Boltzmann's Entropy and Large Deviation Lyapunov Functionals for Closed and Open Macroscopic Systems

Joel L. Lebowitz

Department of Mathematics and Physics
Rutgers University
110 Frelinghuysen Road
Piscataway, NJ 08854 USA

Abstract. I give a brief overview of the resolution of the apparent problem of reconciling time symmetric microscopic dynamic with time asymmetric equations describing the evolution of macroscopic variables. I then show how the large deviation function of the stationary state of the microscopic system can be used as a Lyapunov function for the macroscopic evolution equations.

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Gather ye rosebuds while ye may,
Old time is still a-flying;
And this same flower that smiles today,
Tomorrow will be dying.
Robert Herrick, 1591-1674

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TIME'S ARROW

Every bit of macroscopic matter is composed of an enormous number of atoms which act as quasi-autonomous units. Taking these atoms as classical particles moving according to non-relativistic Hamiltonian equations the complete microscopic (or micro)state of an isolated classical system of N particles is specified by a point X in its phase space Γ,

$$X = (\mathbf{r_1}, \mathbf{v_1}, ... \mathbf{r}_N, \mathbf{v}_N), \quad \mathbf{r}_i \in V \subset \mathbf{R}^d, \quad \mathbf{v}_i \in \mathbf{R}^d \tag{1}$$

and $X(t) = \phi_t X(0)$, where ϕ_t is the evolution operator corresponding to the solution of the Hamiltonian equations of motion. These have the well known time reversal symmetry: setting, $RX = (\mathbf{r_1}, -\mathbf{v}_1, ..., \mathbf{r}_N, -\mathbf{v}_N)$ then

$$RX = \phi_t R \phi_t X, \quad t \in (-\infty, \infty) \tag{2}$$

Suppose now that some property of the system, specified by a function $f(X(t))$, behaves in a particular way as t increases, then there is also a trajectory in which the property

behaves in the time reversed way. Thus, for example, if particle densities get more uniform, say in a way described by the diffusion equation, then there will also be evolutions in which the density gets more nonuniform. So why is one type of evolution, corresponding to "entropy" increase in accord with the second "law", common and the other never seen?

This problem was clearly stated by W. Thomson (later Lord Kelvin) who wrote in 1874 [1]:

"The essence of Joule's discovery is the subjection of physical phenomena to dynamical law. If, then, the motions of every particle of matter in the universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after. The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water; the thermal motions would reconcentrate their energy, and throw the mass up the fall in drops re-forming into a close column of ascending water. ... And if also the materialistic hypothesis of life were true, living creatures would grow backwards, with conscious knowledge of the future, but no memory of the past, and would become again unborn. But the real phenomena of life infinitely transcend human science; and speculation regarding consequences of their imagined reversal is utterly unprofitable."

The explanation of this apparent paradox, due to Thomson, Maxwell and Boltzmann, is based on the great disparity between microscopic and macroscopic scales—with the consequent exponentially large ratios between the number of microstates (phase space volume) corresponding to the different macrostates—and the fact that events are determined not only by differential equations, but also by initial conditions. These provide the ingredients for the emergence of definite time asymmetric behavior in the observed evolution of macroscopic systems, despite the total absence of such asymmetry in the dynamics of individual atoms. (For a more detailed discussion and references see [2],[3].)

Macrostates

To describe the macroscopic state of a system of N atoms in a box V, say $N \gtrsim 10^{20}$, we make use of a much cruder description than that provided by the microstate X. We shall denote by $M(X)$ such a macroscopic description of a macrostate. As an example we may divide V into K cells, where K is large but still $K \ll N$, and specify the number of particles, the momentum and the amount of energy in each cell, with some tolerance.

Clearly there are many $X's$ (in fact a continuum) which correspond to the same M. Let Γ_M be the region in Γ consisting of all microstates X corresponding to a given macrostate M and denote by $|\Gamma_M|$ its Liouville volume.

