

MACROSCOPIC VARIABLES, THERMAL EQUILIBRIUM AND BOLTZMANN ENTROPY

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1 Macroscopic Variables

In classical mechanics a physical quantity is represented by a real valued (measurable) function Y on the phase space Γ . If the micro-state of the system is X , the value of the quantity is

$$Y = Y(X). \quad (1)$$

If the quantity Y is measured and it is found in the interval $Y \pm \Delta Y$ we gather information about the actual micro-state: we know that it is in the region of phase space of those micro-states X such that $Y - \Delta Y \leq Y(X) \leq Y + \Delta Y$.

Not any old function Y on phase space represents a macroscopic quantity. To be a candidate for that, the function has to vary slowly on the macroscopic scale. This is so for locally conserved quantities.

2 Local quantities and Hydrodynamics fields

A local quantity is one which is associated with any (measurable) subset $\Delta \subset \Lambda$ and can be expressed as the integral of a (possibly singular) density. This is so for the following functions on phase space describing the number of particles N , the momentum \mathbf{P} and the energy E of the particles in any (measurable) subset $\Delta \subset \Lambda$:

$$N_X(\Delta) = \int_{\Delta} n_X(\mathbf{r}) d^3\mathbf{r}, \text{ where } n_X(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{Q}_i), \quad (2)$$

$$\mathbf{P}_X(\Delta) = \int_{\Delta} \mathbf{p}_X(\mathbf{r}) d^3\mathbf{r}, \text{ where } \mathbf{p}_X(\mathbf{r}) = \sum_{i=1}^N \mathbf{P}_i \delta(\mathbf{r} - \mathbf{Q}_i), \quad (3)$$

$$E_X(\Delta) = \int_{\Delta} e(\mathbf{r}) d^3\mathbf{r}, \text{ where } e_X(\mathbf{r}) = \sum_{i=1}^N \left(\frac{1}{2m} \mathbf{P}_i^2 + \frac{1}{2} \sum_{i \neq j} V(\mathbf{Q}_i - \mathbf{Q}_j) \right) \delta(\mathbf{r} - \mathbf{Q}_i). \quad (4)$$

We have used the subscript X to express the dependence on the actual microscopic state $X = \{\mathbf{Q}_i, \mathbf{P}_i\}_{i=1}^N$ (In the following, when no confusion will arise, for easiness of notation, we shall drop the subscript X .) N , \mathbf{P} and E are known as the microscopic **hydrodynamics fields** and n , \mathbf{p} , and e as their densities.

Hydrodynamics fields and locally conserved quantities

The hydrodynamics fields are locally conserved, that is, their densities satisfy the continuity equations

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_N = 0, \quad (5)$$

$$\frac{\partial \mathbf{p}}{\partial t} + \nabla \cdot \mathbf{J}_P = 0 \quad (6)$$

$$\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{J}_E = 0, \quad (7)$$

where \mathbf{J}_N , \mathbf{J}_P , and \mathbf{J}_E are the associated flux densities (we leave as an exercise to compute their explicit form). We have used the symbol \mathbf{J}_P for

denoting the momentum flux because it is a tensor related to the stress tensor). The local conservation of the hydrodynamics fields is the reason why they are macroscopically relevant (as opposed to any old function on phase space). In fact, a local excess of a locally conserved quantity cannot disappear locally (which otherwise could happen very rapidly), but can only relax by spreading slowly over the entire system. Then the processes of transport of such quantities are extremely long on the microscopic scale and thus are macroscopically relevant—they are, so to speak, the macroscopic manifestation of the microscopic dynamics.

3 Coarse-graining

Consider for example the number of particles of a gas in standard conditions contained in a cube of side 1 mm, differences in this number of order 10 or even 10^{10} , are differences which do not make any difference. So, the appropriate macroscopic description is not given by Y itself, but by the function \tilde{Y} obtained by suitable coarse-graining.

