Microscopic chaos and macroscopic entropy in fluids

Giovanni Gallavotti
Fisica and I.N.F.N. Roma 1
30 July 2006 ;

Abstract: *In nonequilibrium thermodynamics macroscopic entropy creation plays an important role. Here we study the relationship it bears with the phase space contraction, which has been recently proposed as an apparently alternative quantity.*

1. Phase space contraction and entropy creation

Studying stationary states of mechanical systems in interaction with thermostats the latter are modeled by systems of particles subject to anholonomic constraints. The equations of motion take the form $\dot{x} = f_{\underline{E}}(x)$ where x is a point in phase space and $\underline{E}$ are parameters controlling the size of the acting nonconservative forces.

It has appeared natural to define *entropy creation rate* the divergence $\sigma(x) \stackrel{def}{=} -\sum_j \partial_{x_j} f_{\underline{E}}(x)$. There are other natural definitions of entropy creation rate and here we study their relation with the above phase space divergence. The aim is to find such a relationship for a system that can be considered to be described as a continuum following macroscopic equations.

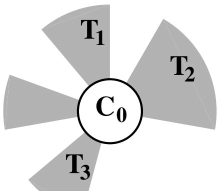

Fig1

Fig.1 Reservoirs occupy finite regions outside $\mathcal{C}_0$, *e.g.* sectors $\mathcal{C}_i \subset R^3$, $i = 1, 2 \ldots$. Their particles are constrained to have a *total* kinetic energy K_i constant, by suitable forces, so that the reservoirs "temperatures" T_i are well defined.

To be concrete and in rather ample generality we imagine a system $\mathcal{C}_0$ of particles enclosed in a container, also called $\mathcal{C}_0$, with elastic boundary conditions surrounded by a few thermostats which consist of particles interacting with the system via short range interactions, through a portion $\partial_i\mathcal{C}_0$ of the surface of $\mathcal{C}_0$, and subject to the constraint that the total kinetic energy of the N_i particles in the i-th thermostat is $K_i = \frac{1}{2}\underline{\dot{X}}_i^2 = \frac{3}{2}N_i k_B T_i$. A symbolic illustration is in Fig.1.

Assuming unit mass, the equations of motion will be

$$\underline{\ddot{X}}_0 = -\partial_{\underline{X}_0}\Big(U_0(\underline{X}_0) + \sum_{j>0} W_{0,j}(\underline{X}_0, \underline{X}_j)\Big) + \underline{E}(\underline{X}_0),$$
$$\underline{\ddot{X}}_i = -\partial_{\underline{X}_i}\Big(U_i(\underline{X}_i) + W_{0,i}(\underline{X}_i, \underline{X}_j)\Big) - \alpha_i \underline{\dot{X}}_i \qquad (1)$$

with α_i such that K_i is a constant. Here $W_{0,i}$ is the interaction potential between particles in $\mathcal{C}_i$ and in $\mathcal{C}_0$, while U_0, U_i are the internal energies of the particles in $\mathcal{C}_0, \mathcal{C}_i$ respectively. We imagine that the energies $W_{i,j}, U_j$ are due to *smooth* translation invariant pair potentials; repulsion from the boundaries of the containers will be elastic reflection. It is assumed, in Eq.(1) that there is no direct interaction between different thermostats: their particles interact directly only with the ones in $\mathcal{C}_0$. Here $\underline{E}(\underline{X}_0)$ denotes possibly present external positional forces stirring the particles in $\mathcal{C}_0$.

Since the work per unit time that particles outside the thermostat $\mathcal{C}_i$ (hence in $\mathcal{C}_0$) exercise on the particles in it, is $-\partial_{\underline{X}_i} W_{0,i}(\underline{X}_0, \underline{X}_i) \cdot \underline{\dot{X}}_i$ and it can be interpreted as the "amount of heat Q_i entering" the thermostat $\mathcal{C}_i$, energy conservation yields

$$\frac{d}{dt}\big(\frac{1}{2}\underline{\dot{X}}_i^2 + U_i\big) \equiv \dot{U}_i = -\alpha_i \underline{\dot{X}}_i^2 + Q_i \qquad (2)$$

and the contraints on the thermostats kinetic energies give $\alpha_i \equiv \frac{Q_i - \dot{U}_i}{3N_i k_B T_i}$.