The equilibrium macrostate M_{eq} is defined as that state for which $|\Gamma_{M_{eq}}| \sim |\Gamma_E|$, the area of the whole energy surface. When $M(X)$ specifies a nonequilibrium state, $|\Gamma_{M(X)}|$ is much smaller. Thus if the system contains N atoms in a volume V then the ratio of $|\Gamma_{M_{eq}}|$, for the macrostate M_{eq} in which there are $(\frac{1}{2} \pm 10^{-10})N$ particles in the left half of the box, to $|\Gamma_M|$ for a macrostate M in which all the particles are in the left half is of order 2^N. For any macroscopic value of N, this is far larger than the ratio of the volume

of the known universe to the volume of one proton. [1]

Boltzmann then argued that given this disparity in the sizes of Γ_M, $|\Gamma_M(X(t))|$ will *typically* increase in a way which *explains* and describes the evolution towards equilibrium of isolated microscopic systems. 'Typical' here means that for any Γ_M the relative volume of the set of microstates X in Γ_M for which $\log|\Gamma_M(X(t))|$ decreases by a macroscopic amount during some time period τ, (no bigger than the age of the universe) goes to zero exponentially in the number of atoms in the system.

ENTROPY AND LYAPUNOV FUNCTION FOR ISOLATED SYSTEM

To make a connection with the Second Law of Clausius, Boltzmann defined the entropy of a macroscopic system with microstate X as

$$S_B(X) = k\log|\Gamma_{M(X)}| \tag{3}$$

and showed that (for a dilute gas) in the equilibrium macrostate M_{eq}, i.e. $X \in \Gamma_{Meq}$, S_B is equal (to leading order in N) to the thermodynamic entropy of Clausius. Following O. Penrose, I shall call $k\log|\Gamma_M(X)|$ the Boltzmann entropy of a system in the macrostate $M(X)$. We can make Boltzmann's argument quantitative if we suppose (assume) that the time evolution of M_t satisfies an autonomous deterministic equation, such as the Navier-Stokes equation or the Boltzmann equation. This means that if $M_{t_1} \to M_{t_2}$, then the microscopic dynamics ϕ_t carries $\Gamma_{M_{t_1}}$ inside $\Gamma_{M_{t_2}}$, i.e. $\phi_{t_2-t_1}\Gamma_{M_{t_1}} \subset \Gamma_{M_{t_2}}$ with *negligible error*. The fact that phase space volume is conserved by the Hamiltonian time evolution implies that $|\Gamma_{M_{t_1}}| \leq |\Gamma_{M_{t_2}}|$ and thus that $S_B(M_{t_2}) \geq S_B(M_{t_1})$ for $t_2 \geq t_1$.

We have thus derived an "$\mathscr{H}$-theorem" or Lyapunov function for any deterministic evolution of the macro-variables arising from the microscopic dynamics of an isolated Hamiltonian system[3].

Example: For spatially uniform equilibrium systems the thermodynamic entropy is extensive

$$S(E, \mathbf{N}, V) = Vs(e, \mathbf{n}). \tag{4}$$

$s(e, .)$ is a concave function of e.

$$\frac{\partial s}{\partial e} = \frac{1}{T}, \quad \frac{\partial}{\partial e}(\frac{1}{T}) = -(1/T^2)\frac{\partial T}{\partial e} \leq 0. \tag{5}$$

For systems in "local thermal equilibrium" (LTE) with local densities $n(x), e(x), \mathbf{u}(\mathbf{x})$

$$S_B(n, \mathbf{u}, e) = \int_V s(e(\mathbf{x}) - \frac{1}{2}mn(\mathbf{x})\mathbf{u}^2(\mathbf{x}), n(\mathbf{x}))d\mathbf{x} = S_{l.e} \tag{6}$$

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[1] This is the reason why properties of an equilibrium system, such as the fraction of particles in a given velocity domain can be obtained, for $N \gg 1$, as an average over the microcanonical ensemble. N.B. This does not depend on the system being ergodic in the mathematical sense as long as N is large enough.

