Morally, it works: on current applications of ergodic concepts in statistical physics

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AUGURI ANGELO!!

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Phys. A 2007; J. Stat. Phys. 2007; Nonlinearity 2007; Phys. Rep. 2008; J. Phys. A 2010; J. Chem. Phys. 2012; Large Deviations in Physics 2014; Reductionism Emergence and Levels of Reality, 2014

Outline

- Something we know (even though not always appreciated)
 - Hamiltonian particle systems
 - Ergodic inconsistencies
 - Sufficient conditions
- 2 Something we are finding out: necessary conditions
 - Dissipation Function Ω
 - Ensemble Response: necessary conditions
 - Steady State Flucutation Relations, T-mixing and Response

3 Discussion

Hamiltonian particle systems Ergodic inconsistencies Sufficient conditions

To describe natural phenomena we make choices, motivated by purpose of description.

Each description at best faithful to some aspects of phenomenon. Different descriptions complement each other.



Gran Sasso: pictures from north are correct and realistic, but do not show south side.

Deterministic and stochastic, hamiltonian and dissipative often contrasted, although complementary and closely related. Today I choose classical mechanics atomism. I must abide by its ruels (convincing or not).

Hamiltonian particle systems Ergodic inconsistencies Sufficient conditions

Hamiltonian particle systems

 $\mathcal{M}=$ space space of "microscopic" phases of system,

e.g.: $\Gamma = (\mathbf{q}, \mathbf{p}) \in \mathcal{M} \subset \mathbb{R}^{6N}$, plus evolution rule: $\dot{\Gamma} = \mathcal{G}(\Gamma)$

 $S^t: \mathcal{M} \to \mathcal{M}$ evolution operator (Γ at time 0, $S^t\Gamma$ at time t).

For instance: adopt Hamiltonian dynamics, successful for several macroscopic objects, in case of assemblies of $N \gg 1$ atoms!

$$\dot{\mathbf{q}} = rac{\partial H}{\partial \mathbf{p}} \;, \;\; \dot{\mathbf{p}} = -rac{\partial H}{\partial \mathbf{q}}$$

For observable \mathcal{O} , assume Γ corresponds to a value $\mathcal{O}(\Gamma) \in \mathbf{R}$.

Macroscopic measurement takes a time T, so let us say it yields average over values $\mathcal{O}(S^t\Gamma)$ taken along trajectory, for a time T.

Which properties of matter are described by our assumptions on atomic dynamics?

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Measurement depends on T (subjective) and on Γ (stochastic). For thermodynamics, microscopic events must occur on time scales much shorter than observation scales, so that:

$$\overline{\mathcal{O}}^{T}(\Gamma) = \frac{1}{T} \int_{0}^{T} \mathcal{O}(S^{t}\Gamma) \, \mathrm{d}t \approx \overline{\mathcal{O}}(\Gamma) = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} \mathcal{O}(S^{t}\Gamma) \, \mathrm{d}t \approx o \in \mathbf{R}$$

For instance: $\overline{\mathcal{O}}^{T}$ indistinguishable from asymptotic mean and almost independent of Γ , if in time T, $\mathcal{O}(S^{t}\Gamma)$ spans range of \mathcal{O} .

Fermi: With increasing time, the system exists successively in all the dynamical states that correspond to the given thermodynamical state. From this point of view we may say that a thermodynamical state **IS** the ensemble of all the dynamical states through which, as a result of the molecular motion, the system is **rapidly** passing.

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Fermi referred to microscopic phases in $\ensuremath{\mathcal{M}}$



Hamiltonian particle systems Ergodic inconsistencies Sufficient conditions

Is this ever the case? Existence of $\overline{\mathcal{O}}(\Gamma)$ proven by Birkhoff. Dependence on Γ problematic.

Ergodic Hypothesis (in its modern form) states that \mathcal{M} is densely explored by almost all trajectories.

Then, in due time $\mathcal{O}(S^t\Gamma)$ certainly spans range of \mathcal{O} . More: there is *invariant* distribution μ , the *ensemble*, such that for *every* observable:

 $\overline{\mathcal{O}}(\Gamma) = \int \mathcal{O}(\Gamma) \, \mathrm{d}\mu(\Gamma) \equiv \langle \mathcal{O} \rangle_{\mu} \,\,, \quad \text{for μ-almost every $\Gamma \in \mathcal{M}$}$

Fermi thought ergodicity (in this metric transitive sense) is generic; he stumbled on the intricate structure of phase space dynamics...

Ensemble phase space descriptions are indeed insidious!

