \dot{\mu}(t) \frac{\partial H}{\partial \mu} \psi$$

Initial condition:

$$\psi(x,0) = \mathrm{e}^{-\beta H(x,\mu(0))} / Z_{\mu(0)}$$

Thus

$$\psi(x,t) = \frac{1}{Z_{\mu(0)}} \mathrm{e}^{-\beta H(x,\mu(t))}$$

Examples

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

- Sudden change in the hamiltonian: $\mu_0 \longrightarrow \mu_1$

$$
\begin{aligned}
\left\langle \mathrm{e}^{-\beta \mathcal{W}} \right\rangle &= \sum_x \mathrm{e}^{-\beta(H(x,\mu_1)-H(x,\mu_0))} \frac{\mathrm{e}^{-\beta H(x,\mu_0)}}{Z_{\mu_0}} \\
&= \frac{1}{Z_{\mu_0}} \sum_x \mathrm{e}^{-\beta H(x,\mu_1)} = \frac{Z_{\mu_1}}{Z_{\mu_0}}
\end{aligned}
$$

Examples

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

- Sudden change in the hamiltonian: $\mu_0 \longrightarrow \mu_1$

$$\begin{aligned}\left\langle \mathrm{e}^{-\beta\mathcal{W}}\right\rangle &= \sum_x \mathrm{e}^{-\beta(H(x,\mu_1)-H(x,\mu_0))}\,\frac{\mathrm{e}^{-\beta H(x,\mu_0)}}{Z_{\mu_0}}\\ &= \frac{1}{Z_{\mu_0}}\sum_x \mathrm{e}^{-\beta H(x,\mu_1)} = \frac{Z_{\mu_1}}{Z_{\mu_0}}\end{aligned}$$

- Adiabatic change: $\mu(t) = \ell(t/t_\mathrm{f})$, $\ell(0) = \mu_0, \qquad \ell(1) = \mu_1$

$$\begin{aligned}\mathcal{W}[\boldsymbol{x}] &\simeq \int_0^{t_\mathrm{f}} \mathrm{d}t' \left\langle \frac{\partial H(x(t'),\mu)}{\partial\mu}\right\rangle_{\mu=\mu(t')} \dot{\mu}(t')\\ &= \int_{\mu_0}^{\mu_1} \mathrm{d}\mu \left\langle \frac{\partial H(x,\mu)}{\partial\mu}\right\rangle_{\mu} = W^{\mathrm{th}}\end{aligned}$$

Comments

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

- $\Delta F = F(\mu_{\mathrm{f}}) - F(\mu_0)$ is the change in the equilibrium free energy with the corresponding values of the parameter μ

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Comments

- $\Delta F = F(\mu_{\mathrm{f}}) - F(\mu_0)$ is the change in the equilibrium free energy with the corresponding values of the parameter μ
- One assumes that the system is initially at equilibrium

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Comments

- $\Delta F = F(\mu_{\mathrm{f}}) - F(\mu_0)$ is the change in the equilibrium free energy with the corresponding values of the parameter μ
- One assumes that the system is initially at equilibrium
- The system is not at equilibrium at the end of the process

Comments

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

- $\Delta F = F(\mu_{\mathrm{f}}) - F(\mu_0)$ is the change in the equilibrium free energy with the corresponding values of the parameter μ
- One assumes that the system is initially at equilibrium
- The system is not at equilibrium at the end of the process
- The average is over all realizations of the process: If the process is deterministic, over the initial conditions

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Derivation: A Markov chain

$$x \in \{1, 2, \ldots, q\} \qquad t \in \{0, 1, 2, \ldots\}$$

Equilibrium distribution determined by hamiltonian $H(x, \mu)$:

$$P^{\mathrm{eq}}(x, \mu) = \frac{\mathrm{e}^{-\beta H(x,\mu)}}{Z_\mu} \qquad Z_\mu = \sum_x \mathrm{e}^{-\beta H(x,\mu)} = \mathrm{e}^{-\beta F(\mu)}$$

Evolution equation for the probabilities:

$$p(x, t+1) = \sum_{x'} W_{xx'}(\mu(t))\, p(x', t)$$

$$\sum_{x'} W_{xx'}(\mu)\, P^{\mathrm{eq}}(x', \mu) = P^{\mathrm{eq}}(x, \mu)$$

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Work and heat in a reversible transformation

$$E(\mu) = \langle H(\mu) \rangle_\mu \qquad \langle A \rangle_\mu = \sum_x A(x)\, P^{\mathrm{eq}}(x,\mu)$$

Manipulation: $\mu \longrightarrow \mu + \mathrm{d}\mu$:

$$\mathrm{d}E(\mu) = \underbrace{\sum_x \mathrm{d}H(x,\mu)\, P^{\mathrm{eq}}(x,\mu(t))}_{\mathrm{d}W} + \underbrace{\sum_x H(x,\mu)\, \mathrm{d}P^{\mathrm{eq}}(x,\mu)}_{\mathrm{d}Q}$$

$$\begin{aligned} \mathrm{d}S^{\mathrm{eq}} &= -k_{\mathrm{B}}\, \mathrm{d}\left(\sum_x P^{\mathrm{eq}}(x,\mu) \ln P^{\mathrm{eq}}(x,\mu) \right) \\ &= -k_{\mathrm{B}} \sum_x \ln P^{\mathrm{eq}}(x,\mu)\, \mathrm{d}P^{\mathrm{eq}}(x,\mu) \\ &= \frac{1}{T} \sum_x H(x,\mu)\, \mathrm{d}P^{\mathrm{eq}}(x,\mu) \end{aligned}$$