Set $x = (\underline{X}_i, \underline{\dot{X}}_i)_{i=0,..}$ and write (1) as $\dot{x} = f_{\underline{E}}(x)$. The divergence $\sigma(x) = -\sum_j \partial_{x_j} f_{\underline{E},j}(x)$ of the equations of motion in phase space is readily computed from (1), see also [1], and is $\sigma(x) = \sum_{i>0} \frac{Q_i}{k_B T_i} + \dot{R}$ or $\sigma(x) = \varepsilon(x) + \dot{R}$ with

$$\varepsilon(x) = \sum_{i>0} \frac{Q_i}{k_B T_i} \qquad (3)$$

where $R = \sum_{i>0}(1 - \frac{1}{3N_i})U_i$ and $\frac{Q_i}{k_B T_i}$ should really be $(1 - \frac{1}{3N_i})\frac{Q_i}{k_B T_i}$: this simplification is made just to simplify the formulae as, in any event, we are interested in cases in which $N_0, N_i \gg 1$.

Remark: (i) The $\varepsilon(x) \stackrel{def}{=} \sum_{i>0} \frac{Q_i}{k_B T_i}$ can be called naturally the *entropy creation rate* and, therefore, Eq.(2) have a physical meaning: *entropy is created at the boundary of the system.* Creation *really* takes place where the walls get in contact with the thermostats, where the temperatures T_i are defined.
(ii) Note that if particles in $\mathcal{C}_0$ were *also* subject to an isokinetic constraint $\frac{1}{2}(\dot{\underline{X}}_0)^2 = \frac{3}{2}N_0 k_B T_0$ phase space contraction would simply be changed by the addition of $\frac{Q_0}{k_B T_0}$ with Q_0 being the work done per unit time by the thermostats in $\mathcal{C}_i$, $i > 0$, on particles in $\mathcal{C}_0$; also R will contain an extra term proportional to $\dot{U}_0$.
(iii) The divergence $\sigma(x)$ is *different* from the entropy creation rate $\varepsilon(x)$. Their difference is a "total time derivative", therefore the time averages $a \stackrel{def}{=} \frac{1}{\tau}\int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \sigma(S_t x)\,dt$ and $a_0 \stackrel{def}{=} \frac{1}{\tau}\int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \varepsilon(S_t x)\,dt$ are related by

$$a = a_0 + \frac{1}{\tau}\big(R(S_{\frac{\tau}{2}}x) - R(S_{-\frac{\tau}{2}}x)\big) \qquad (4)$$

which means that the observables a and a_0 will have the *same* distribution with respect to any stationary distribution in the limit $\tau \to \infty$ if R is a bounded function (as in our case). More general and "singular" interaction potentials could be considered to reach essentially equivalent conclusions, [2].
(iv) Note that also phase space contraction of a system in contact with isokinetic thermostats has a precise physical meaning as it *equals minus the sum of the dimensionless free energy creation rates* $-\frac{\dot{U}_i}{k_B T_i} + \frac{Q_i}{k_B T_i}$ of the thermostats.

2. Macroscopic fluids

The above analysis shows that the two notions of entropy creation rate $\varepsilon(x)$ in Eq.(3) and of phase space contraction $\sigma(x)$ are *related but different.* They have the same stationary average, as they differ by a total derivative $\dot{R}$. This implies that not only the averages of σ and ε are equal but also that the fluctuations of the finite time averages, *i.e.* of a and a_0 in Eq(4), are the same: so that properties known for the fluctuations of σ imply corresponding properties for the fluctuations of the physically meaningful entropy creation rate ε. This is relevant because, in the literature, several results have been derived concerning the fluctuations of the time averages of the phase space contraction, see [4].

Therefore it is of some interest to see what the above mechanical notion of entropy creation rate becomes in a system which can be considered as a continuum in a stationary state and in local equilibrium. In fact for such a system an independent definition of entropy creation is classical, [3]. We check that the two notions coincide.

