Stochastic thermodynamics: an emerging, evolving field



Édgar Roldán ICTP (Trieste, Italy)



United Nations .

- Educational, Scientific and
 - Cultural Organization •



Workshop on Martingales in Finance and Physics

Trieste, 24 May 2019





Stochastic thermodynamics

Standard Thermodynamics: macroscopic systems



Stochastic Thermodynamics: mesoscopic systems



Drifted colloidal particle

Heat engine

Stochastic thermodynamics

An emerging, evolving field studying nonequilibrium fluctuations of mesoscopic systems

Molecular motors

(S Toyabe et al., PNAS 108, 17951 (2011))



Electric circuits (S Ciliberto et al., PRL 110, 180601 (2013))



Colloidal heat engines

IA Martinez et al., Soft Matter 13, 22 (2017)



Quantum dots



Plot of this talk

- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws
- Fluctuation theorems
- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

Plot of this talk

 Curso
 de

 de
 de
 de

 termodinámica
 de
 de

 Jose Aguilar Peris
 de
 de

 Variante Aguilar Peris
 de
 de

 Diagonal Aguilar Designada
 de
 de

 Diagonal Aguilar Designada
 de
 de
 de

 Diagonal Aguilar Designada
 de
 de
 de
 de

 Diagonal Aguilar Designada
 de
 de</td



- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws
- Fluctuation theorems
- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

First Law of Thermodynamics

Heat









First Law of Thermodynamics



First Law of Thermodynamics

 $dE = \delta Q + \delta W$ First Law for infinitesimal changes



generalized

force

Zemansky, Dittman, "Heat and thermodynamics" (1997)

First Law for Heat engines

A system interacting with two thermal baths

 $S_{\rm tot} < 0$ $S_{\rm tot} > 0$

Sadi Carnot

Rudolf Clausius

For any nonequilibrium process

Isothermal processes

Entropy production $S_{ ext{tot}} = \Delta S - (Q/T)$ $F = E - TS = (\Delta E - \Delta F - Q)/T$ $\Delta E = Q + W = (W - \Delta F)/T$ $S_{ ext{tot}} \ge 0$ $W \ge \Delta F$

Non-isothermal Heat engines

Entropy production in a cycle

$$0 = Q_h + Q_c + W$$

 $S_{\text{tot}} = \underbrace{\Delta S}_{=0} -Q_h / T_h - Q_c / T_c \ge 0$ $-\frac{W}{Q_h} \le 1 - \frac{T_c}{T_h}$

Efficiency of Ferrari

 $\eta \leq \eta_C$

Carnot efficiency

Entropy production and irreversibility

Entropy production and irreversibility

Entropy production and irreversibility

Linear irreversible thermodynamics (near equilibrium)

Rate of entropy production

Plot of this talk

- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws
- Fluctuation theorems
- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

Stochastic thermodynamics

C1

K. Sekimoto, "Stochastic energetics" (Springer, 2010)

Langevin equation

$$egin{aligned} &m\ddot{x}(t)=-\gamma\dot{x}(t)-V'(x(t))+f(x(t);t)+\xi(t)\ & ext{Gaussian white noise }&\langle\xi(t)
angle=0\ &\langle\xi(t)\xi(0)
angle=2k_{ ext{B}}T\gamma\delta(t) \end{aligned}$$

Langevin equation

$$egin{aligned} m\ddot{x}(t) &= -\gamma\dot{x}(t) - V'(x(t)) + f(x(t);t) + \xi(t) \ \end{aligned}$$
 Gaussian white noise $\langle \xi(t)
angle = 0 \ \langle \xi(t) \xi(0)
angle = 2k_{
m B}T\gamma\delta(t) \end{aligned}$

Overdamped Langevin equation $(\Delta t \gg m/\gamma)$

$$\gamma \dot{x}(t) = -V'(x(t)) + f(x(t);t) + \xi(t)$$

P. Langevin, Compt. Rendus 146, 530 (1908)

Primer on stochastic calculus

y=x*2

rxn

Stochastic calculus: integration over a trajectory $x_0, x_1, x_2, \ldots, x_n \in \mathbb{R}$

$$I=\int_{x_0}^{x_n}f(x(s))\mathrm{d}x(s)=\lim_{n o\infty}\sum_{i=1}^nf(x_i^*)\Delta x_i \qquad x_i^*\in [x_i,x_{i+1}]$$