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

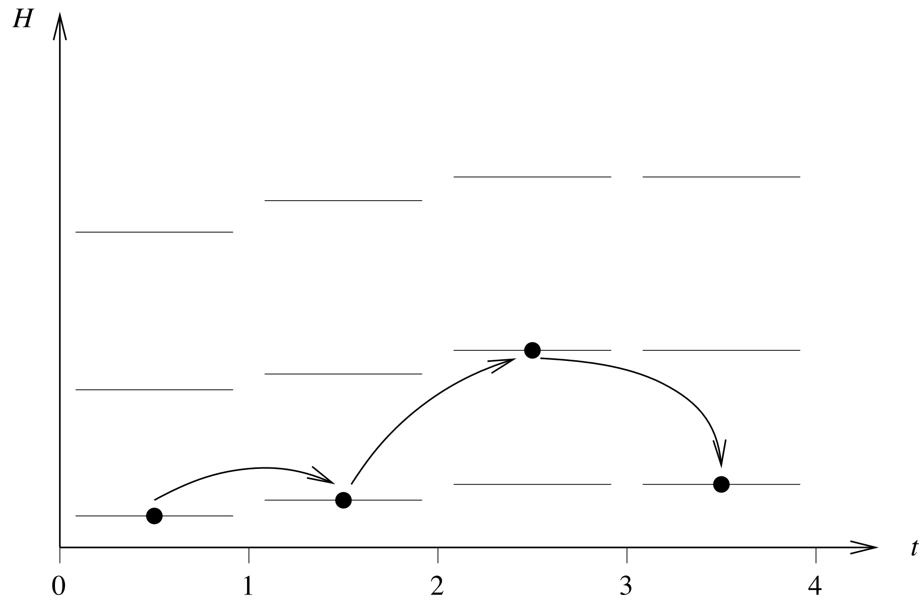
Path work and heat under manipulation

Path $\boldsymbol{x} = (x(0), x(1), x(2), \ldots, x(t_\mathrm{f}))$
Manipulation protocol: $\boldsymbol{\mu} = (\mu(0), \mu(1), \ldots, \mu(t_\mathrm{f} - 1))$

$$\begin{aligned}
\mathcal{W}[\boldsymbol{x}] &= \sum_{t=0}^{t_\mathrm{f}-1} \left[H(x(t+1), \mu(t+1)) - H(x(t+1), \mu(t))\right] \\
\mathcal{Q}[\boldsymbol{x}] &= \sum_{t=0}^{t_\mathrm{f}-1} \left[H(x(t+1), \mu(t)) - H(x(t), \mu(t))\right] \\
\Delta E &= H(x(t_\mathrm{f}), \mu(t_\mathrm{f})) - H(x(0), \mu(0)) = \mathcal{W} + \mathcal{Q}
\end{aligned}$$

N.B. $\mathcal{W}$ and $\mathcal{Q}$ depend on the whole path, ΔE depends only on initial and final states

Path probability



$$\mathcal{P}[\boldsymbol{x} \mid x(0)] = W_{x(t_\mathrm{f}),x(t_\mathrm{f}-1)}(\mu(t_\mathrm{f}-1)) \times \cdots$$
$$\cdots \times W_{x(2),x(1)}(1) W_{x(1),x(0)}(\mu(0))$$

N.B.: The transitions take place with the “old” probability $W_{xx'}(\mu(t-1))$, then the energy changes to $H(x, \mu(t))$

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Reversed path

Time-reversal invariant states: $\mathcal{I}x = x$

$$
\begin{aligned}
\boldsymbol{x} &= (x(0), x(1), \ldots, x(t_{\mathrm{f}}-1), x(t_{\mathrm{f}})) \\
\widehat{\boldsymbol{x}} &= (x(t_{\mathrm{f}}), x(t_{\mathrm{f}}-1), \ldots, x(1), x(0)) \\
\widehat{x}(t) &= x(t_{\mathrm{f}}-t) = x(\widehat{t})
\end{aligned}
$$

Time-reversed protocol:

$$
\widehat{\boldsymbol{\mu}}: \qquad \widehat{\mu}(t) = \mu(t_{\mathrm{f}}-t) = \mu(\widehat{t}) \qquad t = 1, \ldots, t_{\mathrm{f}}
$$

Probability of the reversed transition:

$$
\boxed{\widehat{W}_{xx'}(\mu): \qquad \widehat{W}_{xx'}(\mu) P^{\mathrm{eq}}(x', \mu) = W_{x'x}(\mu) P^{\mathrm{eq}}(x, \mu)}
$$

Reversed path

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

Time-reversal invariant states: $\mathcal{I}x = x$

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\begin{aligned}
\boldsymbol{x} &= (x(0), x(1), \ldots, x(t_\mathrm{f}-1), x(t_\mathrm{f})) \\
\widehat{\boldsymbol{x}} &= (x(t_\mathrm{f}), x(t_\mathrm{f}-1), \ldots, x(1), x(0)) \\
\widehat{x}(t) &= x(t_\mathrm{f}-t) = x(\widehat{t})
\end{aligned}
$$

Time-reversed protocol:

$$
\widehat{\boldsymbol{\mu}} : \qquad \widehat{\mu}(t) = \mu(t_\mathrm{f}-t) = \mu(\widehat{t}) \qquad t = 1, \ldots, t_\mathrm{f}
$$

Probability of the reversed transition:

$$
\boxed{\widehat{W}_{xx'}(\mu) : \qquad \widehat{W}_{xx'}(\mu) P^{\mathrm{eq}}(x', \mu) = W_{x'x}(\mu) P^{\mathrm{eq}}(x, \mu)}
$$

(Detailed balance: $\widehat{W}_{xx'}(\mu) = W_{xx'}(\mu)$)

Probability of the reversed path

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

$$W_{xx'}(\mu(t)) = W_{xx'}(t) \qquad \text{etc.}$$

$$\widehat{W}_{xx'}(t) = W_{x'x}(t_\mathrm{f} - t) \qquad t = 1, \dots t_\mathrm{f}$$

$$\begin{aligned}
\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}} \mid \widehat{x}(0)] &= \widehat{W}_{\widehat{x}(t_\mathrm{f}),\widehat{x}(t_\mathrm{f}-1)}(t_\mathrm{f}) \cdots \widehat{W}_{\widehat{x}(2),\widehat{x}(1)}(2)\widehat{W}_{\widehat{x}(1),\widehat{x}(0)}(1) \\
&= W_{x(1),x(0)}(0)\mathrm{e}^{\beta(H(x(1),\mu(0))-H(x(0),\mu(0)))} \\
&\quad \times W_{x(2),x(1)}(1)\mathrm{e}^{\beta(H(x(2),\mu(1))-H(x(1),\mu(1)))} \times \cdots \\
&\quad \times W_{x(t_\mathrm{f}),x(t_\mathrm{f}-1)}(t_\mathrm{f} - 1) \\
&\qquad \times \mathrm{e}^{\beta(H(x(t_\mathrm{f}),\mu(t_\mathrm{f}-1))-H(x(t_\mathrm{f}-1),\mu(t_\mathrm{f}-1)))} \\
&= \mathcal{P}[\boldsymbol{x} \mid x(0)]\, \mathrm{e}^{\beta \mathcal{Q}[\boldsymbol{x}]}
\end{aligned}$$

Introduction
Fluctuation relations for the work
❖ Nanomanipulation
❖ Manipulating a system out of equilibrium
❖ Jarzynski's relation (1997)
❖ A simple proof
❖ Examples
❖ Comments
❖ Derivation: A Markov chain
❖ Work and heat in a reversible transformation
❖ Path work and heat under manipulation
❖ Path probability
❖ Reversed path
❖ Probability of the reversed path
❖ Crooks's relation (1999)
❖ Dissipation and irreversibility
Applications