Mathematically, the coarse graining of a function can be done in the

following way. Let the values Y of Y be real (or integer) numbers. Divide these values into disjoint intervals ΔY_ν , $\nu = 1, 2, 3, \dots$ and let Y_ν a point in ΔY_ν , for example the middle point (of or a suitable average) of F in ΔY_ν . Then the coarse-graining of Y is the function \tilde{Y} which assumes the constant value Y_ν for all X such that $Y(X) \in \Delta Y_\nu$, that is,

$$\tilde{Y}(x) = \sum_{\nu} Y_\nu \mathbb{1}_{\Delta Y_\nu}(Y(x)) , \quad (8)$$

where $\mathbb{1}_A(y)$ is the characteristic function of the set A , i.e., it is equal to 1 if $y \in A$ and equal to zero otherwise. **Since the box functions are discontinuous and it is preferable to work with smooth functions, we may allow the $\mathbb{1}_{\Delta Y_\nu}$ to be, with any degree of precision, smooth approximations of the characteristic functions.**

A macro-state M_ν is then specified by one of the values Y_ν and

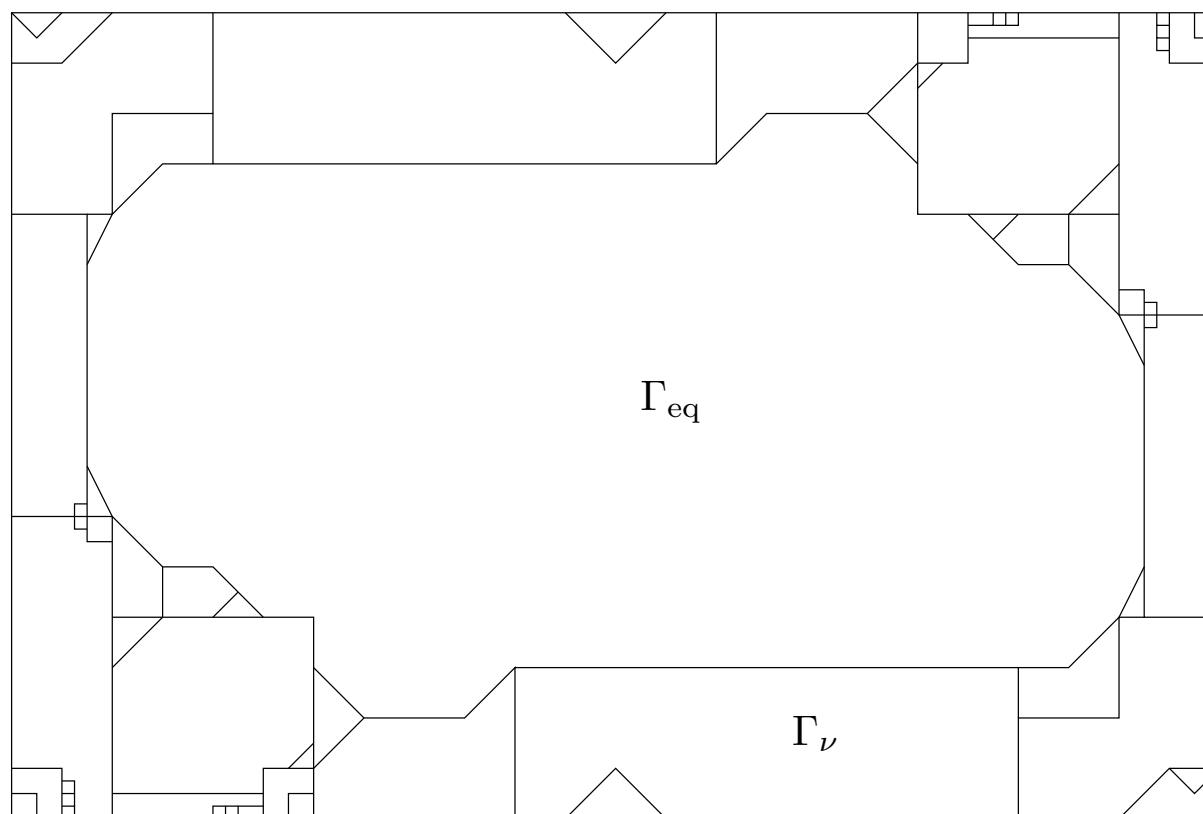
$$\Gamma_{M_\nu} = \{x : \tilde{Y}(x) = Y_\nu\} \quad (9)$$

is the region in Γ_E associated with macro-state M . Clearly, the Γ_M are

disjoint and the decomposition

$$\Gamma_E = \bigcup_{M_\nu} \Gamma_{M_\nu}.$$

(10)



The coarse-graining procedure extends trivially to a family of n macroscopic quantities represented by the functions Y_1, \dots, Y_n . All we have to do is to read eq. (1) and eq. (8) as vector equations, with $Y = (Y_1, \dots, Y_n)$ in eq. (1) representing now the values of the family of functions $Y = (Y_1, \dots, Y_n)$, and ν and ΔY_ν in eq. (8), being now, respectively, the multi-index $\nu = (\nu_1, \dots, \nu_n)$ and the n dimensional box whose edges are the intervals $\Delta Y_{\nu_1}, \dots, \Delta Y_{\nu_n}$.

