Thermostats entropy production and SRB distributions
(`http://ipparco.roma1.infn.it`)

Conference for the 60-th birthday of Giorgio Parisi, 8 Sept. 2008

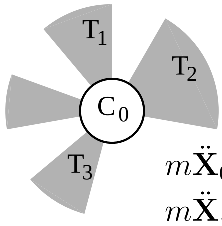
Important development in non equilibrium emerged from simulations since the early 1980's (Nosé, Hoover,Evans-Morriss, Cohen): [1, 2, 3, 4] identification of averages of phase space contraction with entropy production rate.

I dare say that it might be as fundamental as identifcation of temperature with average kinetic energy (Bernoulli, Herapath, Waterstone, Krönig).

Interpretation of the finite time averages? connection with SRB and reciprocity?

Parisi ? (Parisi: 1970's-1980's, see [5])

General thermostats model



$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$

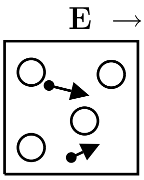
$$m\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \textstyle\sum_j \partial_i W_j(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i(\mathbf{X}_0)$$
$$m\ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i W_j(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

multipliers α_j imply $K_j = \frac{m}{2}\dot{\mathbf{X}}_j^2$ are exactly constants of motion with values $K_j = \frac{3}{2} N_j k_B T_j$, $j = 1, \ldots, n$.

$$\alpha_j(\mathbf{X}, \dot{\mathbf{X}}) = -\frac{(Q_j - \dot{U}_j)}{3N_j k_B T_j}, \qquad Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_{\mathbf{X}_j} W_j(\mathbf{X}_0, \mathbf{X}_j)$$

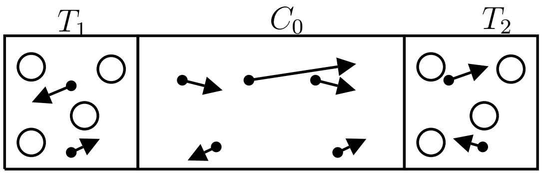
$$\sigma(\mathbf{X}, \dot{\mathbf{X}}) = \sum_{j>0} \frac{(Q_j - \dot{U}_j)}{k_B T_j}, \qquad -\text{“divergence”}$$

Examples



periodic boundary (“*wire*”)
$m\ddot{\mathbf{x}} = \mathbf{E} - \alpha\dot{\mathbf{x}}$

(1) Modern version of classical Drude’s model for electric conductivity.



(2) A model for thermal and electric conduction. Two forces conspire and the $\mathbf{F} = (T_2 - T_1, E)$ characterize strength: matter and heat currents flow.

Alternative models and approaches:

1) infinite thermostats (Ruelle 99, Jarzinsky 99,..,[6, 7]

2) stochastic thermostats (Kurchan 98, Lebowitz-Spohn, Maes 99, Gaspard 06, .. [8, 9, 10, 11])

3) infinite quantum: Feynman-Vernon 63, Eckmann-Pillet-Rey-Bellet 99, ..[12, 13])

4) finite quantum: GG 08, [14, 15]

5) equilibrium-to-equilibrium (Jarzinsky 97, Andrieux-Gaspard 08, [16, 17]

Finite thermostats are best suited for simulations and as a general conjecture statistical properties should be "independent" of thermostats.

Virtually always attention devoted to Onsager reciprocity & Green-Kubo

Microscopic motions are in all possible empirical senses "chaotic".
Paradigm of chaotic motions are the hyperbolic transitive systems.

Chaotic hypothesis (Ruelle 76, Cohen-G 95,[18, 19]) *Attracting sets for mechanical systems are smooth surfaces on which motion is smooth, hyperbolic and transitive.*

It might be at first disturbing. But disturbing assumptions are common:

Periodicity with equal period ("monocyclicity") of the motions was employed in the derivation of the second law from the action principle in Boltzmann.