Consider now an isolated system in LTE (with $\mathbf{u} = 0$ and n constant) in a region V with boundary surface Σ and an energy density profile $e(\mathbf{x})$ satisfying the macroscopic conservation equation

$$\frac{\partial e}{\partial t} = -\nabla \cdot \underline{\mathbf{J}} \tag{7}$$

where $\mathbf{J}(\mathbf{e})$ is the heat flux. When this is given by Fourier's law,

$$\mathbf{J} = -\kappa \nabla \mathbf{T}, \quad \kappa(\mathbf{T}) \geq \mathbf{0}. \tag{8}$$

we then have a closed autonomous equation for e or T. This yields,

$$\begin{aligned}
\frac{dS_{l.e}}{dt} &= \frac{d}{dt} \int_V s d\mathbf{x} \\
&= -\int_V \frac{1}{T} (\nabla \cdot \mathbf{J}) dx = -\int_\Sigma \frac{1}{T} \mathbf{J} \cdot \mathbf{d}\Sigma + \int_{\mathbf{V}} \mathbf{J} \cdot (\nabla \frac{1}{\mathbf{T}}) \mathbf{dx} \geq \mathbf{0},
\end{aligned} \tag{9}$$

since $\mathbf{J} \cdot \mathbf{d}\Sigma = \mathbf{0}$ and $\kappa \geq 0$.

We next consider what happens when the isolated system is not in local equilibrium. (Following that we shall consider situations when the system is not isolated.)

Following Boltzmann, we refine the thermodynamic M used for systems in LTE by noting that the microstate $X = \{\mathbf{r}_i, \mathbf{v}_i\}$, $i = 1, ..., N$, can be considered as a set of N points in the six dimensional "μ-space". We then divide up this μ-space into $\tilde{J}$ cells $\tilde{\Delta}_\alpha$, centered on $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$, of volume $|\tilde{\Delta}_\alpha|$. A macrostate $\tilde{M}$ is then specified by the number of particles in each $\tilde{\Delta}_\alpha$,

$$\tilde{M} = \{N_\alpha\}, \quad \alpha = 1, ..., \tilde{J} << N. \tag{10}$$

For dilute gases one can *neglect*, for typical configurations, the interaction energy between the particles. The coarse grained energy of the system in the state $\tilde{M}$ is given, up to terms independent of f, by

$$\frac{1}{2} m \sum_\alpha N_\alpha \mathbf{v}_\alpha^2 = E \tag{11}$$

with

$$\sum N_\alpha = N \tag{12}$$

The phase space volume associated with such an $\tilde{M}$ is then readily computed to be

$$|\Gamma_{\tilde{M}}| = \Pi_\alpha (N_\alpha!)^{-1} |\tilde{\Delta}_\alpha|^{N_\alpha} \tag{13}$$

Stirling's formula then gives

$$S_B(\tilde{M}) \sim -k \left\{ \sum_\alpha \left(\frac{N_\alpha}{|\tilde{\Delta}_\alpha|} \log \frac{N_\alpha}{|\tilde{\Delta}_\alpha|} \right) |\tilde{\Delta}_\alpha| - N \right\} \tag{14}$$

Using $\tilde{M}$ we can associate with a typical X a coarse grained density $f_X \sim N_\alpha/|\tilde{\Delta}_\alpha|$ in μ-space, i.e. such that $N_\alpha = \int_{\tilde{\Delta}_\alpha} d\mathbf{x}d\mathbf{v}f_X(\mathbf{x},\mathbf{v})$. The Boltzmann entropy is then given by

$$S_B(X) = S_{\text{gas}}(f) = -k \int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v}f(\mathbf{x},\mathbf{v})\log f(\mathbf{x},\mathbf{v}) \tag{15}$$

