Inelastic boundaries of phase spaces.

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1 Physics

1.1 Dynamical system

We consider a *dynamical system* on a phase space $\mathcal{M}$ of dimension $2dN$. The state vector of the system is $\mathbf{x} = (x^0, x^1, ..., x^{dN}) \in \mathcal{M}$. The trajectory is determined by the following differential equation:

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \boldsymbol{\xi}(\mathbf{x}, t). \tag{1}$$

The state vector $\mathbf{x}_t$ at time t is fully determined by the initial condition $\mathbf{x}_0$ because the trajectory is deterministic. The bijective *flow* $\boldsymbol{\varphi}_t$ maps $\mathcal{M}$ onto itself. Generally, we note $\mathbf{x}_t = \mathbf{x}$,so that:

$$\mathbf{x} = \boldsymbol{\varphi}_t(\mathbf{x}_0). \tag{2}$$

1.2 Liouville's equation and compressibility

We follow the trajectory with the Dirac distribution $\delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)$ that ensures 2. Deriving partially with respect to time, we obtain

$$\begin{aligned}\frac{\partial \delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)}{\partial t} &= -\frac{\partial \boldsymbol{\varphi}_t(\mathbf{x}_0)}{\partial t} \nabla \delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right) \\ &= -\nabla \cdot \left[\frac{\partial \mathbf{x}}{\partial t} \delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)\right] \\ &= -\nabla \cdot \left[\boldsymbol{\xi}(\mathbf{x}, t) \delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)\right]\end{aligned}$$

where $\nabla \equiv \frac{\partial}{\partial \mathbf{x}}$ and where we have used the identity[1]: $\nabla\left[h(\mathbf{x})\delta(\mathbf{x} - \mathbf{a})\right] = h(\mathbf{a})\nabla\delta(\mathbf{x} - \mathbf{a})$. This straighforwardly leads to Liouville's equation[2]:

$$\frac{\mathrm{d}\delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)}{\mathrm{d}t} = -\nabla \cdot \boldsymbol{\xi}(\mathbf{x}, t)\delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right). \tag{3}$$

The right hand side of Eq. 3 vanishes for Hamiltonian dynamics because the *phase space compression factor* or *compressibility* $\nabla \cdot \boldsymbol{\xi}$, is equal to zero. We solve Eq. 3 to obtain:

[1] which itself comes from the following: $h(\mathbf{x})\nabla\delta(\mathbf{x} - \mathbf{a}) = h(\mathbf{a})\nabla\delta(\mathbf{x} - \mathbf{a}) - \nabla h(\mathbf{a})\delta(\mathbf{x} - \mathbf{a})$.

[2] We have used: $\frac{\mathrm{d}\delta(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0))}{\mathrm{d}t} = \frac{\partial\delta(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0))}{\partial t} + \boldsymbol{\xi}(\mathbf{x}, t) \cdot \nabla\delta\left(\mathbf{x} - \boldsymbol{\varphi}_t(\mathbf{x}_0)\right)$

$$\delta\left(\mathbf{x}-\boldsymbol{\varphi}_t(\mathbf{x}_0)\right)=\delta\left(\mathbf{x}_0-\boldsymbol{\varphi}_0(\mathbf{x}_0)\right)\exp\left\{-\int_0^t \nabla\cdot\boldsymbol{\xi}\left(\boldsymbol{\varphi}_{t'}(\mathbf{x}_0),t'\right)\mathrm{d}t'\right\}. \tag{4}$$

Eq. 4 justifies the name for the compressibility, because the change of variable in the Dirac distribution (from $\boldsymbol{\varphi}_0$ to $\boldsymbol{\varphi}_t$) has a Jacobian that differs from unity for dissipative systems. Its value, at time t, can be identified by a minor (but useful) modification of Eq. 4:

$$\delta\left(\mathbf{x}-\boldsymbol{\varphi}_t(\mathbf{x}_0)\right)\exp\left\{\int_0^t \nabla\cdot\boldsymbol{\xi}\left(\boldsymbol{\varphi}_{t-t'}^{-1}(\mathbf{x}),t'\right)\mathrm{d}t'\right\}=\delta\left(\mathbf{x}_0-\boldsymbol{\varphi}_0(\mathbf{x}_0)\right). \tag{5}$$