Stratonovich calculus (midpoint rule)

$$\begin{array}{ccc} & & & \\ & & & \\ x_i & & x_{i+1} \end{array} & x_i^* = (x_i + x_{i+1})/2 & & \int_{x_0}^{x_0} f(x(s)) \circ \mathrm{d}x(s) \\ \\ & & & \\ & & \\ & & & \\ x_i & & x_{i+1} \end{array} & x_i^* = x_i & & \int_{x_0}^{x_0} f(x(s)) \cdot \mathrm{d}x(s) \\ \end{array}$$

Stochastic heat

How much heat Q(t) is exchanged between the particle and the bath in a **single** trajectory?

$$0 = -\gamma \dot{x}(t) - V'(x(t)) + f(x(t);t) + \xi(t)$$

Heat absorbed by the x degree of freedom in [t,t+dt]

$$\delta Q(t) = \begin{bmatrix} -\gamma \dot{x}(t) + \xi(t) \end{bmatrix} \circ dx(t)$$
Particle's instataneous
displacement
Environment's force
$$= [V'(x(t)) - f(x(t);t)] \circ dx(t)$$

K. Sekimoto, Prog. Theor. Phys. Suppl. 130, 17 (1998)

O = **Stratonovich** product

Stochastic heat

How much heat Q(t) is exchanged between the particle and the bath in a **single** trajectory?

$$0 = -\gamma \dot{x}(t) - V'(x(t)) + f(x(t);t) + \xi(t)$$

Heat absorbed by the x degree of freedom in [0,t]

$$Q(t) \equiv Q[X_{[0,t]}] = \int_{x(0)}^{x(t)} \left[\frac{\partial V(x(s))}{\partial x} + f(x(s);s) \right] \circ \mathrm{d}x(s)$$

a functional of the stochastic trajectory $X_{[0,t]}$

[not a state function!]

K. Sekimoto, Prog. Theor. Phys. Suppl. 130, 17 (1998)

First law of stochastic thermodynamics

Work exerted on the particle in [t,t+dt]

$$\begin{array}{c}
F \\
V(x,\lambda) \\
\downarrow V(x,\lambda') \\
\downarrow X \\
\delta W(t) = \partial_{\lambda}V(x(t))d\lambda + f(x(t);t) \circ dx(t) \\
\delta Q(t) = [V'(x(t)) - f(x(t);t)] \circ dx(t) \\
\end{array}$$

 $\delta W(t) + \delta Q(t) = \partial_{\lambda} V(x(t)) d\lambda + \partial_{x} V(x(t)) \circ dx(t) = dV(t)$

 $\delta W(t) + \delta Q(t) = \mathrm{d}V(t)$

K. Sekimoto, Prog. Theor. Phys. Suppl. 130, 17 (1998)

Heat and work along a trajectory

Simple case: no external, non-conservative force (f=0)

$$Q(t) = \int_{x(0)}^{x(t)} \frac{\partial V(x(s))}{\partial x} \circ \mathrm{d}x(s) \qquad \qquad W(t) = \int_{x(0)}^{x(t)} \frac{\partial V(x(s))}{\partial \lambda} \mathrm{d}\lambda$$

Colloidal microscopic particle in a harmonic potential

$$W(t) = \int_{x(0)}^{x(t)} \frac{x^2(s)}{2} \mathrm{d}\kappa(s)$$

stochastic

Ideal macroscopic gas in a movable piston

$$W(t) = -\int_{V(0)}^{V(t)} p(s) \mathrm{d}V(s)$$

deterministic

Stochastic entropy

Nonequilibrium system's entropy

$$S(t) \equiv -k_{\rm B} \ln P_t(x(t))$$

Average over many realizations

System entropy change along a single trajectory

Time

t

State

 $P_0(x)$

$$\Delta S(t) = k_{
m B} \ln rac{P_0(x(0))}{P_t(x(t))}$$

Second law? $\Delta S(t) - rac{Q(t)}{T} \equiv S_{
m tot}(t) \ge 0$
U. Seifert, Phys. Rev. Lett. 95(4) 040602 (2005)

Second law and stochastic entropy

System's entropy change $\Delta S(t) = k_{\rm B} \ln \frac{P_0(x(0))}{P_t(x(t))}$

Environment's entropy change $S_e(t) = -rac{Q(t)}{T}$

Stochastic Entropy production

(*key assumption local detailed balance: bath/s in thermal equilibrium)

U. Seifert, Phys. Rev. Lett. 95(4) 040602 (2005)

Second law and stochastic entropy

However, stochastic entropy production $S_{tot}(t)$ can be negative when a rare trajectory occurs !

