Thermostats equivalence in the thermodymamic limit

by Errico Presutti, GG

The evolution of Equilibrium Statistical Mechanics started with the analysis of the thermodynamic limit.

Its importance in Nonequilibrium has been very often mentioned, although it was possible **(but a bad idea)** to discard the problem on the grounds that real systems are finite.

First Noneq. problem is to build a theory of stationary state.

Difficulties: nonequilibrium → nonconservative forces act → systems "heat up" → need to remove heat to achieve stationarity → conceptual difficulty: "how to do that"?. Microscopic mechanincs is not only "conservative" but also reversible.

Paris IHP 17 May 2010: Joel's happy birthday

Thermostat models:

(0) (Lebowitz 1959, Feynman-Vernon 1963): finite system in contact with infinite ones which are "at equilibrium at ∞". It does not require to modify the basic conservative and reversible nature of laws of motion.

(1) (Nosé, Hoover, Evans, Morriss 1982$\sim$1984): finite systems in contact with finite systems subject to forces that constrain their temperature, or energy (or other quantities) constant.

(0): ok

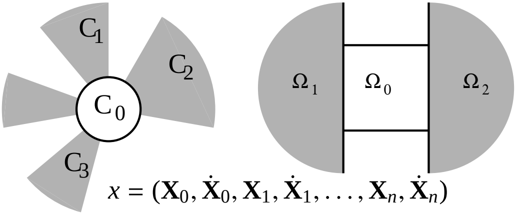
(1): criticized as non-physically meaningful because of the introduction of artificial forces. But the Authors have relentlessly argued that yes the forces are artificial but the results are not because the thermostatting mechanism is irrelevant.

Lebowitz (1959) As was stated in the introduction it is known experimentally, and we hope that it is possible also to prove mathematically for our model, that all important features of the stationary state of a system conducting heat are independent of the details of the interaction with iits surroundings

This reminds: size and ensemble independence of thermodynamic functions in equilibrium

Evans-Searles (following an earlier work by Evans-Sarman) have attempted a general equivalence proof of models like 0&1. Ruelle discusses a special case. Review by Bright-Evans-Searles.

Examples (few out of many varieties: model cases a=0,1)



$$x = (\mathbf{X}_0, \dot{\mathbf{X}}_0, \mathbf{X}_1, \dot{\mathbf{X}}_1, \ldots, \mathbf{X}_n, \dot{\mathbf{X}}_n)$$

$$m\ddot{\mathbf{X}}_{0i} = -\,\partial_i U_0(\mathbf{X}_0) - \sum_{j>0} \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) + \partial_i \Psi(\mathbf{X}_j) + \Phi_i(\mathbf{X}_0)$$

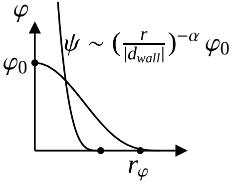
$$m\ddot{\mathbf{X}}_{ji} = -\,\partial_i U_j(\mathbf{X}_j) - \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) + \partial_i \Psi(\mathbf{X}_j) - a\,\alpha_j \dot{\mathbf{X}}_{ji}$$

Interactions (Lebowitz 1959)

$$U_j(\mathbf{X}_j) = \sum_{q,q' \in \mathbf{X}_j} \varphi(q - q'), \qquad j\text{-th thermostat potential}$$

$$U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) = \sum_{q \in \Omega_0, q' \in \Omega_j} \varphi(q - q') \qquad j\text{-th thermostat-system}$$

$$\Psi(X) = \sum_{q \in X} \psi(q) \qquad \text{confining wall potential}$$



Initial state: infinite Gibbs at given density δ_j and temperatures β_j^{-1}

Trying to study precisely the equivalence problem we must

I) check (*i.e* prove) that models (0) (frictionless) are well defined: i.e. model (0) defined first in finite volume Λ shows motions $t \to \mathbf{X}^{0,\Lambda}(t)$ which tend to limit $\mathbf{X}(t)$ as $\Lambda \to \infty$. Thermodynamic limit exists in absence of dissipation.

