Hyperbolic systems and fluctuation theorems

Question: Is Thermodynamics extendible to nonequilibrium phenomena?

Minimal program: extension to stationary states

This means asking more than whether *Temperature,Entropy, Energy …* can be defined.

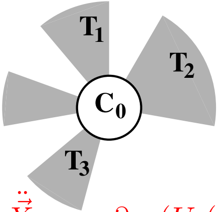
First problem is that to keep a system stationary out of equil. *dissipation* is necessary.

Dissipation requires that the system interacts with *thermostats*.

Should be modeled fundamentally as *infinite systems* capable of sustaining *e.g.* a temperature *gradient*.

This implies that the ambient space has to be 3 dimensional (no harmonic function exists if ≤ 2 in infinite space).

Major advance has been the proposal of treating the thermostats *phenomenologically* (Hoover,Evans '980s).



$$U_i = \sum_{jk} v(q_k - q_j)$$

$$W_{0i} = \sum_{j\in C_0, k\in T_i} v(q_k - q_j)$$

$$\alpha_i = \frac{\sum_{j\in C_0,k\in T_i}(\partial_{q_k} v(q_k-q_j)-\dot U_k)}{k_B T_k}$$

$$\ddot{\vec X}_0 = -\partial_{\vec X_0}(U_0(\vec X_0)+\sum_{i>0} W_{0i}(\vec X_0,\vec X_i)) + \vec E(\vec X_0)$$

$$\ddot{\vec X}_i = -\partial_{\vec X_i}(U_i(\vec X_i)+W_{0i}(\vec X_0,\vec X_i)) - \alpha_i \dot{\vec X}_i$$

α_i s.t. $\frac{m}{2}\sum_{i>0}\dot{\vec X}_i^2 = \frac12 N_i k_B T_i$ const: $\alpha_i = \frac{L_i - \dot U_i}{N_i k_B T_i}$

Prelim.: does it matter? if $d \le 3$ & smooth pair interactions

Theorem: *a.a. data $\vec X$ chosen with a distribution in which the thermostats are in a Gibbs state with temperatures T_i evolved into $\vec X(t)^{[n]}$ by letting move only particles in a ball of radius $r2^n$ with or without $a_i\dot{\vec X}_i$ converge to the SAME $\vec X^\infty$, exponentially fast at fixed distance from 0.* (Presutti, GG)

Open: does the evolution lead to a stationary distribution? only partial unsatisf. answers for finite thermostats.

NEQ Thermodynamics starting point is the Ruelle's principle for fluids: as in equil. $\exists$ a single natural statistics for stationary states: because dynamic is *hyperbolic*.

Chaotic hypothesis: (Cohen, G) *Motions on the attracting set of a chaotic system can be regarded as motions of a smooth transitive reversible hyperbolic system.*

Mathematical meaning: There exist reversible Markovian partitions $\mathcal{P} = (P_1, \ldots, P_n)$. Usable to prove general properties: none proposed since Onsager reciprocity.

History of x on $\mathcal{P}$, $\vec{\sigma} = \{\sigma_i\}_{i=0}^{\infty}$ s.t. $S^i x \in P_{\sigma_i}$ defines an adapted coordinate for x determining x with exponential precision and makes dynamics universal

FT: The stationary distr. of the random variable

$$p=\frac{1}{\tau}\sum_{k=0}^{\tau}\frac{s(S^k\vec X)}{\langle\, s\,\rangle_{srb}},\qquad Prob(p\in\Delta)=e^{\tau\,\max_{p\in\Delta}\zeta(p)+o(\tau)}$$

then $\frac{Prob(p)}{Prob(-p)}=e^{-p\tau\langle\, s\,\rangle}$: more precisely exact symmetry

$$\zeta(-p)=\zeta(p)-p\,\langle\, s\,\rangle_{srb}$$

Importance: $s(\vec X)$, hence p has a physical interpretation: $i.e.$ it is the *entropy increase of the thermostats*.

