Nonequilibrium thermodynamics at the microscale

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• The entropy of a closed system never decreases.
• Clausius inequality
• Carnot limit on the efficiency of heat engines
The entropy of a closed system never decreases.

\[
\frac{dS}{dt} = -mg \frac{dz}{dt} \cdot \frac{1}{T} > 0
\]

Joule experiment (1845)

potential energy of weight
thermal energy of fluid
Scale down to the microscopic level …

Quantify the fluctuations!

fluid
~10^3 molecules

potential energy of weight
thermal energy of fluid

$$\langle \frac{dS}{dt} \rangle > 0$$

$S$
$\tau$
$t$
Distribution of entropy generated

\[ \rho_\tau(S) \]
Distribution of entropy generated

\[ \rho_\tau(-S) \quad \text{and} \quad \rho_\tau(S) \]
Distribution of entropy generated

\[ \rho_\tau(-S) \quad \rho_\tau(S) \]

Fluctuation Theorem

\[ \frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp\left(\frac{S}{k_B}\right) \]

- very general
- valid far from equilibrium
- reduces to linear response near equilibrium

Evans & Searles, PRE 1994
Gallavotti & Cohen PRL 1995
Kurchan, 1998
Lebowitz & Spohn, J Stat Phys 1999
+ many others
Sheared fluid

\[ \frac{dS}{dt} = -\frac{1}{T} \cdot \gamma V P_{xy}(t) \]

\[ S \propto -\overline{P}_{xy} \]

Optically dragged beads


\[ \mathbf{F}_{\text{opt}} = -kr \]

\[ k \sim 0.1 \text{ pN/\mu m} \]

\[ \frac{dS}{dt} = \frac{1}{T} \vec{F}_{\text{opt}} \cdot \vec{v}_{\text{opt}} \]
Demonstration of (integrated) Fluctuation Theorem

\[
\frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp(S/k_B) \quad \rightarrow \quad \frac{P(S_\tau < 0)}{P(S_\tau > 0)} = \langle \exp(-S_\tau/k_B) \rangle_{S_\tau > 0}
\]

Ideally: divide the trajectory into many segments of duration \(\tau\), compute \(S\) for each segment, & construct histogram ...

\[\dot{S}\]

\[\tau\]

\[\text{not enough data!}\]
More recently …

Parameter-dependent potential:

\[ V(z; I) = A \cdot \exp(-\kappa z) + (B + CI) \cdot z \]

Drive the system away from equilibrium with a time-symmetric pulse (*squeeze*, then *relax*)

… measure the work performed on the bead

Illustration of *Clausius inequality*: stretched rubber band

\[ W = \int_{A}^{B} f \, d\lambda \geq W_{\text{rev}} = \Delta F = F_B - F_A \]
Single-molecule pulling experiment

$H_2O$

1. Begin in equilibrium
2. Stretch the molecule
   $W = \text{work performed}$
3. End in equilibrium
4. Repeat

Irreversible process:

$\lambda = A$
$\lambda : A \rightarrow B$
$\lambda = B$
After infinitely many repetitions ...

\[ \Delta F = F_B - F_A \]

\( \rho(W) \)

"violations" of 2nd Law

distribution of work values

average work performed
Nonequilibrium work theorem

\[ \langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \]

\[ \int dW \, \rho(W) e^{-\beta W} \]

\[ \frac{1}{k_B T} \]

- valid far from equilibrium
- fluctuations in W satisfy strong constraint
- nonequilibrium measurements reveal equilibrium properties

Hummer & Szabo, PNAS (2001)
& others
Derivation (isolated system)

microstate $x$ positions, momenta
Hamiltonian $H(x; \lambda)$ internal energy

In equilibrium …

$p^{eq}(x; \lambda) = \frac{1}{Z_\lambda} e^{-\beta H(x; \lambda)}$ Boltzmann-Gibbs distribution

$Z_\lambda = \int dx e^{-\beta H(x; \lambda)}$ partition function

$F_\lambda = -\beta^{-1} \ln Z_\lambda$ free energy
Derivation (isolated system)

One realization …

$0 \leq t \leq \tau$

\[
\begin{align*}
\text{protocol} & \quad \lambda_t \\
\text{trajectory} & \quad x_t \\
\text{work} & \quad W = H(x_\tau; B) - H(x_0; A)
\end{align*}
\]

1st law: \( \Delta E = W + Q \)