II) check (*i.e* prove) that models (1) also have $t \to \mathbf{X}^{1,\Lambda}(t)$ admits a limit $\mathbf{X}(t)$: Thermodynamic limit exists in presence of dissipation

III) check (*i.e* prove) that in both cases the intensive quantities are exact constants of motion (*i.e.* at least at finite times the thermostats temperatures (and other intensive quantities) are constant.

Geometry is essential, and also $d = 3$, to study heat conduction

Kinetic-potential energy density, density and many observables are constant with μ_0 probability 1 at time $t = 0$: examples

$$\lim_{\Lambda\to\infty} \frac{1}{|\Lambda \cap \Omega_j|} K_{j,\Lambda}(x) = \frac{d}{2}\beta_j^{-1}\delta_j$$

$$\lim_{\Lambda\to\infty} \frac{1}{|\Lambda \cap \Omega_j|} N_{j,\Lambda}(x) = \delta_j$$

$$\lim_{\Lambda\to\infty} \frac{1}{|\Lambda \cap \Omega_j|} U_{j,\Lambda}(x) = u_j$$

This should remain true for all $t > 0$ at least (in the thermodynamic limit and keeping in mind that dimension matters).

Frictionless thermostats: “easy” adaptation to new geometry of classics

Existence: Theorem by Caglioti, Marchioro, Pulvirenti (2000)

Remarkable conclusion of a series of works by

Lanford (1968) 1 dimension (a.e. for general states)

Sinai (1971) 1 dimension (a.e. for general states, proving cluster dynamics)

Marchioro, Pellegrinotti, Presutti (1974) (a.e. only for Gibbs states arbitrary dim.)

Dobrushin Fritz (1975) (a.e. for dim.= 2 general states)

$$W(x;\xi,R) \overset{def}{=} \text{total energy} + \text{number of particles in ball } \mathcal{B}(\xi,R)$$

$$\mathcal{E}(x) \overset{def}{=} \sup_{\xi} \sup_{R>(\log_+(\frac{\xi}{r_\varphi}))^{1/d}} \frac{W(x;\xi,R)}{R^d}$$

Let $\mathcal{N}_i(t,n)$= number of particles within r of $q_i^{(n,0)}(t)$ and let $T>0$, $V_1 = \sqrt{\frac{2\varphi_0}{m}}$ and Λ_k= ball of radius $2^k r_\varphi$.

Theorem: *$\exists\, C(\mathcal{E}), c(\mathcal{E})^{-1}, \uparrow \mathcal{E}$, and if $q_i(0) \in \Lambda_k$ $\forall t \le T$,*

(1) $$|\dot{q}^{(n,0)}(t)| \le V_1\, C(\mathcal{E})\, k^{1/2},$$

(2) $$\text{distance}(q_i^{(n,0)}(t), \partial(\cup_j \Omega_j \cap \Lambda)) \ge c(\mathcal{E})\, k^{-3/2\alpha}\, r_\varphi$$

(3) $$\mathcal{N}_i(t,n) \le C(\mathcal{E})\, k^{3/4}$$

(4) $$|x_i^{(n,0)}(t) - x_i^{(0)}(t)| \le C(\mathcal{E})\, r_\varphi\, e^{-c(\mathcal{E})2^{nd/2}}$$

$\forall\, n > k$. The $x^{(0)}(t)$ is unique frictionless motion satisfying 1,2,3

Models (2) (dissipative “unphysical” thermostats) (Presutti, G)

Comparison with frictionless models is made possible via the properties of the entropy production rate.