Consider, in $\mathcal{C}_0$, a system of particles which can be regarded as a continuum in a stationary state and in contact with fixed walls on which, at each boundary point $\boldsymbol{\xi} \in \partial\mathcal{C}_0$, temperature is prescribed at a value $T(\boldsymbol{\xi})$ because the surface element $ds_{\boldsymbol{\xi}}$ is in contact with a thermostat (as idealized in Fig.1). Then the entropy creation rate according to Eq.(3) will be

$$\varepsilon = \int_{\partial\mathcal{C}_0} \frac{Q(\boldsymbol{\xi})}{k_B T(\boldsymbol{\xi})} ds_{\boldsymbol{\xi}}, \qquad (5)$$

where $Q(\boldsymbol{\xi})$ is the amount of work per unit time and unit surface that the fluid performs on the thermostat in contact with the surface element $ds_{\boldsymbol{\xi}}$, while phase space contraction σ will differ from this by $-\frac{d}{dt}\int_{\partial\mathcal{C}_0} \frac{U_{ext}(\boldsymbol{\xi})}{k_B T(\boldsymbol{\xi})}\, ds_{\boldsymbol{\xi}}$ where $U_{ext}(\boldsymbol{\xi})$ is the internal potential energy of the same thermostat.

There are no complete derivations of the Navier Stokes equations, (NS), from molecular models: however all attempts (which achieve the result under reasonable extra assumptions) deal with limiting regimes implying restrictions on initial data involving a length scaling of $O(\delta^{-1})$, a time scaling of $O(\delta^{-2})$, (hence) a velocity scaling $O(\delta)$ and become exact in the limit as $\delta \to 0$.

Here we shall assume that the NS equations can be also obtained from a molecular model under a suitable scaling of space and time variables. We shall therefore consider microscopic initial data with Maxwellian velocity distribution and with position distributions with average fields (of density $\rho(\underline{x})$, of kinetic energy, *i.e.* temperature $T(\underline{x})$, and velocity

$\underline{u}(\underline{x})$) consistent with initial values corresponding to a continuum. And we shall suppose that they evolve so that average velocity, density, kinetic energy satisfy NS with good approximation, and exactly in the limit in which some scaling parameter $\delta \to 0$.

Physically δ is a parameter measuring "how far from a continuum the microscopic structure is"; it can be identified with the ratio between the molecular free path and the length scale of the variation of the macroscopic velocity and temperature fields.

Therefore in the limit $\delta \to 0$ each volume element will contain an infinite number of particles and fluctuations will be suppressed; however the *average* entropy creation will be defined and, by Eq.(3), be

$$\langle\varepsilon\rangle = -\int_{\partial\mathcal{C}_0} \kappa \frac{\underline{n}(\boldsymbol{\xi})\cdot\underline{\partial}\, T(\boldsymbol{\xi})}{k_B T(\boldsymbol{\xi})} ds_{\boldsymbol{\xi}} \tag{6}$$

where κ is the thermal conductivity and the average is intended over a time scale long compared to the microscopic time evolution but macroscopically short.

Suppression of fluctuations will not mean that the averages defining $\underline{u}(\underline{x}), T(\underline{x})$ over such time scales will not continue to vary even in the stationary state. However *global quantities*, *e.g.* $\int_{\mathcal{C}_0} \underline{u}(\underline{x})\, d\underline{x}$ or $\int_{\mathcal{C}_0} \log T(\underline{x})\, d\underline{x}$, will have such averages varying over a longer time scale.

Eq.(6) is the expression corresponding to Eq.(3) derived from molecular dynamics and it must be compared, for compatibility, with the familiar expressions for the entropy creation rate in systems described by macrosopic continua equations, [3].