It was considered also by Clausius, Maxwell, Helmholtz as the basis of the early works on the mechanical interpretation of the second law, CH $\Rightarrow$

if initial data x randomly chosen, near enough to an attracting set *and* with a distr. with (arbitrary) density, a probab. distr, μ exists (SRB dist.)

$$\langle G\rangle = \lim_{T\to\infty}\frac{1}{T}\sum_{j=0}^{T-1} G(S^j x) = \int G(y)\mu(dy), \qquad \text{with probability 1}$$

where $x \to Sx$ is obtained by timing observations on a selected event. *Time averages exist and are uniquely determined.* Hence

$$\sigma(x) = \sum_{j>0}\frac{Q_j - \dot U_j}{k_B T_j} = \varepsilon(x) - \frac{d}{dt}\sum\frac{U_j}{k_B T_j} = \varepsilon(x) + \dot V$$

$$\frac{1}{\tau}\int_0^\tau \sigma(S_t x)dt = \frac{1}{\tau}\int_0^\tau \varepsilon(S_t x)dt + \frac{1}{\tau}(V(\tau) - V(0)) \to \sigma_+ = \varepsilon_+$$

The main result and the power of CH is revealed by its implication of rigorous formulation of a *coarse graining theory* (GG 94,00,05,08, [20, 21, 22, 14].

It turns *rigorously* the SRB distribution into strochastic process and the time evolution into a *Markov chain*, (Sinai 68,94 Bowen 70, Ruelle 73, [23, 24, 25]).

Thus *making possible* and *without approximations* to treat the dynamics by stochastic methods.

The original fluctuation theorem (Cohen-G 95) and the general theory of reciprocity have been based on it.

Suppose

(1) *Reversibility* (above models are such)

$$IS_t = S_{-t} I, \quad I^2 = 1, \qquad \text{isometry}$$

(2) *Dissipativity*: $\langle \sigma \rangle_{SRB} = \sigma_+ > 0$.

(a) *Define: dimensionless (finite time) phase space average contraction*

$$p = \frac{1}{\tau} \sum_{j=0}^{\tau-1} \frac{\sigma(S^j x)}{\sigma_+}, \;\; \textit{or} \;\; p = \frac{1}{\tau} \int_0^\tau \frac{\sigma(S_t x)}{\sigma_+} dt$$

(b) *Define: pattern*: $t \to \varphi(t)$, $t \in [0, \tau]$ and

$$I_\varepsilon \varphi(t) = \varepsilon \varphi(\tau - t), \qquad \textit{antipattern}$$

as its *time-reversed pattern* with parity $\varepsilon = \pm 1$.

Fluctuation theorem: *For observables* $(F_1,\ldots,F_n)$ *with parities* ε_j *and for patterns* $(\varphi_1,\ldots,\varphi_n)$, ($n=0$ Cohen-G 95, $n>0$ GG 97, [19, 26])

$$\frac{prob(F_j(S_tx)\sim_\delta \varphi_j(t),p)}{prob(F_j(S_tx)\sim_\delta I_{\varepsilon_j}\varphi_j(t),-p)}\Big|_{SRB}\sim_{\tau\to\infty} e^{\tau\sigma_+ p}$$

A simple consequence (Bonetto 99, [27]) is an "entropy theorem"

$$\langle e^{-P\tau}\rangle_{SRB}\sim 1,\qquad P\stackrel{def}{=}\frac{1}{\tau}\int_0^\tau \sigma(S_tx)dt\equiv p\sigma_+$$

analogous to the work theorems (Jarzinsky 99, Crooks 99, [16, 28]), but **different** in spite of claims to the contrary.

It is *asymptotic* (rather than time-indep.) and for *stationary* (rather than equilibrium) states. Analogous to earlier results ($n=0$), also *not dealing with stationary states*, Bokhov-Kuzovlev 81, Evans-Searles 94, [29, 30].

Colorfully .. *relative probabilities of patterns observed in a time interval of size* τ *and in presence of an average entropy production* p *are the same as those of the corresponding anti-patterns in presence of the opposite average entropy production rate*,

or … *it "suffices" to change the sign of the entropy production to reverse the arrow of time*,

… *a waterfall will go up, as likely as we see it going down, in a world in which for some reason, or by the deed of a Daemon, the entropy creation rate has changed sign during a long enough time.*

We can also say that the *motion on an attractor is reversible, even in the presence of dissipation, once the dissipation is fixed.*

Variations of this property keep being rediscovered.

