



# Deterministic thermostats: temperature and fluctuation relations

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http://www.rarenoise.lnl.infn.it/

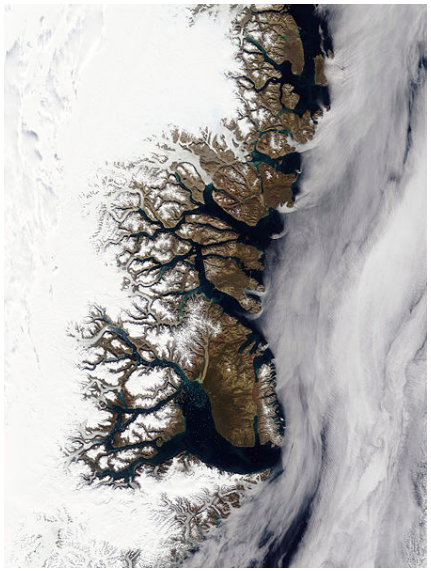
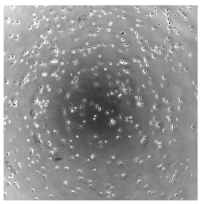
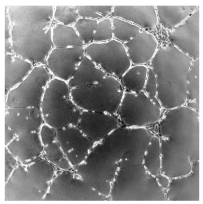
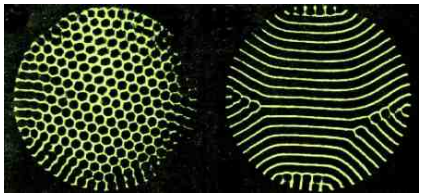
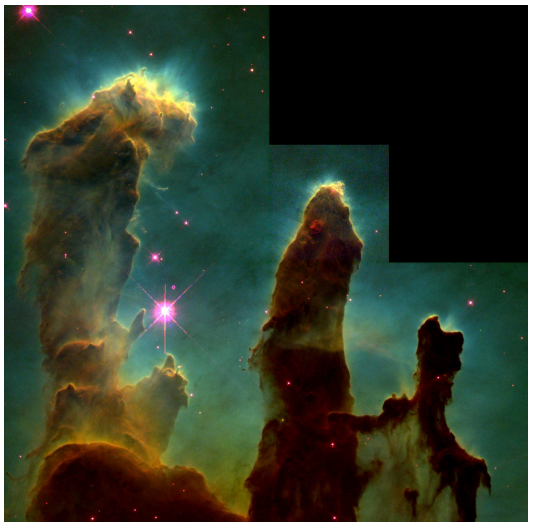
# Outline

1. Local Thermodynamic Equilibrium
2. Dynamics? Ensembles?
3. Fluctuation relations
4. Discussion

# Local Thermodynamic Equilibrium

Variety of nonequilbrium phenomena. As in equilibrium, 3 levels:

- Microscopic (mechanical; reversible);
- Mesoscopic (stochastic/kinetic; fluctuating-irreversible);
- Macroscopic (hydro-thermodynamic; deterministic-irreversible).

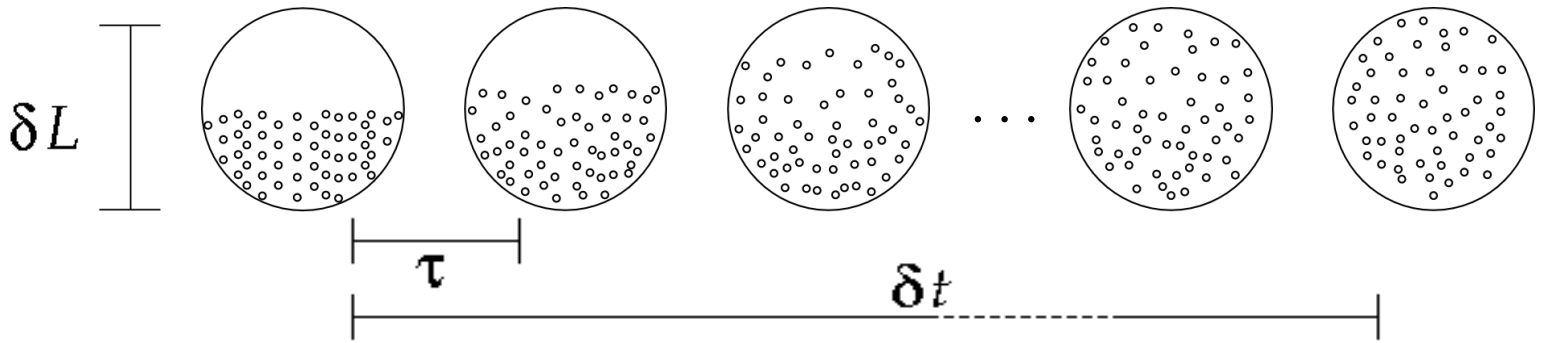

Somewhat unified under hypothesis of

Local Thermodynamic Equilibrium.

Local Thermodynamic Equilibrium: needs vast separation of length and time scales, hence $N \gg 1$ and interactions are prerequisites:

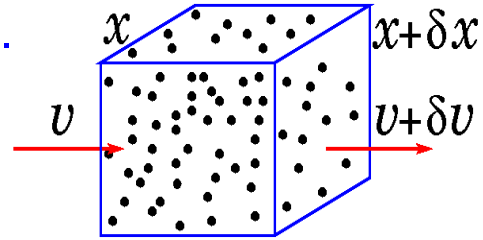
$$\ell \ll \delta L \ll L\,, \qquad \tau \ll \delta t \ll t$$

$\ell =$ mean free path; $\tau =$ mean free time;
$\delta L^3$ contains thermodynamic system $(P, T, \rho)$, infnitesimal for $L$;
$\delta t$ enough to reach equilibrium state in $\delta L^3$;
$L =$ typical system size;
$t =$ typical macroscopic observation time.




LTE: mesoscopic cells reach equilibrium in $\delta t$, infinitesimal for $t$.
Sufficiently fast correlations decay.

LTE: after local relaxation, large $N$ makes irrelevant granularity of matter: uniformly distributed, it appears as a continuum, with continuously varying properties.