Crooks's relation (1999)

$$\mathcal{P}[\boldsymbol{x}] = \mathcal{P}[\boldsymbol{x} \mid x(0)]\, P^{\mathrm{eq}}(x(0), \mu(0))$$

$$\begin{aligned}
\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}] &= \widehat{\mathcal{P}}[\widehat{\boldsymbol{x}} \mid \widehat{x}(0)]\, \mathrm{e}^{-\beta H(\widehat{x}(0), \widehat{\mu}(0))} \big/ Z_{\widehat{\mu}(0)} \\
&= \mathcal{P}[\boldsymbol{x} \mid x(0)]\, \mathrm{e}^{\beta\{\mathcal{Q}[\boldsymbol{x}] - H(x(t_\mathrm{f}), \mu(t_\mathrm{f}))\}} \big/ Z_{\mu(t_\mathrm{f})} \\
&= \mathcal{P}[\boldsymbol{x}]\, \mathrm{e}^{\beta\{\mathcal{Q}[\boldsymbol{x}] - (H(x(t_\mathrm{f}), \mu(t_\mathrm{f})) - H(x(0), \mu(0)))\}} \left(Z_{\mu(0)} \big/ Z_{\mu(t_\mathrm{f})} \right)
\end{aligned}$$

$$\mathcal{Q}[\boldsymbol{x}] - \Delta H = -\mathcal{W}[\boldsymbol{x}] \qquad Z_{\mu(0)} \big/ Z_{\mu(t_\mathrm{f})} = \mathrm{e}^{\beta\, \Delta F}$$

$$\boxed{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}] = \mathcal{P}[\boldsymbol{x}]\, \mathrm{e}^{-\beta(\mathcal{W}[\boldsymbol{x}] - \Delta F)}}$$

Summing over $\boldsymbol{x}$:

$$1 = \left\langle \mathrm{e}^{-\beta(\mathcal{W} - \Delta F)} \right\rangle$$

Dissipation and irreversibility

Introduction

Fluctuation relations for the work

❖ Nanomanipulation

❖ Manipulating a system out of equilibrium

❖ Jarzynski's relation (1997)

❖ A simple proof

❖ Examples

❖ Comments

❖ Derivation: A Markov chain

❖ Work and heat in a reversible transformation

❖ Path work and heat under manipulation

❖ Path probability

❖ Reversed path

❖ Probability of the reversed path

❖ Crooks's relation (1999)

❖ Dissipation and irreversibility

Applications

$$e^{\beta(\mathcal{W}[\boldsymbol{x}]-\Delta F)} = \frac{\mathcal{P}[\boldsymbol{x}]}{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}]}$$

Thus

$$\boxed{W^{\mathrm{d}} = \langle \mathcal{W} \rangle - \Delta F = \beta^{-1} \underbrace{\sum_{\boldsymbol{x}} \mathcal{P}[\boldsymbol{x}] \ln \frac{\mathcal{P}[\boldsymbol{x}]}{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}]}}_{D(\mathcal{P}[\boldsymbol{x}] \| \widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}])}}$$

van den Broeck et al., 2007

Summing over x with a given value of W:

$$W^{\mathrm{d}} = \beta^{-1} \int \mathrm{d}W \; P(W) \ln \frac{P(W)}{\widehat{P}(-W)} = \beta^{-1} D(P(W) \| \widehat{P}(-W))$$

The work distribution

Introduction

Fluctuation relations for the work

Applications

❖ The work distribution

❖ A RNA hairpin

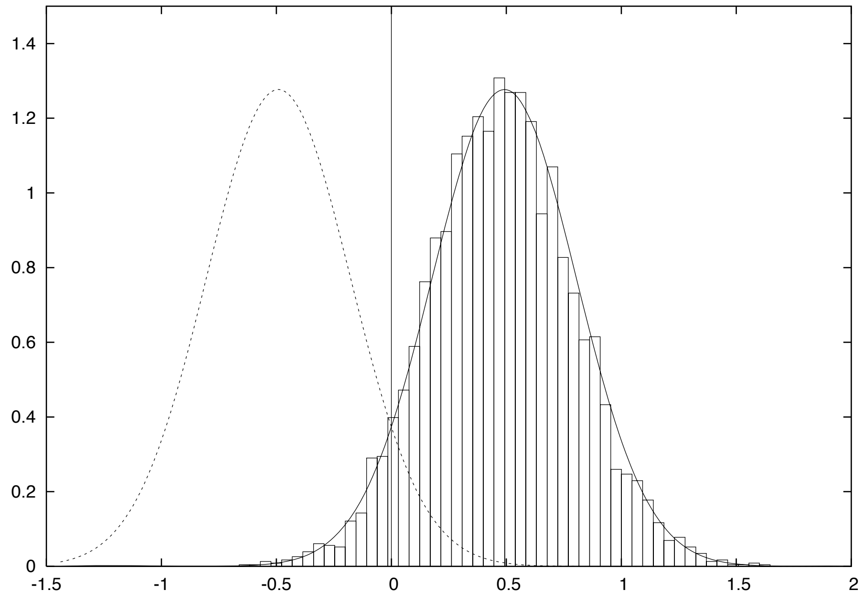
❖ The Ig27 domain of human titin

❖ The free-energy landscape

❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

Nonlinear oscillator: $H(x, \mu) = H_0(x) - \mu x$, $\widehat{\boldsymbol{\mu}} = -\boldsymbol{\mu}$



W

The work distribution

Introduction
Fluctuation relations for the work
Applications
❖ The work distribution
❖ A RNA hairpin
❖ The Ig27 domain of human titin
❖ The free-energy landscape
❖ The Jarzynski estimator: A REM partition function
Fluctuation relations for the entropy production