In the following, when no confusion will arise, we shall omit the “ \sim ”-hat, assuming that the function Y has been already coarse-grained as described above, so that its values Y s are a discrete set. Accordingly, we shall write

$$M = Y \quad \text{and} \quad \Gamma_M = \{x : Y(x) = Y\}. \quad (11)$$

4 Thermal equilibrium

One of the main achievements of statistical mechanics is the proof that for realistic systems with large N that one of the regions $\Gamma_{M_{\text{eq}}}$ of the

partition of phase space induced by the macroscopic variables,

$$\Gamma_E = \bigcup_{M_\nu} \Gamma_{M_\nu},$$

is such that

$$\frac{|\Gamma_{M_{\text{eq}}}|}{|\Gamma_E|} \approx 1, \quad (12)$$

This is the condition that define a ***standard thermodynamic system***. We are thus lead to the following natural characterization of thermodynamic equilibrium in terms of microscopic physics:

Proposition 1 (Thermal equilibrium)

A standard thermodynamic system which is in the microstate X (at some time t) is in ***thermal equilibrium*** (at time t) if X is in $\Gamma_{M_{\text{eq}}}$. The macrostate $\Gamma_{M_{\text{eq}}}$ is called the ***equilibrium macrostate***. When X is not in $\Gamma_{M_{\text{eq}}}$, the system is in a ***nonequilibrium state***.

Indeed, for realistic systems with large N , the estimate eq. (12) can be refined and the results that have been achieved starting with Boltzmann are summarized by the following proposition:

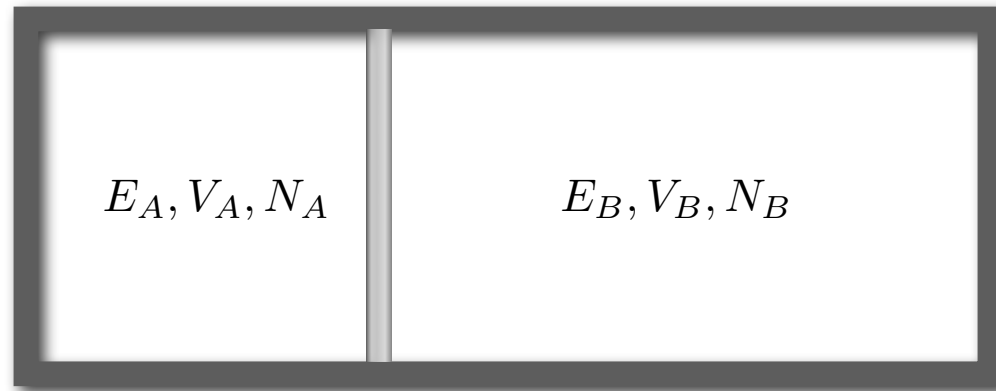
Proposition 2 (Main large deviations' estimate of SM)

The values of the macroscopic variables concentrate around their equilibrium values exponentially with the size of the system.

5 Two systems in thermal contact

To illustrate more concretely the decomposition eq. (10), we consider a macroscopic system of fixed total energy E consisting of two parts, a and b , of energies E_a and E_b , between which energy can flow, but which are

otherwise independent.



The Hamiltonian is

$$H(x) = H_a(x_a) + H_b(x_b) + \lambda V(x_a, x_b), \quad (13)$$

where H_a and H_b are the Hamiltonians of the two systems and λV is a the interaction energy between the two systems. Since the two systems are macroscopic, the interaction energy is much smaller than the energy of the two systems and thus we have the approximation

$$H(x) \approx H_a(x_a) + H_b(x_b), \quad (14)$$

A macroscopic description of the system is then given by the coarse grained energy of one of the two systems, say H_a , since when its value is E_a (with some tolerance δE_a), the energy of the other system is (with the same tolerance δE_a) $E_b = E - E_a$ (having assumed that the total system is isolated and the interaction between the two systems is small).

