

Thermostats and entropy

Recent developments in nonequilibrium S.M. due to

- a) Steady states (rather than approach to equilibrium or to steady)
- b) thermostat models (finite \rightarrow simulations)

Steady State = probability dist. μ : use \Rightarrow *average values*

Collections of μ 's generalize *ensembles* (non eq.)

Empirically a thermostat is a device that fixes, by mechanical action, the temperature in some part of a system under study or in parts of systems interacting with it

In early works the thermostat forces act globally:

$$\ddot{\mathbf{x}}_i = -\partial_{\mathbf{x}_i} U(\mathbf{X}) + \mathbf{E} - \alpha \dot{\mathbf{x}}_i$$

U = potential energy, \mathbf{E} the nonconservative positional force, $\mathbf{X} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$ and α is

$$\alpha = \frac{-\dot{U}(\mathbf{X}) + \mathbf{E} \cdot \dot{\mathbf{X}}}{\dot{\mathbf{X}}^2},$$

so defined that $K = \frac{1}{2}\dot{\mathbf{X}}^2 = \frac{3}{2}Nk_B T$, is exactly constant.

Dating back to early days is another example (“Drude’s thermostat”). “Charged h.c. particles” enclosed in a toral annulus (“electric wire”), subject to a (“electromotive force”) and to collisions among each other or with array of fixed hard sphere obstacles (“crystal background”),

$$\ddot{\mathbf{x}}_i = \text{elastic coll.} + \mathbf{E} + \text{dissipation}$$

dissip. = at collision speed rescaled to $v = \sqrt{3k_B T}$ = thermostat force: av. kinetic energy per particle $\sim \frac{3}{2}k_B T$.

Other model is “viscous thermostat”

$$\ddot{\mathbf{x}}_i = \text{elastic coll.} + \mathbf{E} - \nu \dot{\mathbf{x}}_i$$

ν = constant adjusted so that av. $\langle K \rangle = \frac{3}{2}Nk_B T$. The Nosé-Hoover thermostat .. All are *global*

External models ?

General model with thermostats that are “external” to system \mathcal{C}_0 surrounded by particles interacting via short range interactions, through portions $\partial_i \mathcal{C}_0$ of the surface of \mathcal{C}_0 , and subject to constraint that the N_i particles in i -th thermostat have K.E. $K_i = \frac{1}{2}\dot{\mathbf{X}}_i^2 = \frac{3}{2}N_i k_B T_i$.

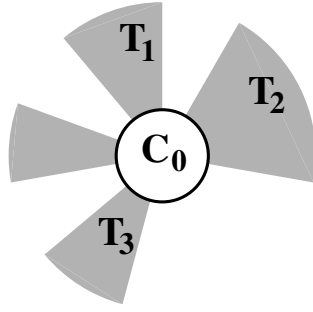


Fig1

Particles in \mathcal{C}_0 (“system”) interact with particles in shaded regions (“thermostats”) ■
 constrained to fixed total K.E.

The equations of motion will be

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

$$\ddot{\mathbf{X}}_i = -\partial_{\mathbf{X}_i} \left(U_i(\mathbf{X}_i) + W_{0,i}(\mathbf{X}_i, \mathbf{X}_j) \right) - \alpha_i \dot{\mathbf{X}}_i$$

with α_i s.t. K_i constant. $W_{0,i}$ interaction potential \mathcal{C}_i - \mathcal{C}_0 , U_0, U_i internal energies.

No direct interaction between thermostats. $\mathbf{E}(\mathbf{X}_0)$ = external positional forces. The constraints give

$$\alpha_i \equiv \frac{Q_i - \dot{U}_i}{3N_i k_B T_i}$$

the work that particles in \mathcal{C}_0 exercise on the particles i -th therm. is $Q_i \stackrel{def}{=} -\partial_{\mathbf{X}_i} W_{0,i}(\mathbf{X}_0, \mathbf{X}_i) \cdot \dot{\mathbf{X}}_i$: is **interpreted** as “amount of heat

Q_i entering" thermostat C_i .

Main feature: thermostats are *external to system proper*

Similar to imagining thermostat infinite with Gibbs states with assigned temperatures T_i at ∞ as their initial states. *Conservative but infinite.*

Other feature is *reversibility*: *i.e.* if $I(\mathbf{X}, \dot{\mathbf{X}}) \stackrel{def}{=} (\mathbf{X}, -\dot{\mathbf{X}})$ is *time reversal* then if $S_t(\mathbf{X}, \dot{\mathbf{X}})$ is solution

$$IS_t \equiv S_{-t}I$$

Entropy and divergence

Equations of motion do not conserve phase space volume and will contract it, at least in average: important exception is equilibrium, if modeled by Hamiltonian eq.

