Thermostats*, BBGKY hierarchy and Fourier law@

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The evolution of Equilibrium Statistical Mechanics started with the analysis of the thermodynamic limit and its importance in Nonequilibrium has also been very often mentioned

First Noneq. problem is to understand that time evolution of individual particles in insensitive to the motion of all but a few other particles near it (of course "near" means within a distance that grows with time).

Difficulties:

(1) nonequilibrium → nonconservative forces act → systems "heat up" → need to remove heat to achieve stationarity →

(2) conceptual difficulty: "how to do that"?. Microscopic mechanics is not only "conservative" but also reversible.

Thermostat models (review by Bonetto, Lebowitz, Rey-Bellet 2000)

(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.

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(0): ok

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

Of course for many the real interest of (1) is that it can be simulated computationally and it led to new developments and ideas.

Once defined the models the next question to address is

Lebowitz (1959) “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 its surroundings”

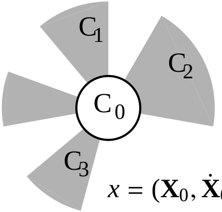
Hence the question is to see whether the models do lead at least to the elementary transport properties in stationary states.

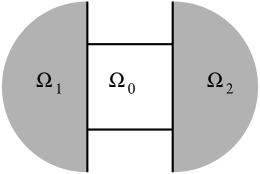
Equivalence

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.

Concrete examples

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





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

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

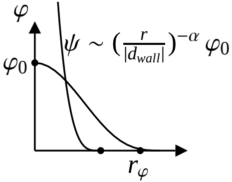
$$m\ddot{\mathbf{X}}_{ji} = -\,\partial_i U_j(\mathbf{X}_j) - \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) + \partial_i \Psi(\mathbf{X}_j) - a\,\alpha_j \dot{\mathbf{X}}_{ji}$$

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).

Existence: Consider the regularized motions in a container Λ_n $\Omega \cap \Lambda_n$, Λ_n = ball or radius $2^n r_\varphi$

Theorem: *With probability* 1 *particles of the initial state* X_0 *evolve so that independently of the regularization box size* n *those intially in* Λ_k *(*$k < n$*)*
(1) do not go too far :

$$|\dot{q}^{(n,0)}(t)| \leq V_1\, C(X_0)\, k^{1/2}$$

(2) nor go too close to the walls

$$\text{distance}(q_i^{(n,0)}(t), \partial(\cup_j \Omega_j \cap \Lambda)) \geq c(X_0)\, k^{-3/2\alpha}\, r_\varphi$$

(3) no accumulation of particles occurs around any particle $q_i^{(n)}(t)$ *initially in* Λ_k

$$\mathcal{N}_i(t,n) \leq C(X_0)\ k^{3/4}$$

(4) Motion insensitive to regularization

$$|x_i^{(n,0)}(t) - x_i^{(0)}(t)| \leq C(X_0)\, r_\varphi\, e^{-c(X_0) 2^{nd/2}}$$

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

Models (1) (dissipative "unphysical" thermostats) (Presutti, G)

Comparison with frictionless possible via entropy production rate properties.

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 $O(1)$ (Sarman, 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 $T_{j,n}(x) \geq c > 0$ **??** i.e. specific kinetic energy positive?

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

(a) specific K.E. stays $> 0 \;\Rightarrow\; \alpha \xrightarrow[n\to\infty]{} 0$ $\Rightarrow$ *unphysical forces disappear*

(b) $\lim_{n\to\infty} S_t^{(n,1)} x = \lim_{n\to\infty} S_t^{(n,0)} x \;\; \forall t > 0$ $\Rightarrow$ *equivalence*.

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

Entropy production $\sigma_0(x) =$ *volume contraction* $\sigma(x)$ + *a time derivative* $-\dot{F}(x)$:

$\Rightarrow$ (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 $\beta_j(S_t x) = \beta_j$

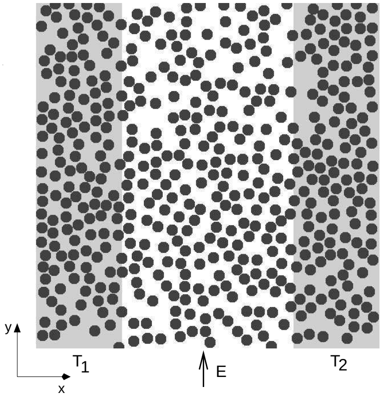
Theorem: *The specific kinetic energy of each thermostat, with μ_0-probability 1, is constant: i.e. thermostats temperatures are constantL.*

More: if Φ is any pair potential with $\varphi + \varepsilon\Phi$ superstable for $|\varepsilon|$ small and $P(\varphi + \varepsilon\Phi)$ (twice) differentiable at $\varepsilon = 0$ (i.e. "no phase trans."))