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For illustration, let $\mathcal{M} = [0,1] imes [0,1]$, $v = (v_x,v_y)$ constant

$$S^t \Gamma = (x + v_x t, y + v_y t) \mod 1$$

 $\Gamma = (x, y) \in \mathcal{M}$

If v_x/v_y is irrational, each trajectory explores densely \mathcal{M} . Only invariant density $\rho(\Gamma) = 1$: *uniform distribution*, $d\mu = dxdy$

Ensembles of Γ 's do not spread to cover uniformly ${\mathcal M}$ so

regarding phase space behaviour as analogous to real space behaviour; ensemble members as analogous to molecules

often leads to state that representing relaxation (*e.g.* ideal gas expanding in its container) requires **more** than ergodicity.

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Mixing: let μ be invariant and $E, F \subset \mathcal{M}$ measurable,



$$\lim_{t\to\infty}\mu\left(E\cap S^{-t}F\right)-\mu(E)\mu(F)=0$$

$$\lim_{t \to \infty} \int \mathcal{O}\left(S^{t} \Gamma\right) \mathcal{Q}\left(\Gamma\right) d\mu - \int \mathcal{O}\left(\Gamma\right) d\mu \int \mathcal{Q}\left(\Gamma\right) d\mu$$

 $=\lim_{t\to\infty}\left\langle \left(\mathcal{O}\circ S^t\right)\mathcal{Q}\right\rangle _{\mu}-\left\langle \mathcal{O}\right\rangle _{\mu}\left\langle \mathcal{Q}\right\rangle _{\mu}=0$

Again, for phase space volumes conserving dynamics, the uniform is the only invariant density, but in a very different fashion: initial ensemble of Γ 's spreads to cover uniformly \mathcal{M} .

Above seems to be confirmed by following little "argument": $d\mu_0(\Gamma) = f_0(\Gamma)d\Gamma$ a non-invaraint *"initial ensemble"* representing initial macrostate (*e.g.* gas confined in left half of box) $d\mu_t(\Gamma) = f_t(\Gamma) d\Gamma$ evolution of μ_0 If (\mathcal{M}, μ, S^t) is mixing, with invariant $d\mu(\Gamma) = d\Gamma$: $\left\langle \mathcal{O} \right\rangle_{t} = \int \mathcal{O}(\Gamma) f_{t}(\Gamma) \mathrm{d}\Gamma = \int \mathcal{O}\left(S^{t}\Gamma\right) f_{0}(\Gamma) \mathrm{d}\Gamma = \left\langle \left(\mathcal{O} \circ S^{t}\right) f_{0} \right\rangle_{\mu}$ $\stackrel{t \to \infty}{\longrightarrow} \langle \mathcal{O} \rangle_{\mu} \langle f_0 \rangle_{\mu} = \langle \mathcal{O} \rangle_{\mu}$

In other words, provided initial state is represented by f_0 and μ is mixing, observable values "relax" to microcanonical averages.

Microcanonical is uniform \Rightarrow gas eventually uniform in container.

Mixing: sufficient for irreversible(!) relaxation to equilibrium.

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Myriads of inconsistencies.

- Mixing stronger than ergodicity, which is almost never verified
- Mixing possible with 2 particles in a square: no notion of



uniform mass distribution; dim \mathcal{M} =8, hard to connect with square (real space); uniform probability density in \mathcal{M} only means ensemble

member on left equally probable as member on right.

- Even for $N \gg 1$, uniform μ only means one Γ out of infinitely many in abstract collection, equally probable as any other Γ : this uniform mass distribution equally likely as that non-uniform mass distribution...
- If f_t evolves, Fermi's statement not realized: average at t over ensemble of (abstract) systems represents no concrete system; different ensemble members yield different time averages.

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Mass density makes sense only for large N, and large N means that mass distributions approximating uniformity are overwhelmingly more "numerous" than those filling only part of container.

More numerous even when phase space probability density is not uniform;

numerosity has no relation with probability distributions and their evolution: just count

Gas may relax to uniform **mass** distribution in isolated container even if **probability** does not evolve towards uniformity in \mathcal{M} . Mixing or ergodic, time averages are the same.

If f evolves, system does not need to. Invariant μ , system evolves.

If f is high in a region of \mathcal{M} and low in another, it does not mean that **mass** density is high or low in a region of real space.

System "relaxes" to by far most numerous state, with negligble fluctuations, both forward and backwards in time. **Just count.**

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Counting with continuum of states?

