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and more recently

Vieri Mastropietro,Guido Gentile,Federico Bonetto,Alessandro Giuliani

It is a great honor to have been selected to share the award with

Kurt Binder

Boltzmann's Heat Theorem and Fluctuation Theorem: from order to chaos

Averages $\langle F\rangle$ observ. depend on control param. $\boldsymbol{\alpha}$, e.g. volume, energy..

Heat Theorem: (HT) *Then can define mechanical quantities* U, V, P, T *so that* $\boldsymbol{\alpha}\to\boldsymbol{\alpha}+d\boldsymbol{\alpha}$ *induces changes* dU*,* dV*, with*

$$\frac{dU+pdV}{T}=\text{exact}$$

if $p=-\text{average}(\partial_V W),\ T=\text{average}(K)$*.*

Assumptions: $H=K(\vec{p}\,)+W(\vec{x}\,)$ and
(a) (1866) all motions are periodic and nonperiodic motions can be regarded periodic with infinite period ([Bo866]).

(a) (1866) all motions are periodic and "nonperiodic motions can be regarded periodic with infinite period" ([Bo866]). (!)
(b) (1868-1871) ergodic hypothesis: motion visits all phase space of given total energy
(c) (1871-1884) theory of statistical ensembles [Bo884].
Modern terminology: *ergodic hypothesis* (EH) $\Rightarrow$ Equil. Stat. Mech.

Guiding idea: HT true for ALL systems with Hamilt. $H = K + W$: *whether having few* (1) *or many* (10^{19}) *degrees of freedom*, as long as EH

I.e. HT = trivial consequence of Hamilt. nature.
It is a *symmetry property*
Equil. States $\equiv$ prob. distr. on phase space providing averages $\langle F\rangle$.

Some (?) universal laws merely reflect symmetry properties which may have deep consequences in large systems: roots of second Law can be found, [Bo866], in the simple properties of the pendulum motion.

Another example: Time reversal; defined as isometric map I anticommuting with evolution

$$I^2 = 1, \qquad S_t I = I S_{-t} \qquad \Big[e.g. \qquad I(\vec{x}, \vec{v}) \longleftrightarrow (\vec{x}, -\vec{v}) \Big]$$

Reciprocal relations of Onsager, *reflect* time reversal.

Time reversal leads to the quantitative form of reciprocity expressed by "fluctuation dissipation theorems", *i.e.* by the Green-Kubo formulae..

Nonequilibrium SM ? Recent progress on NE based on

(a) focus on *steady states* under forcing
(b) focus on *finite thermostats* $\Rightarrow$ simulations NESS in 980's

Main difficulty: microscop. description cannot be Hamiltonian.

In finite thermostats dissipation manifest by nonvanishing divergence

$$\sigma(x) = -\sum \partial_{x_i} f_i(x)$$

of the equations *and of its time average* $\sigma_+ > 0$.

Physical meaning of σ? no direct one: *changes* with coordinates:

$$\sigma'(x) = \sigma(x) - \frac{d}{dt}\Gamma(x)$$

only time averages over long times can have "intrinsic" meaning:

$$\frac{1}{\tau}\int_0^\tau \sigma'(S_t x) = \frac{1}{\tau}\int_0^\tau \sigma(S_t x) + \frac{\Gamma(S_\tau x) - \Gamma(x)}{\tau} \xrightarrow[\tau\to+\infty]{} \frac{1}{\tau}\int_0^\tau \sigma(S_t x)$$

Average $\sigma_+ \stackrel{def}{=} \lim_{\tau\to+\infty} \frac{1}{\tau}\int_0^\tau \sigma(S_t x)$ identified to entropy creation rate

$$\sigma_+ = \langle \sum_j \frac{Q_j}{k_B T_j} \rangle$$

Why? for instance consider general thermostat model

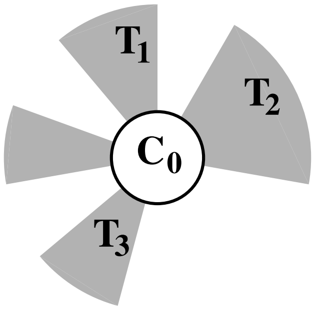

fig.1

Fig.1: $\mathcal{C}_0$ ("system") interact with shaded T_j ("thermostats") constrained fixed K.E.