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

and for all $t > 0$: i.e. the specific potential energy of Φ is a constant.

A natural question is whether there is chance that the system approaches a stationary state. This has been investigated (P.Garrido, GG) in the case of a system of hard disks.



Typical configuration of the model simulated. The disks in the white part (bulk particles) are accelerated in the y direction by a driving field E. The disks at the grey boxes act as thermal baths

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

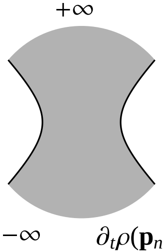


Fig.1: *A hyperboloid-like container* Ω. *Shape is symbolic (d=3)*

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)

$$G_{\mathbf{q}_n}(\mathbf{p}_n) \stackrel{def}{=} \frac{e^{-\frac{1}{2}\beta(\mathbf{q}_n)\mathbf{p}_n\cdot\mathbf{p}_n}}{\sqrt{(2\pi)^{nd}\det\beta(\mathbf{q}_n)^{-1}}}, \qquad :x^k: \stackrel{def}{=} (2C)^{k/2} H_k\left(\frac{x}{\sqrt{2C}}\right)$$

Look for BBGKY solution expanded in Wick (Hermite) monomials:

$$\rho(\mathbf{p}_n, \mathbf{q}_n) = G_{\mathbf{q}_n}(\mathbf{p}_n) \sum_A \rho_A(\mathbf{q}_n) \ :\mathbf{p}_n{}^A:$$

$$:\mathbf{p}_n^A: \stackrel{def}{=} :\prod_{k=1}^{n}\prod_{\alpha=1}^{d}(\overline{p}_{k\,\alpha})^{a_\alpha^k}:, \qquad \overline{p}_k \stackrel{def}{=} -\sqrt{\frac{\beta(q_i)}{2}}p_k$$

BBGKY become a hierarchy in the coefficients $\rho_A(\mathbf{q}_n)$.

Result 0: *In the stationary case the functions $\rho_A(\mathbf{q}_n)$ satisfy a hierarchy of equations: for each $\rho_A(\mathbf{q}_n)$ the hierarchy involves $\rho_{A'}(\mathbf{q}_m)$ with $m = n+1, |A'| = |A|$ or $\rho_{A'}(\mathbf{q}_n)$ with $|A'| = |A|, |A|+2, |A|+4$.*

This result is a simple algebraic check (a key cancellation: $|A| + 6$ is missing)

Even A and odd A have independent equations which could be coupled by boundary conditions: otherwise $\rho_{odd} \equiv 0$ would be possible

Look for solutions $\neq 0$ of the odd correlations. Several exact solutions can be found (disregarding boundary conditions at collisions)

$$\rho_{odd}(\mathbf{q}_n, \mathbf{p}_n) = \delta_{n>1} \sum_{i\alpha} C_{n,i}\, \partial_{i\alpha} \widetilde{F}(\mathbf{q}_n) \cdot \partial_{\overline{p}_{i\alpha}} \frac{:\mathbf{p}_n^A:}{\mathbf{a}^i!}$$

with $\widetilde{F}(\mathbf{q}_n) = \prod_{i=1}^n \widetilde{F}(q_i)$ and with $C_{n,i}(A_1, \ldots, A_n)$ depending only on A_j, $j \neq i$ and arbitrary provided

$$\Delta\widetilde{F} - \frac{1}{2}\frac{\partial\beta \cdot \partial\widetilde{F}}{\beta} = 0 \text{ in } \Omega, \qquad \partial_n \widetilde{F} = 0 \text{ in } \partial\Omega$$

Any relation between $\widetilde{F}$ and β leads to a nonlinear heat equation which becomes $\Delta T = 0$ upon linearization.

Questions

(1) Are there solutions for the even correlations?
(2) How to determine $\widetilde{F}$ and the arbitrary constants?

We consider several possibilities

Collision continuity: if $p_1, p_2 \longleftrightarrow p'_1, p'_2$ is a collision between a particle in q_1 and one in $q_1 + r\omega$ ($\omega \cdot (p_2 - p_1) < 0$)in the direction ω then $\rho(\mathbf{q}_n, \mathbf{p}_n) = \rho(\mathbf{q}_n, \mathbf{p}'_n)$ if $\mathbf{p}'_n$ differs from $\mathbf{p}_n$ with p_1, p_2 are replaced by p'_1, p'_2.

This is a property considered in the literature: however it seems difficult (impossible) to impose and doubtful.

