Stochastic thermodynamics

Udo Seifert

II. Institut für Theoretische Physik, Universität Stuttgart

thanks to:

• F. Berger, J. Mehl, T. Schmiedl and Th. Speck (theory)

• V. Blickle and C. Bechinger (expt's on colloidal particles)

• C. Tietz, S. Schuler and J. Wrachtrup (expt's on single atoms)

LECTURE I

- Classical vs. stochastic thermodynamics

- First law

- General fluctuation theorem and Jarzynski relation

- Optimization
- Perspective

<table>
<thead>
<tr>
<th>Year Range</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
</table>
| 1820 ≈ 1850 | classical thermodynamics         | \[ dW = dU + dQ \]
|            |                                  | \[ dS \geq 0 \]                                                          |
| ≈ 1900     | eq stat phys                     | \[ p_i = \exp[-(E_i - F)/k_BT] \]                                        |
| 1930 ≈ 1960| non-eq: linear response          | Onsager\[\]
|            |                                  | Green-Kubo, FDT                                                          |
| ≥ 1993     | non-eq: beyond linear response   | Fluctuation theorem\[\]
|            | stochastic thermodynamics        | Jarzynski relation                                                      |
Thermodynamics of macroscopic systems [19th cent]

\[ W = \Delta E + Q = \Delta E + T \Delta S_M \]

- First law energy balance:

- Second law:

\[ \Delta S_{\text{tot}} \equiv \Delta S + \Delta S_M > 0 \]

\[ W > \Delta E - T \Delta S \equiv \Delta F \]

\[ W_{\text{diss}} \equiv W - \Delta F > 0 \]
- Macroscopic vs mesoscopic vs molecular machines

[Bustamante et al, Physics Today, July 2005]
• Stochastic thermodynamics for small systems

– First law: how to define work, internal energy and exchanged heat?

– fluctuations imply distributions: \( p(W; \lambda(\tau)) \) ...

– entropy: distribution as well?
Nano-world Experiment: Stretching RNA

[Liphardt et al, Science 296 1832, 2002.]

— distributions of $W_{\text{diss}}$: 

\[ W_{\text{diss}} (k_B T) \]
Mechanically driven systems

Pulling a biomolecule

Colloidal particle in a laser trap
- Flow driven systems

Stretching a polymer (dumbbell)

Tank-treading vesicle in shear flow
- (Bio)chemically driven systems

F1-ATPase


Protein synthesis

1. Transcription
2. Translation
Stochastic thermodynamics applies to such systems where
- non-equilibrium is caused by mechanical or chemical forces
- ambient solution provides a thermal bath of well-defined $T$
- fluctuations are relevant due to small numbers of involved molecules

Main idea: Energy conservation (1$^{st}$ law) and entropy production (2$^{nd}$ law) along a single stochastic trajectory

Precursors:
- notion “stoch th’dyn” by Nicolis, van den Broeck mid ‘80s (ensemble level)
- stochastic energetics (1$^{st}$ law) by Sekimoto late ‘90s
- work theorem(s): Jarzynski, Crooks late ’90s
- fluct’theorem: Evans, Cohen, Galavotti, Kurchan, Lebowitz & Spohn ’90s
- quantities like stochastic entropy by Crooks, Qian, Gaspard in early ’00s
- ...
Paradigm for mechanical driving:

\[
\lambda(\tau) \rightarrow x_1 \rightarrow x_2 \rightarrow x_3 \rightarrow x_4 \rightarrow x_5 \rightarrow x_0
\]

- Langevin dynamics \( \dot{x} = \mu \left[ -V'(x, \lambda) + f(\lambda) \right] + \zeta \quad \langle \zeta \zeta \rangle = 2\mu k_B T \delta(...) \equiv 1 \)

- external protocol \( \lambda(\tau) \)

First law [(Sekimoto, 1997)]:

\[
d w = d u + d q
\]

- applied work: \( d w = \partial_\lambda V(x, \lambda) d\lambda + f(\lambda) dx \)
- internal energy: \( d u = d V \)
- dissipated heat: \( d q = d w - d u = F(x, \lambda) dx = T ds_m \)
- Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$


- work distribution

- non-Gaussian distribution $\Rightarrow$

- Langevin valid beyond lin response

[T. Speck and U.S., PRE 70, 066112, 2004]
Role of external flow and frame invariance

[T. Speck, J. Mehl and U.S., PRL 100 178302, 2008]

Lab frame

\[ V(x, \tau) = k(v\tau - x)^2/2 \]
\[ \dot{x} = \mu k(v\tau - x) + \zeta \]
\[ \dot{w} = \partial_\tau V = kv(v\tau - x(\tau)) \neq 0 \]

comoving frame:
\[ y \equiv x(\tau) - v\tau \]
\[ V(y) = ky^2/2 \]
\[ \dot{y} = -\mu ky - v + \zeta \]
\[ \dot{w} = \partial_\tau V = 0 \quad ?? \]

det balance satisfied: equilibrium ??
Correct definitions of the dynamic quantities

\[
\frac{dw}{dr} = \partial_t V + f \, dr
\]
\[
\frac{dq}{dr} = (-\nabla V + f) \, dr
\]

\text{no flow}  |  flow  \quad u(r) \neq 0

\[
\frac{dw}{dr} \equiv D_t V + f[dr - u dt]
\]
\[
\frac{dq}{dr} \equiv (-\nabla V + f)(dr - u dt)
\]
Path integral representation

- “Boltzmann factor for a whole trajectory”

\[
p[\zeta(\tau)] \sim \exp \left[-\int_0^t d\tau \frac{\zeta^2(\tau)}{4D}\right]
\]

\[
p[x(\tau)\mid x_0] \sim \exp \left[-\int_0^t d\tau \left(\dot{x} - \mu F\right)^2/4D\right]
\]

