Non-equilibrium phenomena and fluctuation relations

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Beijing – 16 March 2012

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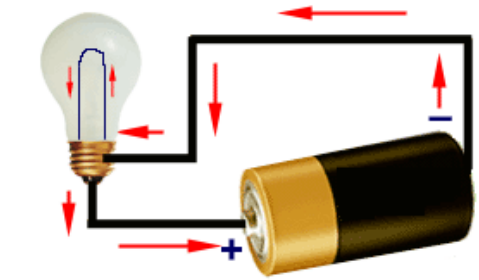
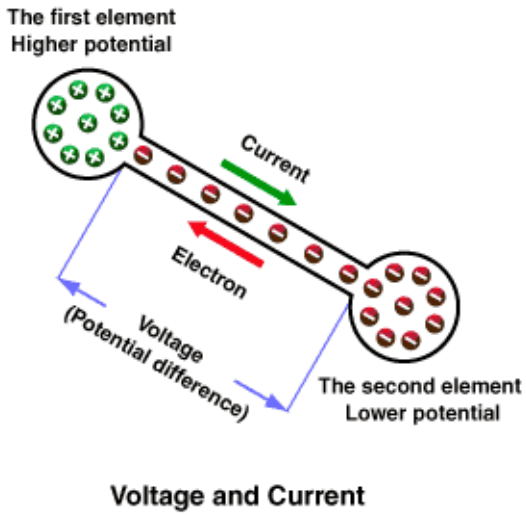
Outline

Electric current I, i.e. flow of electrons due to potential difference ΔV, is a familiar phenomenon. Ohm's law states that

$$I = \Delta V / R \; ; \qquad R = \text{ resistence of the wire}$$





Can one compute R without applying ΔV?

Can one understand nonequilibrium behavior by observing equilibrium properties? (classical question).
May we infer equilibrium properties from nonequilibrium experiments? (modern question).

Mechanical equilibrium: no external or internal net forces.
Otherwise: acceleration, turbulence, waves.

Chemical equilibrium: constant composition, no matter transport.

Thermal equilibrium: state does not change when separated from environment by adiabatic walls. Otherwise: heat flows.

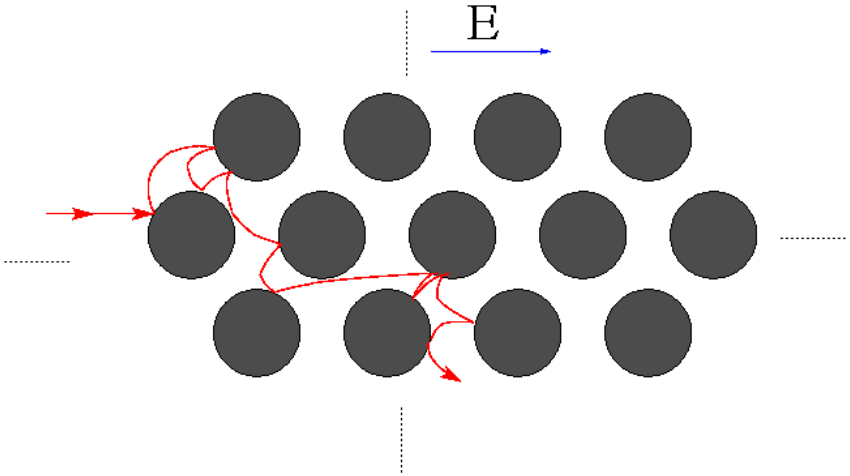
All equilibria $\Rightarrow$ state of Thermodynamic Equilibrium.
Characterized by few global properties (T, P, ρ), constant in time.