Entropy: of thermostats increases by $\left[\dot{\mathbf{X}}_j^2 \stackrel{def}{=} 2K_{j,\Lambda_n}(x) \stackrel{def}{=} d\,N_j k_B T_j(x)\right]$

$$\sigma_0(x) = \sum_{j>0} \frac{Q_j}{k_B T_j(x)}, \qquad Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_{\mathbf{X}_j} U_{0,j}(\mathbf{X}_0, \mathbf{X}_j))$$

Unphysical friction is (for isoenergetic thermostats) infinitesimal

$$\alpha_{j,n} \stackrel{def}{=} \frac{Q_j}{d\,N_j k_B T_j(x)}, \qquad Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_j U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$$

Phase space contraction is not infinitesimal

$$\sigma(\mathbf{x}) = \sum_{\mathbf{j>0}} \frac{\mathbf{Q_j}}{\mathbf{k_B T_j(x)}} + \beta_0(\dot{\mathbf{K}}_0 + \dot{\mathbf{U}}_0 + \dot{\mathbf{\Psi}}_0) \stackrel{\mathbf{def}}{=} \sigma_0(\mathbf{x}) + \dot{\mathbf{F}}(\mathbf{x})$$

Equivalence? (in therm. lim. $\Lambda_n \to \infty$)

Idea: $Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_j U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$ is $O(1)$ (Williams,Searles,Evans 2004)

hence $\alpha_j = \frac{Q_j}{d\, N_j k_B T_{j,n}(x)}$ $\Rightarrow 0$: infinitesimal **as** $n \to \infty$.

But is $T_{j,n}(x) \ge c > 0$ **??**

Theorem (Presutti, G): *with* μ_0*–probability* 1

(a) $\frac{\mathbf{K_{j,\Lambda_n}(S^{(n,1)}x)}}{|\mathbf{\Lambda_n \cap \Omega_j}|} \ge \frac{1}{4}\, d\, \delta_j\, k_B T_j$ *for n large* *(hence* $\alpha \xrightarrow[n\to\infty]{} 0$*).*

(b) $\lim_{n\to\infty} S_t^{(n,1)} x = \lim_{n\to\infty} S_t^{(n,0)} x$ for all $t > 0$.

(c) $\frac{d\mu_t(dx)}{dt} = -\sigma(x)\, \mu_t(dx)$

Entropy production = volume contraction + a time derivative:

$\Rightarrow$ (average&fluctuations of σ) $\equiv$ (average&fluctuations of σ_0)

In other words: very generally phase space contraction can be identified with the physically defined entropy production.

provided $\beta_j(x)$ is a constant of motion as $n \to \infty$ and $\beta_j(S_t x) = \beta_j$ hence

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Theorem: *Let* Γ *be a pair potential and* $\varphi + \varepsilon\Gamma$ *be superstable for* $|\varepsilon|$ *small and* $P(\varphi + \varepsilon\Gamma)$ *(twice) differentiable at* $\varepsilon = 0$ *(i.e. "no phase trans."))*

$$g(S_t x) \stackrel{def}{=} \lim_{\Lambda_n \to \infty} \frac{1}{\Lambda_n \cap \Omega_j} \sum_{q,q' \in x} \Gamma(q(t) - q'(t)) = g$$

with μ_0*-probability* 1 *and for all* $t > 0$*: i.e.* $g(x)$ *constant of motion.*

Method: "*Entropy estimates*" for thermostatted motions

(I) Proof that kinetic energy per particle (in the Λ_n–regularized motion) stays $> \frac{d}{4}\delta_j \beta_j^{-1}$ with μ_0-probability 1 for $t \le \Theta$.

(II) Proof that the number of particles and their (kinetic+wall) energy in a unit box grows at most with a power $\gamma \in (\frac{1}{2}, 1)$ of $(\log_+(|\xi|/r_\varphi))^{\frac{1}{2}} \cdot (\log n)^\gamma$

Combining ideas of Sinai, Fritz-Dobrushin, and Marchioro, Pellegrinotti, Presutti, Pulvirenti (1975,1976).