Experimentally accessible and the Fluctuation Relation is model independent; possibly first non trivial general noneq. property after Onsager reciprocity (OR).

Time reversal leads to many other FRs.

If $F_1(\vec X),\ldots,F_n(\vec X)$ are n TR-odd obs., $(F_i(Ix)=-F_i(x))$, given n patterns $\varphi_1(t),\ldots,\varphi_n(t)$ then

If $F_1(\vec{X}),\ldots,F_n(\vec{X})$ are n TR-odd obs. ($F_i(Ix)=-F_i(x)$), given n patterns $\varphi_1(t),\ldots,\varphi_n(t)$ then

$$\frac{Prob(\{F_i(S^k\vec{X})\overset{\varepsilon}{=}\varphi_i(k)\}_{k=\tau}^{\tau},p)}{Prob(\{F_i(S^k\vec{X})\overset{\varepsilon}{=}-\varphi_i(-k)\}_{k=\tau}^{\tau},-p)} =_{\tau\to\infty} e^{p\,\tau\,\langle\, s\,\rangle}$$

again no free parameters (and independent on F_i).

"*All needed to reverse time is to reverse entropy production*". also $\Rightarrow$ OR & Green-Kubo.

How the CH can be viewed from Physics? it allows to define precisely coarse graining, to count phase space points, to better understand of entropy and finally to a "natural proposal" of quantitative meas. of quasi-static processes.

Coarse graining on a MP $\mathcal{P}=\{P_1,P_2,\ldots,P_s\}$;

MP $\to$ code by $\{\sigma_i\}_{i=-\infty}^{\infty}$ s.t. $x\longleftrightarrow\{\sigma_i\}_{i=-\infty}^{\infty}$ s.t. $S^i x\in P_{\sigma_i}$

Refine $\mathcal{P}\to\mathcal{P}_n$ s.t. "all" F are constants on sets of $\mathcal{P}_n$

Sets in $\mathcal{P}_n = \{P(\sigma_{-n}, \ldots \sigma_n) \stackrel{def}{=} \cap_{-n}^{n} S^{-i} P_{\sigma_i}\}_{\vec\sigma}$

The $P_{\sigma_{-n},\ldots\sigma_n} \equiv P(\vec\sigma)$ will be called coarse grained cells.

The SRB is a distribution with weight $w(\vec\sigma)$ for $P(\vec\sigma)$ and admits an explicit formula

$$w(\vec\sigma) = e^{-\Lambda_{u,n}(\vec\sigma)} \;\Rightarrow\; \mu_{SRB}(P(\vec\sigma)) = \frac{e^{-\Lambda_{u,n}(\vec\sigma)}}{\sum_{\vec\sigma'} e^{-\Lambda_{u,n}(\vec\sigma')}}$$

Interpretation ($\frac{1}{2}$-heuristic): in simulations phase space is discrete and evolution is a map on a finite space.

Discard nonrecurrent points (*i.e.* transient, present in any code): remain those on the "attractor" $\mathcal{A}$.

Thier number in $\mathcal{A} \cap P(\vec\sigma)$ is the fraction of the total $\mathcal{N}$

$$\mathcal{N}(\vec\sigma) = \mathcal{N}\mu_{SRB}(P(\vec\sigma))$$

and evolution is a one cycle permutation of $\mathcal{A}$, "ergodicity"

This unifies equilibrium and nonequilibrium:
In the first case all points are recurrent (ergodicity) and

$$w(\vec{\sigma}) = volume(P(\vec{\sigma})$$

In both cases the stationary dist. is equal weight of the phase space points, *i.e.* SRB $\supset$ Boltzmann.

It becomes possible therefore to count the number of points: is it nonequilibrium Entropy ??

(My) answer NO!: both in equilibrium and nonequilibrium the count is ambiguous: it depends on the precision "ε" of discretization.

BUT equil. ambiguity = an additive constant ("$3N \log \hbar$") independent on the state.