More promising is a stochastic boundary condition at $\pm\infty$

$$\sum_{\alpha=1}^{3} \partial_\alpha \int \rho(p,q) p_\alpha Q(p) d^3p = \int_{\omega\cdot(\pi-p)<0} |\omega \cdot (\pi - p)| \, d^3p d^3\pi$$
$$\cdot \, d\sigma_\omega \Big(Q(p') \, \overline{G}(p') \overline{G}(\pi') \rho_\emptyset(q, q + r\omega) - Q(p) \rho(p, q, \pi, q + r\omega) \Big)$$

with $\overline{G}(p) = \frac{\beta_\pm^{(d+1)/2}}{(2\pi)^{(d-1)/2}} \, p_n \, e^{-\frac{1}{2}\beta_\pm p^2}$.

This may establis a relation between even and odd correlations: and allow us to take $C_n = 0$ for $n \neq 2$ to determine $C_2\widetilde{F}$, once a solution for the even correlations is found. Possible to low order in δ and z_0.

Other geometries can be considered: for instance conic geometry

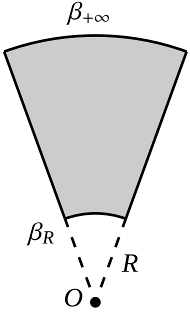


Fig.2: Ω *is a cone with vertex at O truncated at a distance R from its vertex;* $T(q) = T_0 + \tau(q)$ *solves* $\Delta T = 0$ *with* $\partial_n T = 0$ *on* $\partial\Omega$ *and value* τ_- *at bottom of* Ω *and* $\tau_+ = 0$ *at* ∞*: i.e.* $\tau_- = \frac{\delta}{R}, \tau_+ = 0$

with its special case

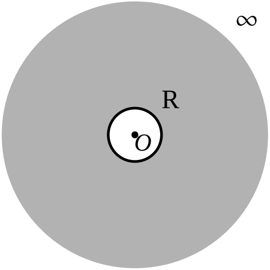


Fig.3: *A special case of Fig.2 the "exterior problem", i.e. the heat conduction outside a ball: a "hot potato" problem. It has an exact solution* $T(q)$*.*

A geometry with a long cylinder which opens up in two reservoirs

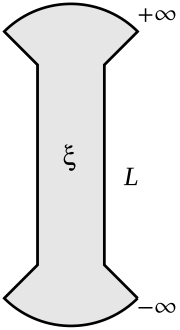
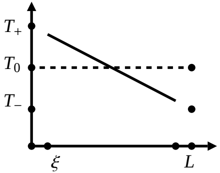
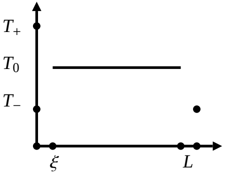


Fig. 4
The container Ω is a cylinder of diameter ξ and height $L \gg \xi \gg r$ continued into two cones extending to ∞.

The interpolating inverse temperature $\beta(q)$ will be close to β_+ at the upper end of the cylinder and close to β_- at the bottom.

In this essentially 1-dimensional geometry the temperature will have some value at the top and the bottom (dictated from the boundary conditions at $\pm\infty$ and the solution of the heat equation) which will be interpolated essentially linearly ("Saint-Venant's principle"), but $\delta T = O(L^{-1})$.





Continuity? It is not clear why the correlation functions of a stationary state shoud be continuous at collisions, *e.g.* why

$$\rho(q_1, p_1, q_1 + r\omega, p_2) = \rho(q_1, p_1', q_1 + r\omega, p_2')$$

if $p_1, p_2 \longleftrightarrow p_1', p_2'$ is a collision at q_1 and $q_1 + r\omega$ $(\omega \cdot (p_2 - p_1) < 0)$ in the direction ω.

True that this is conserved by dynamics; but no contradiction with initial states in which does not hold. On the other hand even if holding at any finite time it might fail to hold in the stationary state via the following scenario

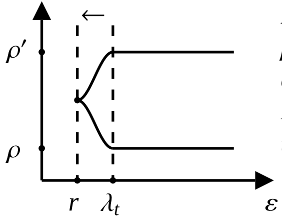


Fig.6: a pair correlations $\rho(\varepsilon)$, $\rho'(\varepsilon)$ discontinuity developing at t large: $\lambda_t \xrightarrow[t\to\infty]{} r$. For $t = +\infty$ $\lambda_t = r$ and discontinuity is sharp.

The problem of which should be the appropriate boundary condition at collisions is therefore open: is continuity a required property? are the multiple collisions relevant (notice that they occurr in the hierarchy).

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