Entropy, Thermostats and Chaotic Hypothesis

Problem: establish relations between time averages of a few observables associated with a system of particles subject to work-performing external forces and to thermostat-forces that keep the energy from building up (→ stationary state)

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`http://ipparco.roma1.infn.it`

References: see Archive

Stationary state = probability distribution μ on phase space $\mathcal{F}$

$$\frac{1}{\tau}\sum_{j=0}^{\tau-1} F(S^j x) \xrightarrow[\tau\to\infty]{} \int_{\mathcal{F}} F(y)\,\mu(dy) \qquad \text{(map)}$$

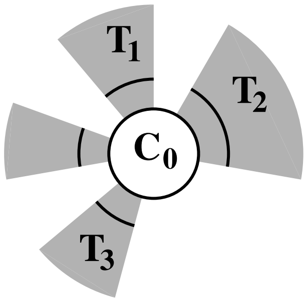
$$\frac{1}{\tau}\int_0^\tau F(S_t x)\,dt \xrightarrow[\tau\to\infty]{} \int_{\mathcal{F}} F(y)\,\mu(dy) \qquad \text{(flow)}$$

a.a. x. Flow: differential equation on $\mathcal{F}$:

$$\dot{x} = \mathbf{f}_{\mathbf{E}}(x)$$

with $\mathbf{f}_{\mathbf{E}}$ internal, external and thermostats forces. Divergence

$$\sigma(x) = -\sum_j \partial_{x_j} f_{\mathbf{E},\mathbf{j}}(x) \neq 0$$



$\mathbf{X_0}$: N_0 part. in $\mathcal{C}_0$ $\mathbf{X_i}, \mathbf{X'_i}$: N_i, N'_i part in $\mathcal{C}_i$ and $\mathcal{C}'_i$, $i = 1, \ldots, n$,
Equations of motion are, for $i = 0$ and $i > 0$ respectively,

$$\ddot{\mathbf{X}}_0 = -\partial_{\mathbf{X_0}}\Big(U_0(\mathbf{X_0}) + \sum\nolimits_{\mathbf{i>0}} \mathbf{W_{0i}}(\mathbf{X_0}, \mathbf{X_i})\Big) + \mathbf{E}(\mathbf{X_0})$$

$$\ddot{\mathbf{X}}_i = -\partial_{\mathbf{X_i}}\Big(U_i(\mathbf{X_i}) + \mathbf{W_{0i}}(\mathbf{X_0}, \mathbf{X_i}) + \mathbf{W_{i,i'}}(\mathbf{X_i}, \mathbf{X_{i'}})\Big)$$

$$\ddot{\mathbf{X}}'_i = -\partial_{\mathbf{X'_i}}\Big(U'_i(\mathbf{X'_i}) + \mathbf{W_{i,i'}}(\mathbf{X_i}, \mathbf{X'_i})\Big) - \alpha_{\mathbf{i}}\, \dot{\mathbf{X}}'_{\mathbf{i}}$$

Thermostat condition ("fixed temperatures")

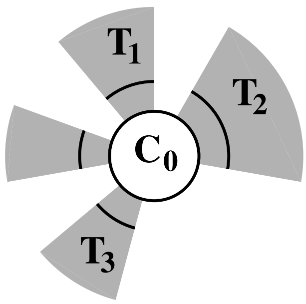
$$\frac{1}{2}\dot{\mathbf{X}}_i'^2 = \frac{3}{2}N_i' k_B T_i \qquad \Rightarrow \qquad \alpha_i = \frac{L_i - \dot{U}_i'}{3\,N_i'\,k_B T_i}$$

L_i = work on $\mathbf{X_i'} \in \mathcal{C}_\mathbf{i}'$, *i.e.* on thermostats.

$$L_i = -\dot{\mathbf{X}}_i' \cdot \partial_{\mathbf{X_i'}} \mathbf{W_{i,i'}}$$

Other thermostats: structure no influence on statistics in $\mathcal{C}_0$.