This is not the case out of equilibrium: still ambiguous by additive constant which is state dependent (in example (GG) depends on density and temp. as ε changes).

Nevertheless $S_{\mathcal{P},\varepsilon} = k_B \log \mathcal{N}_{\mathcal{P},\,\mathcal{A},\,\varepsilon}$ is maximal among all distributions on the attractor.

Simply as it corresponds to equal weights: hence it can play the role of Lyapunov function measuring the distance of an evolving distribution to the SRB; just as in equilibrium !!

What about processes? transforming μ_{ini} into another μ_{fin}? under external parameters $\Phi(t)$ changes of (forces, thermostats temperatures, volume, &tc) as $0 \le t \le +\infty$.

At $0 < t < \infty$ time evolution $x = (\dot{\vec{X}}, \vec{X}) \to x(t) = S_{0,t}x$ is non autonomous evolution. Initial state evolves into μ_t

$$\langle\, F \,\rangle_{\mu_t} = \int_{\mathcal{F}(t)} \mu_t(dx) F(x) \stackrel{def}{=} \int_{\mathcal{F}(0)} \mu_0(dx) F(S_{0,t}^{-1} x)$$

Imagine $\Phi(t)$ stepping from $\Phi(0)$ to $\Phi(\infty)$. Clearly

$$\langle\, F \,\rangle_{\mu_{srb}(t)} \neq \langle\, F \,\rangle_{\mu_t}$$

In the previous model phase space contraction is

$$s(\dot{\vec{X}}, \vec{X}) = \sum_a \frac{\dot{Q}_a}{k_B T_a} - N \frac{\dot{V}_t}{V_t} - \sum_a \frac{\dot{U}_a}{k_B T_a}$$

which dimensionally is a $time^{-1}$.

It is natural (GG) to introduce the quantity

$$t^{-1}_{irreversibiiy} = \frac{1}{N^2} \int_0^{+\infty} \Big(\langle\, s(t)\,\rangle_{\mu_t} - \langle\, s(t)\,\rangle_{SRB,t} \Big)^2 dt$$

By Chaotic Hypothesis μ_t evolve to $\mu_{SRB,t}$ exponentially fast under the "frozen evolution".

Therefore the integral will converge.

The slower the evolution the smaller the integral: it will $\to 0$ as evolution slows down:

$$t_{irreversibility} \to +\infty$$

Interpretation:

$t_{irreversibility}$ is the time necessary to realize that the process is irreversible

This makes sense both in equilibrium thermodynamics and out of equilibrium

Example: Joule-Thomson: (gas expansion in a piston)

S = section; $H_t = H_0 + w\,t$ distance base-moving lid;

$\Omega = S\,H_t$ increases at rate $N\frac{w}{H_t}$.

Hence $\langle\, s_t \,\rangle_t$ is $-N\frac{w}{H_t}$, while $s_t^{srb} \equiv 0$.

$T = \frac{L}{w}$ process duration (to increase height by L)

$$t^{-1}_{irreversibility} = N^{-2}\int_0^T N^2 \Big(\frac{w}{H_t}\Big)^2 dt \xrightarrow[T\to\infty]{} w\frac{L}{H_0(H_0+L)}$$

immediately, if $w = \infty$, irreversibility becomes apparent
never, if $w \to 0$: quasi static $\equiv \infty$-slow.

In any event "quasi staticity" becomes quantitative notion

In the latter example it is customary to estimate the degree of irreversibility at the lift of the lid by the *thermodynamic equilibrium entropy* change between initial and final states.

It would of course be interesting to have a general definition of entropy of a non stationary state (like the states μ_t at times ($t \in (0, \infty)$ in the example just discussed) to allow connecting irreversibility time scale to thermodynamic entropy variation in processes leading from an initial equilibrium state to a final equilibrium state.

It is also not inconceivable a quantitative study of the irreversibiliy of attempts at realizing Carnot cycles.

References