We may be interested in the evolution of a normalized *distribution* of initial conditions $f_0(\mathbf{x}_0)$. Its time evolution reads:

$$f(\mathbf{x},t)=\int \mathrm{d}\mathbf{x}_0 f_0(\mathbf{x}_0)\delta\left(\mathbf{x}-\boldsymbol{\varphi}_t(\mathbf{x}_0)\right). \tag{6}$$

Note that f is normalized at all times: $\int \mathrm{d}\mathbf{x} f(\mathbf{x},t)=1,\forall t$ and that it follows Liouville's equation (Eq. 3). f is the simplest distribution that follows Liouville equation, but it is not the only one.

1.3 Conservation laws

A dynamical system describe trajectories that conserve N_c quantities $h_i(\mathbf{x},t)$ that characterizes the macroscopic state of the system ("change based on invariance"). We note:

$$h_i\left(\mathbf{x},t\right)=0, \qquad \forall t, 1\le i\le I \tag{7}$$

Instead of looking at one system only, we may look at a distribution of systems (which may have several experimental meanings) that follow the same dynamics. In that case, we assume that the initial distribution of state span all accessible state that satisfy Eq. 7 at $t=0$. Therefore, it follows the ensemble distribution density reads

$$f_0(\mathbf{x}_0)=\frac{\prod_i \delta\left(h_i\left(\mathbf{x}_0,0\right)\right)}{\Omega_0}. \tag{8}$$

where the partition function that normalize the distribution generally reads:

$$\Omega_t=\int \mathrm{d}\mathbf{x}\prod_{i=1}^{N_c}\delta\left(h_i\left(\mathbf{x},t\right)\right), \tag{9}$$

and the ensemble average reads $\langle\cdot\rangle=\int \mathrm{d}\mathbf{x} f(\mathbf{x},t)\cdot$

On holonomic and non-holonomic "constraints" Holonomic and non-holonomic constraints are *additional* conservation laws, i.e. that are not guaranted by the dynamical system, but rather imposed on top of it. Therefore, they can be expressed like a conservation law, but one needs to modify the dynamical equations in order to ensure them. Holonomic constraints refer to the one that are integrable (they are about positions and not momenta). Nonholonomic constraints refers to the other one, but some of them can still be integrated, even if they depend on velocities as long as they are homogeneous functions of momenta.

We do not need to resort to such terminology because:

1. "Constraints" are conservation laws once the (maybe non-integrable) final dynamical equation is written down. The distinction with conservation laws is really enshrined in the idea of separating physical conservation laws that are based in symmetry (energy, momentum, etc.) and contingent invariants (e.g. rigid bonds of the H_2O molecules) (J Evans and P Morriss, 2007).

2. We are not interested in integrating a microscopic dynamical system.

3. Their name is problematic as it leads to a confusion with the concept of constraints in biology. Non-holonomic constraints reduce the number of possible microstates accessible in a system. Noting Ω (resp. $\tilde{\Omega}$) their number when the non-holonomic constraint is present (resp. absent), we have $\Omega < \tilde{\Omega}$. This is not how the concept of constraint is defined in the closure of constraints.

1.4 Linking microscopic compressibility to macroscopic entropy variation

We evaluate the average value of the Jacobian in Eq. 5, at time t. We assume that the initial state span all states satisfying the conservation law:

