Quantum Nonequilibrium and Entropy Creation

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

Equil. States $\equiv$ prob. distr. on phase space providing averages $\langle F \rangle$.

Project:
(1) identify the Eq. States (extending Gibbs' equilibrium assumption)
(2) universal laws merely reflect symmetry properties which may have deep consequences in large systems.

Example 1: roots of second Law can be found, [Bo866], in the simple properties of the pendulum motion (Hamiltonian $H = K + V$)
Example 2: 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..

Main difficulty: microscop. description $\dot{x} = f(x)$ 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:

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

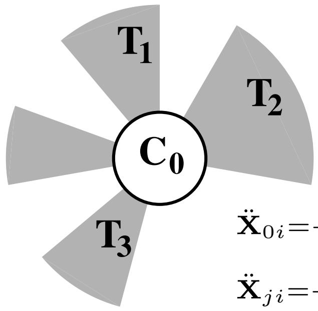
Average $\sigma_+ \stackrel{def}{=} \lim_{\tau\to+\infty} \frac{1}{\tau}\int_0^\tau \sigma(S_t x)$ identified to entropy creation rate

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

Why? for instance consider general thermostat model

Particularly interesting because model independent and **measurable**

A general model for a system in contact with thermostats is in Fig.1



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

$$\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum_j \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i$$

$$\ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

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

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

$$K_i \equiv const \stackrel{def}{=} \frac{3}{2} N_i k_B T_i \qquad \longleftrightarrow \qquad \alpha_i \equiv \frac{Q_i - \dot{U}_i}{3 N_i k_B T_i}$$

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

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

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

[thermostat can even act uniformly inside $\mathcal{C}_0$: eg. electric conduction (Drude)]
Divergence (by algebraic means)

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

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 → 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 $p \stackrel{def}{=} f_1 = \frac{1}{\tau}\int_0^\tau \frac{\sigma(S_t x)}{\sigma_+} dt$. Then

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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 $\frac{1}{\tau}\int_0^\tau \sum_j \frac{Q_j(t)}{k_B T_j} dt$.

$\Rightarrow$ Measurable independently of model.

Some consequences

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

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

Bonetto: similar (but different) from Jarzinsky's relation (and stronger than just positivity of σ_+):

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

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. It is rather general and testable.

Quantum systems?

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

An example of a nanoscale device to measure temperature

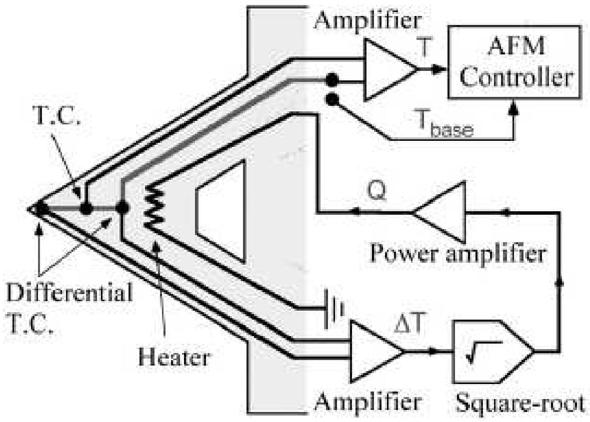

Fig.2

Fig.2: Block diagr. of feedback system from NS02 (Nakabeppu-Suzuki:) a "thermometer" operating above room temperature and performing on a scale of $10\,nm$.

Conceptual problem: what does the measurement apparatus really do?

Thermostat: just a device to keep temperature constant in a system receiving heat from a (stationary state) non equilibrium system.
How that is done precisely *should not matter*.

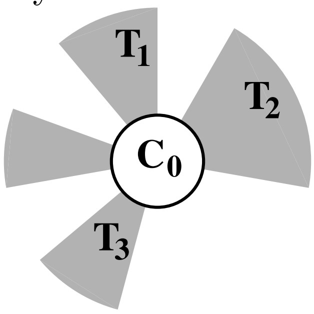

fig.2

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

phase space consists of the points $\big(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0}\big)$:

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

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

Constraint of constant $K_j \Rightarrow$

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

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

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 Crisanti and Ritort as a possible application of FR to define temperature in spin glasses), then setting $p = \int_0^\tau \frac{Q(\tau')}{\langle Q \rangle} \frac{d\tau'}{\tau}$ then $\zeta(p)$ is its large deviation rate and

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

a "device independent" definition of absolute temperature possibly useful in microscale systems.

Check of cancellation in adiabatic approx.

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:

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

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

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

Alternatives: infinite thermostats (Feynman-Vernon, 1963, Eckmann-Pillet-Rey-Bellet 1999, Hänggi-Ingold, 2005). Problem: thermostats must be free systems ⇒ problematic (see Abraham-Baruch-G-MartinLöf, 1972)

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