The equations of motion will be (all masses equal, $\mathbf{E}=$ "stirring forces")

$$
\begin{aligned}
m\ddot{\mathbf{X}}_0 =& -\partial_{\mathbf{X}_0}\Big(U_0(\mathbf{X}_0)+\sum_{j>0} W_{0,j}(\mathbf{X}_0,\mathbf{X}_j)\Big)+\mathbf{E}(\mathbf{X}_0),\\
m\ddot{\mathbf{X}}_i =& -\partial_{\mathbf{X}_i}\Big(U_i(\mathbf{X}_i)+W_{0,i}(\mathbf{X}_0,\mathbf{X}_i)\Big)-\alpha_i\dot{\mathbf{X}}_i
\end{aligned}
$$

$$m\ddot{\mathbf{X}}_0 = -\,\partial_{\mathbf{X}_0}\Big(U_0(\mathbf{X}_0)+\sum_{j>0}W_{0,j}(\mathbf{X}_0,\mathbf{X}_j)\Big)+\mathbf{E}(\mathbf{X}_0),$$
$$m\ddot{\mathbf{X}}_i = -\,\partial_{\mathbf{X}_i}\Big(U_i(\mathbf{X}_i)+W_{0,i}(\mathbf{X}_0,\mathbf{X}_i)\Big)-\alpha_i\dot{\mathbf{X}}_i$$

$\mathbf{E}(\mathbf{X}_0)$ external stirring forces; α_i s.t. $K_i=\frac{3}{2}N_ik_BT_i\equiv \mathit{const}.$

$$K_i\equiv \mathit{const}\overset{def}{=}\frac{3}{2}N_ik_BT_i \qquad\longleftrightarrow\qquad \alpha_i\equiv\frac{Q_i-\dot U_i}{3N_ik_BT_i}$$

$Q_i\equiv$ work per unit time of $\mathcal{C}_0$ on $\mathcal{C}_i$:

$$Q_i\overset{def}{=}-\dot{\mathbf{X}}_i\cdot\partial_{\mathbf{X}_i}W_{0,i}(\mathbf{X}_0,\mathbf{X}_i)$$

Important feature: *preservation of time reversal symmetry !!*.

[thermostat can even act uniformly: eg. electric conduction (Drude)]

Divergence (by algebraic means)

$$\sigma(\mathbf{X},\dot{\mathbf{X}}) \equiv \varepsilon(\mathbf{X},\dot{\mathbf{X}}) + \dot{r}(\mathbf{X}), \qquad \varepsilon(\mathbf{X},\dot{\mathbf{X}}) = \sum_{j=1}^{n} \frac{Q_j}{k_B T_j}, \qquad r = \sum_j \frac{U_j(\mathbf{X}_j)}{k_B T_j}$$

Calorimetry and thermometry measures. No need of equations of motion!

Useful? Fluctuations in average

$$\frac{1}{T}\int_0^T \sigma(S_t x) \equiv \frac{1}{T}\int_0^T \varepsilon(S_t x) + \frac{R(T)-R(0)}{T}$$

Therefore for large T *same fluctuations statistics*. Not just $\langle\sigma\rangle \equiv \langle\varepsilon\rangle$.
A general theory of fluctuations of $\sigma \longleftrightarrow$ general theory of fluct. of ε

Howto?

Need the distribution for averages: i.e. need *extension of EH*.
Ruelle's turbulence theory extension to Stat. Mech. (Cohen-G.)

Chaotic hypothesis (CH) *Motions developing on attracting set of chaotic system may be regarded as motions of transitive hyperbolic system.* $\Rightarrow$

(1) *unique* distribution μ (SRB)*such that outside a set of *zero volume*

$$\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau F(S_t x)dt=\int\mu(dy)F(y)$$

(2) AND μ has an "explicit" express. "similar to the equil. Gibbs distrib."
(3) Nontrivial because μ is concentrated on a 0 volume "attractor"

---

*SRB $\rightarrow$ Sinai-Ruelle-Bowen

Hyperb. systems: *paradigm of chaos* as harmonic oscill. of *order*.
Let $f \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau F(S_t x)dt$

Fluctuation law: *f is in $[a,b]$ with probab. $Prob_\mu(f\in[a,b])$*

$$\lim_{\tau\to\infty}\frac{1}{\tau}\log Prob_\mu(f\in[a,b]) = \max_{f\in[a,b]}\zeta_F(f), \qquad \sim P(f)=e^{\tau\zeta_F(f)}$$

More generally, given n odd observables, let $f_j \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau F_j(S_t x)dt$ $\Rightarrow$,

$$Prob(\mathbf{f}\in\Delta) = Prob((f_1,\ldots,f_n)\in\Delta) \propto_{\tau\to\infty} e^{\tau\max_{\mathbf{f}\in\Delta}\zeta(\mathbf{f})}$$

ζ defined in a convex open set Γ, analytic and convex (Sinai).

ζ is a kind of thermodynamic function.

Possibility of an "explicit" formal expression of μ allows giving an explicit ("uncomputable") expression of stationary averages $\langle F\rangle_\mu$.

