Fluctuations in Nonequilibrium Statistical Mechanics

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Time evolution observed at "timing events": map S of phase space.

Question: Statistics of motion? (probability distr. yielding averages for random data chosen with volume distribution)

Statistics μ:

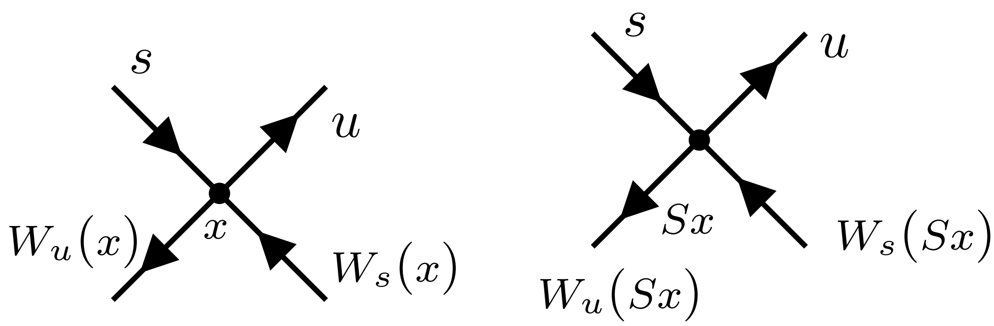
$$\frac{1}{N}\sum_{t=0}^{N-1} F(S^t x) = \int_{phase\ \ space} F(y)\mu(dy)$$

Problem:
Equations of motion $\dot{x} = f(x)$ do not conserve volume (*dissipation is unavoidable*) $\Rightarrow$

$$\text{divergence} \stackrel{def}{=} -\sum_i \frac{\partial}{\partial x_i} f_i(x) \neq 0$$

$\Rightarrow$ if $\sigma_+ > 0$ (dissipation) then μ is on a set of zero volume: SRB statistics is singular.
Is there analogue of the Hamonic oscillators for chaotic systems? *i.e.* systems *very well* understood?

Hyperbolic systems



(1) Continuous in x
(2) Contracting or (resp.) expanding by $\le \lambda < 1$
(3) One dense orbit (to exclude trivially disconnected systems)

Hyperb. syst. admit a statistics SRB: singular but with formal expression. Can be used to write averages; *not to compute them*! as in equilibrium one can write but not compute microcanonical averages! *but formal expressions can be used to derive relations*: *e.g.* exhibit symmetries.

A fundamental symmetry: *time reversal* T or PCTe: operation I with $I^2 = 1$ and $IS = S^{-1} I$.

Reflected in hyperb. syst. $\Rightarrow$ *Fluctuation theorem*

Be $F_1(x), \ldots, F_n(x)$ even/odd: $F_i(Ix) = \pm F_i(x)$
Let $\sigma(x) = -divergence(x)$ *and* $\sigma_+ \stackrel{def}{=} \langle\sigma\rangle_{SRB}$

Given τ *and "patterns"* $t \to \varphi_i(t)$, $t \in (-\frac{\tau}{2}, \frac{\tau}{2})$

$$p = \frac{1}{\tau} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{\sigma(S_t x)}{\sigma_+} dt$$

"dimensionless phase space contraction"

$$\frac{P_\tau(\, F_j(S_t x) \sim \varphi_j(t), p)}{P_\tau(\, F_j(S_t x) \sim \pm\varphi_j(-t), -p)} = e^{p\sigma_+ \tau + O(1)}$$

$P_\tau =$ *SRB probability, for* $|p| < p^*$

Special case

$$\frac{P_\tau(p)}{P_\tau(-p)} = e^{\zeta(p)\tau + O(1)} \quad {\scriptstyle and} \ \zeta(-p) = \zeta(p) - p\sigma_+$$

(Cohen,Evans,Morriss (exp) Cohen,G (theory)

What about *real systems*: like the ergodic hypothesis not sastisfied. But behavior is nevertheless chaotic. So

Chaotic Hypothesis: *Motion on the attractor can be regarded as "hyperbolic" (Anosov)*
(Ruelle 73, Cohen-G 95)

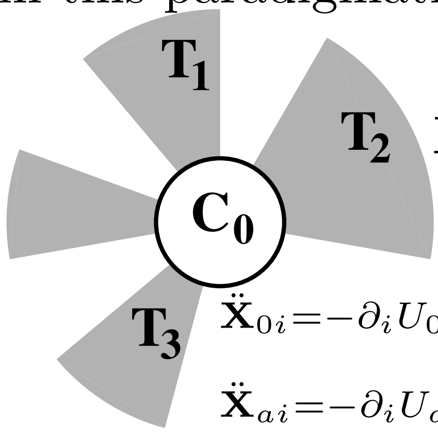
(*Ambitious* $\rightarrow$ identification btwnn
Equilibrium and Nonequilibrium $\Rightarrow$ ergodic)

$+$ *reversibility*, *i.e.* $I^2 = 1$, $IS_t = S_{-t}I \to$ **FT**

What about reversibility? we are not used to think of dissipating systems as reversible (Drude's model of electrical conductivity, friction, Navier Stokes fluids...).

Nevertheless microscopic revers. implies that any macrosc. model which is irreversible must be *equivalent* to a reversible one. Remarkably taking this seriously leads to *identify* phase space contraction with *entropy creation rate.* Discovered in the '980s in special cases and recently becoming more and more clear (Hoover, Evas, Morriss et al).