For a physical interpretation to average value of phase space contraction restrict to systems with guaranteed existence of averages.

Chaotic hypothesis (CH): *Motions developing on the attracting set of a chaotic system can be regarded as motions of trans. hyperbolic (also called “Anosov”) system.*

\Rightarrow all smooth observables $F(\mathbf{X}, \dot{\mathbf{X}})$ on phase space all initial data near an attracting set, *with the exception of a set of data with 0 total volume*, admit time av. independent of initial data and define 1-que probability distribution μ

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T F(S_t(\mathbf{X}, \dot{\mathbf{X}})) dt = \int F(\mathbf{Y}, \dot{\mathbf{Y}}) \mu(d\mathbf{Y}, d\dot{\mathbf{Y}})$$

μ is called *SRB distribution*.

If $\sigma(\mathbf{X}, \dot{\mathbf{X}}) = -$ *divergence of the equations of motion*, we call σ_+ its time average *i.e.* its μ -integral with respect to μ : system is *dissipative* if $\sigma_+ > 0$.

Since the early works it was clear that there should be a relation between entropy and phase space contraction. However in general the two notions are not identical.

Phase space contraction rate, for velocity–position is

$$\sigma(\dot{\mathbf{X}}, \mathbf{X}) = \varepsilon(\dot{\mathbf{X}}, \mathbf{X}) + \dot{R}(\mathbf{X})$$

where, remarkably, $\varepsilon(\dot{\mathbf{X}}, \mathbf{X})$ is given by

$$\varepsilon(\dot{\mathbf{X}}, \mathbf{X}) = \sum_{j>0} \frac{Q_j}{k_B T_j}$$

and can be interpreted as the *entropy creation rate*, because of the meaning of Q_i (work performed by system in \mathcal{C}_0 on thermostat \mathcal{C}_i , while $R(\mathbf{X}) = \sum_{j>0} \frac{U_j}{k_B T_j}$.

An additive total derivative, $\dot{R}(\mathbf{X})$, of a bounded quantity is like additive constant in equilibrium. It does not affect the long time fluctuations

\Rightarrow average contraction and the average entropy creation have *same average* $\sigma_+ \equiv \varepsilon_+$ and, if $\varepsilon_+ \neq 0$, the *same large deviations rate function* $\zeta(p)$ for

$$p = \frac{1}{\sigma_+\tau} \int_0^\tau \sigma(S_t(\dot{\mathbf{X}}, \mathbf{X}))dt \text{ and } \frac{1}{\varepsilon_+\tau} \int_0^\tau \varepsilon(S_t(\dot{\mathbf{X}}, \mathbf{X}))dt$$

the latter is measurable as it concerns heat exchanges.

Remarkable because (thermostats being reversible) $p = \frac{1}{\tau} \int_0^\tau \frac{\sigma(S_t(\dot{\mathbf{X}}, \mathbf{X}))}{\sigma_+} dt$ satisfies the *fluctuation relation*, by the *fluctuation theorem* ([GC95]): namely

$$\zeta(-p) = \zeta(p) - p\sigma_+, \quad \text{for all } |p| < p^*,$$

where $p^* \geq 1$: \Rightarrow possibility of test CH in experiments.

Quantum systems

At first seems impossible: in quantum systems average K.E. is *not* identified with temperature; and all motions are quasi periodic, so that no chaos is possible.

A way out, explored in the literature: thermostats as infinite systems. However recent progress in N.E.S.M. was sparked by the introduction of *finite size* thermostats.

Consider Fig.1 when quantum nature of particles in \mathcal{C}_0 cannot be neglected. Let H be the operator on $L_2(\mathcal{C}_0^{3N_0})$, space of symmetric or antisymmetric wave functions Ψ ,

$$H = -\frac{\hbar^2}{2}\Delta_{\mathbf{X}_0} + U_0(\mathbf{X}_0) + \sum_{j>0} (U_{0j}(\mathbf{X}_0, \mathbf{X}_j) + U_j(\mathbf{X}_j))$$

its spectrum consists of $E_n = E_n(\{\mathbf{X}_j\}_{j>0})$, for \mathbf{X}_j fixed. And a system–reservoirs model can be the *dynamical system* on the space of the variables $(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0})$ defined by ($\langle \cdot \rangle_\Psi$ is expectation in the state Ψ)

$$\begin{aligned} -i\hbar\dot{\Psi}(\mathbf{X}_0) &= (H\Psi)(\mathbf{X}_0), \quad \text{and for } j > 0 \\ \ddot{\mathbf{X}}_j &= -\left(\partial_j U_j(\mathbf{X}_j) + \langle \partial_j U_j(\mathbf{X}_0, \mathbf{X}_j) \rangle_\Psi\right) - \alpha_j \dot{\mathbf{X}}_j \\ \alpha_j &\stackrel{def}{=} \frac{\langle W_j \rangle_\Psi - \dot{U}_j}{2K_j}, \quad W_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_j U_{0j}(\mathbf{X}_0, \mathbf{X}_j) \end{aligned}$$