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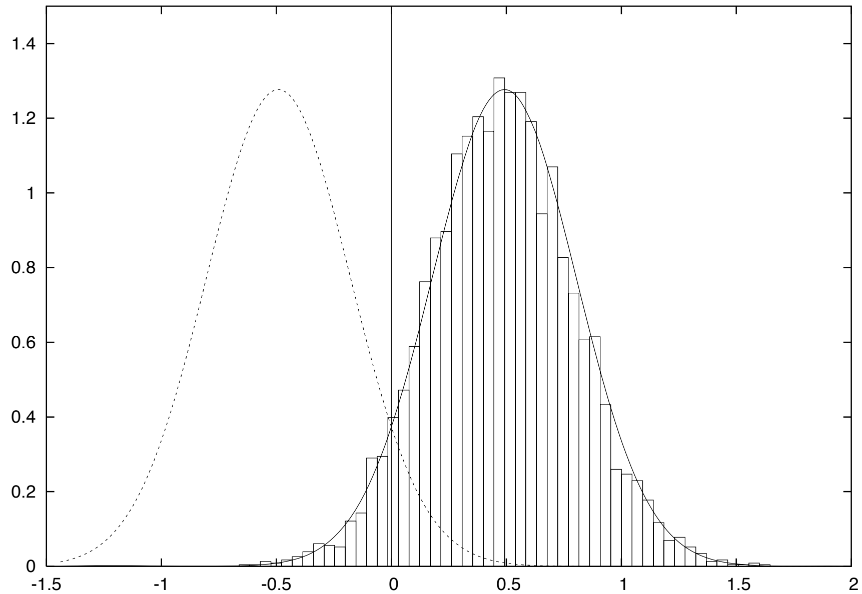

W

Dotted line: $P(W)\,\mathrm{e}^{-\beta W} = P(-W)$

The value of W that contributes most to Jarzynski's equality is the most probable in the inverse manipulation

The work distribution

Introduction
Fluctuation relations for the work
Applications
❖ The work distribution
❖ A RNA hairpin
❖ The Ig27 domain of human titin
❖ The free-energy landscape
❖ The Jarzynski estimator: A REM partition function
Fluctuation relations for the entropy production

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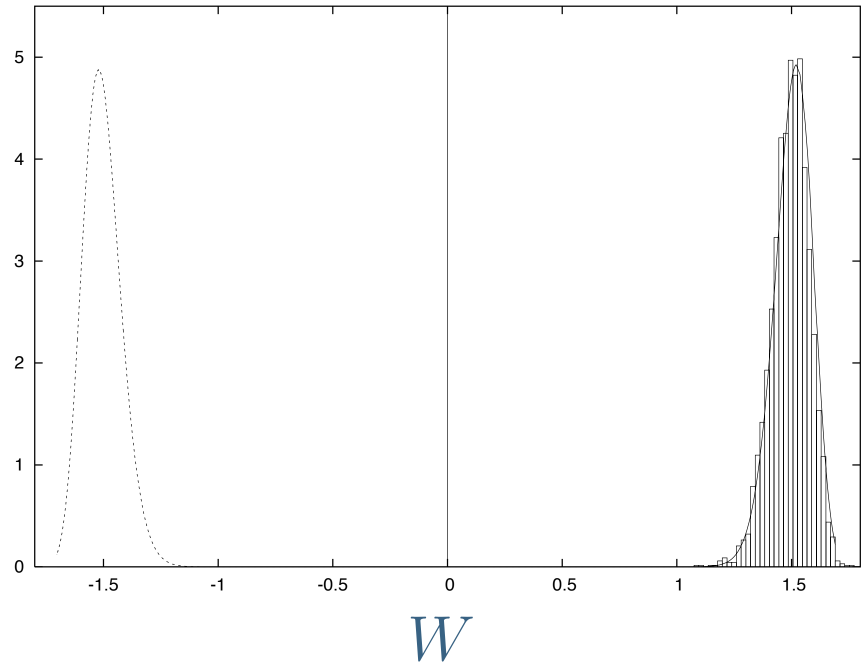


For larger systems, fluctuations which contribute to Jarzynski's equality are exceedingly rare

A RNA hairpin

Collin et al., 2005

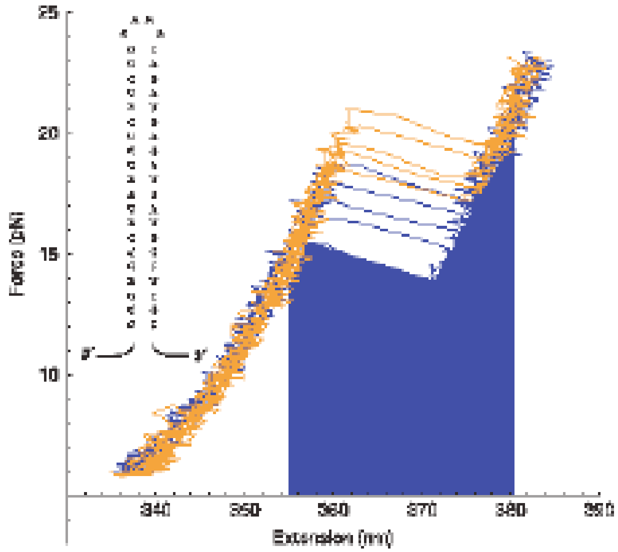


Figure 1 | Force–extension curves. The stochasticity of the unfolding and refolding processes is characterized by a distribution of unfolding or refolding work trajectories. Five unfolding (orange) and refolding (blue) force–extension curves for the RNA hairpin are shown (loading rate of 7.5 pN s^{-1}). The blue area under the curve represents the work returned to the machine as the molecule switches from the unfolded to the folded state. The RNA sequence is shown as an inset.

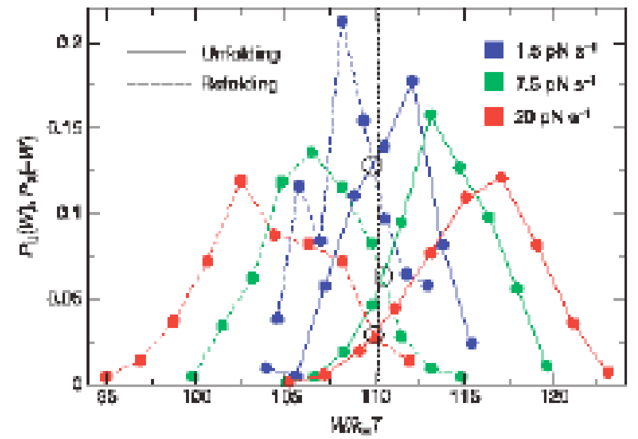


Figure 2 | Test of the CFT using an RNA hairpin. Work distributions for RNA unfolding (continuous lines) and refolding (dashed lines). We plot negative work, $P_R(-W)$, for refolding. Statistics: 130 pulls and three molecules ($r = 1.5$ pN s^{-1}), 380 pulls and four molecules ($r = 7.5$ pN s^{-1}), 700 pulls and three molecules ($r = 20.0$ pN s^{-1}), for a total of ten separate experiments. Good reproducibility was obtained among molecules (see Supplementary Fig. S2). Work values were binned into about ten equally spaced intervals. Unfolding and refolding distributions at different speeds show a common crossing around $\Delta G = 110.3 k_B T$.