This is a really fundamental remark that might turn out comparable to the identification of temperature with average kinetic energy. Exemplified in this paradigmatic example.



$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$

$$\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum_a \partial_i U_a(\mathbf{X}_0, \mathbf{X}_i) + \mathbf{F}_i$$

$$\ddot{\mathbf{X}}_{ai} = -\partial_i U_a(\mathbf{X}_a) - \partial_i U_a(\mathbf{X}_0, \mathbf{X}_i) - \alpha_a \dot{\mathbf{X}}_a$$

$\alpha_a = \textit{Gauss for } K_a = \frac{1}{2} \sum_i \dot{\mathbf{X}}_{ia}^2 = \frac{3}{2} k_B T_a \, N_a$

$\alpha_a = (\textit{exercise}) = \frac{W_a - \dot{U}_a}{3 N_a k_B T_a}$

$W_a = -\sum \dot{\mathbf{X}}_a \cdot \boldsymbol{\partial}_{\mathbf{X}_a} U_a(\mathbf{X}_0, \mathbf{X}_a)$, $W_a = \dot{Q}_a =$ heat

Divergence $= \sigma(\mathbf{X}) = (\textit{exercize}) = \sigma_0(\mathbf{X}) + \dot{U}(\mathbf{X})$

$\sigma(\mathbf{X}) = \ {\scriptstyle (exercize)} \ = \sigma_0(\mathbf{X}) + \dot U(\mathbf{X})$
$\sigma_0(\mathbf{X}) = \sum_{a=1}^n \frac{\dot Q_a}{k_B T_a},\ U(\mathbf{X}) = \sum_{a=1}^n \frac{\dot U_a}{k_B T_a}$

If volume $V^N \times R^{3N}$ changes
$\sigma^\Gamma(\mathbf{X}) = \sigma_0(\mathbf{X}) + \dot U - N\frac{\dot V_t}{V_t}$

Assume U_a bounded and thermostats *efficient*
$\lim_{t\to\infty} \frac{1}{t}\int_0^t F(S_t\mathbf{X}) = \int_{\mathcal{F}} F(\mathbf{Y})\,\mu(d\mathbf{Y})$, then

$$\sigma_+ = \langle\sigma\rangle_\mu \equiv \langle\sigma_0\rangle + \lim_{t\to\infty}\frac{U(t)-U(0)}{t} \equiv \langle\sigma_0\rangle$$

$$\mathrm{CH} \to \mathrm{FT} : \zeta(-p) = \zeta(p) - p\sigma_+$$

$$p = p_0 + \frac{U(t)-U(0)}{t\sigma_+} \ \Rightarrow\ FT\ for\ p_0!$$

$p_0 =$ entropy increase of thermostats: measurable

$\frac{U(t)-U(0)}{t} \to 0$ is very large ! (CvZ,BGGZ) but σ_+ and p_0 bear no more reference to thermostats and have time scale of $O(surface)$

In simuations the FR can be tested well (necessary because systems are *not* hyperbolic) and has always been confirmed.

In experiments this is more difficult because the fluctuations are very large and therefore it is necessary to look at small parts.

This leads to interpretation problems. Ideas:

1) SRB distributions equivalence: as in equilibrium there shall be equivalence of ensembles. Reversible models can be $\sim$ irreversible ones.

2) look at small subsystems: *IF* well defined then they can be regarded as special cases of the paradigmatic case: in this way one can for instance check that in the Navier-Stokes equations the microscopic phase space contraction equals the classical entropy creation rate ("up to a total derivative")

3) FR $\Rightarrow \langle e^{\int_0^t \sigma(S_t x)dt} \rangle = e^{O(1)}$: similar to Jarzynski's inequality. But very different as it applies to stationary *nonequilibria*. Could be used in experiments.

Def Irreversibility time scale for process Π

$\varepsilon(X) \stackrel{def}{=} \sigma_0(\mathbf{X}) - N\frac{\dot V_t}{V_t}$

Quasi static $\Pi:\ \mathbf{F}(t) = \mathbf{F}_0 + (1-e^{-\gamma t})(\mathbf{F}_\infty - \mathbf{F}_0)$

Stationary μ_0 evolves to μ_t and to μ_∞.

$\mu_{srb,t}$ = SRB parameters "frozen" at value taken at time t. Let *irreversibility time scale* for Π

$\frac{1}{\tau(\Pi)} \stackrel{def}{=} \frac{1}{N^2}\int_0^\infty \big(\langle\varepsilon_t\rangle_{\mu_t} - \langle\varepsilon_t^0\rangle_{\mu_{srb,t}}\big)^2 dt$

If quasi static $\tau(\Pi) = O(\gamma^{-1}\log\gamma^{-1}) \xrightarrow[\gamma\to 0]{} \infty$ (*i.e.* $\to$ reversible)

If "Joule-Thomson" with vol. doubling at speed w it is $\tau(\Pi) = O(\frac{L}{w})$

If "Joule-Thomson" with volume *suddenly* larger $\tau(\Pi) = 0$

If "Joule-Thomson" with volume side from L to $L(1+\delta)$ at speed w: $\tau(\Pi) = \frac{L}{w\delta}$

References: see *Statistical Mechanics and Fluid mechanics* books, (Springer–Verlag) **freely downloadable** and

`http://ipparco.roma1.infn.it`
`http://math.rutgers.edu/ giovanni`