Finite thermostats in nonequilibrium (classical and quantum)

Progress (recent) due to

(a) Study of stationary states out of equilibrium, [EM89].

(b) Modeling thermostats in terms of finite systems, [No84],[Ho85]

Finite thermostats have been essential.
Rationale: properties should not depend on how thermostats are imagined to work.

Equations of motion: NOT Hamiltonian $\Rightarrow$ phase space contraction

$$\sigma(x) \stackrel{def}{=} -\operatorname{div} f(x) = -\sum_{i=1}^{3N} \partial_i f_i(x)$$

$\sigma(x)$ no direct physical meaning: as *changes* with coordinates:

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

only long time averages 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 $\sigma_+ \stackrel{def}{=} \lim_{\tau\to+\infty} \frac{1}{\tau}\int_0^\tau \sigma(S_t x)$ interpreted as *entropy creation*

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

Important achievement: mechanical meaning of entropy creation

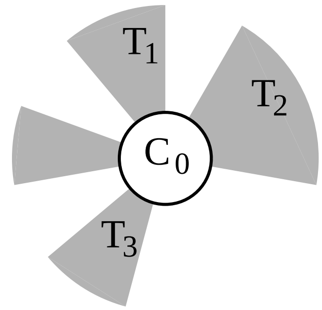

fig.1

Fig.1: Particles in $\mathcal{C}_0$ ("system") interact with particles in shaded regions ("thermostats") constrained to fixed total kinetic energy.

The equations of motion will be (all masses equal)

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

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with $\alpha_i \Rightarrow K_i = \frac{3}{2}N_ik_BT_i$ is a constant. $\mathbf{E}(\mathbf{X}_0)$ stirring forces.

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

where Q_i is work per unit time of $\mathcal{C}_0$ on $\mathcal{C}_i$ = "*heat*"

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

Gauss' principle *preserves time-reversal symmetry*;
time reversibility is unrelated to dissipation

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

Measurable by calorimetric and thermometric experiments. No need of of the equations of motion.

Important feature: preservation of time reversal symmetry.

Useful? Finite time averages:

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

Therefore for large T *same fluctuations statistics*. Not just $\langle\sigma\rangle \equiv \langle\varepsilon\rangle$

General theory of fluctuations of $\sigma \longleftrightarrow$ general theory of fluct. of ε.

Chaotic hypothesis (CH): *Motions developing on the attracting set of a chaotic system can be regarded as motions of a transitive hyperbolic (also called "Anosov") system.*[GC95]

(From Ruelle's "Nature of turbulence"). *Dynamical systems* $\Rightarrow$:

(1) Existence of averages and "volume" statistics μ (SRB statistics)

$$\frac{1}{T}\int_0^T F(S_t x)\,dt \xrightarrow[T\to\infty]{} \int_{\mathcal{A}} F(y)\mu(dy) \stackrel{def}{=} \langle F\rangle$$

(2) Coarse graining rigorous $\rightarrow$ SRB = equidistribution on attracting set ($\Rightarrow$ variational principle and existence of Lyapunov function)

(3) μ admits an explicit representation so that averages can be written and compared (*without computing them*)

(4) large deviations law holds: $f_j \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau F_j(S_t x)dt$

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

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

(5) Let $F_1(x) = \frac{\varepsilon(x)}{\langle\varepsilon\rangle}$. Call $p = \frac{1}{\tau}\int_0^\tau \frac{\varepsilon(S_t x)}{\langle\varepsilon\rangle}$: $\Rightarrow \zeta(p)$

(6) in *time reversal invariant* cases FT (CG): (F_j odd)

$$\zeta(-\mathbf{f}) = \zeta(\mathbf{f}) - \langle\varepsilon\rangle p \qquad \longleftrightarrow \qquad \frac{Prob(\mathbf{f})}{Prob(-\mathbf{f})} = e^{p\sigma_+\tau}$$

provided $\sigma = \varphi(\mathbf{F})$ and $\langle\varepsilon\rangle > 0$ (e.g. $F_1 = \sigma$). No free parameters.