E.g. $\mathcal{C}_i'$ could be *infinite* in equilibrium at temperature T_i.



Divergence of the equations **easily** is $-\sigma(x)$ with

$$\sigma(x) = \sum_{i>0} \Big(\frac{L_i}{k_B T_i} - \frac{\dot U'_i}{k_B T_i}\Big)\frac{3N'_i - 1}{3N'_i} \stackrel{def}{=} \sum_{i>0} \frac{L_i}{k_B T_i} + \dot\Phi$$

But $L_i = -\dot X'_i \cdot \partial_{X'_i} W_{i,i'} \equiv +\dot X_i \cdot \partial_{X_i} W_{i,i'} - \dot W_{i,i'} = -L'_i - \dot W_{i,i'}$

$$\textit{Energy conservation} \text{ and } L_{0i} \stackrel{def}{=} -\dot{\mathbf{X}}_i \cdot \partial_{\mathbf{X_i}} W_{0i} \to$$

$$L'_i \equiv -L_{0i} + \frac{d}{dt}\Big(\frac12 \dot X_i^2 + U_i\Big) = -Q_i + \dot\Phi'$$

$L_{0i} \equiv Q_i$ work $\mathcal{C}_0$ on $\mathcal{C}_i$: $\equiv$ *heat* from $\mathcal{C}_0 \to \mathcal{C}_i \to$ thermostats $\mathcal{C}'_i$.

$$\varepsilon(x) \stackrel{def}{=} \sum_{i>0} \frac{Q_i}{k_B T_i} \qquad \Rightarrow \qquad \sigma(x) = \varepsilon(x) + \dot R$$

where $R(x) = -\sum_i \frac{(W_{i,i'} + U'_i + U_i + \frac12 \dot X_i{}^2)}{k_B T_i}$.

$\sigma(x)$ is *entropy creation*: large time same as $\varepsilon(x) = \sum_{i>0} \frac{Q_i}{k_B T_i}$

Difference $\frac{1}{\tau}(R(S_\tau x) - R(x)) \xrightarrow[\tau\to\infty]{}$, IF R is bounded.

Strong assumption.
"Efficiency"; violation interesting, [CvZ02,BGGZ05,Ga06,GG06].

Chaotic Hypothesis: *Motions developing on the attracting set of a chaotic system can be regarded as a transitive hyperbolic system.*

General: statistics μ uniquely determined probability.
Entropy creation rate to be

$$\varepsilon_+ = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \sigma(S_t x)\, dt = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau \varepsilon(S_t x)\, dt$$

Assume *dissipativity*: $\varepsilon_+ > 0$

$$p \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau \frac{\varepsilon(S_t x)}{\varepsilon_+}\,dt$$

"dim.less phase space contraction".

A general property $a = \frac{1}{\tau}\int_0^\tau F(S_t x)\,dt$

$$P_\mu(a\in\Delta) = \exp(\tau \max_{a\in\Delta} \zeta_F(a) + O(1))$$

for $\Delta\subset(a_-,a_+)$, where $\zeta_F(a)$ defined, analytic and convex.
$\zeta_F(a) = -\infty$ naturally for $a\not\in[a_-,a_+]$: *large deviations rate*

Reversible $\Rightarrow$ isometry I s.t. $IS_t = S_{-t}I$ or $IS = S^{-1}I$.
F odd, *i.e.* $F(Ix) = -F(x)$: fluctuation interval $[-a^*,a^*]$.

Fluctuation $\sigma(x)/\varepsilon_+$ and of $\varepsilon(x)/\varepsilon_+$ is **same** and, [CG95],[Ge98],

Fluctuation theorem: $\zeta(-p) = \zeta(p) - p\sigma_+$**,** $|p| < p^*$**.**

By CH FT holds for dimless contraction of any reversible chaotic motion with a dense attractor (call FR)

In particular to the model: where $\varepsilon(x) \stackrel{def}{=} \sum_{a>0} \frac{Q_a}{k_B T_a}$ has a physical meaning and can be measured in experiments even without equations of motion

The quantity $\varepsilon(x)$ is *local*; depends only on the microscopic conf. of $\mathcal{C}_0$ and of the walls $\mathcal{C}_i$. One can also imagine FR remains valid with ∞-thermostats

Quite a few tests of CH and FR [BGGZ06] (granular materials).