A RNA hairpin

Introduction

Fluctuation relations for the work

Applications

❖ The work distribution

❖ A RNA hairpin

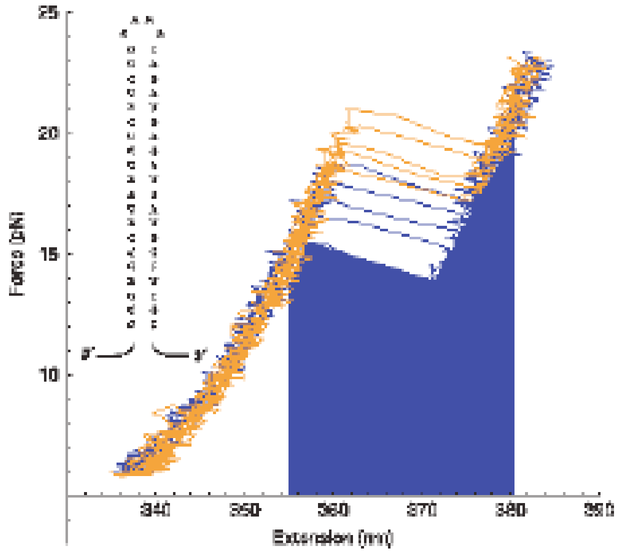
❖ The Ig27 domain of human titin

❖ The free-energy landscape

❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

Collin et al., 2005



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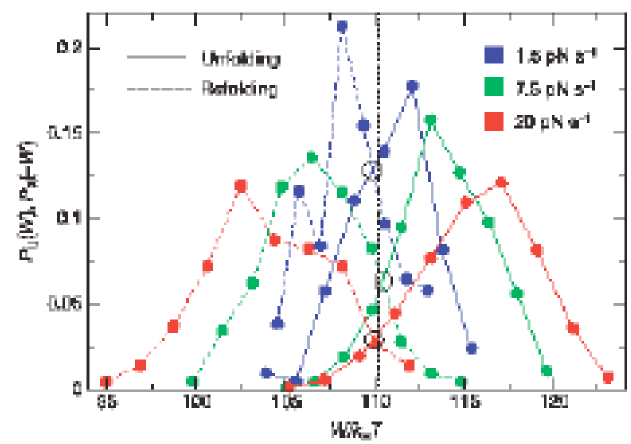

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$$\widehat{P}(-\Delta F) = P(\Delta F)$$

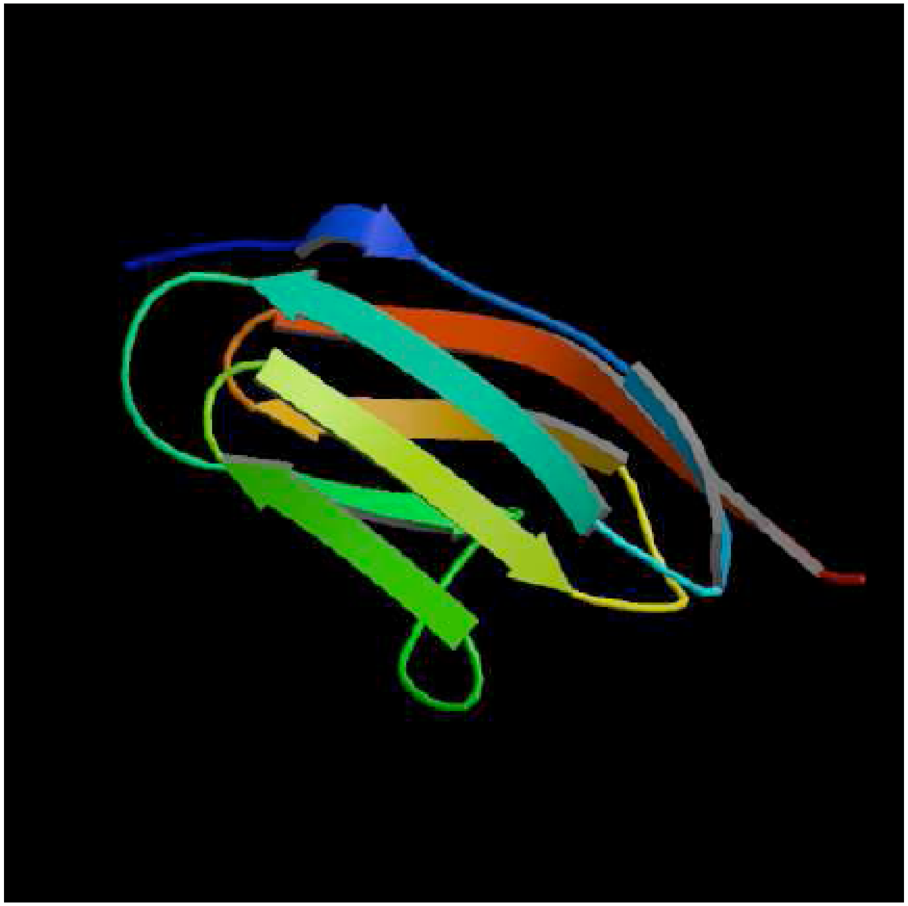
Introduction

Fluctuation relations for the work

Applications
❖ The work distribution
❖ A RNA hairpin
❖ The Ig27 domain of human titin
❖ The free-energy landscape
❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