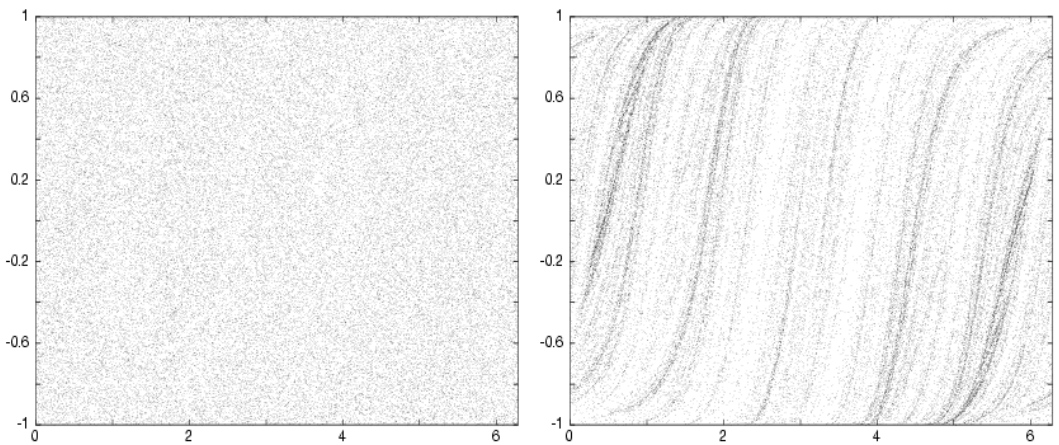
If not in equilibrium, many system still described by $(T(\mathbf{x}), P(\mathbf{x}), \rho(\mathbf{x}))$ at all different locations $\mathbf{x}$:

Local Thermodynamic Equilibrium.

If not in equilibrium, and not interacting with environment, state typically evolves towards equilibrium.

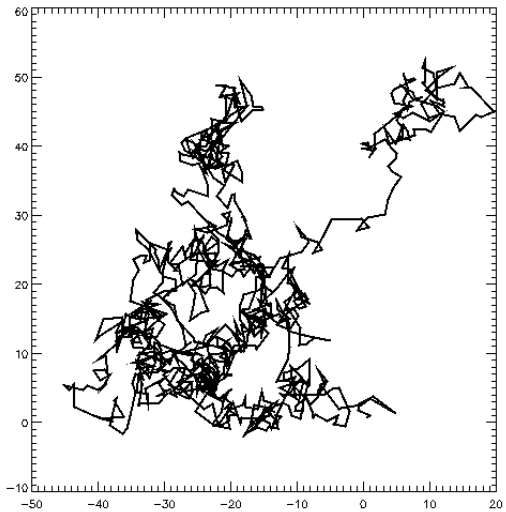
Coupling with environment may prevent relaxation to equilibrium: energy is dissipated and nonequilibrium steady states may be realized.





Coupling allows pattern formation and ordered structures: the most common situation in nature.

Brownian motion is equilibrium process (motion persists indefinitely, goes nowhere, no work, no energy dissipation).



It shows one can adopt three different levels of description
of physical phenomena, and unifies them:

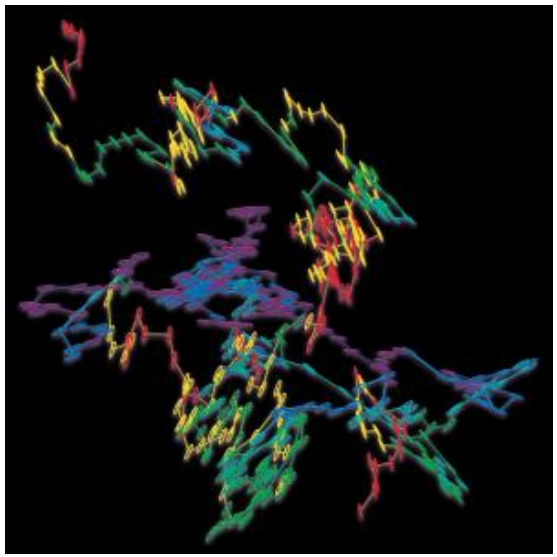
- Macroscopic $\longrightarrow$ irreversible, deterministic (fluid viscosity)
- Mesoscopic $\longrightarrow$ irreversible, stochastic (pollen scale)
- Microscopic $\longrightarrow$ reversible, deterministic (molecular scale)

The Fluctuation Dissipation Relation (FDR), which is of very wide applicability (most equilibrium phenomena) shows this and obtains nonequilibrium from equilibrium.

Einstein obtained first FDR, giving a theory of Brownian motion, to prove that matter is made of atoms.

Fluctuations: variation of physical quantity around its mean (equilibrium)

Dissipation: how system responds to external actions (non-equilibrium)



$\langle \mathbf{x}^2(t) \rangle \sim 6Dt$ (fluctuation/meso).