... now take average of \( e^{-\beta W} \) over many realizations
\[
W(x_0) = H(x_\tau(x_0); B) - H(x_0; A)
\]

\[
\langle e^{-\beta W} \rangle = \int dx_0 \frac{1}{Z_A} e^{-\beta H(x_0; A)} e^{-\beta W(x_0)}
\]

\[
= \frac{1}{Z_A} \int dx_0 e^{-\beta H(x_\tau(x_0); B)}
\]

\[
= \frac{1}{Z_A} \int dx_\tau \left| \frac{\partial x_\tau}{\partial x_0} \right|^{-1} e^{-\beta H(x_\tau; B)}
\]

\[
= \frac{Z_B}{Z_A} = e^{-\beta \Delta F}
\]

QED
Various derivations

- G. Hummer & A. Szabo PNAS 2001
- S. Mukamel PRL 2003 ... & others

Hamiltonian evolution, Markov processes, Langevin dynamics, deterministic thermostats, quantum dynamics ... robust

see also S. Park & K. Schulten, J. Chem. Phys. 2004

related result:
G.N. Bochkov & Y.E. Kuzovlev JETP 1977
Experimental verification: unfolding a single RNA molecule


unfolding / refolding cycles

hysteresis (irreversibility)
Results: equilibrium $\Delta F$ from nonequilibrium work values

- three pulling rates: $2$-5 pN/s, $34$ pN/s, $52$ pN/s
- $\sim 300$ cycles at each rate
- slow cycles (reversible) used to determine $\Delta F$

\[ \langle W \rangle - \Delta F \]

\[ \langle W \rangle - \frac{\beta}{2} \sigma_w^2 - \Delta F \]


\[ -\beta^{-1} \ln \langle e^{-\beta W} \rangle - \Delta F \]
What is the probability that the 2nd law will be “violated” by at least $\zeta$ units of energy?

\[ P[W < \Delta F - \zeta] = \int_{-\infty}^{\Delta F - \zeta} dW \, \rho(W) \]
\[ \leq \int_{-\infty}^{\Delta F - \zeta} dW \, \rho(W) e^{\beta(\Delta F - \zeta - W)} \]
\[ \leq e^{\beta(\Delta F - \zeta)} \int_{-\infty}^{+\infty} dW \, \rho(W) e^{-\beta W} = \exp(-\zeta / kT) \]
Crooks fluctuation theorem

Forward process … \( \lambda : A \to B \) (unfolding)
Reverse process … \( \lambda : B \to A \) (folding)

\[
\frac{\rho_{A \to B}(+W)}{\rho_{B \to A}(-W)} = \exp[\beta(W - \Delta F)]
\]


Experimental verification:
3-helix junction of ribosomal RNA of *E. coli*

Collin *et al*, Nature 2005

\[ W_{\text{diss}} \approx 50 k_B T \]
\[
\frac{\rho_{A \rightarrow B}(+W)}{\rho_{B \rightarrow A}(-W)} = \exp[\beta(W - \Delta F)]
\]

\[
\ln \frac{\rho_{A \rightarrow B}(+W)}{\rho_{B \rightarrow A}(-W)} = \beta(W - \Delta F)
\]
Macroscopic machines

steam engine

Carnot cycle

textbook thermodynamics
What are the underlying thermodynamics?
How is chemical energy converted to mechanical motion?
Simple explanation of molecular machines

\[ \dot{x} = \Delta x / \tau \]
\[ \dot{\eta} = \Delta \eta / \tau \]

\[ p^e_{\tau} (+\Delta x, +\Delta \eta) = p^e_{\tau} (-\Delta x, -\Delta \eta) \]
(detailed balance)

however ...

\[ \langle \Delta x \cdot \Delta \eta \rangle \neq 0 \] (generically)

increase \( c_{\text{ATP}} \) \( \Rightarrow + \dot{\eta} \Rightarrow + \dot{x} \) motion!

A similar argument can be made far from equilibrium.
Minimal molecular motors

Van den Broeck, Meurs, Kawai

“Triangula”

“Triangulita”

Directed motion? YES!
Summary

New & interesting thermodynamics at the microscale

- Fluctuation theorem
  \[
  \frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp\left(\frac{S}{k_B}\right)
  \]
  symmetry between entropy generation & consumption

- Nonequilibrium work theorem
  \[
  \left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}
  \]
  equilibrium thermodynamic information encoded in fluctuations far from equilibrium

- Molecular motors “generic”