We consider here a viscous and thermally conducting fluid with density ρ and in local equilibrium. Thus the local equilibrium entropy density s depends on temperature and density $s = s(T,\rho)$. Then, if $\underset{\approx}{\tau}'$ is the stress tensor $\tau'_{ij} = (\partial_i u_j + \partial_j u_i)$ in terms of the velocity field $\underline{u}$, η is the dynamical viscosity and $U(\underline{x})$ is the internal energy density, the NS equation are, [4, p.6,18],

$$\begin{aligned}
&(1)\quad \partial_t\rho + \underline{\partial}\cdot(\rho\underline{u}) = 0\\
&(2)\quad \partial_t\underline{u} + \underset{\sim}{u}\cdot\underset{\sim}{\partial}\,\underline{u} = -\frac{1}{\rho}\underline{\partial}\, p + \frac{\eta}{\rho}\Delta\underline{u} + \underline{g}\\
&(3)\quad \partial_t U + \underline{\partial}\cdot(\underline{u}U) = \eta\,\underset{\approx}{\tau}'\,\underset{\sim}{\partial}\,\underset{\sim}{u} + \kappa\Delta T - p\,\underline{\partial}\cdot\underline{u}\\
&(4)\quad T\,(\partial_t s + \underline{\partial}\cdot(\underline{u}s)) = \eta\,\underset{\approx}{\tau}'\,\underset{\sim}{\partial}\,\underset{\sim}{u} + \kappa\Delta T
\end{aligned} \tag{7}$$

The conditions at the boundary of the fluid container $\mathcal{C}_0$ will be time independent, $T = T(\boldsymbol{\xi}), \underline{n}(\boldsymbol{\xi})\cdot\underline{u}(\boldsymbol{\xi}) = 0$ with $\underline{n}$ = outer normal (elastic boundary), or $\underline{u} = \underline{0}$ (no slip boundary). Here $\underline{g}$ is a (nonconservative) external force generating the fluid motion and p is the physical pressure.

As mentioned, Eq.(7) are macroscopic equations that can be valid only in some limiting regime. Given a system of particles with short range pair interactions let δ be a dimensionless scaling parameter; then a typical conjecture is: for suitably restricted and close to local equilibrium initial data (see [4, p.21] for examples) *on time scales of $O(\delta^{-2})$ and space scales $O(\delta^{-1})$ the evolution follows the incompressible NS equation*, [4, p.30].

The classical entropy creation rate in nonequilibrium thermodynamics of an *incompressible fluid* is

$$k_B\langle\varepsilon\rangle = \int_{\mathcal{C}_0}\Big(\kappa\,\big(\frac{\underline{\partial}T}{T}\big)^2 + \eta\,\frac{1}{T}\underset{\approx}{\tau}'\,\underset{\sim}{\partial u}\Big)\, d\underline{x}. \tag{8}$$

By integration by parts and use of the first and fourth of (7), $k_B\langle\varepsilon\rangle_\mu$ becomes, if $S \stackrel{def}{=} \int_{\mathcal{C}_0} s\, d\underline{x}$,

$$\begin{aligned}
&\int_{\mathcal{C}_0}\Big(-\kappa\,\underline{\partial}T\cdot\underline{\partial}T^{-1} + \eta\,\frac{1}{T}\underset{\approx}{\tau}'\,\underset{\sim}{\partial u}\Big)\, d\underline{x} =\\
&= -\int_{\partial\mathcal{C}_0}\kappa\,\frac{\underline{n}\cdot\underline{\partial}T}{T}\, ds_{\boldsymbol{\xi}} + \int_{\mathcal{C}_0}\frac{(\kappa\Delta T + \eta\,\underset{\approx}{\tau}'\underset{\sim}{\partial u})}{T} d\underline{x} =\\
&= -\int_{\partial\mathcal{C}_0}\kappa\,\frac{\underline{n}\cdot\underline{\partial}T}{T}\, ds_{\boldsymbol{\xi}} + \dot S + \int_{\mathcal{C}_0}\underline{u}\cdot\underline{\partial}s\, d\underline{x} =\\
&= -\int_{\partial\mathcal{C}_0}\kappa\,\frac{\underline{\partial}T\cdot\underline{n}}{T}\, ds_{\boldsymbol{\xi}} + \dot S
\end{aligned} \tag{9}$$

i.e. it *still leads to* the expression Eq.(6), "local on the boundary" or "localized at the contact between system and thermostats", since $\underline{u}\cdot\underline{n} \equiv 0$ by the boundary conditions, *plus* the time derivative of the total "thermodynamic entropy" of the fluid.