Thus, local balances are valid:

Corresponding macroscopic description
is based on linear equations, like
Fick's law for tracer diffusion or Ohm's low for electric current

$$J_n(x,t) = -D\frac{\partial n}{\partial x}(x,t)\ , \quad J_e(x,t) = \kappa E$$

with entropy sources

$$\sigma_s(x,t) = \frac{D}{n(x,t)}\left[\frac{\partial n}{\partial x}(x,t)\right]^2\ , \quad \sigma_s(x,t) = \frac{JE}{k_B T}$$

Nonlinear generalizations, still in LTE.

In LTE, hydrodynamic laws hold; container shape does **NOT** matter (only boundary conditions).
In macroscopic world, very hard to break LTE and continuum mechanics reigns (transport, pattern formation, turbulence, etc.)

Beyond LTE, Boltzmann's Kinetic theory of (rarefied) gases.
Works well even in extreme situations, like neutron transport.

Rests on stosszahl-ansatz, and $\ell \ll L$.

Walls are still merely boundary conditions.

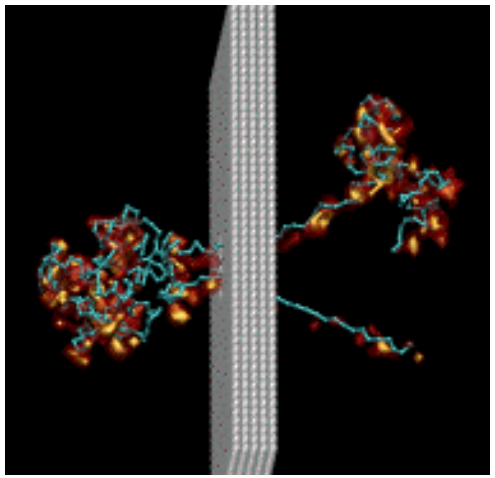
**Further away from equilibrium?** In meso- and micro-scopic media, walls play significant role in determining transport laws: inter-particle and particle-wall interactions count the same.

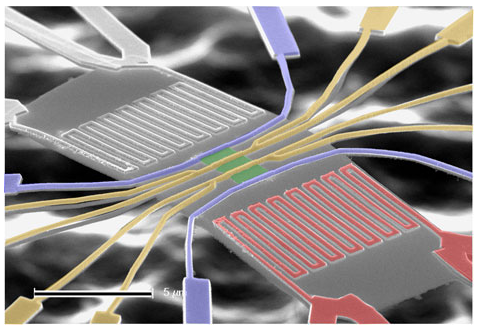
Rarefied conditions, $\ell \sim L$.
Highly confined (almost 1-D).
High gradients (reduced chaos).
Correlations destroy LTE,
produce anomalous transport
e.g. of matter (membranes)
and heat (nanowires).

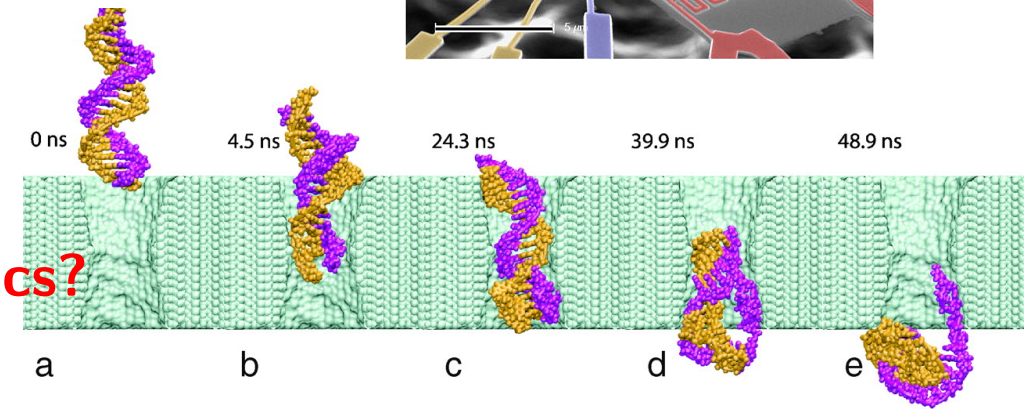
**Dynamics succeeds**
**in many circumstances.**

Possible starting point for
comprehensive theory of
nonequilibrium phenomena.

**Which nonequilibrium dynamics?**







- How does transition from dynamics to thermodynamics take place?
- What if it does not take place (e.g. in bio- nano-systems)?

Introduce Transport Exponent $\gamma$ as: $\left\langle \mathbf{r}^2(t) \right\rangle \sim t^{2\nu}$

Inter-particle interactions have stronger influence on transition than defocussing particle-wall interactions: not bound to occur at fixed positions, efficiently break correlations.

Chaos neither sufficient nor necessary.

How should linear response theory be modified?

Need models to test various hypothesis.

Given that

$$D_{ii} = \lim_{t\to\infty} \frac{\langle (x_i(t) - x_i(0))^2 \rangle}{2t} = \int_0^\infty C_{ii}(t)\, dt\,, \quad C_{ii}(t) = \langle v_i(t) v_i(0) \rangle$$

super-diffusion occurs if

- variance of velocity is not finite ($\langle v^2 \rangle = \infty$)
- correlations persist ($C_{ii}(t) \sim t^{-\beta}$, $\beta < 1$)

FDR relates mean velocity and position responses to an external perturbing force $\mathbf{F}$, to the velocity autocorrelation:

$$\langle v(t) \rangle_{\mathbf{F}} \propto \int_0^t C_v(t')dt'$$

$$\langle x(t) \rangle_{\mathbf{F}} = \int_0^t \langle v(t') \rangle_{\mathbf{F}} dt' \propto \int_0^t \int_0^t C_v(t' - t'')dt'dt'' = \langle x(t)^2 \rangle_0 \sim t^{2\nu}$$

Not rigorous; theoretically, numerically, experimentally confirmed in some subdiffusive case [MBK99,GSGWS96,VPV08].

Various works show that transient anomalous diffusion is often realized, even when asymptotically normal diffusion sets in. It is then to be seen whether the asymptotic regime is experimentally relevant.