FT extends Green-Kubo and Onsager reciprocity (GG 97, [31]) if:

$$(1)\quad j_i(x)=\frac{\partial\sigma(x)}{\partial E_i},\qquad (2)\quad J_i=\langle j_i\rangle_{SRB},\qquad (3)\quad \underline{\textbf{if } \sigma(x)=0 \textbf{ for } \mathbf{E}=0}$$

$$\Rightarrow\qquad L_{ij}\stackrel{def}{=}\frac{\partial J_j}{\partial_{E_i}}|_{\mathbf{E}=0}=L_{ji},\qquad L_{ij}=\frac{1}{2}\int_{-\infty}^{\infty}\langle j_i(S_t x)j_j(x)\rangle dt$$

which follow from FT when it degenerates into triviality ($\mathbf{E}=0$).

Questions: (3) can fail in two ways

(a) $\frac{\partial\sigma(x)}{\partial E_i}=0$;
(b) $\sigma|_{\mathbf{E=0}}\neq 0$.

Does this restrict the interpretation of phase space contraction as entropy production rate? Does FT always constitute an extension of GK?

Remark: phase space contraction *depends* on the coordinate system and *therefore it cannot have a direct physical meaning.*
For instance in the case of the above finite thermostats $\neq$ phase contraction

$$\sigma(x) = \sum_{j>0} \frac{Q_j - \dot{U}_j}{k_B T_j} = \varepsilon(x) - \frac{d}{dt} \sum \frac{U_j}{k_B T_j} = \varepsilon(x) + \dot{V}$$

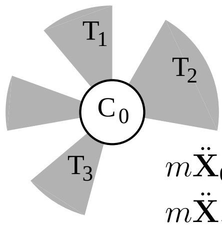
However if differs from instantaneous entropy prod. by a derivative, hence

$$\frac{1}{\tau}\int_0^\tau \sigma(S_t x)dt = \frac{1}{\tau}\int_0^\tau \varepsilon(S_t x)dt + \frac{1}{\tau}(V(\tau) - V(0)) \to \sigma_+ = \varepsilon_+$$

In general: changing coordinates or metric alters σ by a *time derivative*, $\sigma \to \overline{\sigma} = \sigma + \dot{O}$ as in the example above: no effect on long time averages.

$\Rightarrow$ all statistical properties of $\sigma, \overline{\sigma}$ and ε coincide: the long time averages of σ have a physical meaning and be identified with entropy production rates.

Therefore GK formulae can still follow from FT if
(1) currents can be generated by a function which satisfies FT and
(2) vanishes at $\mathbf{E}=0$. Again



$$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$$

$$m\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum_j \partial_i W_j(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i(\mathbf{X}_0)$$
$$m\ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i W_j(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

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

$$\sigma_{\mathbf{E}=0} \neq 0, \qquad \partial_{E_i} \sigma \equiv 0$$

So σ does not seem right. However if H_0 is total energy (kin.+poten.)

Altering σ by a time derivative $\sigma \to \sigma - \beta \dot{H}_0$ (for any β) gives (by the "*vis viva theorem*")

$$\dot{H}_0 = \mathbf{E} \cdot \dot{\mathbf{X}}_0 - \sum_{j>0} \alpha_j \dot{\mathbf{X}}_j^2 = \mathbf{E} \cdot \dot{\mathbf{X}}_0 + \sum_{j>0} (Q_j - \dot{U}_j)$$

$\Rightarrow$ phase space contraction is *statistically equivalent* to

$$\overline{\sigma}(x) = \sigma(x) - \beta \dot{H}_0(x) = \sum_{j>0} \frac{Q_j - \dot{U}_j}{k_B T_j} - \beta\, \mathbf{E} \cdot \dot{\mathbf{X}}_0 - \beta \sum_{j>0} (Q_j - \dot{U}_j)$$

hence to $\varepsilon(x) = \sum_{j>0} \frac{Q_j}{k_B T_j}$, the *entropy production.*.