Let $||x|| \stackrel{def}{=} \max_{\xi\in\Lambda_n} \frac{\max(N_{C_\xi}(x),\varepsilon_{C_\xi}(x))}{(\log_+(\xi/r_\varphi))^{1/2}}$ where

$C_\xi \stackrel{def}{=}$ unit cube centered at ξ, $N_{C_\xi}(x)$= number of particles in C_ξ,

$\varepsilon^2_{C_\xi} \stackrel{def}{=} \max_{q\in C_\xi}(\frac{1}{2}\dot{q}^2 + \psi(q))$. kinetic+wall energy

1) Given $1 > \gamma > \frac{1}{2}$, define for x s.t. $\mathcal{E}(x) \le E$, the **stopping time** $\tau(x)$

$$T_n(x) \stackrel{def}{=} \max\{t :\ t \le \Theta :\ \forall\, \tau < t,$$
$$\frac{K_{j,n}(S_\tau^{(n,1)}x)}{\varphi_0} > \kappa 2^{nd}, \quad \|S_t^{(n,1)}x\|_n < (\log n)^\gamma\}.$$

2) show that before the stopping time frictionless evolution and thermostatted evolution are very close for particles starting within Λ_k provided the cut-off $n \gg k$; hence entropy production remains uniformly bounded

3) Check that the μ_0-probability of $\mathcal{B} \stackrel{def}{=} \{x\,|\,x \in \mathcal{X}_E \text{ and } T_n(x) \le \Theta\}$ is

$$\mu_0(\mathcal{B}) \le\ C\, e^{-c(\log n)^{2\gamma}}.$$

Via large deviations estimates based on the entropy production control: which allows us the use the initial equilibrium distribution.

The next step is to study existence of stationary states with temperatures at $\pm\infty$ different: $\rho_{\pm\infty}(\mathbf{q}_n)$ correspond to $\rho_\pm, \beta_\pm$.

Lebowitz (1959): We try to find Γ-space ensembles that will represent systems not in equilibrium in the same way that microcanonical, canonical, g.c. ensembles represent systems in equilibrium ... And there is of course no *priori* assurance that such a parallel can be made

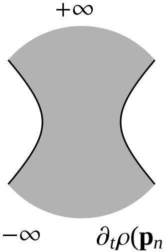

Fig.1: *A hyperboloid-like container* Ω. *Shape is symbolic (d=3)*

Stationary BBGKY hierarchy (hard core):

$$\partial_t \rho(\mathbf{p}_n, \mathbf{q}_n) = 0 = \sum_{i=1}^{n} \Big(-p_i \cdot \partial_i \rho(\mathbf{p}_n, \mathbf{q}_n)$$

$$+ \int_{\sigma(q_i, \mathbf{q}'_n)} \omega \cdot (\pi - p_i)\, \rho(\mathbf{p}_n, \mathbf{q}_n, \pi, q_i + r\omega) d\sigma_\omega\, d\pi \Big)$$

Work in progress (Gentile,Giuliani,G,Presutti) for the 81-th birthday.

Estimate the probability of $\mathcal{X}_n \stackrel{def}{=} \{\mathcal{E}(x) \le E;\ T_n(x) < \Theta\}$.

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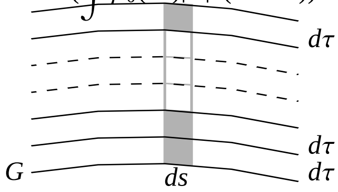
(2) $\Rightarrow$ bound on the *max entropy production within the stopping time*:
$|\int_0^{\tau_n(x)} \sigma(S_t^{(n,1)} x) dt| \le C'$ with C' depending only on E.

For inst. estimate probab. that kinetic energy becomes $G = 1/2$ of its μ_0-almost sure asympt. value. $G = \frac{1}{4} N_j d\beta_j^{-1}$. IF μ_0 were invariant

$$ds d\tau \stackrel{def}{=} \Big(\int \mu_0(dx) |\dot{K}| \delta(K - G)\Big) d\tau$$



Remark: *all shaded volumes would have the same μ_0 volume* !

