Fluctuations and frictionless thermostats in nonequilibrium statistical mechanics

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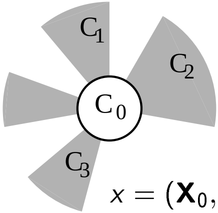
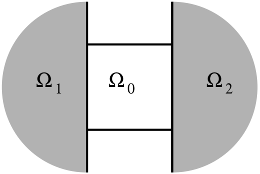
Thermostat models (Feynman-Vernon 1963): finite system in contact with infinite. Examples





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

Initial state: $\mu_0(dx) \stackrel{def}{=} C e^{-\sum_{j=0}^{\nu} \beta_j H_j(\mathbf{X}_j, \dot{\mathbf{X}}_j)} \prod_j \frac{d\mathbf{X}_j \, d\dot{\mathbf{X}}_j}{N_j!}$

Equations

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

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

$$U_j(\mathbf{X}_j) = \sum_{q,q' \in \mathbf{X}_j} \varphi(q - q'), \qquad \Psi(X) = \sum_{q \in X} \psi(q)$$

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

Initial state: infinite Gibbs;
With given chemical potentials λ_j and temperatures β_j^{-1}

No phase transitions $\Rightarrow$ kinetic-potential energy density, density and many observables constant with μ_0-probability 1 at time $t = 0$

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

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

Thermostats in thermodynamic limit:

Cut-off in a ball Λ_n (side size $2^n r_\varphi$) then limit $n \to \infty$.

Time evolution $S_t^{(0)} x = \lim_{n\to\infty} S_t^{(n,0)} x$

[Caglioti, Marchioro, Pulvirenti et al (2000)]

4 Thermostats have fixed

temperature, density, energy density at all times (actually expect all intensive observables). In particular

$$\lim_{\Lambda\to\infty}\frac{1}{|\Lambda\cap\Omega_j|}K_{j,\Lambda}(S_t^{(0)}x)=\frac{d}{2}\beta_j^{-1}\delta_j$$

in absence of phase transitions (GP)

Entropy: thermostats entropy increases by

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

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

$\mathcal{E}(x)\stackrel{def}{=}\sup_\xi\sup_{R>(\log_+(\frac{\xi}{r_\varphi}))^{1/d}}\frac{W(x;\xi,R)}{R^d}<+\infty$ with μ_0-prob. 1.

theorem $\exists C, c^{-1}$: *frictionless evolution of* $q_i(0) \in \Lambda_k$ ($v_1 = \sqrt{\frac{\varphi_0}{m}}$)

$$\begin{aligned}
&(1) \qquad \text{velocity} \le\ v_1\, C\, k^{1/2},\\
&(2) \qquad \text{distance to walls} \ge\ r_\varphi\, c\, k^{-3/2\alpha}\\
&(3) \qquad \text{interacting particles} \le\ C\ k^{3/4}\\
&(4) \qquad |x_i^{(n,0)}(t) - x_i^{(0)}(t)| \le\ C\, r_\varphi\, e^{-c2^{nd/2}}
\end{aligned}$$

$\forall\, n > k$. *The* $x^{(0)}(t)$ *is the unique solution of the frictionless equations satisfying the bounds 1,2,3. (CMP,(GP))*

Q1: is the temperature fixed for $t > 0$? are intensive quantities constants of motion? (yes: (GP)).

Q2: Alternative models (Λ_n–regularized): necessary for simulations

Simulations provided insights (Nosé, Hoover, Evans, Morriss, Cohen) in 980-90's,

Nonequilibrium statistical mech.: extending thermodynamics to stationary states

Chaotic hypothesis: *motion is hyperbolic* (Ruelle, Cohen-G)

Stationary states described by "ensembles" = families of stationary distributions μ.

Look for universal properties: "**model-independent** relations between averages"

Examples: equilibrium $\to$ Second law: $\frac{dU+pdV}{T}$ = "exact"

Onsager reciprocity (time reversal symmetry)

Finite thermostats & Chaotic Hypothesis & Time reversal $\Rightarrow$

"Fluctuation theorem": *probability that (odd) observables* $F(x)$ *follow patterns* $\varphi(t)$*:* $F(S_t x)=\varphi(t)$ *for* $t\in[-\frac12\tau,\frac12\tau]$ *while entropy production is* $s=\frac{1}{2\tau}\int_{-\tau}^{\tau}\sigma(S_t x)dt$ *satisfies*

$$\frac{P(F(S_t x)=\varphi(t)|s)}{P(F(S_t x)=-\varphi(-t)|-s)}=_{\tau\to\infty}1$$

Conditioned to given entropy production a "pattern" has the same probability of the reversed "pattern" conditioned to the opposite entropy production.

(Cohen-G,G)

Amount of entropy production $\longleftrightarrow$ "arrow of time"

$$\frac{P(F(S_t x) = \varphi(t)|s)}{P(F(S_t x) = -\varphi(-t)| - s)} =_{\tau\to\infty} 1$$

To invert time "just" change the sign of s.