Extending Onsager-Machlup's theory and Reciprocity + Green-Kubo

Fluctuation patterns: probability that the successive $F(S_t x)$ follow, for $t \in [-\tau, \tau]$, a preassigned *pattern* $\varphi(t)$, [Ga97].

In a reversible hyperbolic and transitive system consider n observables $F_1, \ldots, F_n$ with $F_j(Ix) = \pm F_j(x)$. Given n functions $\varphi_j(t)$, $t \in [-\frac{\tau}{2}, \frac{\tau}{2}]$:

probability that $F_j(S_t x) \sim \varphi_j(t)$ for $t \in [-\frac{\tau}{2}, \frac{\tau}{2}]$? FPT theorem:

Fluctuation Patterns Theorem: *Under assumptions of FT given F_j, φ_j, and given $\varepsilon > 0$ and an interval $\Delta \subset (-p^*, p^*)$ SRB-probability*

$$\frac{P_\mu(|F_j(S_t x) - \varphi_j(t)|_{j=1,\ldots,n} < \varepsilon, p \in \Delta)}{P_\mu(|F_j(S_t x) \mp \varphi_j(-t)|_{j=1,\ldots,n} < \varepsilon, -p \in \Delta)} =$$
$$= \exp(\tau \max_{p\in\Delta} p\,\sigma_+ + O(1))$$

FPT means "all that has to be done to change the time arrow is to change the sign of the entropy production", *i.e.* the *time reversed processes occur with equal likelyhood as the direct processes if conditioned to the opposite entropy creation.*

Application, [Ga96a,Ga96] with $j_j(x) = \partial_{E_j}\sigma(x)$ is *Green–Kubo formulae* hence Onsager recip.

Jarzinsky, Bonetto and Fluctuation relations

Bonetto's forml., BF, [Ga00]: FT or FR imply $\langle e^{-\int_0^\tau \varepsilon(S_t x)\,dt}\rangle_{SRB}$ **bounded** as $\tau\to\infty$: *would be exactly* 1 if FR true finite τ.

Jarzinsky's forml., JF: Let γ be a function $H(,p,q,t)$ interpolating between $H_0(p,q)$ and $H_1(p,q)$, called a "protocol γ". Let $S_{0,t}(p,q)$ be the time evolution of (p,q) under the time dependent protocol. Let $(p',q') = S_{0,1}(p,q)$ and $W(p',q') = H_1(S_{0,1}(p,q)) - H_0(p,q)$:

$$\frac{Z_0}{Z_1} e^{-\beta W(p',q')}\frac{e^{-\beta H_0(p,q)}}{Z_0} dp dq \equiv \frac{e^{-\beta H_1(p',q')}dp'dq'}{Z_1},\ \textit{hence}$$
$$\langle e^{-\beta W}\rangle_{\mu_0} = \frac{Z_1}{Z_0} = e^{-\beta \Delta F(\beta)}$$

ΔF = free energy variation between equilibria H_1 and H_0.

JF is *exact*, an instance of the Monte Carlo method. It can be implemented *without actually knowing* neither H_0 nor H_1 nor the *protocol* $H(p,q,t)$ to evaluate ΔF. *But* BF and JF quite different:

(1) $\int_0^\tau \sigma(S_t x)\,dt$ is entropy creation not energy variation W (W "work done by the machines implementing the protocol").

(2) average is SRB of a stationary state, out of equilibrium, not a canonical equilibrium state.

(3) the BF says that $\langle e^{-\int_0^\tau \varepsilon(S_t x)\,dt}\rangle_{SRB}$ is bounded as $\tau \to \infty$ rather than being 1 exactly.