Negative stochastic entropy production

$$\dot{x}(t) = v + \sqrt{2D}\xi(t)$$
$$\Rightarrow S_{\text{tot}}(t) = \frac{k_{\text{B}}v}{D}[x(t) - x(0)]$$

t

Stochastic entropy production

Equilibrium : $S_{tot}(t) = 0 \Rightarrow \langle S_{tot}(t) \rangle = 0$

Nonequilibria: $\langle S_{\text{tot}}(t) \rangle \geq 0$

Relation to financial concepts

Dynamical trajectory

Financial Asset

Particle's position

Time

Price of Gold

1975 1980 1985 1990 1995 2000 2005

Plot of this talk

- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws

- Fluctuation theorems
- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

Jarzynski's equality

Non-equilibrium equality for any protocol arbitrarily far from equilibrium

$$\langle e^{-\beta W(t)} \rangle = e^{-\beta \Delta F}$$

where W(t) is the **nonequilibrium** work $W(t) = \int_{x(0)}^{x(t)} \frac{\partial V(x(s))}{\partial \lambda} d\lambda$

and the equilibrium free energy change $\Delta F = -k_{\rm B}T \ln(Z_{\rm fin}/Z_{\rm ini})$ C. Jarzynski, Phys. Rev. Lett. **78**, 269 (1997)

Jarzynski's equality

Non-equilibrium equality for any protocol arbitrarily far from equilibrium

$$\langle e^{-\beta[W(t)-\Delta F]} \rangle = 1$$

Jensen's inequality $\langle e^x
angle \geq e^{\langle x
angle}$ $\langle W(t)
angle \geq \Delta F$

Probability for "second law violations"

$$\Pr(W(t) - \Delta F \le -\xi) \le e^{-\xi/k_{\rm B}T}$$

4 October 2019 Jarzynski @ ICTP Colloquium

C. Jarzynski, Phys. Rev. Lett. 78, 269 (1997)

Jarzynski's equality

J Liphardt, S Dumont, SB Smith, I Tinoco, C Bustamante, Science 296 (5574), 1832 (2002)

Crooks theorem

Forward process

work distribution

Backward process

$$P_t(W) = P(W(t) = W)$$
 $ilde{\lambda}(au) = \lambda(t- au) \quad au \in [0,t]$

work distribution $\tilde{P}_t(W) = \tilde{P}(W(t) = W)$

 $\lambda(\tau)$ $\tau \in [0,t]$

Asymmetry relation between forward and backward work distributions:

$$\frac{P_t(W)}{\tilde{P}_t(-W)} = e^{-\beta(W - \Delta F)}$$

$$\Rightarrow \langle e^{-\beta W(t)} \rangle = e^{-\beta \Delta F}$$

G. E. Crooks, Phys. Rev. E 60, 2721 (2000)

Crooks theorem

D. Collin, F. Ritort, et. al, Nature 437, 231 (2005)

Detailed and integral fluctuation theorem

Entropy production along a stochastic trajectory of finite time duration in a generic non-equilibrium (stationary or non-stationary) process

- Diffusion processes e.g. Langevin
- Discrete systems e.g. continuous-time Markov processes
- Non-Markovian stochastic processes

Detailed and integral fluctuation theorem

Entropy production along a stochastic trajectory of finite time duration in a generic non-equilibrium (stationary or non-stationary) process

- Diffusion processes e.g. Langevin
- Discrete systems e.g. continuous-time Markov processes
- Non-Markovian stochastic processes

U. Seifert, Phys. Rev. Lett. 95(4) 040602 (2005)

$$S_{ ext{tot}}(t) = k_{ ext{B}} \ln \left| rac{\mathrm{d}\mathcal{P}}{\mathrm{d}(\tilde{\mathcal{P}} \circ \Theta)} \right|_{\mathcal{F}_{t}}(\omega)$$

Radon - Nykodim derivative

$$\left\langle \frac{\mathrm{d}Q}{\mathrm{d}P} \right\rangle_P = \left\langle e^{-S_{\mathrm{tot}}(t)/k_{\mathrm{B}}} \right\rangle = 1$$

Smell of Martingales....

Detailed and integral fluctuation theorem

Experimental tests: electrical circuits, colloidal particles, nanoelectronic devices...

(a)

Reviews: S. Ciliberto, PRX 7, 021051 (2017); Martinez.Soft Matter '17

Plot of this talk

- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws
- Fluctuation theorems

- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

Maxwell's demon

Review: J. M. R. Parrondo, J. M. Horowitz, & T. Sagawa, Nature Physics 11, 131-139 (2015)

 $\langle W \rangle - \Delta F \ge 0$

 $-\Delta F \ge -\kappa_{\rm B} T H(p)$ $H(p) = -\sum_{i=1,2} p_i \ln p_i = \ln 2$

Sagawa-Ueda fluctuation theorems

T. Sagawa, M. Ueda, Phys. Rev. Lett. 104, 090602 (2010)

Finance and feedback control

Plot of this talk

- Brief review of classical "textbook" thermodynamics
- Stochastic thermodynamics: first and second laws
- Fluctuation theorems
- Maxwell's demons and feedback control
- The latest: Uncertainty relations and Martingales

Generation of P is driven by free energy consumption

Is there a fundamental relation between the uncertainty (in the number of produced P's) and the free energy cost to sustain the bimolecular process?