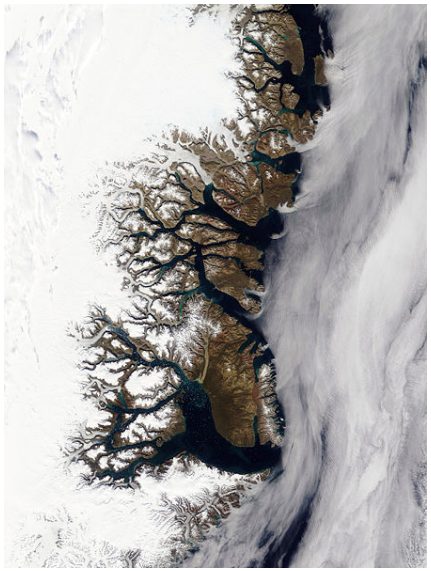
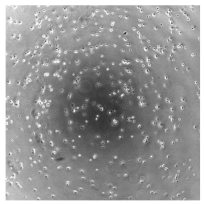
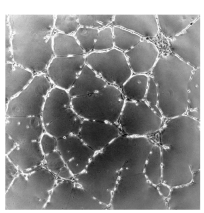
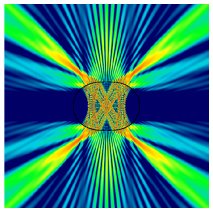
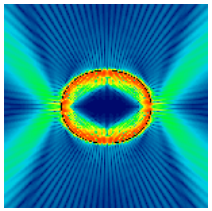
FDR: $D = \frac{RT}{6\pi\eta a} \cdot \frac{1}{N_A}$; N_A (micro)

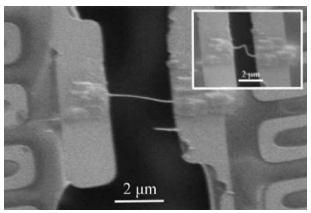
η = viscosity (dissipation/macro: response to drag).

Idea: pollen subject to deterministic viscous force & stochastic molecular impacts;

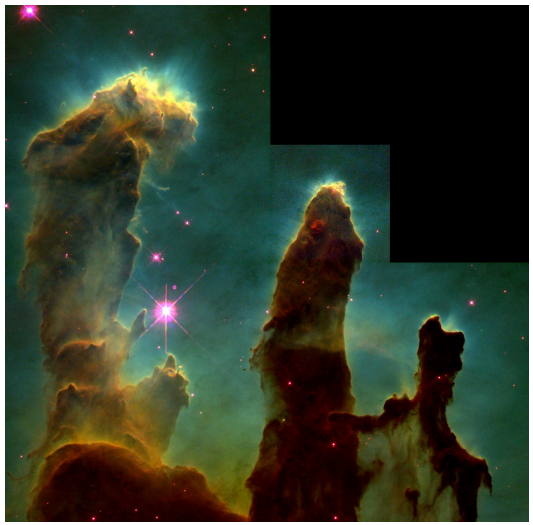
pollen - fluid equilibrium: energy equipartition: $m\langle v_x^2 \rangle = RT/N_a$.

Variety of nonequilbrium phenomena is huge.