Then

$$M = E_a \quad \text{and} \quad \Gamma_{E_a} = \{x : H_a(x) = E_a, H_b(x) = E - E_a\}, \quad (15)$$

whence the partition eq. (10).

The size of the macrostate is

$$|\Gamma_{E_a}| = \Omega_a(E_a)\Omega_b(E - E_a), \quad (16)$$

(since the two systems are weakly dependent) Assuming that the **TL** is finite and well behaved (concavity of s), we have

$$|\Gamma_{E_a}| \asymp e^{N_a s_a(e_a)} e^{N_b s_b(e - e_a)}, \quad e_a = E_a/N, \quad e = E/N \quad (17)$$

Let us now consider the volume of the total energy shell $\Gamma_{E, \delta E}$. By convolution

$$|\Gamma_E| = \Omega(E)\delta E = \int \Omega_a(E_a)\Omega_b(E - E_a)dE_a$$

So, in the **TL**

$$|\Gamma_E| \asymp \int e^{N[x_a s_a(e_a) + x_b s_b(e - e_a)]} de$$

where x_a and x_b are the fractions of particles in a and b (which we assume for simplicity to be fixed) and thus of order one. By Laplace method

$$\int e^{N(x_a s_a(e_a) + x_b s_b(e - e_a))} de \asymp \exp \left\{ N \max_{e_a} (x_a s_a(e_a) + x_b s_b(e - e_a)) \right\}$$

The maximum is achieved for $e_a = \varepsilon$ solution of the equation

$$\frac{\partial s_a}{\partial e_a} = \frac{\partial s_b}{\partial e_b} \quad (18)$$

whence (restoring N_a and N_b)

$$|\Gamma_E| \asymp e^{N x_a s_a(\varepsilon) + N x_b s_b(\varepsilon)}$$

Thus we obtain for the ratio between the volume of the macrostate E_a and the total volume

$$\frac{|\Gamma_{E_a}|}{|\Gamma_E|} \asymp e^{N \Delta s} \quad (19)$$

where

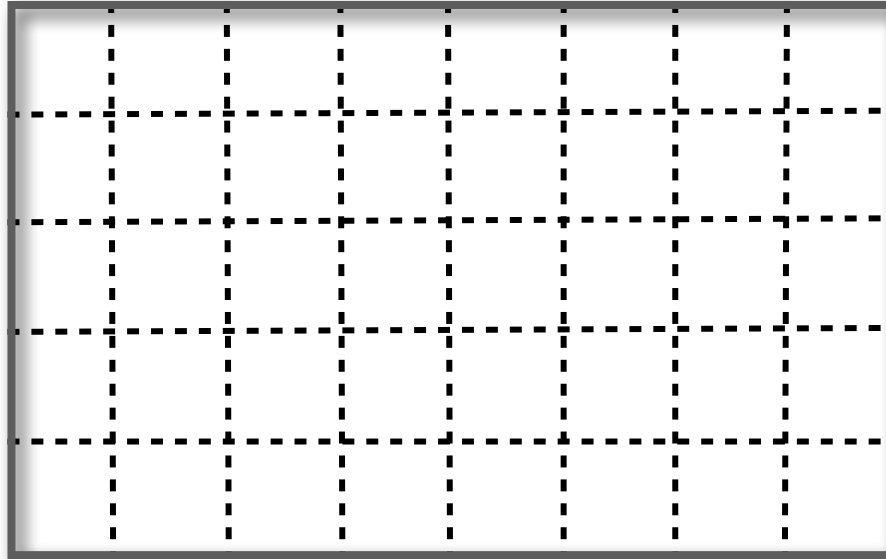
$$\Delta s = (x_a s_a(e_a) - x_a s_a(\varepsilon)) + (x_b s_b(e - e_a) - x_b s_b(e - \varepsilon)) < 0 \quad (20)$$

Thus the macrostate $E_a = N_a \varepsilon$ (with some tolerance δE_a) is the equilibrium macrostate. Non equilibrium macrostates have a relative volume that is exponentially small in the number of particles