A. C. Barato, U. Seifert, PRL 114(15), 158101 (2015); J. M. Horowitz, T. R. Gingrich, PRE 96(2), 020103 (2017)

$$\frac{d}{dt}P(x,t) = k_+P(x-1,t) + k_-P(x+1,t) - (k_+ - k_-)P(x,t)$$

Velocity
$$J \equiv \langle x \rangle / t = (k_+ - k_-)$$

Dispersion
$$D \equiv (\langle x^2 \rangle - \langle x \rangle^2)/(2t) = (k_+ + k_-)/2$$

Relative uncertainty
$$\epsilon^2 \equiv \frac{\langle x^2 \rangle - \langle x \rangle^2}{\langle x \rangle^2} = \frac{2D}{J^2 t} = \frac{k_+ + k_-}{(k_+ - k_-)^2} t^{-1}$$

A. C. Barato, U. Seifert, PRL 114(15), 158101 (2015); J. M. Horowitz, T. R. Gingrich, PRE 96(2), 020103 (2017)

Relative uncertainty
$$\epsilon^2 \equiv \frac{\langle x^2 \rangle - \langle x \rangle^2}{\langle x \rangle^2} = \frac{2D}{J^2 t} = \frac{k_+ + k_-}{(k_+ - k_-)^2} t^{-1}$$

Thermodynamic Affinity $\implies \mathcal{A} = (\mu_S - \mu_P)/(k_B T) = \ln(k_+/k_-)$

Rate of entropy production $\sigma = \mathcal{A}(k_+ - k_-)$ Total dissipated heat (cost) $\mathcal{C} = k_B T \sigma t = \langle S_{tot}(t) \rangle$

> Total cost × relative uncertainty $C\epsilon^2 = k_B T \mathcal{A} \operatorname{coth}[\mathcal{A}/2] \ge 2k_B T$

A. C. Barato, U. Seifert, PRL 114(15), 158101 (2015);

Universal cost-uncertainty tradeoff for time-integrated currents in non-equilibrium stationary Markov processes

A. C. Barato, U. Seifert, PRL 114(15), 158101 (2015)

Continuous time

$$\frac{\operatorname{var}(J(t))}{\langle J(t)\rangle^2} \geq \frac{2k_{\mathrm{B}}}{\langle S(t)\rangle}$$

J. M. Horowitz, T. R. Gingrich, PRE **96**(2), 020103 (2017)

Discrete time

$$\frac{\operatorname{var}(J(t))}{\langle J(t)\rangle^2} \ge \frac{2\Delta S}{e^{\Delta S/k_{\rm B}} - 1}$$

K. Proesmans, C.Van den Broeck, EPL 119(2), 20001 (2017)

Consequence of joint fluctuation theorem

$$\frac{P_t(S_{\text{tot}},J)}{P_t(-S_{\text{tot}},-J)} = e^{S_{\text{tot}}/k_{\text{B}}}$$

Y Hasegawa, T Van Vu ar Xiv: 1902.06376 (2019)

Why martingales?

Most fluctuation theorems concern events that take place at a fixed time

However, most interesting stuff happens at random stopping times

Execution of cellular functions e.g. bacterial cell cycle

Why martingales?

Extreme-value statistics of active molecular processes

Two Refreshing Views of Fluctuation Theorems Through Kinematics Elements and Exponential Martingale

Raphaël Chetrite · Shamik Gupta

Statistics of Infima and Stopping Times of Entropy Production and Applications to Active Molecular Processes

Izaak Neri,^{1,2} Édgar Roldán,^{1,3} and Frank Jülicher¹

Thanks!

Collaborators on Thermodynamics with Martingales

Izaak Neri Shamik Gupta Simone Pigolotti Raphael Chetrite Frank Julicher

My current team Roman Belousov Ashwin Gopal QLS members Shilpi Singh Ivan Khaymovich Dmitry Golubev Joonas Peltonen Jukka Pekola

Thanks also to

Ali Hassanali Nawaz Qaisrani Narjes Ansari Gennaro Tucci Andrea Gambassi Takahiro Sagawa Andre Barato

Gonzalo Manzano

Rosario Fazio

Ken Sekimoto

Karel Proesmans

Alexandre Guillet