In discrete case, counting is *natural*: possible square arrangements of $10^3 \times 10^3$ black and white pixels: 2^{10^6} pictures. Dull movie:

- Pictures projected at constant pace (25 frames a second)
- according to deterministic sequence.
- Movie goes through all pictures and starts again; period $> 10^{301020}$ years. \mathcal{M} contains all photos ever shot, including Angelo's face...
- Remotely regular photos are very small fraction of totality; overwhelming majority look gray, approximately half black and half white.





I. Pitowsky: in continuous case, Lebesgue naturally extends counting (proceed from binary representation of [0, 1]).

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For rarefied gases, phase space idiosyncrasies are irrelevant:

- a) systems with $N \gg 1$;
- b) several physical observables, and special;
- c) no problem if ensemble averages do not coincide with time averages on small sets of trajectories.

Khinchin: let $H = \sum_{n=1}^{N} H_n(\mathbf{q}_n, \mathbf{p}_n)$ and consider sum functions $f(\Gamma) = \sum_{n=1}^{N} f_n(\mathbf{q}_n, \mathbf{p}_n)$ (e.g. P,T of rarefied gas).

In microcanonical cases

$$\operatorname{Prob}\left(\frac{|\overline{f} - \langle f \rangle|}{|\langle f \rangle|} \ge K_1 N^{-1/4}\right) \le K_2 N^{-1/4} ,$$

Statistical properties needed for (equilibrium) thermodynamics only due to some kind of randomness and $N \gg 1$.

Microscopic dynamics: irrelevant!

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One way or another, irreversibility and relaxation to equilibrium for single systems is **sufficiently** justified by counting; details of micro-dynamics and ensembles not necessary.

One could argue that not all systems are rarefied and not all observables are sum functions (Prigogine). But...

Morally it works! (AV)

Conjecture. AV refers to:

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The above is (appears to be) the simplest framework reconciling classical hamiltonian atomism with observations.

Merit: it is sufficient but rather minimal.

However, other scenarios may be envisaged.

And what about dissipation?

Dissipation amounts to constraints which make typical vanishing subvolumes of the phase space, e.g. the rarest equilibrium current fluctuations become the steady state value.

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$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i \mathbf{F}_e$$
; $\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \mathbf{F}_e - \alpha \mathbf{p}_i$

 $\alpha(\Gamma) =$ deterministic time reversible term to add or remove energy

 \propto phase space volumes contraction rate \propto dissipative flux J Model chosen because phase space volumes contraction related to expression for SRB probability distribution of Anosov systems (formalized by Gallavotti-Cohen '95).

Like mixing: Anosov apparently **sufficient**, but almost never verified; even assuming it **morally**, it misses physical scales, observables of interest, etc. while FR for energy dissipation tested and commonly verified within physically relevant regimes.

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Question: if FR verified for physically relevant variables and scales, which mechanisms are at work? Necessary conditions unveil unavoidable physics.

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Dissipation Function Ω Ensemble Response: necessary conditions Steady State Flucutation Relations, T-mixing and Response

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Reversible: $S^t i = iS^{-t}$, where i = time reversal involution,

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Let $f^{(0)} =$ initial distribution.

Dissipation function:

 $\Omega^{(0)} = -G \cdot \partial_{\Gamma} \ln f^{(0)} - \Lambda$

 $\Omega_{t,t+\tau}^{(0)}(\Gamma) = \int_t^{t+\tau} \Omega^{(0)}(S^s\Gamma) \mathrm{d}s = \ln \frac{f^{(0)}(S^t\Gamma)}{f^{(0)}(S^{t+\tau}\Gamma)} - \int_t^{t+\tau} \Lambda(S^s\Gamma) \mathrm{d}s$

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Transient FRs and Response

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

The definition of $\boldsymbol{\Omega}$ and time reversibility yield

$$\frac{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in \mathcal{A}_{\delta}^{+})}{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in \mathcal{A}_{\delta}^{-})} = \frac{\int_{\mathcal{A}_{\delta}^{+}} f^{(0)}(\Gamma) \mathrm{d}\Gamma}{\int_{\mathcal{A}_{\delta}^{-}} f^{(0)}(\Gamma) \mathrm{d}\Gamma} = \exp\left\{\tau\left[\mathcal{A} + \epsilon(\mathcal{A}, \delta, \tau)\right]\right\}$$

where $\epsilon(A, \delta, \tau) \leq \delta$

Transient Ω -FR: (unbreakable) identity for a property of $f^{(0)}$, $\forall \tau$ only time reversibility and symmetry of $f^{(0)}$.

Dissipation Function Ω Ensemble Response: necessary conditions Steady State Flucutation Relations, T-mixing and Response

Trivial identities, transient FRs describe **ensembles** of experiments whose initial conditions are distributed as $f^{(0)}$ (like Jarzynski etc). Obtain equilibrium properties from nonequilibrium dynamics, closing circle with Fluctuation Dissipation Relation. Unbreakable. Revealed (for instance) deterioration of lubricant in this microscope.