6 Local equilibrium

When N is very large, we can give a coarse-grained description of a system of total constant energy E by characterizing its macro-state M in terms of the coarse grained hydrodynamic fields. We divide Λ into cells (e.g., cubes) Δ_α , $\alpha = 1, \dots, J$, centered around the points r_α ,

$$\Lambda = \bigcup_{\alpha=1}^J \Delta_\alpha.$$



Assume that J is large, but still $J \ll N$, so that so that each cell contains a very large number of particles. Then a macro-state M is specified by the (coarse-grained) values of the energy E_α , momentum \mathbf{P}_α and number of particles N_α in each cell Δ_α (analogously to what we have done above for the region Δ_a),

$$M = \{N_\alpha, \mathbf{P}_\alpha, E_\alpha\}_{\alpha=1}^J, \quad \Gamma_M = \left\{ X : \{N_X(\Delta_\alpha) = N_\alpha, \mathbf{P}_X(\Delta_\alpha) = \mathbf{P}_\alpha, E(\Delta_\alpha) = E_\alpha\}_{\alpha=1}^J \right\}, \quad (21)$$

whence eq. (10).

Proceeding as before . . .

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Equilibrium macrostate

$$S_{\text{tot}}(\{E_\alpha\}, \{\mathbf{P}_\alpha\}, \{N_\alpha\}) = \sum_{\alpha} S_{\alpha}(E_{\alpha}, \mathbf{P}_{\alpha}, N_{\alpha}). \quad (22)$$

Equilibrium macrostate: maximum of S_{tot}

We maximize the functional using Lagrange multipliers,

$$S_{\text{tot}}(\{E_\alpha\}, \{\mathbf{P}_\alpha\}, \{N_\alpha\}, \eta, \xi, \zeta) = \sum_{\alpha} S_{\alpha}(E_{\alpha}, \mathbf{P}_{\alpha}, N_{\alpha}) - \eta \sum_{\alpha} E_{\alpha} - \xi \cdot \sum_{\alpha} \mathbf{P}_{\alpha} - \zeta \sum_{\alpha} N_{\alpha}.$$

Then

$$\begin{aligned} \frac{\partial S_{\text{tot}}}{\partial E_{\alpha}} &= \frac{\partial S_{\alpha}}{\partial E_{\alpha}} - \eta = 0 \\ \frac{\partial S_{\text{tot}}}{\partial \mathbf{P}_{\alpha}} &= \frac{\partial S_{\alpha}}{\partial \mathbf{P}_{\alpha}} - \xi = 0 \\ \frac{\partial S_{\text{tot}}}{\partial N_{\alpha}} &= \frac{\partial S_{\alpha}}{\partial N_{\alpha}} - \zeta = 0 \end{aligned}$$

Note

$$S(E, \mathbf{P}) = S_0 \left(E - \frac{\mathbf{P}^2}{2M} \right) \quad (23)$$

$$\frac{\partial S}{\partial \mathbf{P}} = -\frac{\mathbf{P}}{M} \frac{\partial S_0}{\partial E} = -\mathbf{v} \frac{\partial S_0}{\partial E} \quad (24)$$

where \mathbf{v} is the velocity of the system.

Continuum limit (local equilibrium)

$$S(e, n, \mathbf{p}) = \int_{\Lambda} s(e(\mathbf{r}), n(\mathbf{r}), \mathbf{p}(\mathbf{r})) d^3 \mathbf{r} . \quad (25)$$

7 Boltzmann's Entropy

Boltzmann associated with each microscopic state X of a macroscopic system, be it gas, fluid or solid, a number $\mathcal{S}_B(X)$, given, up to multiplicative and additive constants (in particular we set Boltzmann's constant,

κ_B , equal to unity), by

$$\mathcal{S}_B(X) = S_B(M(X)) \quad (26a)$$

with

$$S_B(M) = \log |\Gamma_M| . \quad (26b)$$

$\mathcal{S}_B(X)$ is known as *Boltzmann entropy* of a classical system in the microstate X . We have deliberately written eq. (26) as two equations to emphasize their logical independence.

Boltzmann then provided arguments to explain the observation, embodied in the second law of thermodynamics, that when a constraint is lifted, an isolated macroscopic system will evolve toward a state with greater entropy. (See above.)

8 Equilibrium entropy

Boltzmann's entropy of the equilibrium macrostate M_{eq} is

$$S_B = \log |\Gamma_{eq}| , \quad (27)$$

Since (as we have argued above)

$$|\Gamma_{eq}| \asymp |\Gamma_E|$$

we have

$$S_{eq} = \log \Omega(E). \quad (28)$$

9 Ergodicity is neither necessary nor sufficient

It has been argued that the ergodic theorem is essential to justify equilibrium statistical mechanics.