The maximum of $S_{\text{gas}}(f)$ over all f which satisfy the constraints,

$$\int_V d\mathbf{x} \int_{\mathbf{R}^3} d\mathbf{v}f(\mathbf{x},\mathbf{v}) = N \tag{16}$$

$$\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v}\frac{1}{2}m\mathbf{v}^2 f(\mathbf{x},\mathbf{v}) = E \tag{17}$$

gives the equilibrium distribution, which is readily seen to be the Maxwell distribution

$$f_{eq} = \frac{N}{V}(2\pi kT/m)^{-3/2}\exp[-m\mathbf{v}^2/2kT] \tag{18}$$

where $kT = 2/3(E/N)$. In this case S_B coincides with the Clausius entropy

$$S_{\text{gas}}(f_{eq}) = S(E,N,V) = Nk[\frac{3}{2}\log T - \log(N/V)] + \text{Const.} \tag{19}$$

When $f \neq f_{eq}$ then f and consequently $S_{\text{gas}}(f)$ will change in time. The second law, now says that *typical $X \in \Gamma_{\tilde{M}}$*, at the initial time $t = 0$, will have an $\tilde{M}_t = \tilde{M}(X_t)$ such that $S_B(\tilde{M}(X_t)) \geq S_B(\tilde{M}(X_{t'}))$, for $t \geq t'$. This means that $S_{\text{gas}}(f_t) \geq S_{\text{gas}}(f_{t'})$, for $t \geq t'$. This is exactly what happens for a dilute gas described by the Boltzmann equation for which

$$\frac{d}{dt}S_{\text{gas}}(f_t) \geq 0, \quad \text{Boltzmann's} \quad \mathscr{H}-\text{theorem} \tag{20}$$

i.e. $S_{\text{gas}}(f)$ is a Lyapunov function,

As put by Boltzmann: "In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state"[4].

Remark: It is important to distinguish between the empirical μ-space density profile $f_{X_t}(\mathbf{x},\mathbf{v})$ and another object with the same name, the marginal one-particle (probability) distribution $F_1(\mathbf{x},\mathbf{v},t)$ obtained from an N-particle ensemble density evolving according to the Liouville equation. An instructive example is a macroscopic system of N noninteracting point particles, moving among a periodic array of scatterers in a macroscopic volume V. Starting with a nonuniform initial density $f_{X_0}(\mathbf{x},\mathbf{v})$ the time evolved $f_{X_t}(\mathbf{x},\mathbf{v})$ will approach an f which depends only on $|\mathbf{v}|$ and which will have a larger $S_{\text{gas}}(f)$, while $\int \int F_1 \log F_1 d\mathbf{x}d\mathbf{v}$ remains constant in time. The obvious evolution equation for f_{X_t} for this system, namely the one-particle Liouville equation, in fact does not describe the evolution of f_{X_t} for times after which $F_1(\mathbf{x},\mathbf{v},t)$ has developed structure on the microscopic scale.

The Boltzmann Entropy of Dense Fluids Not in LTE

Consider now the case when the interaction potential energy Φ between the particles is not negligible. The region $\Gamma_{\tilde{M}}$ will then include phase points with widely differing total energies. The set of microstate X of a system with a specified energy, $H(X) = E$ will then correspond to a small fraction of $\Gamma_{\tilde{M}(X)}$. In fact a little thought shows that most of Γ_f corresponds to the largest energies compatible with $f(\mathbf{x}, \mathbf{v})$. The macrostate M specified by both f and E will then have a Boltzmann entropy consisting of a momentum part and a configurational part. For a system of hard spheres where $E = K$ the Boltzmann entropy can be written as the sum,