Indirect access to non-accessible quantities.

Ubiquitous $\Omega^{(0)}$.

What about steady state FRs? What about statistics of fluctuations along single, long evolution?

Move from statistics of $\mu^{(0)}$ to statistics of steady state μ_{∞} , provided it exists.



Figure 2.9. This photo was taken in June 2005, after the system was significantly modified. The components in the photo are: (1) Nihon Diaphot 300 inverted microscope, (2) Microscope objectives, (3) Microscope stage, (4) Coherrent Compass 400M Laser, (5) BEOC Laser Stabiliser, (6) MT11F0 CCO Comera, (7) Physik Instrumente Piero Translator, (8) replacement control computer with custom written Labview software, (9) Sample Cell 1011 in in-house.

Trivial identities, transient FRs describe **ensembles** of experiments whose initial conditions are distributed as $f^{(0)}$ (like Jarzynski etc). Obtain equilibrium properties from nonequilibrium dynamics, closing circle with Fluctuation Dissipation Relation. Unbreakable. Revealed (for instance) deterioration of lubricant in this microscope.

Indirect access to non-accessible quantities.

Ubiquitous $\Omega^{(0)}$.

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Dissipation Function Ω Ensemble Response: necessary conditions Steady State Flucutation Relations, T-mixing and Response

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Steady state FRs

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

Take
$$t \to \infty$$
 to let $\mu^{(t)} \to \mu_{\infty}$.

Then $au o \infty$ should kill $\ln \langle .
angle_{\overline{\Omega}_{t,t+ au}^{(0)} \in A_{\delta}^+}^{(0)}$

But $t o \infty$ before au, hence $\Omega_{0,t}^{(0)}$, $\ln \langle ... \rangle_{\overline{\Omega}_{t,t+ au}^{(0)} \in A_{\delta}^{+}}^{(0)}$ may diverge.

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Image: A image: A

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Dissipation Function Ω Ensemble Response: necessary conditions Steady State Flucutation Relations, T-mixing and Response

$${f f} = {1\over au} \ln \langle ...
angle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+ au} \in {\cal A}^+_{\delta}}$$

does not diverge with t, we have:

steady state FR with $O(1/\tau)$ correction, for **Dissipation Function.**

What kind of condition is this?

Necessary condition. If it diverges: FR is violated!

Moreover, suppose "f⁽⁰⁾-correlations" decay instantaneously:

$$\left\langle e^{-\Omega^{(0)}_{0,t}}\cdot e^{-\Omega^{(0)}_{t+ au,2t+ au}}
ight
angle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+ au}\in A^+_{\delta}}=1$$

Steady state FR immediately verified.

Condition on correlations with respect to initial ensemble.

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 Something we know (even though not always appreciated)
 Dissipation Function Ω

 Something we are finding out: necessary conditions
 Ensemble Response: necessary conditions

 Steady State Flucutation Relations, T-mixing and Response

New property concerning: initial (equilibrium) distribution $f^{(0)}$ and nonequilibrium dynamics S^t , which we call **T**-mixing:

$$\lim_{t\to\infty} \left[\left\langle \left(\mathcal{O} \circ S^t \right) \mathcal{P} \right\rangle^{(0)} - \left\langle \mathcal{O} \right\rangle^{(t)} \left\langle \mathcal{P} \right\rangle^{(0)} \right] = 0$$

Many exact and completely general relations involving Ω , e.g.:

Average Response

$$\langle \mathcal{O}
angle^{(t)} = \langle \mathcal{O}
angle^{(0)} + \int_0^t \mathrm{d} s \left\langle \left(\mathcal{O} \circ S^s
ight) \Omega^{(0)}
ight
angle^{(0)}$$

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Because $\langle \Omega^{(0)} \rangle^{(0)} = 0$, T-mixing means: $\langle (\mathcal{O} \circ S^t) \Omega^{(0)} \rangle^{(0)} \to 0$ We call Ω T-mixing the situation in which

$$\langle \mathcal{O} \rangle^{(\infty)} = \langle \mathcal{O} \rangle^{(0)} + \int_0^\infty \mathrm{d}s \left\langle \left(\mathcal{O} \circ S^s \right) \Omega^{(0)} \right\rangle^{(0)}$$
 exists

 $\Omega\mathsf{T} ext{-mixing}$ necessary for convergence of ensemble response.

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 Ω T-mixing **necessary** for convergence of ensemble response.