Assume average phase space contraction positive $\sigma_+>0$ **and** *time reversal symmetry*; let $F_1\equiv\frac{\sigma}{\sigma_+}$ and $p\stackrel{def}{=}f_1=\frac1\tau\int_0^\tau\frac{\sigma(S_tx)}{\sigma_+}dt$. Then

---

Fluctuation Theorem (FT): (Cohen, G.)

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

More generally $\zeta(-p,-f_2,\ldots,-f_n)=\zeta(p,f_2,\ldots,f_n)-p\sigma_+$

Interest?
Physical interpretation of $p\sigma_+$ as entropy creation $\frac1\tau\int_0^\tau\sum_j\frac{Q_j(t)}{k_BT_j}dt$.
$\Rightarrow$ Measurable independently of model.

Some consequences

(1) In *stationary states* of reversible dynamics heat exchanges constrained

$$\langle e^{-\int_0^\tau \sum_j \frac{Q_j(t)}{k_B T_j}\, dt} \rangle = 1, \qquad (\frac{1}{\tau} \log \langle \cdot \rangle \xrightarrow[\tau\to\infty]{} 0)$$

Bonetto: stronger than Ruelle's:

$$\sum_{j=1}^{n} \frac{\langle Q_j \rangle}{k_B T_j} \ge 0$$

Not to be confused with the formulae of Bockhov-Kuzovlev (and the later developments) dealing with properties of equilibrium distributions or of distributions with density in phase space.

(2) FR implies Fluctuation-Dissipation Theorem

Fluids

(1) Fluid equations are not reversible. Equivalence conjecture:

$$\dot{\mathbf{u}} + \underset{\sim}{\mathbf{u}} \cdot \underset{\sim}{\partial}\, \mathbf{u} = \nu \Delta \mathbf{u} - \partial\, p + \mathbf{g},$$

$$\dot{\mathbf{u}} + \underset{\sim}{\mathbf{u}} \cdot \underset{\sim}{\partial}\, \mathbf{u} = \alpha(\mathbf{u}) \Delta \mathbf{u} - \partial\, p + \mathbf{g}, \qquad \alpha = \frac{\int \mathbf{u}\cdot\mathbf{g}}{\int (\partial\,\mathbf{u})^2} \Rightarrow \int \mathbf{u}^2 = \mathcal{E} = const$$

Same statistics for "local observables": F local $\Rightarrow$ F depends on finitely many Fourier comp. of $\mathbf{u}$.

Same statistics $\Rightarrow$ as $R \to \infty$ if $\mathcal{E}$ is chosen $= \langle \int \mathbf{u}^2 \rangle_{\mu_\nu}$ (equivalence): "Gaussian NS eq." or "GNS". So far *only numerical tests in strongly cut off equations and* $d = 2$ (Rondoni,Segre).

Problem: can reversibility be detected? Assume K41

K41 $\Rightarrow$ # of degrees of freedom is # of $\mathbf{k}$'s s.t. $|\mathbf{k}| < R^{\frac{3}{4}}$

Divergence: $\sigma \sim \nu\,\sum_{\mathbf{k}} 2|\mathbf{k}|^2 = \nu\,(\frac{2\pi}{L})^2\,\frac{8\pi}{5}\,R^{15/4}$
By FT probability (relative) to see "*wrong*" friction *for a time* τ is

$$Prob_{srb} \sim \exp\big(-\tau\nu\frac{32\pi^3}{5L^2}R^{\frac{15}{4}}\big) = e^{-g\tau}$$

$$\begin{cases} \quad\nu = 1.5\,10^{-2}\,\dfrac{cm^2}{sec}, \quad v = 10.\,\dfrac{cm}{sec} \quad L = 100.\,cm \\ \quad R = 6.67\,10^4, \quad g = 3.66\,10^{14}\,sec^{-1} \\ \\ Prob_{srb} = e^{-g\tau} = e^{-3.66\,10^8}, \qquad \text{if} \quad \tau = 10^{-6} \end{cases}$$

Viscosity is $-\nu$ during $10^{-6}s$ (*say*) with probability P above:
similar to the recurrence times estimates.

Quantum systems?

temperature? *finite* Thermostats? are CH and FT possible?