Many reports on fast diffusion, e.g. of water in carbon natubes.

Well known slow transport in *single-file diffusion*.

# Dynamics? Ensembles?

Equilibrium: Hamiltonian dynamics and Ergodic Hypothesis:

$\dot{\Gamma} = G(\Gamma)$ in $\mathcal{M}$ with solution $S^\tau \Gamma$.

Observable $\mathcal{O}$, time average of appropriate microscopic quantity $\mathcal{Q}$, equals phase space average, with proper probability distribution (*ensembles*) $\mu$:

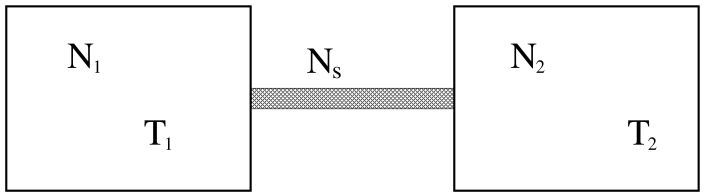
$$\mathcal{O} = \lim_{t\to\infty} \frac{1}{t} \int_0^t \mathcal{Q}(S^\tau \Gamma) d\tau = \int_{\mathcal{M}} \mathcal{Q}(\Gamma) d\mu(\Gamma) \quad a.e.\ \Gamma$$

Why it works, is a long story (mathematical ergodic theory: too much and too little), but classical ensembles work very well.

**Which nonequilibrium *ensembles*?**

What about nonequilibrium ensembles? Need model.

Ideally, infinite reservoirs must be given. How to represent them?




Algorithms to compute transport coefficients etc.?

Need dynamical models to test various hypothesis and develop theory, in particular far from LTE.

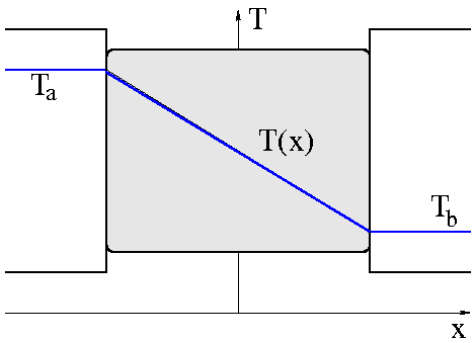
**Deterministic Thermostats** devised to efficiently compute transport coefficients.
Idea: details of heat removal irrelevant for phenomenon of interest.

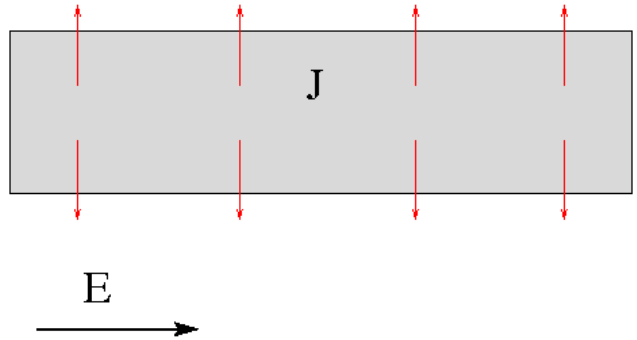
Molecular dynamics computes properties of systems by simulation of microscopic particle dynamics:

$$\dot{\mathbf{q}}_i = \mathbf{p}_i/m;\ \dot{\mathbf{p}}_i = \mathbf{F}_i;\ i = 1, ..., N$$

and use of statistical mechanical relations.

To reach nonequilibrium steady state, energy pumped in system by external drivings must be passed to reservoirs.




Nonequilibrium molecular dynamics achives goal replacing:

boundary or bulk drivings + reservoirs

by

mechanical forces + p.b.c. + *fictitious* thermostatting forces

**Thermostatting** term added to equations of motion, introduced through appropriate constraints, dissipates excess energy. Simplest case:

**Gauss' principle of least constraint (1829).** *Consider $N$ point particles of mass $m_i$, subjected to frictionless bilateral constraints $\mathbf{\Phi}_i$ and external forces $\mathbf{F}_i$. Of all motions allowed by the constraints, the* **natural** *one minimizes the "curvature"*

$$C = \sum_{i=1}^{N} m_i \left( \ddot{\mathbf{q}}_i - \frac{\mathbf{F}_i}{m_i} \right)^2 = \sum_{i=1}^{N} \frac{1}{m_i} \mathbf{\Phi}_i^2 \ .$$

According to Gauss, the "Curvature" $C$ is minimized by the accelerations of real motions or, equivalently, real motions minimize the action of the constraints.

In case of holonomic constraints, consistent with least action principle (Hamiltonian eqs).

Non holonomic constraints result in non Hamiltonian eqs.
$N$-particles with external field $\mathbf{F}_i^{ext}$, interactions $\mathbf{F}_i^{int}(\mathbf{q})$:

$$\begin{cases} \dot{\mathbf{q}}_i = \mathbf{p}_i/m \\ \dot{\mathbf{p}}_i = \mathbf{F}_i^{int}(\mathbf{q}) + \mathbf{F}_i^{ext}(\mathbf{q}) - \alpha(\Gamma)\mathbf{p}_i \end{cases}$$

Simple constraints: isokinetic fixes $K = \sum_i \mathbf{p}_i^2/2m$;
isoenergetic fixes $H_0 = K + \Phi^{int}$

$$\alpha_{IK}(\Gamma) = \frac{1}{2K}\sum_{i=1}^{N} \dot{\mathbf{q}}_i \cdot \left(\mathbf{F}_i^{int} + \mathbf{F}_i^{ext}\right) = \beta\dot{\Phi}^{int}(\mathbf{q}) + \beta\sum_{i=1}^{N} \dot{\mathbf{q}}_i \cdot \mathbf{F}_i^{ext}$$

$$\alpha_{IE}(\Gamma) = \frac{1}{2K}\sum_{i=1}^{N} \dot{\mathbf{q}}_i \cdot \mathbf{F}_i^{ext}$$