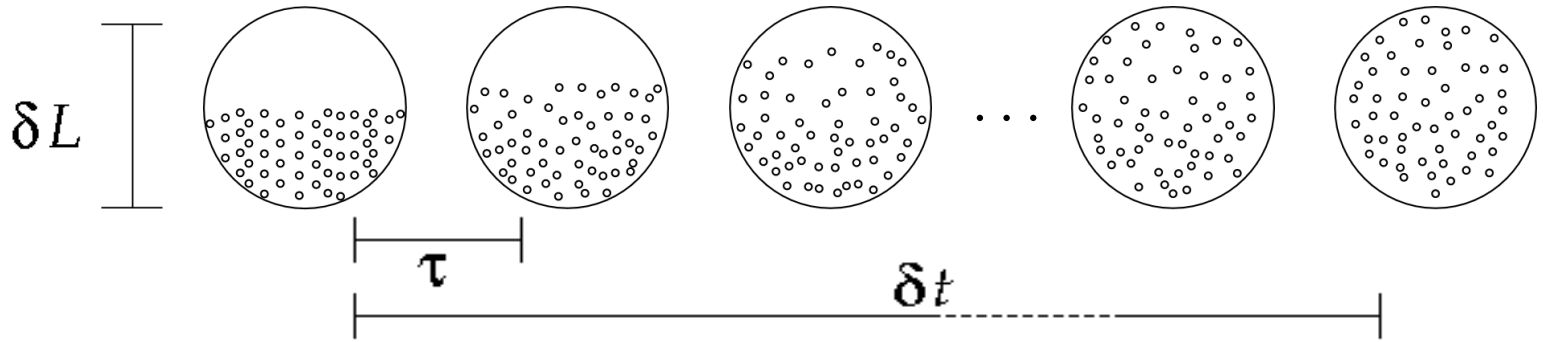
Somewhat unified under hypothesis of

Local Thermodynamic Equilibrium

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

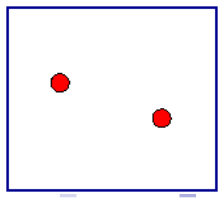
$$\ell \ll \delta L \ll L\,, \qquad \tau \ll \delta t \ll t$$

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



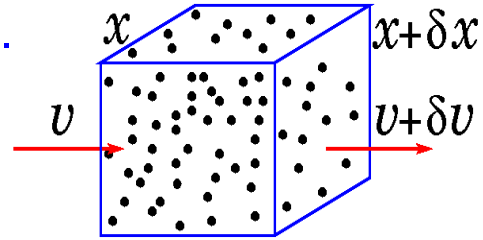
LTE **if** mesoscopic cells reach equilibrium in δt, infinitesimal for t.

Sufficiently fast correlations decay. Condition met here
but no notion of uniform distribution, no relaxation:



LTE $\neq$ invariant measure.

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 Kinetic theory; even in extreme situations (neutron transport). Rests on stosszahl-ansatz, $N \gg 1$, $\ell \ll L$.

Common feature: laws unaffected by containers walls, mere "boundary conditions".

Further away from equilibrium? In meso- and micro-scopic media, walls contribute to determining transport laws: both inter-particle and particle-wall interactions matter.

Low dimensionality often associated with anomalous transport.

Fluctuations

Let isolated system in equilibrium be made of small subsystem S + reservoir R.

Extensive variable X of S fluctuates, other extensive variables fixed.
Probability of $X < x$ given by canonical distribution:

$$P(X < x) = e^{-\psi(h)} \int_{-\infty}^{x} e^{-hx'} dN(x')$$

$h =$ intensive thermodynamic field conjugated to X,
$N(x) =$ cumulative number of microstates with $X < x$

$$e^{\psi(h)} = \int_{-\infty}^{\infty} e^{-hx} dN(x)$$

Relation between unobservable fluctuations of X and observable non-fluctuating thermodyamic quantities. We then have:
$\psi =$ thermodynamic potential, Legendre transform of entropy.

Consider Hamiltonian $\mathcal{H}(\mathbf{P},\mathbf{Q}) = \mathcal{H}_0(\mathbf{P},\mathbf{Q}) + \lambda A(\mathbf{P},\mathbf{Q})$ with small perturbation λA. To linear order, canonical ensemble:

$$f(\mathbf{P},\mathbf{Q}) = \frac{\exp(-\beta\mathcal{H})}{\int d\mathbf{P}d\mathbf{Q}\exp(-\beta\mathcal{H})} \simeq \frac{\exp(-\beta\mathcal{H}_0)}{\int d\mathbf{P}d\mathbf{Q}\exp(-\beta\mathcal{H}_0)} \frac{1-\lambda\beta A(\mathbf{P},\mathbf{Q})}{1-\lambda\beta\langle A(\mathbf{P},\mathbf{Q})\rangle_0}$$

$$= f_0(\mathbf{P},\mathbf{Q})\big(1-\lambda\beta\left[A(\mathbf{P},\mathbf{Q}) - \langle A(\mathbf{P},\mathbf{Q})\rangle_0\right]\big)$$