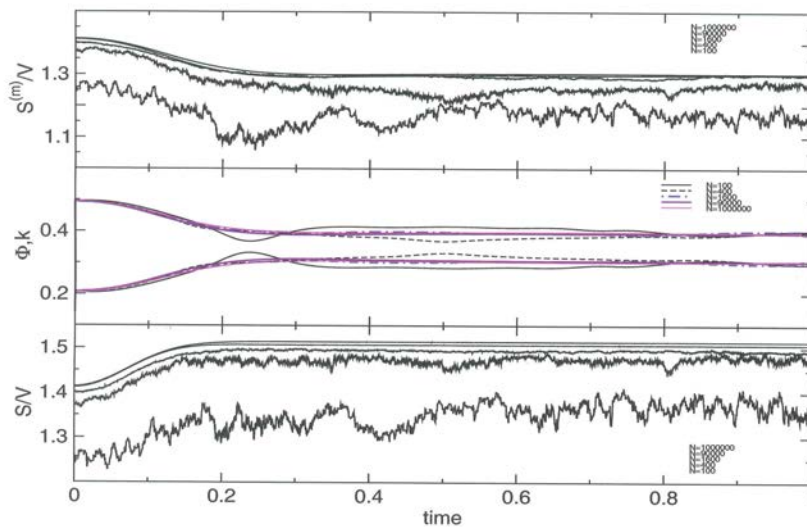$$S_{hs}(f) = S^{(m)}(f) + \mathscr{S}_{hs}^{(c)}(n) \tag{21}$$

where $S^{(m)}$ is the momentum part

$$S^{(m)}(f) = -\int_V d\mathbf{x} \int d\mathbf{v} f(\mathbf{x}, \mathbf{v}) log[f(\mathbf{x}, \mathbf{v})/n(\mathbf{x})] \tag{22}$$

and $\mathscr{S}_{hs}^{(c)}(n)$ is the configurational part of the entropy of an equilibrium system of hard spheres kept at a nonuniform density $n(\mathbf{x}) = \int f(\mathbf{x}, \mathbf{v}) d\mathbf{v}$ by some external potential $U(\mathbf{x})$.

$S_{hs}(f)$ was proven by Resibois (in a different form) to be a Lyapunov function for the modified Enskog equation c.f.[3],

$$\frac{d}{dt} S_{hs}(f_t) \geq 0 \tag{23}$$

The decrease of $S^{(m)}(f_t)$ and increase of the total $S(f_t, E)$ is shown in Fig. 1. Based on molecular dynamic simulations for different number of particles N in a periodic box, Fig.1 shows the time evolution of $S^{(m)}$, of the potential and kinetic energies and of the total entropy S for a Lennard-Jones system started at $t = 0$ in a state where the kinetic energy is "too high"[5]. This corresponds to a situation considered by Jaynes, c.f.[3].

OPEN SYSTEMS

For an open system, say one in contact with a "heat bath" at a specified temperature $\bar{T}$, the entropy of the system alone is clearly no longer an increasing function, e.g. we can start the system at an energy E_o corresponding to a temperature $T_o > \bar{T}$. In terms of the macroscopic equation for the energy density or temperature the entropy is no longer a Lyapunov function since the energy flux across the boundaries no longer vanishes, and can be either positive or negative.

So what do we do for a Lyapunov function?

A simple way which works for the case when there is only one heat bath is to observe that the *total* entropy production in system plus reservoir can be written as, see (9),

$$\frac{dS_{total}}{dl} = \frac{dS_{l.e}}{dt} + \int_\Sigma (1/\bar{T}) \mathbf{J} \cdot \mathbf{d}\sum \tag{24}$$

$$= \frac{d}{dt}[S_{l.e} - (1/\bar{T})E_{l.e}] = \frac{d}{dt}(-\mathscr{F}) \tag{25}$$

$$= \int_V \mathbf{J} \cdot \nabla(\frac{\mathbf{1}}{\mathbf{T}})\mathbf{dx} \geq \mathbf{0} \tag{26}$$

where $\mathscr{F}$, given by the terms in the square brackett in (25), is now the "Lyapunov function".