As phase space contraction rate $\chi = -\text{div}\,\dot{\Gamma} \propto -\alpha$

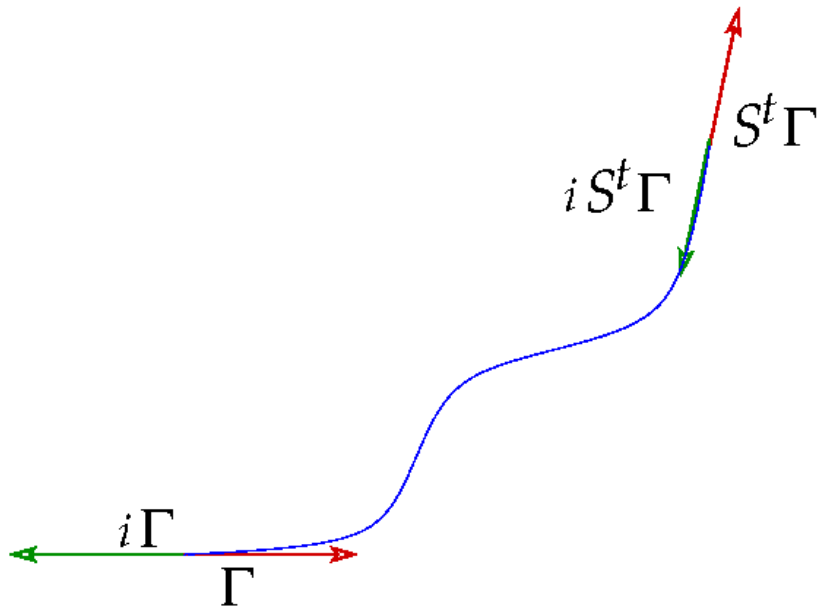
$$\sigma_{IE} \propto \chi_{IE}$$

$$\sigma_{IK} \propto \chi_{IK} - \text{extra (conservative) term}$$

$\alpha(\Gamma)\mathbf{p}_i$ makes dynamics dissipative, hence system reaches steady state, but time reversal invariant.

$S^t : \mathcal{M} \to \mathcal{M}$ evolution operator,
$t \in \boldsymbol{R}$; $S^t\Gamma$ phase after time $t$.
$i : \mathcal{M} \to \mathcal{M}$ time reversal involution ($i^2 = \text{Id}$).
Time reversal invariant if

$$iS^t\Gamma = S^{-t}i\Gamma \;, \forall \Gamma \in \mathcal{M}$$



## Nosè-Hoover thermostat

Defined by following transformations of momenta and time variables:

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s} \; ; \quad \tilde{t} = \int_0^t \frac{d\tau}{s}$$

$$\frac{d\mathbf{q}_i}{d\tilde{t}} = \frac{\tilde{\mathbf{p}}_i}{m} \; ; \quad \frac{d\tilde{\mathbf{p}}_i}{d\tilde{t}} = \mathbf{F}_i - \zeta \tilde{\mathbf{p}}_i \; ; \quad \frac{d\zeta}{d\tilde{t}} = \frac{1}{\tau^2}\left(\frac{K(\tilde{\mathbf{p}})}{K_0} - 1\right) \; ; \quad \frac{ds}{dt} = \zeta s \, .$$

$K_0$ = value chosen for the time average of kinetic energy $K(\tilde{\mathbf{p}})$,
$\tau$ = relaxation time.

In the small $\tau$ limit, Nosè-Hoover dynamics approximate Gaussian *IK* dynamics.

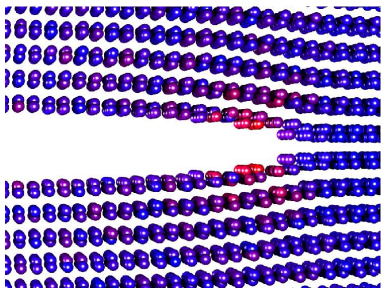
In equilibrium, Hamiltonian and reproduces canonical ensemble: equilibrium at fixed $T$ instead of fixed $E$; closed system.

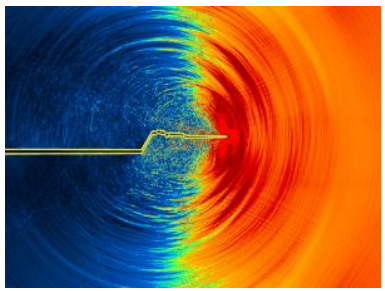
Dynamics dissipative, but time reversal invariant.

Successful in calculation of transport coefficients, defects in crystals, friction of surfaces, atomic clusters, biological macromolecules, etc. Difficulties only if:

- interatomic forces too complicated;
- number of simulated particles must be too large;
- simulation must be times too long.

Otherwise, commonly used to understand results of experiments; in place of (expensive or practically impossible) experiments:
fracture fronts *inside* solids,
nuclear fuel pellets
thermal dilation etc.





One may use deterministic thermostats also to fix the **Configurational Temperature** $T$. In microcanonical ensemble,

$$e^{S(E)} = \int_{\Sigma(E)} \frac{m(d\Sigma)}{\|\nabla\mathcal{H}\|} , \qquad \frac{1}{T(E)} = \frac{dS}{dE}$$

implies

$$k_B T \equiv \lim_{t\to\infty} \frac{1}{t} \int_0^t \frac{\nabla\mathcal{H}\cdot\mathbf{B}}{\nabla\cdot\mathbf{B}} , \qquad \nabla = \frac{\partial}{\partial\Gamma} \qquad (2.1)$$

$\mathbf{B} = (0, \mathbf{p})$ yields usual kinetic temperature, $\mathbf{B} = (\mathbf{F}, 0)$ purely configurational.

Useful when kinetic $T$ makes no sense (nonequilibirum fluids of large flexible polymers).

Mimic Nosé-Hoover to obtain eqs. of motion:

$$\frac{\mathrm{d}\mathbf{q}}{\mathrm{d}t} = \frac{\mathbf{p}}{m} - \xi\mathbf{F} ; \qquad \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \mathbf{F} ; \qquad \frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{Q}\left(\mathbf{F}\cdot\mathbf{F} - kT\nabla\cdot\mathbf{F}\right)$$

Liouville eq. in phase space $(\mathbf{q}, \mathbf{p}, \xi)$:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = f\xi\nabla \cdot \mathbf{F}$$

implies canonical distribution is preserved by dynamics: closed.