$$\begin{aligned}
\left\langle \exp\left\{\int_0^t \nabla\cdot\boldsymbol{\xi}\left(\boldsymbol{\varphi}_{t-t'}^{-1}(\mathbf{x}),t'\right)\mathrm{d}t'\right\}\right\rangle &= \int \mathrm{d}\mathbf{x}\exp\left\{\int_0^t \nabla\cdot\boldsymbol{\xi}\left(\boldsymbol{\varphi}_{t-t'}^{-1}(\mathbf{x}),t'\right)\mathrm{d}t'\right\} f(\mathbf{x},t)\\
\text{Eq. 5} &= \int \mathrm{d}\mathbf{x} f(\mathbf{x}_0,0)\\
\text{Eq.8} &= \int \mathrm{d}\mathbf{x}\frac{\prod_i \delta\left(h_i\left(\mathbf{x}_0,0\right)\right)}{\Omega_0}\\
\text{Eq. 7} &= \frac{1}{\Omega_0}\int \mathrm{d}\mathbf{x}\prod_i \delta\left(h_i\left(\mathbf{x},t\right)\right)\\
&= \frac{\Omega_t}{\Omega_0}
\end{aligned}$$

We have obtained the following nonequilibrium result: given an initial "equilibrium" state, the part of the Jacobian that is path dependent can be written as follows:

$$\left\langle \exp\left\{\int_0^t \nabla\cdot\boldsymbol{\xi}\left(\boldsymbol{\varphi}_{t-t'}^{-1}(\mathbf{x}),t'\right)\mathrm{d}t'\right\}\right\rangle = \exp\left\{\frac{S_t - S_0}{k_B}\right\}. \tag{10}$$

where $S_t = k_B \ln \Omega_t$ is the (Boltzmann) entropy of the system at time t. The result does not assume that the system is at equilibrium at t. Rather, it is because we initially span all accessible states satisfying the constraint of Eq. 7 that we are still considering all possible states satisfying the same condition at later time. What is the physical meaning of the Jacobian?

Remark on Gibbs' entropy Because f satisfies Liouville equation, we have

$$\frac{\mathrm{d}\ln f(\mathbf{x},t)}{\mathrm{d}t} = -\nabla\cdot\boldsymbol{\xi}(\mathbf{x},t), \tag{11}$$

and therefore, by direct integration, we also get:

$$\left\langle \frac{f\left(\boldsymbol{\varphi}_t^{-1}(\mathbf{x}),0\right)}{f(\mathbf{x},t)} \right\rangle = \exp\left\{\frac{S_t - S_0}{k_B}\right\}. \tag{12}$$

Define the "stochastic entropy" $s(\mathbf{x},t) = -k_B \ln f(\mathbf{x},t)$, whose ensemble average is Gibbs' entropy:

$$S^{\mathrm{G}}(\mathbf{x},t) = \langle s(\mathbf{x},t)\rangle = -k_B \int \mathrm{d}\mathbf{x} f(\mathbf{x},t) \ln f(\mathbf{x},t). \tag{13}$$

Then, we can also read:

$$\left\langle \exp\left\{\frac{s(\mathbf{x},t) - s\left(\boldsymbol{\varphi}_t^{-1}(\mathbf{x}),0\right)}{k_B}\right\} \right\rangle = \exp\left\{\frac{S_t - S_0}{k_B}\right\}. \tag{14}$$

1.5 Inelastic systems and non-Hamiltonian dynamics

We consider a system described by a Hamiltonian $\mathcal{H}$, *driven* into states with internal energy $E(t)$. The first conserved quantity reads:

$$h_1(\mathbf{x},t) = E(t) - \mathcal{H}(\mathbf{x},t) = 0 \tag{15}$$

To change its internal energy, the system needs to be open. It receives energy from the outside ($\partial\mathcal{H}/\partial t \neq 0$). Expliciting the total derivative of $\mathcal{H}$ leads to:

$$\frac{\mathrm{d}\mathcal{H}(\mathbf{x},t)}{\mathrm{d}t} = \frac{\partial\mathcal{H}(\mathbf{x},t)}{\partial t'} + \nabla\mathcal{H}(\mathbf{x},t)\cdot\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t}. \tag{16}$$

Inserting Eq. 1 and Eq. 15, we are looking for $\boldsymbol{\xi}$ so that the first law of thermodynamics ($\mathrm{d}E = \delta W + \delta Q$) is microscopically satisfied. It reads:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\partial\mathcal{H}}{\partial t} + \nabla\mathcal{H}\cdot\boldsymbol{\xi}, \tag{17}$$