Origin: $\frac{P(s)}{P(-s)} = e^{\tau s}$ (Cohen,G):

FT is an extension of Onsager reciprocity and Green-Kubo (G)

Finite thermostats. Equations in Λ_n:

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

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

With $\alpha_{j,n}$ so fixed that $U_{j,\Lambda_n} + K_{j,\Lambda_n} = E_{j,\Lambda_n}$ is exact constant

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

with $m\dot{\mathbf{X}}_j^2 \stackrel{def}{=} 2K_{j,\Lambda_n}(x) \stackrel{def}{=} d\,N_j k_B T_j(x)$

Gauss least contraint ! Unphysical? can we change the mechanical laws ?

Equivalence? (required in thermodynamic limit $\Lambda_n \to \infty$)

Idea: $Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_j U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$ involves forces across the boundary of test system $\Rightarrow O(1)$ while $N_j = O(2^{dn}) = \mathrm{volume}(\Lambda_n)$

$$\alpha_j = \frac{Q_j}{d\, N_j k_B T_{j,n}(x)} \quad \textbf{tends to } 0 \textbf{ as} \quad n \to \infty$$

"Mean field". Problem: But is $T_j(x) \geq c > 0$?? (non-trivial)

$\alpha_j = \frac{Q_j}{d\, N_j k_B T_{j,n}(x)}$

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

(a) yes: $\frac{1}{2} k_B T_j(x) N_j \ge \frac{1}{4} N_j \beta_j^{-1}$ *(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) $\frac{d\mu_0(dx)}{dt} = -\sigma(x)\mu_0(dx)$ and

$$\sigma(x) = \sum_{j>0} \frac{Q_j}{k_B T_j(x)} + \beta_0(\dot K_0 + \dot U_0 + \dot\Psi_0) \stackrel{def}{=} \sigma_0(x) + \dot F(x)$$

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Entropy production differs by a time derivative of a bounded observable from the volume contraction:

$\Rightarrow$ average of $\sigma \equiv$ average of σ_0 *provided* $\beta_j(x)$ is a constant of motion as $n \to \infty$ and $\beta_j(S_t x) = \beta_j$

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

Method: "*Entropy estimates*" for thermostatted motions

(I) Proof that kinetic energy per particle (in the Λ_n–regularized motion) stays $> \frac{d}{4}\beta_j^{-1}$ 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 $(\log_+(|\xi|/r_\varphi)) \cdot (\log n)$

This is based on combining an idea of Sinai, and one of Marchioro, Pellegrinotti, Presutti, Pulvirenti (1975,1976), and Fritz-Dobrushin (1976). Let

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

C_ξ= unit cube centered at ξ,

$N_{C_\xi}(x)$= number of particles in C_ξ,

$\varepsilon^2_{C_\xi} = \max_{q\in C_\xi}(\frac12\dot q^2+\psi(q))$.

Ideas of the analysis follow.

1) Define for x s.t. $\mathcal{E}(x) \le E$, the **stopping time** $\tau(x)$

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

2) show that before reaching the stopping time the frictionless evolution and the thermostatted evolution are very close for particles starting within Λ_k provided the cut-off $n \gg k$.

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

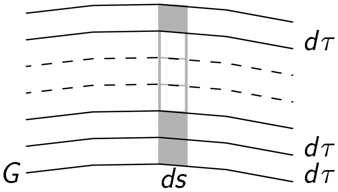
$$\mu_0(\mathcal{B}) \le \ C\, e^{-c(\log n)^{2\gamma}}.$$

Via large deviations estimates. *Key*: entropy production is a quantitative estimate of how far from invariant is μ_0 thus reducing estimates to *equilibrium estimates* (GP).

17 Estimate the probability of $\mathcal{X}_n \stackrel{def}{=} \{\mathcal{E}(x) \le E;\ T_n(x) < \Theta\}$. From (2) derive a bound on the *max entropy production within the stopping time* as $|\int_0^{\tau_n(x)} \sigma(S_t^{(n,1)}x)dt| \le C'$ with C' depending only on E.

For inst. estimate probab. that kinetic energy becomes smaller than 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

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



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

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

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

Hence $\le e^{C'}\Theta \int \mu_0(dx)\delta(K-(G-\eta))|\dot{K}|$, for $\varepsilon \ge \eta \ge 0 \Rightarrow$ (any $\varepsilon > \eta > 0$!)

$$\le C\frac{1}{\varepsilon}\int_0^{\varepsilon} d\eta \int \mu_0(dx)\,\delta(K-(G-\eta))\,|\dot{K}|$$

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

$$\le \frac{1}{\varepsilon}\int \mu_0(dx)\,\chi(G-\eta \le K \le G)\,|\dot{K}|$$

$$\le \frac{1}{\varepsilon}\sqrt{\mu_0(\chi(G-\eta \le K \le G))}\,\sqrt{\mu_0(\dot{K}^2)} \le e^{-\gamma|\Lambda_n|}$$

with $\gamma > 0$: *summable* $\Rightarrow$ "Borel-Cantelli".

Reference

G. Gallavotti, E. Presutti:
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