Existence of average value of $\xi$ implies that:

$$\overline{\dot{\xi}} = 0 = \frac{1}{Q}\left(\overline{\mathbf{F}\cdot\mathbf{F}} - kT\overline{\nabla\cdot\mathbf{F}}\right) \quad \Rightarrow \quad kT = \frac{\overline{\mathbf{F}\cdot\mathbf{F}}}{\overline{\nabla\cdot\mathbf{F}}}$$

i.e. system $T \equiv$ configurational $T$.

$\mathbf{F}$ has no component $\perp$ to bond lengths or other holonomic constraints, so these constraints not broken by dynamics.

Temperature for Gaussian isokinetic dynamics: Coordinate transform leads to Hamiltonian version of *IK* dynamics. One particle. Replace $\mathbf{p}$ with $\boldsymbol{\pi} = \mathbf{p}\exp\left(-\phi/2R\right)$, $\phi = \phi^{ext} + \phi^{int}$ $R =$ parameter.

$$\mathcal{H}(\mathbf{q},\boldsymbol{\pi}) = \frac{e^{\phi/2R}}{2m}\boldsymbol{\pi}^2 - R\ e^{-\phi/2R}\ , \qquad (2.2)$$

leads to:

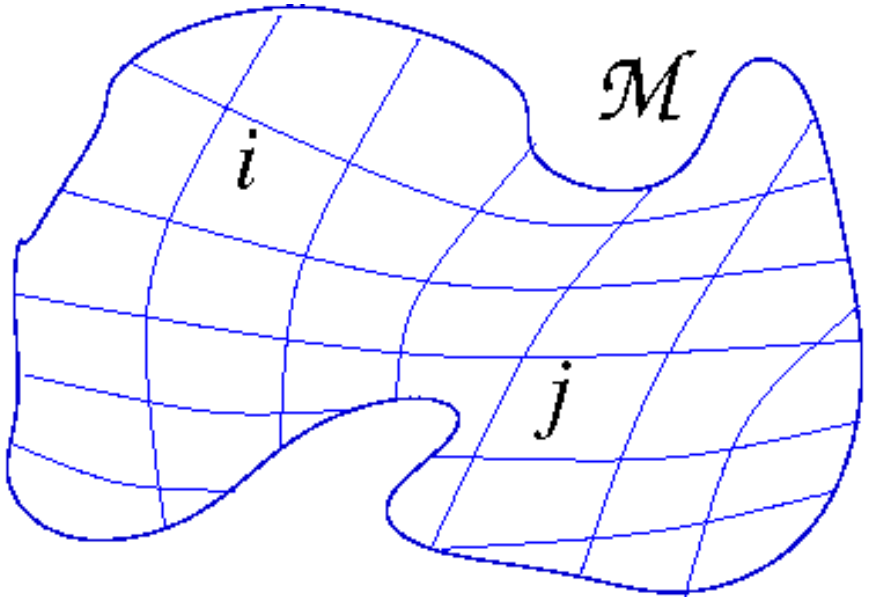
$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}\ , \quad \dot{\mathbf{p}} = \frac{d\mathbf{p}}{d\boldsymbol{\pi}}\frac{d\boldsymbol{\pi}}{dt} = \mathbf{F}^{ext} + \mathbf{F}^{int} - \frac{(\mathbf{F}^{ext} + \mathbf{F}^{int})\cdot\mathbf{p}}{\mathbf{p}^2}\mathbf{p}\ . \qquad (2.3)$$

the *IK* equations for a 1-particle system.
$T$ approaches $T_\perp = \sum_{i=1}^{N}\mathbf{p}_{i,\perp}^2/dNm$, in large $N$ limit, $\mathbf{p}_{i,\perp}$ component of $\mathbf{p}_i$ orthogonal to $\mathbf{F}^{ext}$. $T_\perp$ may be good temperature for simple liquids.

# Fluctuation relations

Which probability distributions describe steady states of NEMD models? If $\Phi$ is one observable

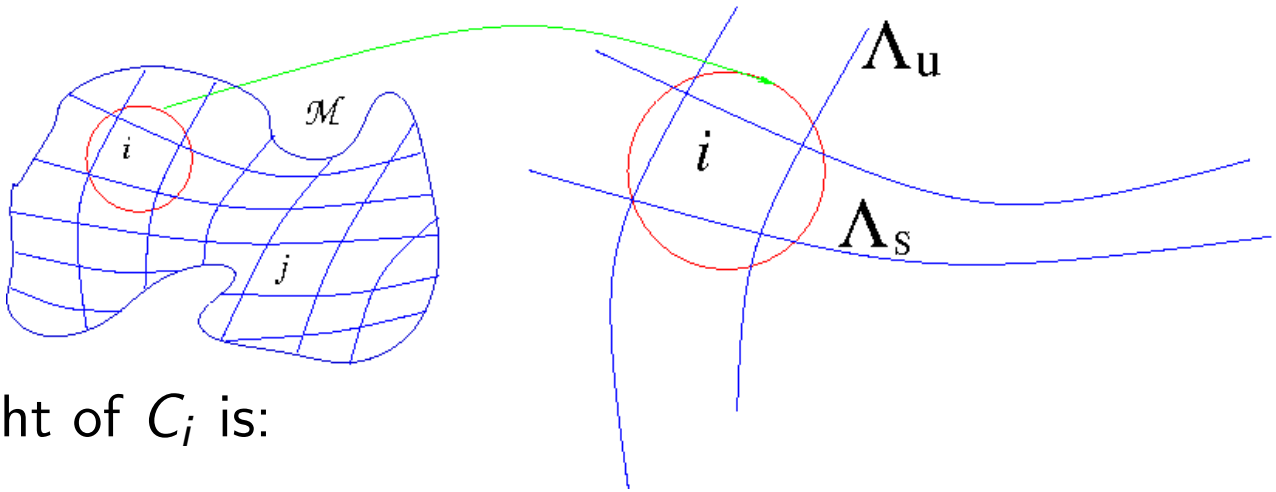
$$\langle \Phi \rangle = \lim_{T \to \infty} \frac{1}{t} \int \Phi(S^t x) dt = \int_\Omega \Phi(x) \mu(dx)$$




$$\langle \Phi \rangle \approx \sum_i \Phi(x_i) P(C_i)$$

**Theorem (Sinai, 1968):** *Every transitive Anosov system admits Markov partitions.*

Attribute weights to cells of a Markov partition of $\Omega$; limit of finer and finer partitions: SRB measure.