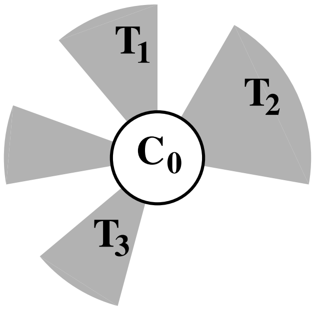

fig.2

H operator on $L_2(\mathcal{C}_0^{3N_0})$, symm. or antisymm. waves Ψ,

$$H = -\frac{\hbar^2}{2}\Delta_{\mathbf{X}_0} + U_0(\mathbf{X}_0) + \sum_{j>0}\big(U_{0j}(\mathbf{X}_0,\mathbf{X}_j) + U_j(\mathbf{X}_j) + K_j\big)$$

Dynamical system on $\big(\Psi, (\{\mathbf{X}_j\},\, \{\dot{\mathbf{X}}_j\})_{j>0}\big)$:

$$-i\hbar\dot\Psi(\mathbf{X}_0) = \,(H\Psi)(\mathbf{X}_0),$$

$$\ddot{\mathbf{X}}_j = -\Big(\partial_j U_j(\mathbf{X}_j) + \langle \partial_j U_j(\mathbf{X}_0,\mathbf{X}_j)\rangle_\Psi\Big) - \alpha_j \dot{\mathbf{X}}_j \qquad j>0$$

Constraint of constant K_j

$$\alpha_j \stackrel{def}{=} \frac{\langle W_j\rangle_\Psi - \dot U_j}{2K_j}, \qquad W_j \stackrel{def}{=} -\dot{\mathbf{X}}_j\cdot\partial_j U_{0j}(\mathbf{X}_0,\mathbf{X}_j)$$

$$\sigma(\mathbf{x},\dot{\mathbf{x}}) \equiv \varepsilon(\mathbf{X},\dot{\mathbf{X}}) + \dot r(\mathbf{x}) = \sum_{j>0}\frac{Q_j}{k_B T_j} + \ldots$$

Chaotic and reversible $\Rightarrow$ FT

Consistency: single thermostat equivalent to Gibbs?

Attempt: probability proportional to $d\Psi\, d\mathbf{X}_1\, d\dot{\mathbf{X}}_1$ times

$$\sum_{n=1}^{\infty} e^{-\beta E_n} \delta(\Psi - \Psi_n(\mathbf{X}_1)\, e^{i\varphi_n})\, d\varphi_n\, \delta(\dot{\mathbf{X}}_1^2 - 2K_1)$$

Stationary in the *adiabatic approximation only.*

$$\langle O\rangle_\mu = Z^{-1} \int \sum_{n=1}^{\infty} e^{-\beta E_n(\mathbf{X}_1)} \langle \Psi_n(\mathbf{X}_1)|O|\Psi_n(\mathbf{X}_1)\rangle \delta(\dot{\mathbf{X}}_1^2 - 2K_1) d\mathbf{X}_1 d\dot{\mathbf{X}}_1$$
$$= Z^{-1} \int \mathrm{Tr}\left(e^{-\beta_1 H(\mathbf{X}_1)} O\right) \delta(\dot{\mathbf{X}}_1^2 - 2K_1) d\mathbf{X}_1 d\dot{\mathbf{X}}_1$$

Nevertheless if *adiabatic approximation* (*i.e.* classical motion in therm. is on a time scale *much slower* than the quantum evolution of the system).

Conjecture: true SRB is *also* equiv. to Gibbs at temp. $(k_B\beta)^{-1}$

$\Rightarrow$ possibility of defining the temperature via the FT if Q is measurable or Q if T is measurable (originally suggested by Cugliandolo and Kurchan as a possible application of FT to define temperature in spin glasses)

$$\frac{\zeta(p)-\zeta(-p)}{p}=\frac{\langle Q\rangle}{k_BT}$$

a "device independent" definition of absolute temperature possibly useful in microscale systems empirically thermostatted by a single thermostat and subject to action of a nonconservative stirring force.

Eigenstates at time 0 evolve following variations of Hamiltonian $H(\mathbf{X}(t))$ due to thermostats particles motion, without changing quantum numbers. [Under time evolution a time $t > 0$ infinitesimal:

$$\begin{aligned}
&\mathbf{X}_1 \;\to\; \mathbf{X}_1 + t\dot{\mathbf{X}}_1 + O(t^2)\\
&E_n(\mathbf{X}_1) \;\to\; E_n + t\, e_n + O(t^2) \qquad \text{with}\\
&e_n \stackrel{def}{=} \langle \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_{01}\rangle_{\Psi_n} + t\dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_1 = -t\,(Q_1 + \dot{U}_1)\\
&e^{-\beta E_n(\mathbf{X}_1)} \;\to\; e^{-\beta t e_n}
\end{aligned}$$

thermostat phase space contracts by $e^{t\sigma} \equiv e^{t\frac{3N_1 e_n}{2K_1}}$

Therefore if β is chosen such that $\beta = \frac{3N_1}{2K_1} \equiv (k_B T_1)^{-1}$ the distribution $\langle\cdot\rangle_\mu$ is stationary.]

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