Usually the following motivation is given:

When you are measuring a macroscopic variable $Y = f(X)$ the experimental measurement is not instantaneous; if the experiment begins at time $t = 0$ and complete at time $t = T$, what the experiment measure is effectively the time average

$$\frac{1}{T} \int_0^T f(X_t) dt,$$

where T is a macroscopic time determined by the response time of the measurement's apparatus. Since T is macroscopic, the limit $T \rightarrow \infty$ is justified.

However,

- T needed for the ergodic theorem is the time required to explore a large portion of the space of phases, i.e., a time whose order of the return time of Poincaré. For a macroscopic system,

$$T \sim 10^{10^{23}}$$

Clearly, it can not have any relationship with the response time of an apparatus! Thus, *the ergodic hypothesis is not sufficient to justify why the equilibrium value of a variable is given by its macroscopic microcanonical average.*

- The crucial point of Boltzmann's analysis is that

$$|\Gamma_{eq}| \asymp |\Gamma_E|$$

This means that as long as the microstate remains in the equilibrium macrostate, the details of the temporal evolution are irrelevant, and a macroscopic variable , during its temporal evolution remains typically constant, apart from small fluctuations that are negligible on a macroscopic scale. Thus, ***the macroscopic variables are constant on Γ_E and their microcanonical average reproduces their constant value. Therefore the ergodic hypothesis is not necessary.***

10 Autonomous evolution of the macro-state

To decide whether a certain macroscopic description is appropriate, e.g., whether the hydrodynamic or the kinetic description is appropriate for the system at hand, one should consider the time evolution of the macrostates

$$M_0 = M(X_0) \longrightarrow M_t = M(X_t), \quad (29)$$

where $X_t = T^t(X_0)$ is the Hamiltonian evolution of the initial micro-state X_0 . The macroscopic description provided by M will be satisfactory if the

evolution eq. (29) of the macro-state is autonomous, i.e., is given by a flow in space \mathbb{M} of all macrostates. This important fact has been proven for the hydrodynamics fields in a suitable regime (local equilibrium) and only for special models.

11 H-theorem

Given the disparity in size of Γ_Y for the various values Y , the temporal evolution of the macrostate will be such that $|\Gamma_Y(X_t)|$, and therefore $S_B(X_t)$ typically increases, in agreement with the second law of thermodynamics. Assuming **local thermodynamic equilibrium**, this fact can easily be demonstrated (Lebowitz-Goldstein).

Consider the case in which Y_t satisfies a deterministic evolution autonomous, such as the diffusion equation for $Y = n(\mathbf{r})$. This means that if such evolution leads

$$M_{t_1} \rightarrow M_{t_2},$$

then the microscopic dynamics ϕ_t takes $\Gamma_{Y_{t_1}}$ **inside** $\Gamma_{Y_{t_2}}$, namely

$$\phi_{t_2-t_1}(\Gamma_{M_{t_1}}) \subseteq \Gamma_{M_{t_2}},$$

with a negligible error.

Now, the fact that the phase space volume is preserved by the Hamiltonian flow implies that

$$|\Gamma_{M_{t_1}}| \leq |\Gamma_{M_{t_2}}|$$

and then from the definition of Boltzmann's entropy that

$$S_B(M_{t_2}) \geq S_B(M_{t_1}) \tag{30}$$

for $t_2 \geq t_1$.

The theorem just proven is an instance of **H-theorem**¹

The explicit form for the rate of change of $S_B(M_t)$ (including the positivity in the strict sense) depends on the detailed macroscopic evolution

¹This is terminology introduced by Ludwig Boltzmann in 1872 to describe the tendency to increase in the quantity H (capital "eta", for entropy) in a nearly-ideal gas of molecules.

equation. The fact that $\Gamma_{M_{eq}}$ coincides substantially for large N with all energy surface $H(X) = E$ also explains the evolution towards equilibrium, and persistence in this condition, for an isolated macroscopic system.

The emergence of a defined asymmetric behavior over time in the time evolution of macroscopic systems, despite the total absence of such asymmetry in the dynamics of microscopic, is thus a consequence of big disparities between the microscopic and the macroscopic, together with the fact (or the very reasonable assumption) that what we observe in Nature is a typical behavior, corresponding initial conditions typical.