The Ig27 domain of human titin



89 aminoacids, $\epsilon/k_{\mathrm{B}} = 43$ K

The free-energy landscape

Introduction

Fluctuation relations for the work

Applications

❖ The work distribution

❖ A RNA hairpin

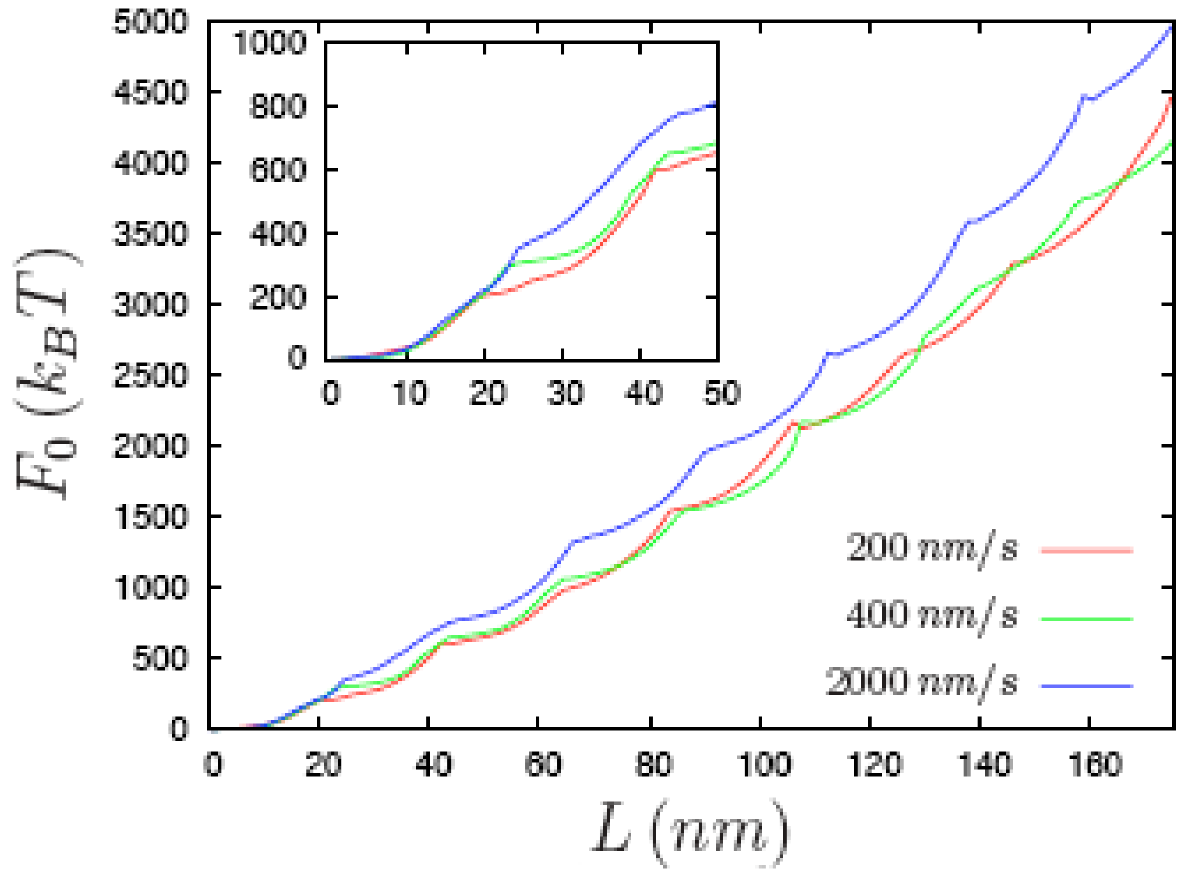
❖ The Ig27 domain of human titin

❖ The free-energy landscape

❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

A. Imparato, S. Luccioli, A. Torcini, 2007



The Jarzynski estimator: A REM partition function

Introduction

Fluctuation relations for the work

Applications

❖ The work distribution

❖ A RNA hairpin

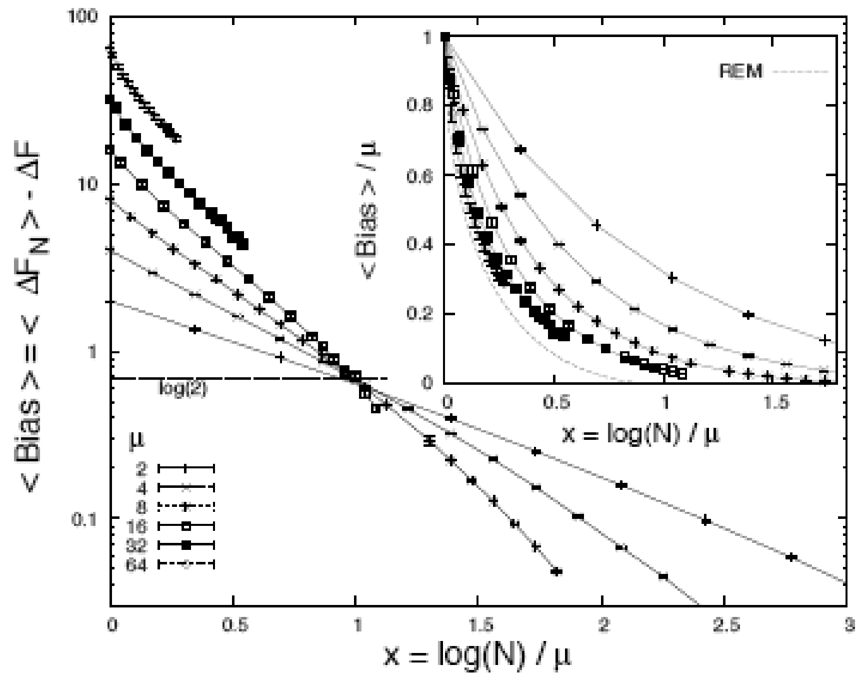
❖ The Ig27 domain of human titin

❖ The free-energy landscape

❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

Palassini and Ritort, 2008



$$\Delta F_N = -\frac{1}{N\beta}\sum_{k=1}^{N} e^{-\beta W_k}$$

The Jarzynski estimator: A REM partition function

Introduction

Fluctuation relations for the work

Applications

❖ The work distribution

❖ A RNA hairpin

❖ The Ig27 domain of human titin

❖ The free-energy landscape

❖ The Jarzynski estimator: A REM partition function

Fluctuation relations for the entropy production

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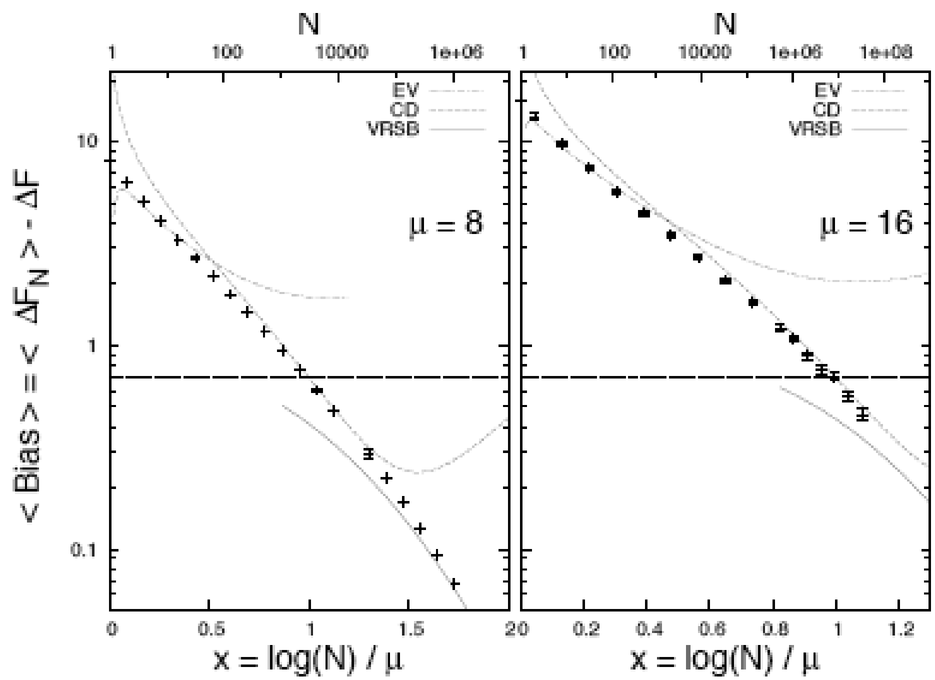

