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 depend on the special way thermostats are imagined to work.

Equations of motion: NOT Hamiltonian ⇒ phase space contraction

\[ \sigma(x) \overset{\text{def}}{=} - \text{div } f(x) = - \sum_{j=1}^{3N} \partial_i f_i(x) \]
\( \sigma(x) \) 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 \( \sigma_{+} \) defined as

\[
\sigma_{+} = \lim_{\tau \to +\infty} \frac{1}{\tau} \int_{0}^{\tau} \sigma(S_{t}x) \text{ identified to entropy creation rate}
\]

\[
\sigma_{+} = \langle \sum_{j} \frac{Q_{j}}{T_{j}} \rangle
\]

Several reasons: for instance consider general thermostat model
Fig.1: 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)

$$m \ddot{X}_0 = - \partial_{X_0} \left( U_0(X_0) + \sum_{j>0} W_{0,j}(X_0, X_j) \right) + E(X_0),$$

$$m \ddot{X}_i = - \partial_{X_i} \left( U_i(X_i) + W_{0,i}(X_0, X_i) \right) - \alpha_i \dot{X}_i$$
\[
m \ddot{X}_0 = - \partial_{X_0} \left( U_0(X_0) + \sum_{j>0} W_{0,j}(X_0, X_j) \right) + E(X_0),
\]
\[
m \ddot{X}_i = - \partial_{X_i} \left( U_i(X_i) + W_{0,i}(X_0, X_i) \right) - \alpha_i \dot{X}_i
\]

with \( \alpha_i \) such that \( K_i = \frac{3}{2} N_i k_B T_i \) is a constant. \( E(X_0) \) are external positional forces stirring \( C_0 \). The constraints on the thermostats give

\[
K_i \equiv \text{const} \overset{\text{def}}{=} \frac{3}{2} N_i k_B T_i \quad \iff \quad \alpha_i \overset{\text{def}}{=} \frac{Q_i - \dot{U}_i}{3 N_i k_B T_i}
\]

where \( Q_i \) is the work per unit time that particles outside the thermostat \( C_i \) (hence in \( C_0 \)) exercise on the particles in it, is

\[
Q_i \overset{\text{def}}{=} - \dot{X}_i \cdot \partial_{X_i} W_{0,i}(X_0, X_i)
\]

The model identifies the “temperature of the thermostats”,

30/giugno/2007; 18:19
\[ \sigma(\mathbf{x}, \dot{\mathbf{x}}) = \varepsilon(\mathbf{x}, \dot{\mathbf{x}}) + \dot{r}(\mathbf{x}, \dot{\mathbf{x}}), \quad \varepsilon(\mathbf{x}, \dot{\mathbf{x}}) = \sum_{j=1}^{n} \frac{Q_j}{k_B T_j}, \quad r = \sum_{j} \frac{u_j}{k_B T_j}. \]

Measurable by calorimetric and thermometric experiments. No need of 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 $\varepsilon$

**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 $\mu$ (SRB statistics)

$$\frac{1}{T} \int_0^T F(S_t x) \, dt \xrightarrow{T \to \infty} \int_A F(y) \mu(dy) \overset{\text{def}}{=} \langle F \rangle$$

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

3. $\mu$ admits an explicit representation so that averages can be written and compared (without computing them)
large deviations law holds: $f_j \overset{\text{def}}{=} \frac{1}{\tau} \int_0^\tau F_j(S_t x) dt$

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

\(\zeta\) defined in a convex open set \(\Gamma\), 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]): \((F_j\ \text{odd})\)

$$\zeta(-f) = \zeta(f) - \langle \varepsilon \rangle p \quad \leftrightarrow \quad \frac{\text{Prob}(f)}{\text{Prob}(-f)} = e^{p\sigma+\tau}$$

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

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

\[ \dot{u} + u \cdot \nabla u = \nu \Delta u - \partial p + g, \]
\[ \dot{u} + u \cdot \nabla u = \alpha(u) \Delta u - \partial p + g, \quad \alpha = \frac{\int u \cdot g}{(\nabla u)^2} \Rightarrow \int u^2 = \mathcal{E} = \text{const} \]

Same statistics for “local observables”: \( F \) local \( \Rightarrow \) \( F \) depends on finitely many Fourier comp. of \( u \).