$\langle\rangle_0$ for $\lambda = 0$. For generic observable B, to same order:

$$\begin{aligned}\langle\Delta B\rangle_0 &= \int d\mathbf{P}d\mathbf{Q}B(\mathbf{P},\mathbf{Q})\big[f(\mathbf{P},\mathbf{Q}) - f_0(\mathbf{P},\mathbf{Q})\big] \\ &\simeq -\lambda\beta\big(\langle BA\rangle_0 - \langle B\rangle_0\langle A\rangle_0\big)\ .\end{aligned}$$

response of B from equilibrium B-A correlation. If $B = A = \mathcal{H}_0$:

$$\frac{\partial\langle\mathcal{H}_0\rangle_0}{\partial\beta} = \lim_{\lambda\to 0}\frac{\langle\Delta\mathcal{H}_0\rangle_0}{\lambda\beta} = -\big(\langle\mathcal{H}_0^2\rangle_0 - \langle\mathcal{H}_0\rangle_0^2\big) = -k_B T^2 C_V$$

Heat capacity, i.e. response to energy perturbation, linked to equilibrium energy fluctuations.

Perturb $\mathcal{H}_0$ with spatially uniform force h along x. Average velocity reaches steady state, because drift current is balanced by diffusion current. Let $B(\mathbf{P},\mathbf{Q}) = \frac{1}{m}\sum_j p_j^x$,

$$\langle \Delta B(t) \rangle = \beta \frac{h}{m^2} \int_0^t dt' \sum_{jk} \left\langle p_j^x(t_0) p_k^x(t-t') \right\rangle_0$$

Assuming momenta of different particles uncorrelated in equilibrium:

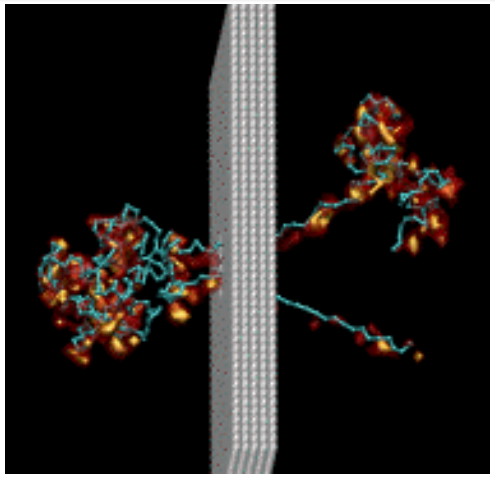
$$\langle \Delta B(t) \rangle = \beta \frac{h}{m^2} \int_0^t dt' \sum_{j} \left\langle p_j^x(t_0) p_j^x(t-t') \right\rangle_0$$

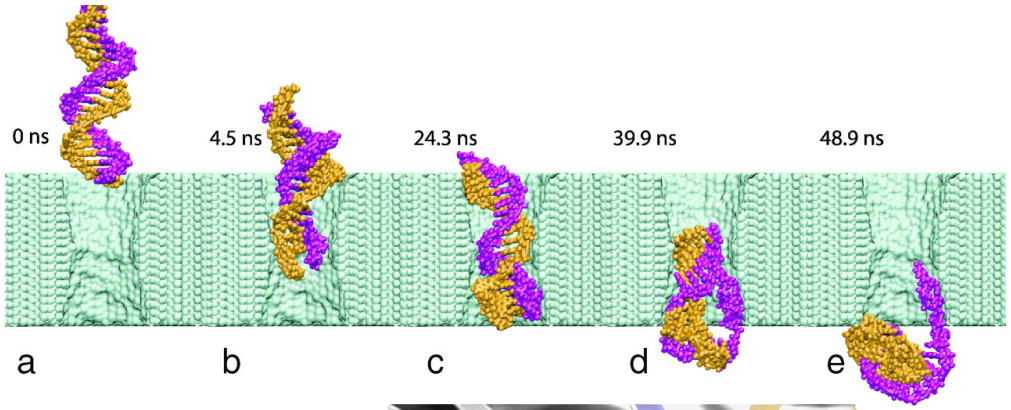
As mobility μ is defined by $\lim_{t\to\infty}\langle \Delta B(t)\rangle = \mu h$,

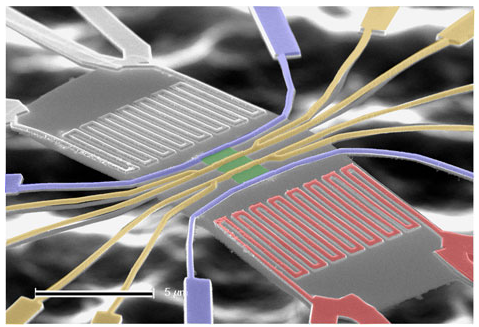
$$\mu = \frac{\beta}{m^2} \int_0^\infty dt' \sum_{j} \left\langle p_j^x(0) p_j^x(t') \right\rangle_0 \qquad \text{Green-Kubo relation}$$

Einstein relation $D = \mu/\beta$.