Weight of $C_i$ is:

$\Lambda^{-1}_{w_i,u,\tau} = 1/|\text{Jacobian of dynamics restricted to } W^u|$,

$w_i = \{S^t x_i\}_{t=-\tau/2}^{\tau/2}$, large $\tau$, $x_i \in C_i$.

$w$'s can be periodic: $\Rightarrow \Lambda^{-1}_{w,u} = \exp(-\tau \sum_l^+ \lambda_{w,l})$,

$\sum^+$ summation over positive $\lambda_{w,i}$

For one NEMD model of isoenergetic shear, Evans-Cohen-Morriss (1993) proposed and tested this Fluctuation Relation:

$$\frac{\text{Prob.}\left(\overline{E}_\tau = A\right)}{\text{Prob.}\left(\overline{E}_\tau = -A\right)} = \exp\left[A\tau\right]$$

$\overline{E}_\tau =$ average entropy production rate in long time interval $\tau$.

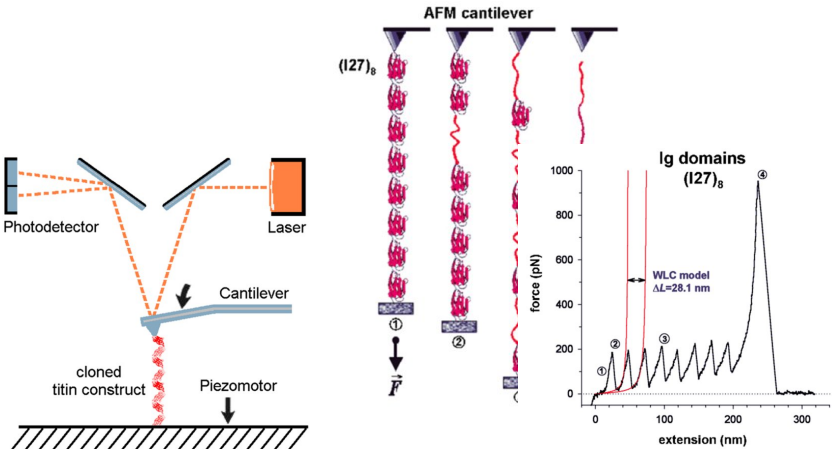
Obtained from theory of chaotic dynamical systems.
Related to ergodic theory by Gallavotti and Cohen (1995) who formulated the Chaotic Hypothesis.

Quantifies second law.

Step towards comprehensive theory of nonequilibrium phenomena: extends thermodynamic relations far from equilibrium.

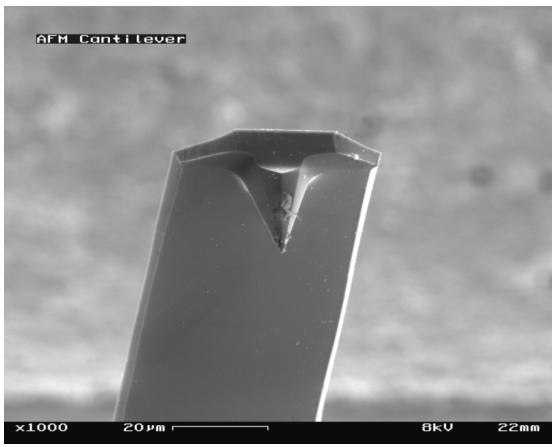
Fluctuations not observed in macroscopic systems, but observable in microscopic ones, such as nano-tech and bio-physical systems.

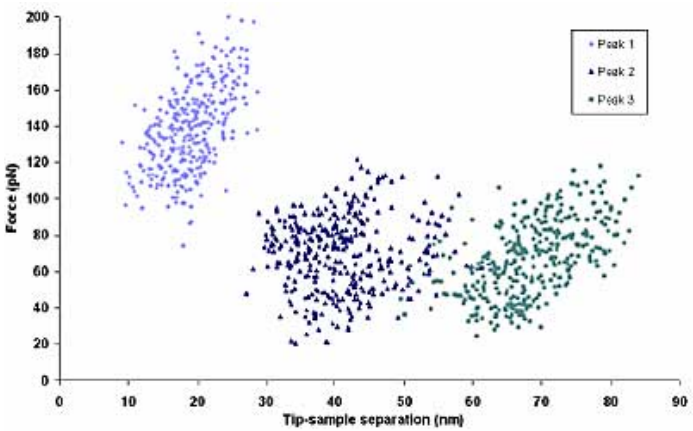
Gibbs free energy of proteins, via Jarzynski Equality: equilibrium properties from nonequilibrium experiments, canonical ensemble




$$\left\langle e^{-\beta W} \right\rangle_{A \to B} = e^{-\beta[F(B)-F(A)]}$$

$F(B) - F(A)$ = free energy difference between equilibrium with $\lambda = A$, and equilibrium with $\lambda = B$.



$\dot{\Gamma} = G(\Gamma)$ in phase space $\mathcal{M}$, $\Gamma = (\mathbf{q}, \mathbf{p})$, reversible.
$S^t\Gamma$ =solution with i.c. $\Gamma$. $i$ =time reversal operation.