What does Ω T-mixing mean?

Correlations between \mathcal{O} and *dissipation*, $\Omega^{(0)}$, i.e. correlations with initial ensemble (possibly **macrostate**) rapidly vanish.

That's why (average) convergence to steady state follows.

Different from **microscopic** correlations decay **within** mixing steady state.

Too bad! Ensemble results are worthless, aren't they?

It depends:

i. collections of small systems, e.g. colloidal particles, in a fluid;ii. in general: conditions in which microstates (in the sense of intervals of values of observables) are not rapidly explored.

They make ensembles real and single system results irrelevant. Let us investigate further this possibility.

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 Discussion
 Steady State Flucutation Relations, T-mixing and Response

T-mixing implies unique ensemble average, independent of initial ensemble: take

$$\mathcal{O}$$
 and $\mathcal{Q} = h_0/f_0$, with $h_0 \ge 0$, $h_0(\Gamma) = 0$ if $f_0(\Gamma) = 0$, $\int h_0 = 1$.

$$\begin{split} &\lim_{t\to\infty} \left[\langle \mathcal{O} \rangle_t^{(h_0)} - \langle \mathcal{O} \rangle_t^{(f_0)} \right] = \\ &\lim_{t\to\infty} \left[\int \mathrm{d}\Gamma f_0(\Gamma) \mathcal{O} \left(S^t \Gamma \right) \mathcal{Q}(\Gamma) - \int \mathrm{d}\Gamma f_0(\Gamma) \mathcal{O} \left(S^t \Gamma \right) \int \mathrm{d}\Gamma f_0(\Gamma) \mathcal{Q}(\Gamma) \right] \end{split}$$

-0

 f_0 is for equilibrium, so smooth, almost constant on small balls, fills \mathcal{M} . Then, h_0 can be (normalized) constant on balls.

If all such ensembles h_0 are T-mixing with \mathcal{O} : Done!

If single system required, problems: Fermi, riddled spaces etc. Time average along different single trajectories may differ.

Nevertheless: different basins uniformly intertwined with each other everywhere in phase space!

Dissipation Function Ω Ensemble Response: necessary conditions Steady State Flucutation Relations, T-mixing and Response

Step further:
$$E_o^{\mathcal{O}} = \left\{ \Gamma \in \mathcal{M} : \overline{\mathcal{O}}(\Gamma) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \mathcal{O}(S^t \Gamma) \, \mathrm{d}t = o \right\}$$

$$\mu_0\left(\bigcup_{o\in R} E_o^{\mathcal{O}}\right) = 1, \qquad E_o^{\mathcal{O}} \cap E_{o'}^{\mathcal{O}} = \emptyset, \qquad S^{-t}E_o^{\mathcal{O}} = E_o^{\mathcal{O}}$$

Characteristic function $\chi_o^{\mathcal{O}}$ of $E_o^{\mathcal{O}}$ trivially verifies Ω T-mixing. If it also verifies T-mixing:

$$\mu_0\left(E_o^{\mathcal{O}}\right) - \mu_0\left(E_o^{\mathcal{O}}\right)^2 = \mu_0\left(E_o^{\mathcal{O}} \cap S^{-t}E_o^{\mathcal{O}}\right) - \mu_0\left(S^{-t}E_o^{\mathcal{O}}\right)\mu_0\left(E_o^{\mathcal{O}}\right) \xrightarrow[t \to \infty]{} 0$$

i.e. $\mu_0\left(E_o^{\mathcal{O}}
ight)=0$ or 1 ; "= 1" for one and only one $o\in R$.

T-mixing for $\chi_o^{\mathcal{O}}$ sufficient & necessary for single system relaxation. Tuned to observables of interest, does not imply metric transitivity.

$$\mu_0 \equiv {\sf counting!}$$

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Discussion

- Stationary macrostate = ensemble of values of O summarized by measurement. NOT subjective (A.V. et al. Phys. A 2007).
- Ergodic notions refer to trajectories and probabilities on \mathcal{M} : provide "sufficient" conditions for relaxation/response. Such conditions are too strong and not even sufficient: incorrect physical scales, confusion mass-probability etc.
- For certain observables of conservative $N \gg 1$ systems, one only needs COUNTING. What about dissipation?
- In minimal framework for steady state FRs, **T-mixing** necessary as decay of **macroscopic** correlations.
- ΩT-mixing necessary+sufficient for ensemble relaxation to steady state, useful in non-thermodynamic cases. General response relation based on ubiquitous dissipation function Ω.
- T-mixing for $E_o^{\mathcal{O}}$ turns ensemble into single system relations.
- How is T-mixing related to N?