JF: very useful in equilibrium problems.

In a steady state with entropy at rate ε_+ (*e.g.* **a living organism peacefully feeding on a background**) CH $\to$ FR $\to$ BF gives informations on heat produced: could check that all relevant heat transfers have been properly taken into account.

Def Irreversibility time scale for process Π

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

Quasi static $\Pi: \ \mathbf{F(t)} = \mathbf{F_0} + (\mathbf{1} - \mathbf{e}^{-\gamma \mathbf{t}})(\mathbf{F}_\infty - \mathbf{F_0})$

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: $\tau(\Pi) = \frac{L}{w\delta}$

Is the definition of Entropy consistent with Nonequilibrium Thermodynamics?

$$\varepsilon(x) = \sum_{i>0} \frac{Q_i}{k_B T_i} \Rightarrow \int_{\partial\mathcal{C}_0} \frac{Q(\boldsymbol{\xi})}{k_B T(\boldsymbol{\xi})} ds_{\boldsymbol{\xi}}$$

$$\langle\varepsilon\rangle = -\int_{\partial\mathcal{C}_0} \kappa \frac{\mathbf{n}(\boldsymbol{\xi}) \cdot \partial \mathbf{T}(\boldsymbol{\xi})}{\mathbf{k_B T}(\boldsymbol{\xi})} ds_{\boldsymbol{\xi}}$$

The fluid equations are

$$(1)\;\; \underline{\partial} \cdot \underline{u} = 0$$

$$(2)\;\; \partial_t \underline{u} + \underset{\sim}{u} \cdot \underset{\sim}{\partial} \underline{u} = -\frac{1}{\rho} \underline{\partial} p + \nu \Delta \underline{u} + \underline{g}$$

$$(3)\;\; \rho\, c\, (\partial_t T + \underline{u} \cdot \underline{\partial} T) \;=\; \eta\, \underset{\approx}{\tau}{}' \underline{\partial}\underset{\sim}{u} + \kappa \Delta T$$

Classical entropy production:

$$k_B \langle\varepsilon\rangle_\mu = \int_{\mathcal{C}_0} \Big(\kappa \,\big(\frac{\underline{\partial} T}{T}\big)^2 + \eta\, \frac{1}{T} \underset{\approx}{\tau}{}'\, \underline{\partial}\underset{\sim}{u}\Big)\, d\underline{x}$$

By integration by parts and use of the first and third $k_B \langle\varepsilon\rangle_\mu$ becomes the previous expression.
Entropy is created at the contact with the thermostats.

$$
\begin{aligned}
&\int_{\mathcal{C}_0} \Big(- \kappa\, \underline{\partial} T \ \cdot \ \underline{\partial} T^{-1} + \eta\, \frac{1}{T} \underset{\approx}{\tau}\,'\, \underline{\partial} \underset{\sim}{u} \Big)\, d\underline{x} = \\
&- \int_{\partial \mathcal{C}_0} \kappa\, \frac{\underline{n} \cdot \underline{\partial} T}{T}\, ds_{\boldsymbol{\xi}} + \int_{\mathcal{C}_0} \frac{1}{T} (\kappa \Delta T + \eta\, \underset{\approx}{\tau}\,' \underline{\partial} \underset{\sim}{u}) d\underline{x} = \\
&- \int_{\partial \mathcal{C}_0} \kappa\, \frac{\underline{n} \cdot \underline{\partial} T}{T}\, ds_{\boldsymbol{\xi}} + \int_{\mathcal{C}_0} \frac{\underline{u} \cdot \underline{\partial} T}{T\, c\, \rho}\, d\underline{x} = \\
&- \int_{\partial \mathcal{C}_0} \kappa\, \frac{\underline{\partial} T \cdot \underline{n}}{T}\, ds_{\boldsymbol{\xi}} - \int_{\partial \mathcal{C}_0} \underline{u} \cdot \underline{n} \frac{\log T}{c\, \rho} ds_{\boldsymbol{\xi}}
\end{aligned}
$$