**Dissipation function:**

$$\overline{\Omega}_{t,t+\tau}(\Gamma) = \frac{1}{\tau}\Omega_{0,\tau}(\Gamma) \equiv \frac{1}{\tau}\int_t^{t+\tau} \Omega(S^s\Gamma)ds$$

$$= \frac{1}{\tau}\left[\ln \frac{f(S^t\Gamma)}{f(S^{t+\tau}\Gamma)} - \int_t^{t+\tau} \Lambda(S^s\Gamma)ds\right]$$

$f$ = phase space probability density [even for $i$: $f(i\Gamma) = f(\Gamma)$]

$\Lambda$ = phase space volume variation rate $= \nabla \cdot \dot{\Gamma}$

$\Omega$ = dissipation rate $= F_e J/k_B T$ (for properly chosen $f$, as in equilibrium, as in Jarzynski)

Let

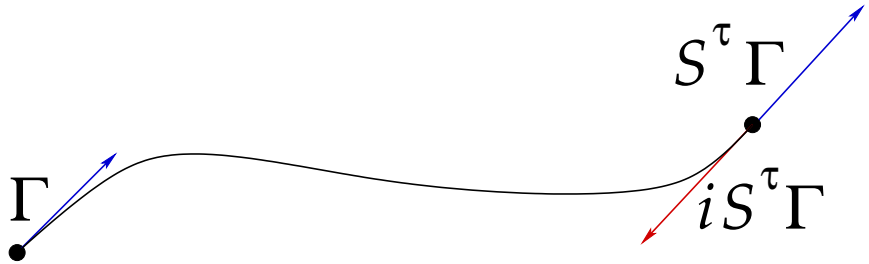
$$A_\delta^+ = (A-\delta, A+\delta)$$
$$A_\delta^- = (-A-\delta, -A+\delta)$$

Consider

$$\frac{\mathrm{Prob}(A_\delta^+)}{\mathrm{Prob}(A_\delta^-)} = \frac{\int_{\{\overline{\Omega}_{0,\tau}\in A_\delta^+\}} f(\Gamma)d\Gamma}{\int_{\{\overline{\Omega}_{0,\tau}\in A_\delta^-\}} f(\Gamma)d\Gamma} \equiv \frac{\mu(\{\overline{\Omega}_{0,\tau}\in A_\delta^+\})}{\mu(\{\overline{\Omega}_{0,\tau}\in A_\delta^-\})}$$

Observe that

$$\{\Gamma : \overline{\Omega}_{0,\tau}\in A_\delta^-\} = iS^\tau\{\Gamma : \overline{\Omega}_{0,\tau}\in A_\delta^+\}$$




Introduce $\Gamma = iS^\tau X$ and its jacobian

$$J_{0,\tau} = \left|\frac{d\Gamma}{dX}\right| = \exp\left(\int_0^\tau \Lambda(S^s X)ds\right) \equiv \exp\left(\Lambda_{0,\tau}\right)$$

$$\text{Prob}(A_\delta^-) = \int_{\{\overline{\Omega}_{0,\tau} \in A_\delta^-\}} f(\Gamma) d\Gamma = \int_{\{\overline{\Omega}_{0,\tau} \in A_\delta^+\}} f(iS^\tau X)\, e^{\Lambda_{0,\tau}(X)} dX$$

$$= \int_{\{\overline{\Omega}_{0,\tau} \in A_\delta^+\}} f(X)\, e^{-\Omega_{0,\tau}(X)} dX = e^{-[A+\epsilon(\delta,\tau)]\tau} \int_{\{\overline{\Omega}_{0,\tau} \in A_\delta^+\}} f(X) dX$$

which leads to

$$\frac{\text{Prob}(A_\delta^+)}{\text{Prob}(A_\delta^-)} = \exp\{\tau\,[A + \epsilon(\delta,\tau)]\} \qquad \epsilon \leq \delta$$

Called *transient* fluctuation relation: concerns initial state $f$ and not steady state (invariant measure). Holds for all $\tau$.

The transient relation describes the statisitcs of an **ensemble** of experiments, all beginning in the same initial state $f$.

Just a coordinate transformation, for time reversal invariant dynamics.

Can be experimentally verified. E.g. optical tweezers and colloidal particles (Evans et al. PRL 2002).

What about steady state fluctuation relations?

What about the statistics of fluctuations along a single, but long, evolution?

Wants to move from statistics of initial ensemble $\mu$ to statistics of steady state $\mu_\infty$, *provided it exists*.

Let averaging start at time $t$

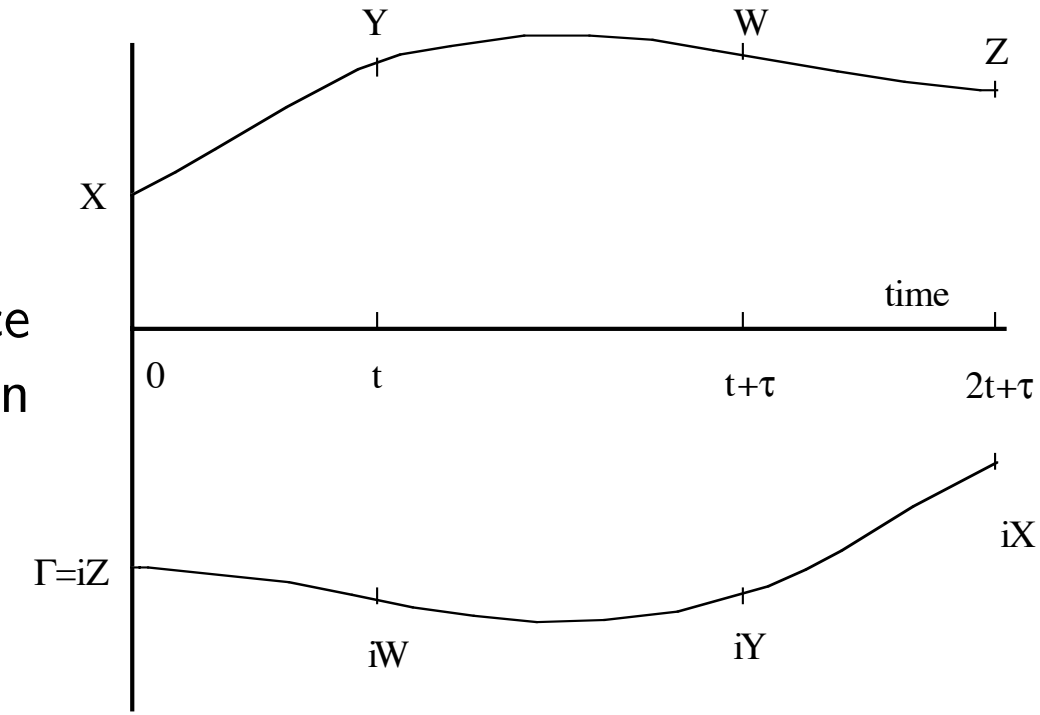
$$\frac{1}{\tau} \ln \frac{\mu(\{\overline{\Omega}_{t,t+\tau} \in A_\delta^+\})}{\mu(\{\overline{\Omega}_{t,t+\tau} \in A_\delta^-\})}$$