The above rests on the LTE assumption.
What if this does not hold (e.g. in bio-nano-systems)?
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).
For instance, consider transport of matter. Introduce Transport Exponent ν as: $\left\langle \mathbf{r}^2(t) \right\rangle \sim t^{\nu}$
How does liner response need to be modified?







In the standard case, one has:

$$D = \lim_{t\to\infty} \frac{\langle (x(t) - x(0))^2 \rangle}{2t} = \int_0^\infty C(t)\, dt \ , \quad C(t) = \langle v(t) v(0) \rangle$$

We have anomalous diffusion if

- variance of positions is not finite ($\langle x^2 \rangle = 0$ or $\langle v^2 \rangle = \infty$)
- velocity correlations persist ($C(t) \sim t^{-\beta}$, $\beta < 1$)

Therefore, one could think that mean velocity and position response to external perturbing force **F** may be related to velocity autocorrelation as in standard case, except that:

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

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

with $\nu \neq 1$

Although the above argument is correct in the case of normally diffusing systems, in general it is not rigorous, and in the case of anomalous diffusion it easily leads to inconsistencies.

In some subdiffusive case, however, its conclusions have been theoretically, numerically and experimentally confirmed.

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*.

Consider evolution $S^t\mathbf{x}$ mixing, with invariant probability density

$$\bar{A}(x) = \lim_{t\to\infty} \int_0^t A(S^\tau x) d\tau = \int A(y)\rho(y) = \langle A \rangle_\rho$$

Perturb initial state so that $\rho'(x) = \rho(x - \delta x)$.
Study $\delta\langle (S^t x)_i \rangle = \langle (S^t x)_i \rangle_{\rho'} - \langle (S^t x)_i \rangle_\rho$. One obtains

$$\delta\langle (S^t x)_i \rangle = \langle (S^t x)_i F(x, \delta x) \rangle_\rho \ , \quad F(x, \delta x) = \frac{\rho(x - \delta x) - \rho(x)}{\rho(x)}$$

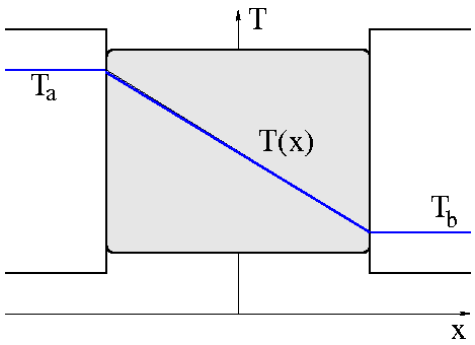
To linear order, for generic $A(\mathbf{x})$

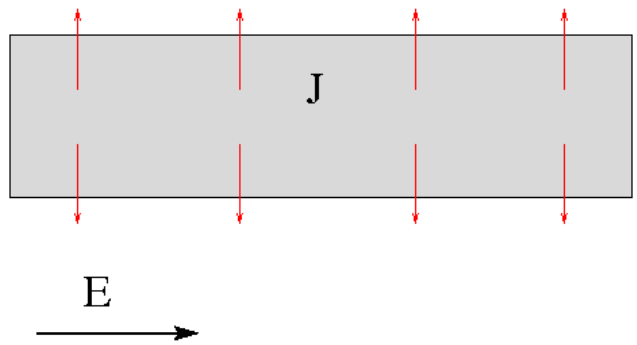
$$\delta\langle A(t) \rangle = -\sum_{j=1}^{N} \left\langle A(S^t x) \left. \frac{\partial \ln \rho}{\partial x_j} \right|_x \right\rangle \delta x_j$$

Linearization of initial perturbed density, and smoothness of ρ.

What if we also do work on our systems?