**Same statistics** \( \Rightarrow \) as \( R \to \infty \) if \( \mathcal{E} \) is chosen = \( \langle u^2 \rangle_{\mu, \nu} \) (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 ⇒ # of degrees of freedom is # of $k$’s s.t. $|k| < R^{\frac{3}{4}}$

Divergence: $\sigma \sim \nu \sum_k 2|k|^2 = \nu \left(\frac{2\pi}{L}\right)^2 \frac{8\pi}{5} R^{15/4}$

By FT probability (relative) to see “wrong” friction for a time $\tau$ is

$$P_{\text{sr}_b} \sim \exp \left( -\tau \nu \frac{32\pi^3}{5L^2} R^{\frac{15}{4}} \right)$$

\[
\begin{align*}
\text{cgs units: cm, sec (data for air)}
\frac{\nu}{\text{sec}} &= 1.5 \times 10^{-2} \frac{cm^2}{sec}, \quad \nu = 10. \frac{cm}{sec} \quad L = 100. cm \\
R &= 6.67 \times 10^4, \quad g = 3.66 \times 10^{14} \text{sec}^{-1} \\
P_{\text{sr}_b} &= e^{-g\tau} = e^{-3.66 \times 10^8}, \quad \text{if } \tau = 10^{-6}
\end{align*}
\]

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)

\[ k_B \langle \varepsilon \rangle = k_B \varepsilon_{\text{classic}} + \dot{S}, \]
\[ k_B \varepsilon_{\text{classic}} = \int_{C_0} \left( \kappa \left( \frac{\partial T}{T} \right)^2 + \eta \frac{1}{T} \tau' \cdot \partial u \right) dx \]

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? (⇒ CH & FT)
A natural model is in the previous Figure 1
H operator on $L_2(C_0^{3N_0})$, (symm./antisymm.) wave funct.s $\Psi$,

$$H = -\frac{\hbar^2}{2} \Delta x_0 + U_0(x_0) + \sum_{j>0} \left(U_{0j}(x_0, x_j) + U_j(x_j) + K_j\right)$$
Spectrum consists of eigenvalues $E_n = E_n(\{X_j\}_{j>0})$, for $X_j$ fixed. Dynamical sys. on $(\Psi, (\{X_j\}, \{\dot{X}_j\})_{j>0})$ defined by $(\langle \cdot \rangle_{\Psi} \equiv \langle \Psi | \cdot | \Psi \rangle)$

$$-i\hbar \dot{\Psi}(X_0) = (H\Psi)(X_0), \quad \text{and for } j > 0,$$
$$\dot{X}_j = -\left( \partial_j U_j(X_j) + \langle \partial_j U_j(X_0, X_j) \rangle_{\Psi} \right) - \alpha_j \dot{X}_j$$
$$\alpha_j \overset{\text{def}}{=} \frac{\langle W_j \rangle_{\Psi} - \dot{U}_j}{2K_j}, \quad W_j \overset{\text{def}}{=} -\dot{X}_j \cdot \partial_j U_{0j}(X_0, X_j)$$

Evolution keeps $K_j \equiv \frac{1}{2} \dot{X}_j^2$ exactly constant (defining therm. temperatures $T_j$ via $K_j = \frac{3}{2} k_B T_j N_j$, as classical case).

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

Divergence: $\sigma(x) = \sum_j \frac{Q_j}{k_B T_j} + \frac{\dot{U}_j}{k_B T_1}$ (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 \( \mu \): 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 \( T_1 \).

\[
\langle O \rangle_{\mu} = Z^{-1} \int \sum_{n=1}^{\infty} e^{-\beta E_n(\mathbf{X}_1)} \langle \Psi_n(\mathbf{X}_1) | O | \Psi_n(\mathbf{X}_1) \rangle \delta(\dot{\mathbf{X}}_1^2 - 2K_1) \, d\mathbf{X}_1 \, d\dot{\mathbf{X}}_1
\]
\[ \langle O \rangle = Z^{-1} \int \sum_{n=1}^{\infty} e^{-\beta E_n(X_1)} \langle \Psi_n(X_1) | O | \Psi_n(X_1) \rangle \delta(\dot{X}_1^2 - 2K_1) dX_1 \dot{X}_1 \]

However, it 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 \( H(X(t)) \) due to thermostats particles motion, without changing quantum numbers.
Under time evolution a time \( t > 0 \) infitesimal:

\[
\begin{align*}
X_1 &\to X_1 + t \dot{X}_1 + O(t^2) \\
E_n(X_1) &\to E_n + t e_n + O(t^2) \quad \text{with} \\
e_n &\overset{\text{def}}{=} \langle \dot{X}_1 \cdot \partial_{X_1} U_{01} \rangle_{\Psi_n} + t \dot{X}_1 \cdot \partial_{X_1} U_1 = -t (Q_1 + \dot{U}_1) \\
e^{-\beta E_n(X_1)} &\to e^{-\beta t e_n}
\end{align*}
\]

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

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

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