Use conservation of phase space probabilities to move evolution from sets to probabilities:

$$\mu_t(S^t E) = \mu(E)$$

which yields

$$\frac{1}{\tau} \ln \frac{\mu_t(\{\overline{\Omega}_{0,\tau} \in A_\delta^+\})}{\mu_t(\{\overline{\Omega}_{0,\tau} \in A_\delta^-\})}$$




Split trajectory as $t + \tau + t$.

$$\{\Gamma : \overline{\Omega}_{t,t+\tau}(\Gamma) \in A_\delta^-\} = iS^{t+\tau+t}\{X : \overline{\Omega}_{t,t+\tau}(X) \in A_\delta^+\}$$

Change coordinates: $\Gamma = iS^{t+\tau+t}X$

$$\left|\frac{d\Gamma}{dX}\right| = e^{\Lambda_{0,t}(X)} \cdot e^{\Lambda_{t,t+\tau}(X)} \cdot e^{\Lambda_{t+\tau,2t+\tau}(X)}$$

$$\frac{1}{\tau} \ln \frac{\mu_t(\{\overline{\Omega}_{0,\tau} \in A_\delta^+\})}{\mu_t(\{\overline{\Omega}_{0,\tau} \in A_\delta^-\})} = A + \epsilon(\delta, t, A, \tau) + -\frac{1}{\tau} \ln \left\langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \right\rangle_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+}$$

Large $\tau$ kills strange term. $t \longrightarrow \infty$ implies $\mu_t \longrightarrow \mu_\infty$.

Trouble: $t \longrightarrow \infty$ before $\tau$, hence $\Omega_{0,t} = \int_0^t \Omega dt$ may diverge.

But this can be controlled, thanks to some correlations decay.

Similarly, one obtains other relations

**Transient $\phi$-FR.** $$\frac{P(\phi_{0,\tau} \in A_\delta^+)}{P(\phi_{0,\tau} \in A_\delta^-)} = \frac{1}{\langle e^{-\Omega_{0,\tau}} \rangle_{\phi_{0,\tau} \in A_\delta^+}}$$

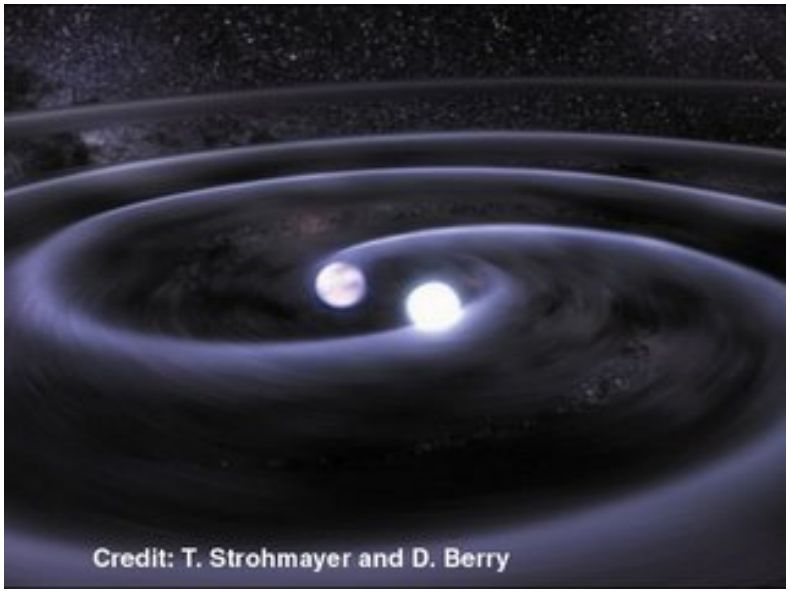
**Steady State $\phi$-FR.** *For any $\gamma$,* sufficiently large $\tau$ *yields*

$$\frac{1}{\tau} \ln \frac{P_\infty(\phi_{t,t+\tau} \in A_\delta^+)}{P_\infty(\phi_{t,t+\tau} \in A_\delta^-)} = -\frac{1}{\tau} \ln \langle e^{-\Omega_{t,t+\tau}} \rangle_{\phi_{t,t+\tau} \in A_\delta^+} + \gamma$$

**Dissipation relation.** $$\langle \mathcal{O}(t) \rangle = \int_0^t ds \langle \Omega(0) \mathcal{O}(s) \rangle$$

Where $\phi$ is any time-odd observable, and $\mathcal{O}$ any observable, e.g. the current and the thermal dilation.

# Truly unobservable in macroscopic systems?




**RareNoise**

**Problems in Detection of Gravitational Waves**

ERC funded project to understand nonequilibrium fluctuations in macroscopic objects, such gravitational antennas.

http://www.rarenoise.lnl.infn.it/

# Discussion

- Nonequilibrium phenomena are most common in nature
- Current understanding closely related to understanding of equilibrium phenomena, via response theory, Fluctuation Dissipation Theorem and Flcutuation Relations
- Flcutuation Relations quantify 2nd law, extend well beyond LTE, and may then suggest a comprehensive theory of nonequilibrium phenomena
- Flcutuation Relations useful in understanding states of matter at the mesoscopic scale (nano-tech and bio-physical systems), where LTE fails, and perhaps more...
- Deterministic dynamics allows operational definitions microscopic of temperature when this concept not fully clear.