- “time reversal” \( \tilde{x}(\tau) \equiv x(t - \tau) \) and \( \tilde{\lambda}(\tau) \equiv \lambda(t - \tau) \)

- Ratio of forward to reversed path

\[
\frac{p[x(\tau)\mid x_0]}{\tilde{p}[\tilde{x}(\tau)\mid \tilde{x}_0]} = \frac{\exp \left[-\int_0^t d\tau \left(\dot{x} - \mu F\right)^2/4D\right]}{\exp \left[-\int_0^t d\tau \left(\dot{\tilde{x}} - \mu \tilde{F}\right)^2/4D\right]}
\]

\[= \exp \beta \int_0^t d\tau \dot{x}F = \exp \beta q[x(\tau)] = \exp \Delta s_m\]
- General fluctuation theorem

[U.S., PRL 95, 040602, 2005; generalizing Jarzynski, Crooks, Maes]

\[ 1 = \sum_{\tilde{x}(\tau), \tilde{x}_0} \tilde{p}[\tilde{x}(\tau)|\tilde{x}_0] \ p_1(\tilde{x}_0) \]

\[ = \sum_{x(\tau), x_0} p[x(\tau)|x_0] \ p_0(x_0) \frac{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0] \ p_1(\tilde{x}_0)}{p[x(\tau)|x_0] \ p_0(x_0)} \]

\[ = \langle \exp[-\beta q[x(\tau)] + \ln \frac{p_1(x_t)}{p_0(x_0)} - \Delta s_m] \rangle \]

- for arbitrary initial condition \( p_0(x) \)
- for arbitrary (normalized) function \( p_1(x_t) \)
- Jarzynski relation (PRL, 1997)

\[ \lambda \]

\[ t \]

\[ \lambda_0 \]

\[ \frac{\langle W \rangle_{\lambda(\tau)}}{p_0(x_0)} \geq \Delta F \equiv F(\lambda_t) - F(\lambda_0) \]

- Short proof: 

\[ 1 = \langle \exp[-q[x(\tau)] + \ln \frac{p_1(x_t)}{p_0(x_0)}] \rangle_{-\Delta s_m} \]

* \[ p_0(x_0) \equiv \exp[-(V(x_0, \lambda_0) - F(\lambda_0))] \]

* \[ p_1(x_t) \equiv \exp[-(V(x_t, \lambda_t) - F(\lambda_t))] \]

- within stochastic dynamics an identity!
• Jarzynski (cont’d) \( (k_B T = 1) \)

\[
\expval{e^{-W}}_{\lambda(\tau)} = e^{-\Delta F}
\]

- start with initial thermal distribution
- valid for any protocol \( \lambda(\tau) \)
- valid beyond linear response
- allows to extract free energy differences from non-eq data
- “implies” a variant of the second law

\[
\expval{e^x} \geq \expval{x} \Rightarrow \expval{W} \geq \Delta F
\]
Dissipated work $W_d \equiv W - \Delta G$

- $\langle \exp[-W_d] \rangle \equiv \int_{-\infty}^{+\infty} dW_d \; p(W_d) \exp[-W_d] = 1$

- red events “violate the second law” (??)

- Special case: Gaussian distribution

$$p(W_d) \sim \exp[-(W_d - \langle W_d \rangle)^2/2\sigma^2] \quad \text{with} \quad \langle W_d \rangle = \sigma^2/2$$

* scenario 1: slow driving of any process

Scenario 2: linear equations of motion and arbitrary driving


- different protocols

* linear: \( \lambda(\tau) = \tau L/t \)  \( \Rightarrow \langle W_d \rangle = (N\gamma/3)L^2/t \)

* periodic: \( \lambda(\tau) = L \sin \pi\tau/2t \)  \( \Rightarrow \langle W_d \rangle = \left[\pi^2/8\right](N\gamma/3)L^2/t \)
Optimal finite-time processes in stochastic thermodynamics


- optimal protocol $\lambda^*(\tau)$ minimizes $\langle W \rangle$ for given $\lambda_i, \lambda_f$ and finite $t$
• Ex 1: Moving a laser trap \( V(x, \lambda) = (x - \lambda(\tau))^2/2 \)

\[- \lambda^*(\tau) \text{ requires jumps at beginning and end} \quad \Delta \lambda = \lambda_f/(t+2) \]

\[- \text{gain} \quad 1 \geq W^*(t)/W^{lin}(t) \geq 0.88 \]
Ex 2: Stiffening trap \[ V(x, \lambda) = \lambda(\tau)x^2/2 \]

- jumps are generic
- should help to improve convergence of \( \langle \exp(-W) \rangle \)
- generalization: underdamped dynamics \( \Rightarrow \) delta-peaks

• Heat engines at maximal power

  – Carnot (1824)

  \[ \eta_c \equiv 1 - \frac{T_c}{T_h} \]

  but zero power

  – Curzon-Ahlborn (1975)

  \[ -Q_h = \alpha (T_h - T_h^m) \]

  \[ Q_c = \beta (T_c^m - T_c) \]

  \[ \eta_{ca} \equiv 1 - \sqrt{\frac{T_c}{T_h}} \]

  – recent claims for universality(?)

  – what about fluctuations?
- Brownian heat engine at maximal power

[T. Schmiedl and U.S., EPL 81, 20003, (2008)]

\[ \eta^* = \frac{\eta_c}{2-\alpha \eta_c} \quad \text{with} \quad \alpha = 1/2 \quad \text{for temp-independent mobility} \]

- Curzon-Ahlborn neither universal nor a bound
Optimizing potentials for temperature ratchets