

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

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

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:

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

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

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

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

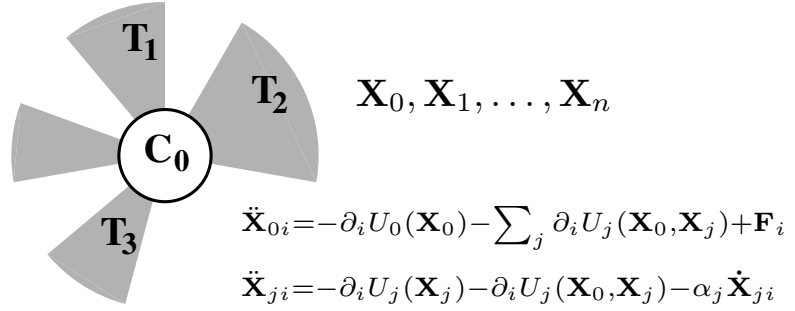


Fig.1: \mathcal{C}_0 (“system”) interact with shaded T_j (“thermostats”) constrained fixed K.E.

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

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

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

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

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*

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

(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. $Prob_\mu(f \in [a, b])$

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

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

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

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

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

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

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

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

$$\langle e^{-\int_0^\tau \sum_j \frac{Q_j(t)}{k_B T_j} dt} \rangle = 1, \quad \left(\frac{1}{\tau} \log \langle \cdot \rangle \xrightarrow{\tau \rightarrow \infty} 0 \right)$$

Bonetto: stronger than positivity of σ_+ :

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

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: rather general and testable.

Quantum systems?

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

An example of a nanoscale device to measure temperature

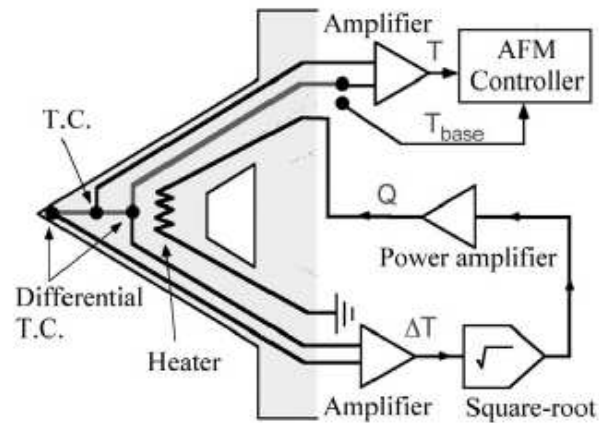


Fig.2

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*.

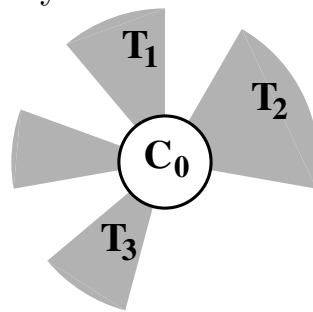


fig.2

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

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

Dynamical system

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

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

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

Constraint of constant K_j

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

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

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*.

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

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), 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 empirically thermostatted by a single thermostat and subject to action of a nonconservative stirring force.

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:

$$\mathbf{X}_1 \rightarrow \mathbf{X}_1 + t\dot{\mathbf{X}}_1 + O(t^2)$$

$$E_n(\mathbf{X}_1) \rightarrow E_n + t e_n + O(t^2) \quad \text{with}$$

$$e_n \stackrel{\text{def}}{=} \langle \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_{01} \rangle_{\Psi_n} + t \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_1 = -t(Q_1 + \dot{U}_1)$$

$$e^{-\beta E_n(\mathbf{X}_1)} \rightarrow e^{-\beta t e_n}$$

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.

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

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