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

Idea: details of heat removal irrelevant for phenomenon of interest.

N-particles with external field $\mathbf{F}_i^{ext}$, interactions $\mathbf{F}_i^{int}(\mathbf{q})$:

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

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

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

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

$\alpha\mathbf{p}_i$ makes dynamics dissipative, but time reversal invariant.
Efficiently compute transport coefficients.

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

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

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

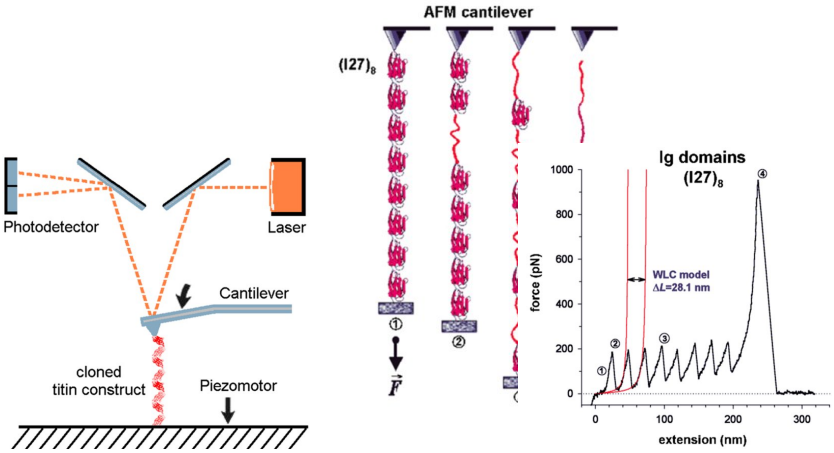
Quantifies second law.

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

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

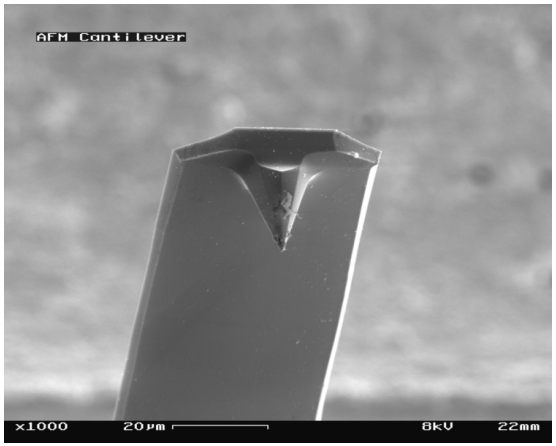
Fluctuations not observed in macroscopic systems, but observable in microscopic ones, such as nano-tech and bio-physical systems.

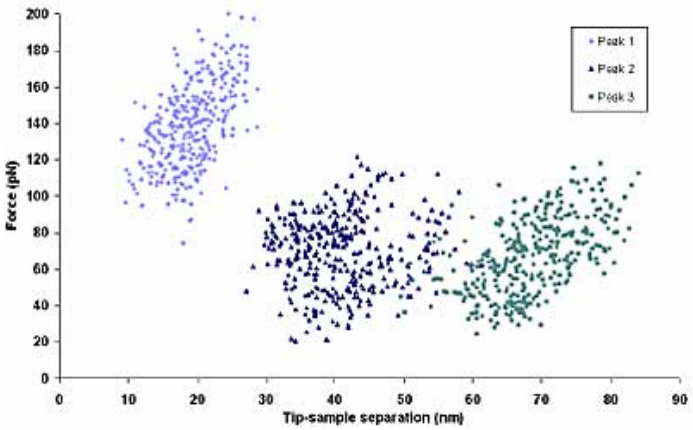
Gibbs free energy of proteins, via Jarzynski Equality: equilibrium properties from nonequilibrium experiments.



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

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





- Nonequilibrium phenomena are most common in nature
- Current understanding closely related to notion of local equilibrium phenomena.
- Fluctuations yield response

Geometry effects and correlations lasting over scales comparable with medium size, interesting e.g. relevance for nano- bio-sciences.

- Flcutuation Relations extend well beyond LTE, quantify 2nd law, suggest 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, but also in macroscopic bodies (GW).

Phys. Rep. **461** 111 (2008); Phys. Rev. Lett. **103** 010601 (2009)