Then $\mu_0(\mathcal{X}_n)$ is bounded, if $C \ge |\int_0^{\tau_n(x)} \sigma(S_{-t}x)dt|$, by:

$$e^{C'}\Theta \int ds|\dot{K}| \equiv e^{C'}\Theta \int \mu_0(dx)\delta(K-G)|\dot{K}|$$

thus, *by a large (kinetic energy) deviation estimate*

$$\le\ e^{-\gamma|\Lambda_n|}$$

with $\gamma > 0$: *summable* $\Rightarrow$ “Borel-Cantelli” (after a similar bound on the second item appearing in definition of stopping time) yields that the stopping time must be Θ with μ_0-prob 1.

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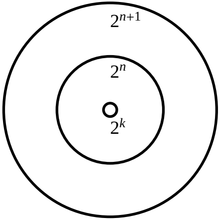
Some Details

Convergence $x_i^{(n,0)}(t) \to \overline{x}_i^{(0)}(t), \qquad q_i(0) \in \Lambda_k$

$$u_k^n(t) \stackrel{def}{=} \max_{q_i(0)\in\Lambda_k} |q_i^{(n,0)}(t) - q_i^{(n+1,0)}(t)|$$



Relation: $q_i^{(n,0)}(t) = q_i^{(n,0)}(0) + \dot{q}_i^{(n,0)}(0)\, t + \int_0^t f_i(x^{(n,0)}(\tau)d\tau \to$ comparison

subtract: n and $n+1$ relations $(\eta = \frac{3}{2} + \frac{3}{\alpha}) \;\Rightarrow$

$$u_k^n(t) \leq Cn^\eta \int_0^t u_{k_1}^n(\tau)d\tau \qquad k_1 = k + C\sqrt{n}$$

#iteration steps $\gg \ell = 2^{n/2} \;\Rightarrow\; |u_k^n(t)| \leq C\frac{(n^\eta\Theta)^\ell}{\ell!}$

Why not “same” for thermostatted dynamics ?

$$u_k^n(t) \le Cn^\eta \int_0^\Theta u_{k_1}^n(\tau)d\tau + C2^{-nd} \qquad k_1 = k + C\sqrt{n}$$

#iteration steps is same $\gg \ell = 2^{n/2}$ BUT error $Ce^{C\,n^\eta\,\Theta}\,2^{-n\,d} \to \infty$

Up to Stopping time properties

$$|\dot q_i^{(n,1)}(t)| \le C\,V_1\,(k\,\log n)^\gamma, \qquad |q_i^{(n,1)}(t)| \le r_\varphi\,(2^k + C\,(k\,\log n)^\gamma)$$

$$\Rightarrow \mathcal{N} \le C\,(k\log n)^{d\gamma}, \quad \rho \ge c\,(k\log n)^{-2(d\gamma+1)/\alpha}$$

Only $(k\log n)^\eta$ particles interact with $q_i \in \Lambda_k$

Compare $x^{(n,1)}(t)$ and $x^{(n,0)}(t)$ ℓ times $2^{k_\ell} = 2^k + \ell\,C\,(k\log n)^\gamma$

Compare $x^{(n,1)}(t)$ and $x^{(n,0)}(t)$ ℓ times $2^{k_\ell} = 2^k + \ell\, C\,(k\log n)^\gamma$ with $\ell = \ell^* \sim 2^n/(\log n)^\gamma$ (ℓ^* is largest s.t. $2^{k_\ell} < 2^{k+1}$)

$$\frac{u_{k_\ell}(t,n)}{r_\varphi} \leq C\,(k\log n)^\eta\,(2^{-nd} + \int_0^t \frac{u_{k_{\ell+1}}(s,n)ds}{r_\varphi \Theta})$$

Iterate. This time the Lyapunov exponent is small

$$\frac{u_k(t,n)}{r_\varphi} \leq e^{C\,(k\ \log n)^\eta} C(k\log n)^\eta 2^{-dn} + \frac{(C\,(k\ \log n)^\eta)^{\ell^*}}{\ell^*!}\,C\,(2^k + k(\log n)^\gamma + k^{1/2})$$