This procedure fails when the system is in contact with more than one heat bath and $\bar{T}$ is not constant on the boundary Σ in which case the entropy production is not zero in the stationary state.

To proceed we now recall that, as noted by Boltzmann and Einstein, the relative Boltzmann entropy $\mathscr{S}(M) \equiv S_B(M) - S_B(M_{eq})$ is equal to the log of the probability of finding the system in the macrostate $M = \{e(x)\}$,

$$P(M) \sim exp[S_B(M) - S_B(M_{eq})] = exp\{-\mathscr{F}(M)\} \tag{27}$$

This probability is with respect to the uniform (microcanonical) measure on the energy surface of the isolated system, which is stationary under the microscopic Hamiltonian time evolution.

$\mathscr{S}(M)$ thus coincides, in the limit of large system size and M macroscopically distinct from M_{eq} (the latter includes states which only differ by "normal" fluctuations) with the negative of the usual large deviation functional (LDF) of probability theory for $\mu_{st}(X) \sim \delta(H(X) - E)$, i.e. for the microcanonical ensemble.

The same is true for the Lyapunov function $\mathscr{F}$ for the system in contact with a single heat bath at temperature $\bar{T}$, where

$$\mathscr{F}(\{e(x)\}) = [E - \bar{T}S_{l.e}]/\bar{T} \tag{28}$$

is again the LDF of the stationary measure for the system in contact with a heat bath. This is now the canonical ensemble at temperature $\bar{T}$.

$$\mu_{st} \sim exp[-H(X)/\bar{T}] \tag{29}$$

The above analysis can be readily generalized to the macrostate $M = \{e(\mathbf{x}), \mathbf{n}(\mathbf{x}), \underline{\mathbf{u}}(\mathbf{x})\}$ whose time evolution is governed by the Navier-Stokes equations. In fact one expects that the LDF for the stationary measure will always be a Lyapunov function for the macroscopic equation [6, 7]. An example which exploits this fact to derive new Lyapunov functions is given in the next section[8].

LYAPUNOV FUNCTION FOR A SYSTEM IN CONTACT WITH SEVERAL PARTICLE RESERVOIRS

Let σ be a smooth increasing function. We consider the PDE on a regular domain $V \subset \mathbb{R}^d$

$$\frac{\partial \rho(t,\mathbf{x})}{\partial t} = \nabla^2\left(\sigma\big(\rho(t,x)\big)\right), \tag{30}$$

with Dirichlet boundary conditions on Σ specified by the reservoirs, i.e. $\rho(t,x) = \bar{\rho}(x)$ for $x \in \Sigma$ where $\bar{\rho}(x)$ is the stationary profile in all of V. Let

$$F_u(v) = \int_u^v dz \log \frac{\sigma(z)}{\sigma(u)}. \tag{31}$$

We define the functional

$$\mathscr{F}(\sigma) = \int_V dx\, F_{(\mathbf{u})}(\sigma(\mathbf{x})). \tag{32}$$

A straightforward but lengthy computation then shows that $\frac{\partial \mathscr{F}(\rho)}{\partial t} \geq 0$ where we used the fact that on the boundary $\frac{\rho(t,x)}{\bar{\rho}(x)} = 1$.

The function $\mathscr{F}$ defined in (32) is the LDF for the "zero range process" in contact with particle reservoirs at different densities. For this model the NESS is known explicitely and thus permits the explicit computation of the LDF [8].

The same computation will go through with a field

$$\frac{\partial \rho(t,x)}{\partial_t} = \nabla^2 \sigma(\rho(t,\mathbf{x})) - E\nabla \sigma(\rho(t,\mathbf{x})). \tag{33}$$

One could also treat mixed Dirichlet/Neumann boundary conditions.

ACKNOWLEDGMENTS

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