Finite thermostats in nonequilibrium (classical and quantum)

Progress (recent) due to

(a) Study of stationary states out of equilibrium (as opposed to deviation and return to equilibrium), [EM89].

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

Finite thermostats have been essential. Rationale: the properties of the system should not ϒdepend on the special way thermostats are imagined to work.

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

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

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

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

only 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

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

Several reasons: for instance consider general thermostat model

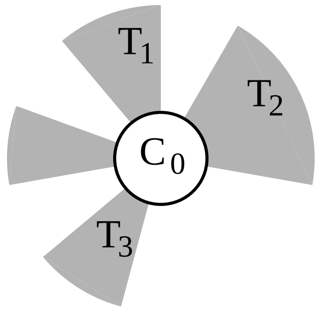

fig.1

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)

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

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

with α_i such that $K_i=\frac{3}{2}N_ik_BT_i$ is a constant. $\mathbf{E}(\mathbf{X}_0)$ are external positional forces stirring $\mathcal{C}_0$. The contraints on the thermostats give

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

where Q_i is the work per unit time that particles outside the thermostat $\mathcal{C}_i$ (hence in $\mathcal{C}_0$) exercise on the particles in it, is

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

The model identifies the "temperature of the thermostats",

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

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

Important feature: preservation of time reversal symmetry.

Useful? 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 fluctuations 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 Dynamical systems:

(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 $\to$ 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.

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

(6) in *time reversal invariant* cases FT ([GC95]): (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.

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. $|\mathbf{k}| < R^{\frac34}$

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

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

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

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*.

Model with finite thermostat?? and Dynamical system? ($\Rightarrow$ **CH & FT**)
A natural model is in the previous Figure 1

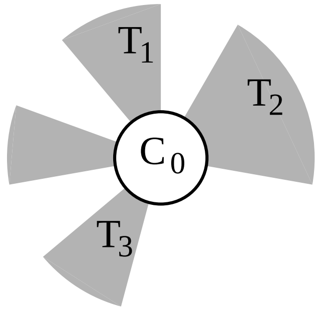

fig.1

H operator on $L_2(\mathcal{C}_0^{3N_0})$, (symm./antisymm.) wave funct.s Ψ,

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

Spectrum consists of eigenvalues $E_n = E_n(\{\mathbf{X}_j\}_{j>0})$, for $\mathbf{X}_j$ fixed.
dynamical sys. on $\big(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0}\big)$ defined by ($\langle\cdot\rangle_\Psi \equiv \langle\Psi|\cdot|\Psi\rangle$)

$$\begin{aligned}
&-i\hbar\dot\Psi(\mathbf{X}_0) = \,(H\Psi)(\mathbf{X}_0), \quad \text{ and for } j>0\\
&\ddot{\mathbf{X}}_j = -\Big(\partial_j U_j(\mathbf{X}_j) + \langle\partial_j U_j(\mathbf{X}_0,\mathbf{X}_j)\rangle_\Psi\Big) - \alpha_j\dot{\mathbf{X}}_j\\
&\alpha_j \stackrel{def}{=} \frac{\langle W_j\rangle_\Psi - \dot U_j}{2K_j}, \qquad W_j \stackrel{def}{=} -\dot{\mathbf{X}}_j\cdot\partial_j U_{0j}(\mathbf{X}_0,\mathbf{X}_j)
\end{aligned}$$

Evolution keeps $K_j \equiv \frac12\dot{\mathbf{X}}_j^2$ exactly constant (defining therm. temperatures T_j via $K_j = \frac32 k_B T_j N_j$, as classical case).

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

Divergence: $\sigma(x) = \sum_j \frac{Q_j}{k_B T_j} + \frac{\dot U_1}{k_B T_1}$ (*same as classical*)

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

Consistency: *system interacting with a single thermostat* the SRB distribution should be equivalent to the 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.

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

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

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.* the classical motion of the thermostat particles is on a time scale much slower than the quantum evolution of the system).

Eigenstates at time 0 evolve following the variations of Hamiltonian $H(\mathbf{X}(t))$ due to thermostats particles motion, without changing quantum numbers.

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

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

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.]

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