Let's first see what happens if we keep Hamilton's dynamics. We split the variables and operators in position and momenta. We note $\mathbf{x} = (\mathbf{q},\mathbf{p})$ and $\nabla = (\nabla_{\mathbf{q}},\nabla_{\mathbf{p}})$ where $\nabla_{\mathbf{q}} \equiv \frac{\partial}{\partial\mathbf{q}}$ and $\nabla_{\mathbf{p}} \equiv \frac{\partial}{\partial\mathbf{p}}$. An Hamiltonian dynamics would be obtained by using $\boldsymbol{\xi} = \overline{\nabla}_{\pm}\mathcal{H}$ where $\overline{\nabla}_{\pm} = (\nabla_{\mathbf{p}}, -\nabla_{\mathbf{q}})$. However, we can check the orthogonality relation $\nabla\mathcal{H}\cdot\overline{\nabla}_{\pm}\mathcal{H} = \{\mathcal{H},\mathcal{H}\} = 0$ due to the null value of the Poisson bracket. Inserting $\boldsymbol{\xi} = \overline{\nabla}_{\pm}\mathcal{H}$ in Eq. 16 with the use of Eq. 1, we can check that, given our conservation law, we cannot use Hamilton's equation without having to close the system ($\partial\mathcal{H}/\partial t = 0$). Regarding entropy variation, we can check that$\overline{\nabla}_{\pm}\mathcal{H}$ is divergent-free because $\nabla\cdot\overline{\nabla}_{\pm} = 0$. Therefore, the compressibility is null ($\nabla\cdot\boldsymbol{\xi} = 0$) and entropy (when macrostates are defined as microcanonical energy shells) does not vary.

To ensure the first law (Eq. 17) we need to add a *non-conservative* external force that provides a dissipative channel for the system. We pose:

$$\boldsymbol{\xi} = \overline{\nabla}_{\pm}\mathcal{H} + \gamma\hat{\mathbf{F}}, \tag{18}$$

where the vector field $\hat{\mathbf{F}} = (0, \mathbf{F})$ contains the conservative force $\mathbf{F}(\mathbf{q})$ that is not affected by the dynamics. We call the *inelastic coefficient* the adimensional factor $\gamma(\mathbf{x}, t)$: even if $\mathbf{F}$ is conservative ($\nabla_{\mathbf{p}}\mathbf{F} = 0$) we do introduce a non-conservative force $\gamma\mathbf{F}$ into the system. Inserting Eq. 18 in Eq. 17, we find the inelastic coefficient that ensures the energy conservation of the system:

$$\gamma = \frac{1}{\hat{\mathbf{F}} \cdot \nabla \mathcal{H}} \left(\frac{\mathrm{d}E}{\mathrm{d}t} - \frac{\partial \mathcal{H}}{\partial t} \right). \tag{19}$$

Eq. 18 and Eq. 19 are valid for *any* force field $\hat{\mathbf{F}}$ that works on the system *if* $\mathrm{d}E \neq \delta W_{\mathrm{ext}}$, where $\delta W_{\mathrm{ext}} = \frac{\partial \mathcal{H}}{\partial t}\mathrm{d}t$ is the infinitesimal work supplied to the system from the outside. More precisely, in our case, we can define the microscopic power $\mathcal{P}_{\mathbf{F}}(\mathbf{x}, t)$ of $\mathbf{F}$, which is related to the infinitesimal work of $\mathbf{F}$ as $\delta W_{\mathbf{F}} = \mathbf{F} \cdot \mathrm{d}\mathbf{q} = \mathcal{P}_{\mathbf{F}}\mathrm{d}t$, and that reads:

$$\mathcal{P}_{\mathbf{F}} = \mathbf{F} \cdot \nabla_{\mathbf{p}} \mathcal{K} \tag{20}$$

where $\mathcal{K}$ is the kinetic part of $\mathcal{H} = \mathcal{U}(\mathbf{x}, t) + \mathcal{K}(\mathbf{x}, t)$, that contains all the momenta dependency. Taking the divergence of Eq. 18, we find an expression for the compressibility[3]:

$$\nabla \cdot \boldsymbol{\xi} = \mathbf{F} \cdot \nabla_{\mathbf{p}} \gamma. \tag{21}$$

How does this expression connects to more familiar expressions of microscopic entropy production, which never resort to a conservative force $\mathbf{F}$ nor the idea of inelastic collisions?