Therefore $\overline{\sigma}$ *satisfies the FT* and *at the same time* generates all thermodynamic currents

$$j_j(x) = \frac{\partial \overline{\sigma}(x)}{\partial T_j} = -\frac{Q_j}{k_B T_j^2}, \qquad j_i(x) = \frac{\partial \overline{\sigma}(x)}{\partial E_i} = -\frac{1}{k_B T} \dot{\mathbf{X}}_{0,j}$$

The generating function for the currents:

$$\overline{\sigma} = \sum_{j>0} \frac{Q_j - \dot{U}_j}{k_B T_j} - \beta\,\mathbf{E}\cdot\dot{\mathbf{X}}_0 - \beta\,\sum_{j>0}(Q_j - \dot{U}_j)$$

vanishes for vanishing "thermodynamic forces"

$$\mathbf{F} = (T_1 - T, \ldots, T_n - T, E_1, \ldots, E_q) = \mathbf{0}$$

Since it satisfies the FT and vanishes at 0 forces *it follows*, (GG 97), [32], that the above currents satisfy reciprocity and Green-Kubo.

Heuristic construction and meaning of SRB. Coarse graining.

$\Rightarrow$ symbolic dynamics. $\exists\ \mathcal{E} = (E_0, \ldots, E_q)$ partition with "transition" or "compatibility" matrix

$$M_{\xi\xi'} = 1,\ \text{if}\ SE^0_\xi \cap E^0_{\xi'} \neq \emptyset, \qquad M_{\xi\xi'} = 0 \text{ otherwise}$$

(1) transitive ($M^{\overline{\ell}}_{\xi\xi'} > 0$)..
(2) Markovian: $1 \longleftrightarrow 1$ correspondence btwn compatile sequences and points (but a zero volume set).

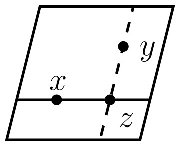
Call E_ξ "coarse cells"

(a) If $\boldsymbol{\xi} = (\ldots, \xi_{-1}, \xi_0, \xi_1, \ldots)$, $M_{\xi_i\,\xi_{i+1}} \equiv 1 \;\; \longleftrightarrow \exists\, x$ and $S^i x \in E_{\xi_i}$.

(b) If $\boldsymbol{\xi}, \boldsymbol{\xi}'$ corresp. x, x' and agree between $-\tau$ e $\tau \Rightarrow d(x, x') \le Ce^{-\lambda n}$

(c) E_ξ is foliated by W_s (W_i), smooth & connected, with histories eventually equal in the future (past) and $x, y \in W_s \Rightarrow d(S^n x, S^n y) \le Ce^{-n\lambda}$.

(d) If $x, y \in E_\xi \Rightarrow z = W_i(x) \cap W_s(y) \Rightarrow d(S^k y, S^k z) \xrightarrow[k\to\infty]{} 0$ exponent.



W_i is asymptotically attracting.

Let τ so large that *all* interesting observ. F are constant in the cells

$(\widetilde{\boldsymbol{\xi}} \stackrel{def}{=} (\xi_{-\tau}, \ldots, \xi_\tau))$

$$E(\widetilde{\boldsymbol{\xi}}) \stackrel{def}{=} S^\tau E_{\xi_{-\tau}} \cap S^{\tau-1} E_{\xi_{-\tau+1}} \cap \ldots \cap S^{-\tau} E_{\xi_\tau} = \text{“\textit{coarse cells}”}$$

Problem: time evolution *cannot be a permutation* (cells too large)

Immagine phase space discretized (Boltzmann) in *microcells*. As in simulations: a point $\to$ 64 bits per each of the $\mathcal{N}$ coordinates: $2^{64}\mathcal{N}$.

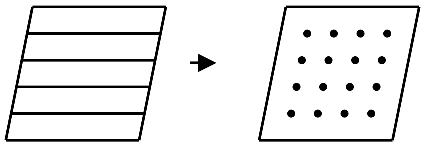
We wish $\langle F \rangle$.

The set $\mathcal{A}$ of recurrent points is the *attractor*. Transitivity (generalization of “ergodic hypothesis”) $\Rightarrow$ 1-cycle permutation.