$$\Delta F_N = -\frac{1}{N\beta}\sum_{k=1}^{N} \mathrm{e}^{-\beta W_k}$$

Entropy produced in a transition

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

Detailed balance:

$$
\begin{aligned}
W_{xx'}\,\mathrm{e}^{-\beta H(x')} &= W_{x'x}\,\mathrm{e}^{-\beta H(x)} \\
&\Downarrow \\
\frac{W_{xx'}}{W_{x'x}} &= \mathrm{e}^{-\beta(H(x)-H(x'))} = \mathrm{e}^{-\beta Q_{xx'}} = \mathrm{e}^{\Delta S^{\mathrm{bath}}_{xx'}/k_{\mathrm{B}}}
\end{aligned}
$$

Generalize by definition: (units $k_{\mathrm{B}} = 1$)

$$
\Delta S^{\mathrm{bath}}_{xx'} = \ln \frac{W_{xx'}}{\widehat{W}_{x'x}}
$$

$$
\frac{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}} \mid \widehat{x}(0)]}{\mathcal{P}[\boldsymbol{x} \mid x(0)]} = \prod_{t=0}^{t_{\mathrm{f}}-1} \frac{\widehat{W}_{x(t)x(t+1)}}{W_{x(t+1)x(t)}} = \mathrm{e}^{-\Delta\mathcal{S}^{\mathrm{bath}}[\boldsymbol{x}]}
$$

Seifert's relation

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Define $\pi_0(x)$ and $\widehat{\pi}_0(x)$ arbitrary but normalized, $\mathcal{P}[\boldsymbol{x}] = \mathcal{P}[\boldsymbol{x} \mid x(0)]\pi_0(x(0))$ etc.:

$$\boxed{\ln \frac{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}]}{\mathcal{P}[\boldsymbol{x}]} = -\Delta \mathcal{S}^{\mathrm{bath}}[\boldsymbol{x}] + \ln \frac{\widehat{\pi}_0(\widehat{x}(0))}{\pi_0(x(0))}}$$

Seifert 2005

Fluctuation theorem I (Seifert)

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

Let $p(x,t)$ be the solution of

$$p(x,t+1) = \sum_{x'} W_{xx'}(t)p(x',t) \qquad p(x,0) = p_0(x)$$

$$\pi_0(x) = p_0(x) \qquad \widehat{\pi}_0(x) = p(x,t_\mathrm{f})$$

Define $S(x,t) = -\ln p(x,t)$, then

$$\begin{aligned} \ln \frac{\widehat{\pi}_0(\widehat{x}(0))}{\pi_0(x(0))} &= \ln \frac{p(x(t_\mathrm{f}),t_\mathrm{f})}{p(x(0),0)} = -\Delta S \\ \Delta \mathcal{S}^{\mathrm{tot}} &= \Delta \mathcal{S}^{\mathrm{bath}} + \Delta S \end{aligned}$$

$$\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}] = \mathcal{P}[\boldsymbol{x}]\mathrm{e}^{-\Delta \mathcal{S}^{\mathrm{tot}}[\boldsymbol{x}]} \Rightarrow \boxed{\left\langle \mathrm{e}^{-\Delta \mathcal{S}^{\mathrm{tot}}} \right\rangle = 1}$$

Comments

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

- Entropy becomes a fluctuating quantity, related to a single trajectory rather than to an ensemble

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

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- There is a nonzero probability for $\Delta\mathcal{S}^{\mathrm{tot}} < 0$!

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- Jensen's inequality: $\left\langle \mathrm{e}^{X} \right\rangle \geq \mathrm{e}^{\langle X \rangle}$:

$$\left\langle \Delta\mathcal{S}^{\mathrm{tot}} \right\rangle \geq -\ln \left\langle \mathrm{e}^{-\Delta\mathcal{S}^{\mathrm{tot}}} \right\rangle = 0$$

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Comments

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- $\Delta S < 0$ can be interpreted as a "transient violation" of the 2nd principle

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Comments

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- $\Delta S < 0$ can be interpreted as a "transient violation" of the 2nd principle
- Transient violations are related to Loschmidt's reversibility paradox

Fluctuation theorem II (Jarzynski)

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Let $\pi_0(x) = P^{\mathrm{eq}}(x, \mu_0)$, $\widehat{\pi}_0(x) = P^{\mathrm{eq}}(x, \mu_1)$, $\beta = 1/k_{\mathrm{B}}T$:

$$\ln \frac{\widehat{\pi}_0(\widehat{x}(0))}{\pi_0(x(0))} = \mathrm{e}^R = \mathrm{e}^{\beta \Delta F - \beta(H(x(t_{\mathrm{f}}),\mu_1) - H(x(0),\mu_0))}$$

$$\begin{aligned} \Delta \mathcal{S} &= -\beta \mathcal{Q} \\ R &= \beta \left[\mathcal{Q} + \Delta F - \Delta H(x, \mu) \right] \\ &= -\beta \left(\mathcal{W}[\boldsymbol{x}] - \Delta F \right) \end{aligned}$$

$$\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}] = \mathcal{P}[\boldsymbol{x}]\, \mathrm{e}^R \Rightarrow \boxed{\left\langle \mathrm{e}^{-\beta \mathcal{W}} \right\rangle = \mathrm{e}^{-\beta\, \Delta F}}$$

Steady states out of equilibrium

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

$$\widehat{W}_{x'x} = W_{x'x}$$

Detailed balance is violated:

$$W_{xy}W_{yz}W_{zx} \neq W_{zy}W_{yx}W_{xz} \qquad \exists x, y, z$$

Thus $\nexists H(x)$: $\quad W_{x'x}/W_{xx'} = \mathrm{e}^{-\beta(H(x')-H(x))}$

Steady state distribution:

$$\sum_{x'} W_{xx'}p^{\mathrm{ss}}(x') = p^{\mathrm{ss}}(x)$$

Fluctuation theorem III (Evans-Searles)