1.6 The inelastic contribution

Using Eq. 19, we can express the gradient $\nabla\gamma$ in Eq. 21. It reads:

$$\begin{aligned}
\nabla \cdot \boldsymbol{\xi} &= -\mathbf{F} \cdot \frac{\nabla_{\mathbf{p}} \left(\frac{\partial \mathcal{K}}{\partial t} \right) \mathcal{P}_{\mathbf{F}} + \left(\frac{\mathrm{d}E}{\mathrm{d}t} - \frac{\partial \mathcal{H}}{\partial t} \right) \nabla_{\mathbf{p}} \mathcal{P}_{\mathbf{F}}}{\mathcal{P}_{\mathbf{F}}^2} && (22) \\
&= -\frac{1}{\mathcal{P}_{\mathbf{F}}} \left(\frac{\partial \mathcal{P}_{\mathbf{F}}}{\partial t} + \gamma \mathbf{F} \cdot \nabla_{\mathbf{p}} \mathcal{P}_{\mathbf{F}} \right) && (23) \\
&= \nabla \cdot \boldsymbol{\xi}|_{\mathrm{elastic}} + \nabla \cdot \boldsymbol{\xi}|_{\mathrm{inelastic}}. && (24)
\end{aligned}$$

On the second line, we have used the fact that $\frac{\partial^2 \mathcal{H}}{\partial \mathbf{x} \partial t} = \frac{\partial^2 \mathcal{H}}{\partial t \partial \mathbf{x}}$ and the explicit time-independence of $\mathbf{F}$.

The second term of Eq. 23 explictely involves the inelastic coefficient γ and therefore refers to heat transfer. However, the first one is independent of γ, which seems to imply that there could be another entropy variation in a conservative system ($\gamma = 0$). This paradox is resolved by the fact, $\gamma = 0$ implies $\frac{\partial \mathcal{K}}{\partial t} = \frac{\mathrm{d}E}{\mathrm{d}t} - \frac{\partial \mathcal{U}}{\partial t}$ according to Eq. 19, which is independent of momenta : the second term also requires $\gamma = 0$. However, its effect on the compressibility is physically different from the the one that involves the dissipative channel.

Let's first dwell on the second term, $\nabla \cdot \boldsymbol{\xi}|_{\mathrm{inelastic}}$. After, some straightforward algebra, the first term of Eq. 22, can be written as follows:

[3] We use: $\nabla \cdot (\gamma \hat{\mathbf{F}}) = \gamma \nabla \cdot \hat{\mathbf{F}} + \hat{\mathbf{F}} \cdot \nabla \gamma$.

$$\nabla \cdot \boldsymbol{\xi}|_{\text{inelastic}} = \left(\frac{\mathrm{d}E}{\mathrm{d}t} - \frac{\partial \mathcal{H}}{\partial t}\right) \nabla_{\mathbf{p}} \cdot \left(\frac{\mathbf{F}}{\mathcal{P}_{\mathbf{F}}}\right). \tag{25}$$

Regarding the prefactor in Eq. 25, the insertion of Eq. 18 into the first law (Eq. 17) allows us to equate the following quantities:

$$\mathrm{d}E - \delta W_{\text{ext}} = \gamma \delta W_{\mathbf{F}} = \delta Q. \tag{26}$$

Regarding the divergence in Eq. 25, it can be linked to the microscopic instantaneous temperature $\mathcal{T}(\mathbf{x})$ definition in the microcanonical ensemble. More precisely, we can show that (Rugh, 1997, 1998; Adib, 2005):

$$\nabla_{\mathbf{p}} \cdot \left(\frac{\mathbf{F}}{\mathcal{P}_{\mathbf{F}}}\right) = \frac{1}{k_B \mathcal{T}}, \tag{27}$$

where, upon ensemble averaging: $\langle \frac{1}{\mathcal{T}} \rangle_{N,V,E} = \frac{1}{T(E)} = \frac{\partial S(E)}{\partial E}$.