Then averages are computed with a uniform distribution!

$$\langle F \rangle = \frac{\sum_{\widetilde{\boldsymbol{\xi}}} \mathcal{N}(\widetilde{\boldsymbol{\xi}}) F(\widetilde{\boldsymbol{\xi}})}{\sum_{\widetilde{\boldsymbol{\xi}}} \mathcal{N}(\widetilde{\boldsymbol{\xi}})}$$

In the discrete representation $\mathcal{A}$ appears, in each coarse cell, as a family of points regularly arranged on a finite number of unstable manifolds



The number $\mathcal{N}(\widetilde{\boldsymbol{\xi}})$ is subject to a strong compatibility constraint.

If $x \in E(\widetilde{\boldsymbol{\xi}})$ prefixed, let $\Lambda_i(\widetilde{\boldsymbol{\xi}})$ the coefficient of expansion of the surface $W_i(x)$ for the map $S^{2\tau}$ (as map of $S^{-\tau}x$ into $S^{\tau}x$).

$$\text{Compatibility} \Rightarrow \mathcal{N}(\widetilde{\boldsymbol{\xi}}) = \, cost\, \Lambda_i(\widetilde{\boldsymbol{\xi}})^{-1}$$

hence if $\lambda_i(\widetilde{\boldsymbol{\xi}}) \stackrel{def}{=} \log \Lambda_i(\widetilde{\boldsymbol{\xi}})$

$$\langle F \rangle = \frac{\sum_{\widetilde{\boldsymbol{\xi}}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})} F(\widetilde{\boldsymbol{\xi}})}{\sum_{\widetilde{\boldsymbol{\xi}}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})}}$$

espressing the SRB distribution.

Applications? Fluctuation theorem of CG (*very different from* Evans-Searles), Onsager reciprocity, Green-Kubo.

Can count the number of microcells! equal to entropy in equilibrium, NOT a function of state otherwise. *No entropy defined out of equilibrium.* (Ga 01) [33]. However there exist Lyapunov functions (Garrido-Goldstein-Lebowitz 05) [34, 35]

Remark 1: Besides the derivation of GK other applications:

(1) Heat conduction (Dorfman-Gaspard-Gilbert 02, Eckmann-Young 06, Gaspard-Gilbert 08, [36, 37, 38])

(2) Macroscopic non equilibrium properties Derrida-Lebowitz-Speer 02, Bertini et al. 01), [39]

(3) Applications to nanosystems (Gaspard 06)[10]

Remark 2: The FT theorem that $\overline{\sigma}(x)$ actually is the phase space contraction of the distribution on phase space with weight $e^{-\beta H_0(x)}$

$$\overline{\mu}(dx) = const\, e^{-\beta H_0(x)} \prod_{j>0} \delta(K_j(x) - \frac{3}{2} N_j T_j)\, dx$$

which is not the SRB distribution. *Unless* $n = 1$ $T_1 = T_0 = T$ and $\mathbf{E} = \mathbf{0}$: then it becomes the invariant distribution is (Evans-Morriss 90) [3]

$$\mu_0(dx) = const\, e^{-\beta H_0(x)} \prod_{j>0} \overline{\delta}(K_j(x) - \frac{3}{2} N_j T)\, dx.$$

Proof of FT:
If evolution is reversible (as in above models) $\exists I$ such that $I^2 = 1$, $IS = S^{-1}I$.
Then $\lambda_i(I\widetilde{\boldsymbol{\xi}}) = -\lambda_s(\widetilde{\boldsymbol{\xi}})$

Hence if $p = \frac{1}{\tau}\sum_{j=0}^{\tau-1}\frac{\sigma(S^j x)}{\sigma_+}$, $\sigma_+ = \langle\sigma\rangle > 0$