Evolution maintains the kinetic energies $K_j \equiv \frac{1}{2} \dot{\mathbf{X}}_j^2$ exactly constant so they define thermostats temperatures T_j via $K_j = \frac{3}{2} k_B T_j N_j$, as in the classical case.

The formal volume element $\mu_0(\{d\Psi\}) \times \nu(d\mathbf{X} d\dot{\mathbf{X}})$ with

$$\mu_0(d\Psi) \stackrel{def}{=} \left(\prod_{\mathbf{x}_0} d\Psi(\mathbf{x}_0) \right) \delta \left(\int_{\mathcal{C}_0} |\Psi(\mathbf{Y})|^2 d\mathbf{Y} - 1 \right)$$

$$\nu(d\mathbf{X} d\dot{\mathbf{X}}) \stackrel{def}{=} \prod_{j>0} \left(d\mathbf{X}_j d\dot{\mathbf{X}}_j \delta(\dot{\mathbf{X}}_j^2 - 3N_j k_B T_j) \right)$$

conserved, by the unitary property of the wave functions evolution, just as in the classical case, *up to the volume contraction in the thermostats*.

Solutions *will not be quasi periodic* and the Chaotic Hypothesis can be assumed: hence dynamics should select an invariant distribution μ , the SRB.

Furthermore reversibility will imply the fluctuation relation for the phase space contraction given again by $\sigma = \sum_j \frac{Q_j}{k_B T_j} + \dot{R}$ with $Q_j = \langle W_j \rangle_\Psi$.

Check: if only one thermostat and no forces. At least one stationary distribution equivalent to canonical distribution at the temperature T_1 associated with the (constant) K.E. of thermostat: $K_1 = \frac{3}{2}k_B T_1 N_1$. **Candidate** is

$$\sum_{n=1}^{\infty} e^{-\beta E_n} \delta(\Psi - \Psi_n(\mathbf{X}_1) e^{i\varphi_n}) d\varphi_n \delta(\dot{\mathbf{X}}_1^2 - 2K_1)$$

where $\Psi =$ wave functions in \mathcal{C}_0 and \dot{X}_1, X_1 positions and velocities of therm. particles and $\varphi_n \in [0, 2\pi]$ is a phase, $E_n = E_n(\mathbf{X}_1) = n$ -th level of $H(\mathbf{X}_1)$ with $\Psi_n(\mathbf{X}_1)$ the eigenfunction. However the above is not invariant under evolution. Difficult to find explicit invariant distribution.

Nevertheless under *adiabatic approximation* eigenstates of Hamiltonian at time 0 simply follow the variations of $H(\mathbf{X}(t))$ due to the motion of the thermostats particles without changing quantum numbers (rather than evolving following the Schödinger equation and become, therefore, *different* from the eigenfunctions of $H(\mathbf{X}(t))$).

Hence in *adiabatic limit* (classical motion of thermostat particles on a time scale much faster than the quantum evolution) distribution is *invariant* as the variation of the energy levels (supposed non degenerate) is compensated by the phase space contraction in thermostat.

Under evolution \mathbf{X}_1 at time $\varepsilon > 0$ becomes $\mathbf{X}_1 + \varepsilon \dot{\mathbf{X}}_1 + O(\varepsilon^2)$ and, if non degeneracy, $E_n(\mathbf{X}_1)$ changes, by perturbation analysis, into $E_n + \varepsilon e_n + O(\varepsilon^2)$ with

$$e_n \stackrel{def}{=} -\varepsilon \langle \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_{01} \rangle_{\Psi_n} - \varepsilon \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_1$$

and at the same time phase space contracts by $e^{-\varepsilon \frac{3N_1 e_n}{2k_1}}$. *Therefore if β is chosen such that $\beta = (k_B T_1)^{-1}$ distribution is stationary.*

In adiabatic approximation, interaction with single thermostat at T_1 admits at least one stationary state. This is, by construction, a Gibbs state of thermodynamic equilibrium with a special kind (random $\mathbf{X}_1, \dot{\mathbf{X}}_1$) of boundary condition and temperature T_1 .

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12