Gathering the last three equations and inserting in Eq. 10, we find that

$$\int_0^\tau \nabla \cdot \boldsymbol{\xi}|_{\text{inelastic}} \mathrm{d}t = \int_A^B \frac{\delta Q}{k_B \mathcal{T}}, \tag{28}$$

where we have considered a process happening on a timescale τ, whose energy follows the trajectory $E(t)$, and for which $E(0) = E_A$ and $E(\tau) = E_B$. We find a familiar expression for the inelastic contribution to the compressibility (and therefore entropy variation). Note that the inelastic contribution depends is proportional to the *time integral of the inelastic power of the force* $\mathbf{F}$.

1.7 The elastic contribution

The elastic contribution to the compressibility reads:

$$\int_0^\tau \nabla \cdot \boldsymbol{\xi}|_{\text{elastic}} \mathrm{d}t = -\int_0^\tau \frac{1}{\mathcal{P}_{\mathbf{F}}} \frac{\partial \mathcal{P}_{\mathbf{F}}}{\partial t} \mathrm{d}t. \tag{29}$$

It therefore depends on the *relative variation of the elastic work* $\delta W_{\mathbf{F}}$ ***due to external kinetic energy variations.*** Indeed, $\mathbf{F}$ having not explicit time-dependence, variations of the power of $\mathbf{F}$ come from kinetic “impulses” towards regions were $\mathbf{F}$ works. This contribution is often neglected (see e.g. footnote in (Adib, 2005)). We introduce the *constraining factor* δC:

$$\delta C(\mathbf{x}, t) = \frac{\mathbf{F} \cdot \partial_t \nabla_{\mathbf{p}} \mathcal{K}}{\mathbf{F} \cdot \nabla_{\mathbf{p}} \mathcal{K}}.$$

1.8 A model

We adopt a general expression for the kinetic energy, which allows us to control the momenta of each particle:

$$\mathcal{K}(\mathbf{p}, t) = \sum_{i=1}^{dN} \lambda_i(t) \frac{p_i^2}{2m_i}. \tag{30}$$

where $\lambda_i(t)$ are positive parameters, N the number of particles and d the dimension. We introduce a vector which contains the microscopic work of $\mathbf{F}$ on the particle i:

$$\delta\mathbf{w_F} = (\delta w_{\mathbf{F}\to i})_{1\leq i\leq dN} = (F_i(\mathbf{q})p_i/m_i\mathrm{d}t)_{1\leq i\leq dN} \, ,$$

We can now specify Eq. 29 by introducing the *constraining factor* δC:

$$\delta C(\mathbf{x}, t) = \frac{\sum_i \delta w_{\mathbf{F}\to i}\mathrm{d}\lambda_i}{\sum_i \delta w_{\mathbf{F}\to i}\lambda_i(t)} = \frac{\delta\mathbf{w_F}\cdot\mathrm{d}\boldsymbol{\lambda}}{\delta\mathbf{w_F}\cdot\boldsymbol{\lambda}}. \tag{31}$$

1.9 Fluctuation theorem in the microcanonical ensemble with inelastic collisions.

Adding both the elastic and inelastic contribution, Eq. 28 and Eq. 29 gives the following fluctuation theorem:

$$\exp\left\{\frac{S_\tau - S_0}{k_B}\right\} = \left\langle \exp\left\{\int_0^\tau \frac{\mathrm{d}E - \delta W_{\mathrm{ext}}}{k_B\mathcal{T}} - \delta C\right\}\right\rangle \tag{32}$$

References

D. J Evans and G. P Morriss, *Statistical Mechanics of Nonequilbrium Liquids* (ANU Press, 2007).

H. H. Rugh, Physical Review Letters **78**, 772 (1997).

H. H. Rugh, Journal of Physics A: Mathematical and General **31**, 7761 (1998).

A. B. Adib, Physical Review E **71**, 056128 (2005).