(7) Bonetto formula: $\langle \exp - \int_0^T \frac{\sum_j Q_j}{k_B T_j}\rangle = 1$

Not to be confused with the formulae of Evans-Searles and Jarzynski resp. dealing with properties of the equilibrium distributions

The latter actually started in 1981 by a remarkable work of Bockhov-Kuzovlev (by Hänggi) and were not extended to steady states possibly because at the time the SRB theory on the nature of turbulence was not well known

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

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

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

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

Compatibility? near equil. entropy creation independently defined (DeGroot-Mazur)

$$
\begin{aligned}
k_B\langle\varepsilon\rangle =& k_B\varepsilon_{classic}+\dot S,\\
k_B\varepsilon_{classic} =& \int_{\mathcal{C}_0}\Big(\kappa\,\big(\frac{\partial T}{T}\big)^2+\eta\,\frac{1}{T}\underset{\sim}{\boldsymbol{\tau}}'\cdot\underset{\sim}{\partial}\mathbf{u}\Big)\,d\mathbf{x}
\end{aligned}
$$

Quantum systems: temperature and heat are defined by the special apparata that measure them.
However important in *meso-physics* and *nano-physics*.
Finite thermostat?? and Dynamical system? ($\Rightarrow$ **CH & FT**)
A natural model is in the previous Figure 1

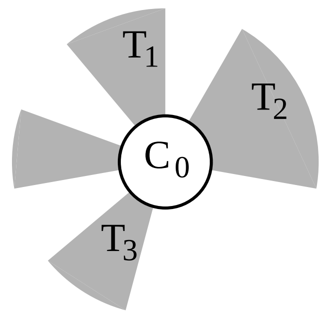

fig.1

H operator on $L_2(\mathcal{C}_0^{3N_0})$, (symm./antisymm.) wave funct.s 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 sys. on $\big(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0}\big)$ (if $\langle\cdot\rangle_\Psi \equiv \langle\Psi|\cdot|\Psi\rangle$)

$$-i\hbar\dot{\Psi}(\mathbf{X}_0) = (H(\{\mathbf{X}_j\}_{j>0})\Psi)(\mathbf{X}_0), j > 0$$

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

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

Evolution: $K_j \equiv \frac{1}{2}\dot{\mathbf{X}}_j^2 \stackrel{def}{=} \frac{3}{2}k_B T_j N_j$ exact constant, as classical).

NOT a time dep. Schrödinger eq.: *essential interaction syst-thermos.*

Divergence: $\sigma(x) = \sum_j \big(\frac{Q_j}{k_B T_j} + \frac{\dot{U}_j}{k_B T_j}\big)$ (*same as classical*)

Equations are reversible and chaotic: CH $\Rightarrow$ SRB + FT

Consistency: *system with a single thermostat* $\rightarrow$ SRB distrib. should be equivalent to a canonical distribution. (*True in classical case*).

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

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

$\Rightarrow$ expectation of O is a Gibbs state of therm. equil. with a special kind (random $\mathbf{X}_1, \dot{\mathbf{X}}_1$) of boundary condition and temperature T_1.

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

$$\langle O\rangle = Z_0^{-1}\int \Big(\mathrm{Tr}\, e^{-\beta H(\mathbf{X}_1)}\, O\Big)\, d\mathbf{X}_1$$

However is not invariant under evolution: difficult to exhibit explicitly an invariant distribution (why should it be easy? *Aesopus*)

Nevertheless if *adiabatic approximation* (*i.e.* classical motion in thermostat on a time scale much slower than quantum evolution).

Eigenstates at time 0 follow variations of Hamiltonian $H(\mathbf{X}_1(t))$ due to thermostats motion, without changing quantum numbers.
Conjecture: true SRB is *also* equivalent to Gibbs at temp. $(k_B\beta)^{-1}$

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

In presence of forcing and a single thermostat measure $\langle Q \rangle$ and *if*

$$\zeta(-p) - \zeta(p) = -p\sigma_+$$

use slope σ_+ to set

$$k_B T = \frac{\langle Q \rangle}{\sigma_+}$$

[Under time evolution a time $t > 0$ infinitesimal:

$$\begin{aligned}
&\mathbf{X}_1 \;\to\; \mathbf{X}_1 + t\dot{\mathbf{X}}_1 + O(t^2)\\
&E_n(\mathbf{X}_1) \;\to\; E_n + t\,e_n + O(t^2) \qquad \text{with}\\
&e_n \stackrel{def}{=} \langle \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_{01} \rangle_{\Psi_n} + t\dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_1 = -t\,(Q_1 + \dot{U}_1)\\
&e^{-\beta E_n(\mathbf{X}_1)} \;\to\; e^{-\beta t e_n}\\
&\text{thermostat phase space contracts by } e^{t\sigma} \equiv e^{t\frac{3N_1 e_n}{2K_1}}
\end{aligned}$$

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.*]