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Choose $\pi_0(x) = \widehat{\pi}_0(x) = p^{\mathrm{ss}}(x)$

$$\ln \frac{\widehat{\mathcal{P}}[\widehat{\boldsymbol{x}}]}{\mathcal{P}[\boldsymbol{x}]} = -\Delta\mathcal{S}^{\mathrm{bath}}[\boldsymbol{x}] - \Delta S^{\mathrm{ss}}$$

Total entropy production:

$$\Delta\mathcal{S}^{\mathrm{tot}} = \Delta\mathcal{S}^{\mathrm{bath}}[\boldsymbol{x}] + \Delta S^{\mathrm{ss}}$$

Summing over all paths $\boldsymbol{x}$ with a given value of $\Delta\mathcal{S}^{\mathrm{tot}}$ yields the **fluctuation theorem**:

$$\boxed{\frac{p(-\Delta\mathcal{S}^{\mathrm{tot}})}{p(\Delta\mathcal{S}^{\mathrm{tot}})} = \mathrm{e}^{-\Delta\mathcal{S}^{\mathrm{tot}}}}$$

Comments

- The fluctuation theorem holds for finite times, but starting from the steady state

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Comments

- The fluctuation theorem holds for finite times, but starting from the steady state
- Since ΔS is bounded, but $\Delta \mathcal{S}^{\text{bath}}$ grows, we have for large t_{f}

$$\Delta \mathcal{S}^{\text{tot}} \simeq \Delta \mathcal{S}^{\text{bath}}$$

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

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$$\Delta\mathcal{S}^{\mathrm{tot}} \simeq \Delta\mathcal{S}^{\mathrm{bath}}$$

- Large-deviation function $\phi(s)$:

$$p(\Delta\mathcal{S}^{\mathrm{tot}}) \propto \mathrm{e}^{-t_{\mathrm{f}}\phi(\Delta\mathcal{S}^{\mathrm{tot}}/t_{\mathrm{f}})}$$

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Comments

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$$p(\Delta\mathcal{S}^{\mathrm{tot}}) \propto \mathrm{e}^{-t_{\mathrm{f}}\phi(\Delta\mathcal{S}^{\mathrm{tot}}/t_{\mathrm{f}})}$$

Gallavotti-Cohen relation:

$$\boxed{\phi(-s) = \phi(s) + s}$$

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

Housekeeping entropy production (heat)

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

Stationary system:

$$
\begin{aligned}
\Delta\mathcal{S}_{x'x} &= \ln \frac{W_{x'x}}{W_{xx'}} \\
&= \underbrace{\ln \frac{W_{x'x} p^{\mathrm{ss}}(x)}{W_{xx'} p^{\mathrm{ss}}(x')}}_{\Delta\mathcal{S}^{\mathrm{hk}}} - \underbrace{\ln \frac{p^{\mathrm{ss}}(x)}{p^{\mathrm{ss}}(x')}}_{\Delta S^{\mathrm{ex}}}
\end{aligned}
$$

N.B.: If detailed balance is satisfied:

$$W_{xx'} p^{\mathrm{ss}}(x') = W_{x'x} p^{\mathrm{ss}}(x)$$

then

$$-\Delta\mathcal{S}^{\mathrm{hk}}_{x'x} = 0 \qquad \forall x, x'$$

Average housekeeping heat

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

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❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

$$
\begin{aligned}
\varphi_{x'x} &= \mathrm{Prob}^{\mathrm{ss}}(x \longrightarrow x') = W_{x'x} p^{\mathrm{ss}}(x) \\
\varphi_{x'x} &\geq 0 \qquad \sum_{x'x} \varphi_{x'x} = 1 \\
\widehat{\varphi}_{x'x} &= \varphi_{xx'} \qquad \sum_{x'x} \widehat{\varphi}_{x'x} = \sum_{xx'} \varphi_{xx'} = 1
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \Delta \mathcal{S}^{\mathrm{hk}} \right\rangle^{\mathrm{ss}} &= \sum_{xx'} \ln \frac{W_{x'x} p^{\mathrm{ss}}(x)}{W_{xx'} p^{\mathrm{ss}}(x')} W_{x'x} p^{\mathrm{ss}}(x) \\
&= \sum_{xx'} \ln \frac{\varphi_{x'x}}{\varphi_{xx'}} \varphi_{x'x} = D(\widehat{\varphi} \| \varphi) \geq 0
\end{aligned}
$$

Fluctuation theorem for the housekeeping heat

Since

$$\Delta\mathcal{S}^{\mathrm{hk}}_{x'x} = \ln \frac{\varphi_{x'x}}{\varphi_{xx'}}$$

we have

$$\begin{aligned}\left\langle \mathrm{e}^{-\Delta\mathcal{S}^{\mathrm{hk}}} \right\rangle &= \sum_{xx'} \frac{\varphi_{xx'}}{\varphi_{x'x}} \varphi_{x'x} \\ &= \sum_{xx'} \varphi_{xx'} = 1\end{aligned}$$

Speck and Seifert, 2005

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Conclusions

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

- Fluctuation relations for the entropy are more general than the corresponding ones for the work

Conclusions

- Fluctuation relations for the entropy are more general than the corresponding ones for the work
- They provide hope for a characterization of non equilibrium steady states

Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

Conclusions

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

- Fluctuation relations for the entropy are more general than the corresponding ones for the work
- They provide hope for a characterization of non equilibrium steady states
- The field is still unsettled

Bibliography: Work fluctuations

Introduction

Fluctuation relations for the work

Applications

Fluctuation relations for the entropy production

❖ Entropy produced in a transition

❖ Seifert's relation

❖ Fluctuation theorem I (Seifert)

❖ Comments

❖ Fluctuation theorem II (Jarzynski)

❖ Steady states out of equilibrium

❖ Fluctuation theorem III (Evans-Searles)

❖ Comments

❖ Housekeeping entropy production (heat)

❖ Average housekeeping heat

❖ Fluctuation theorem for the housekeeping heat

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Introduction
Fluctuation relations for the work
Applications
Fluctuation relations for the entropy production
❖ Entropy produced in a transition
❖ Seifert's relation
❖ Fluctuation theorem I (Seifert)
❖ Comments
❖ Fluctuation theorem II (Jarzynski)
❖ Steady states out of equilibrium
❖ Fluctuation theorem III (Evans-Searles)
❖ Comments
❖ Housekeeping entropy production (heat)
❖ Average housekeeping heat
❖ Fluctuation theorem for the housekeeping heat

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