$$\frac{P_\tau(p)}{P_\tau(-p)} = \frac{\sum_{\widetilde{\boldsymbol{\xi}},p\,\text{fixed}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})}}{\sum_{\widetilde{\boldsymbol{\xi}},-p\,\text{fixed}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})}} = \frac{\sum_{\widetilde{\boldsymbol{\xi}},p\,\text{fixed}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})}}{\sum_{\widetilde{\boldsymbol{\xi}},p\,\text{fixed}} e^{-\lambda_i(I\widetilde{\boldsymbol{\xi}})}} = \frac{\sum_{\widetilde{\boldsymbol{\xi}},p\,\text{fixed}} e^{-\lambda_i(\widetilde{\boldsymbol{\xi}})}}{\sum_{\widetilde{\boldsymbol{\xi}},p\,\text{fixed}} e^{\lambda_s(\widetilde{\boldsymbol{\xi}})}} = e^{\tau\,p\,\sigma_+}$$

because $-\lambda_i(\widetilde{\boldsymbol{\xi}}) - \lambda_s(\widetilde{\boldsymbol{\xi}}) = p\sigma_+\tau$.

In terms of large deviations (*Fluct. Theorem*): $\exists p^*$

$$\zeta(-p) = \zeta(p) - p\sigma_+, \qquad \forall p \in (-p^*, p^*)$$

no parameters, model independent (provided reversible).

Verifiable in simulations and, in principle, in experiments, because of the interpretation of σ as entropy creation rate.

Remark 3: Thermostats isokinetic or Hamiltonian (or other)? [40]
Often: request to give a Hamiltonian interpretation to isokinetic thermostats
Note that the thermostat force if $-\alpha\dot{\mathbf{X}}_j$ with

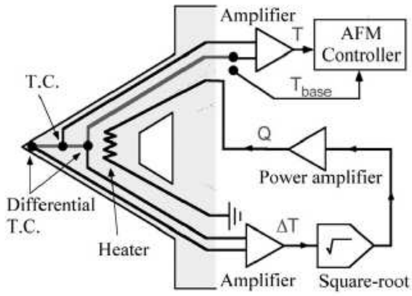
$$\alpha_j(\mathbf{X},\dot{\mathbf{X}}) = -\frac{(Q_j - \dot{U}_j)}{3N_j k_B T_j}, \qquad Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j\cdot\partial_{\mathbf{X}_j} W_j(\mathbf{X}_0,\mathbf{X}_j)$$

$$\sigma(\mathbf{X},\dot{\mathbf{X}}) = \sum_{j>0}\frac{(Q_j - \dot{U}_j)}{k_B T_j}, \qquad -\text{"divergence"}$$

and Q_j has size of order $O(L^2)$ if L is the surface of C_0, while $\dot{U}_j$ has a size that should be of order $O(L_j^{\frac{3}{2}})$ where L_j is the size of the container at temperature T_j. Hence in the limit $L_j\to\infty$ the multiplier $\alpha_j \xrightarrow[L_j\to\infty]{} 0$ and the motion becomes Hamiltonian. But the $\varepsilon(x)$ is extensive and equal to $\varepsilon(x)=\sum_j\frac{Q_j}{k_BT_j}$.

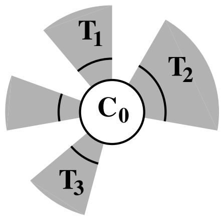
The time scale to see non Hamiltonian behavior tends to 0 with L_j. Similar to "weak limit approximation" justification of stochastic therm.

Equivalence conjectures: GG ([41, after (2.2),(2.5),(2.10),(5.27)], [42, Sec.5], [20],[43, Sec.8],[44, Sec.6,comment8],[45], [21, Sec.9.11],[46, 47]).



Block diagr. of feedback system from [48] (Nakabeppu-Suzuki:) a "thermometer" operating above room temperature and performing on a scale of $10\,nm = 100A^o$ (the size of one Hydrogen atom is .1nm or $1\,A^o$).

Conceptual problem: what does the measurement apparatus really do?



"Thermostats", or reservoirs, occupy finite regions outside C_0, *e.g.* sectors $C'_i \subset R^3$, $i = 1, 2\ldots$, marked T_i located beyond "buffers" $\mathcal{C}_a$: the buffers (representing the *walls* separating the system from the thermostats) simply have their boundaries marked. The reservoir particles are constrained to have a *total* kinetic energy K_i constant, by suitable forces $\boldsymbol{\vartheta}_i$, so that their "temperatures" T_i, are well defined, [49]. Buffers and reservoirs have *arbitrary sizes.*

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