Remarks: (i) An identical analysis can be performed for *Rayleigh's convection model*, widely used to test

ideas on turbulence since [5]: the result is the same because the extra term that would appear in Eq.(9), see [4, p. 47], would be proportional to $\int_{\mathcal{C}_0} u_z d\underline{x}$ which vanishes because the motion has no net momentum in the z direction.
(ii) It should be noted that in the limit $\delta \to 0$, *i.e.* when the NS equations are expected to become rigorously exact, the Eq.(8) simplifies: only the first term in *r.h.s.* remains because the velocity $\underline{u}$ scales as $O(\delta)$, [4, p.26].

3. Incompressible continua viewpoint

The above analysis leads to a further natural question: whether the phase space contraction and the entropy creation rate can be computed if we imagine, as it is tempting to do, the small macroscopic volume elements of an incompressible fluid *in local equilibrium and observed on a short but macroscopic time scale* as a collection of small thermostats in contact with reservoirs consisting in the neighboring volume elements: would the results be consistent?

However the volume elements $E = d\underline{x}$ are not separated by walls, hence they can exchange particles, and they also move. In order to be able to treat volume elements as systems on their own we imagine that their size is ξ with ξ macroscopically small but microscopically large: certainly such length scale ξ is $\ll L = \big(\frac{1}{T}\frac{\partial T}{\partial x}\big)^{-1}$ where L is the macroscopic scale of the container $\mathcal{C}_0$.

Furthermore we have to assume that molecules diffuse in a characteristic evolution time, over a distance $\ll \xi$. The diffusion coefficient is $D = O(\frac{k_B T}{mr^2\rho v})$ with v the average speed, $v = O(v_{sound})$, m the mass of the molecules, r their radius and ρ the numerical density, and a characteristic time scale is $\theta = \frac{mD}{k_B T}$. The distance traveled by diffusion in the latter time scale is $(D\theta)^{\frac{1}{2}}$ ($\sim 10^{-2}$cm in air at normal conditions). In stationary turbulence ξ has also to be small compared to the Kolmogorov scale.

Finally we assume that the local quantities, velocity field and temperature field, $\underline{u}(\underline{x}), T(\underline{x})$, evolve on a time scale much slower than the microscopic time scale θ and can be considered constant on that time scale. Then the expression Eq.(8) should be regarded as an average over a long microscopic time but over a short macroscopic time.

If the conditions that allow us to consider a volume element in a fluid as a thermostated system in a stationary state in contact with thermostats made of the neighboring elements, *i.e.* that the quantity δ introduced after (7) is small and the diffusion across the elements boundaries is not so important to make the identity of the volume elements ill defined (*i.e.* $\delta \ll \xi \ll L$) we can apply the analysis leading from Eq.(1) to Eq.(3) and conclude that *up to a total derivative* $\dot R$ the phase space contraction of the total system, *i.e.* fluid plus thermostats, is

$$\varepsilon(x) = \sum_E \sum_{E'} \frac{Q_{E,E'}}{k_B T_{E'}} \tag{10}$$

where $Q_{E,E'}$ is the amount of work that the particles in a given volume element E perform over the neighboring elements E', see Eq.(3).

We assume that the local average kinetic energies can be regarded as non fluctuating (*i.e.* we assume to be close to thermal equilibrium): this is an assumption that appears often (if tacitly) in nonequilibrium thermodynamics and it will be used here to deduce that the average values of products of temperatures and velocities equal the products of the averages.

If the average heat current is $-\kappa\,\underline{\partial} T$ and the element E is imagined with the bases orthogonal to the gradient of T, the average contribution to $Q_{E,E'}$ for E' adjacent to the upper base of E is $-\kappa\,\underline{\partial} T\cdot\underline{n}\,\xi^2$ (ξ^2 = area of the base) and it is opposite to the contribution from the lower base; therefore the quantity $\sum_{E'} \frac{Q_{E,E'}}{T_{E'}}$ has average

$$-\kappa\,\underline{\partial} T\cdot\underline{n}\xi^2\,(\frac{1}{T_+} - \frac{1}{T_-}) = -\kappa\underline{\partial} T\cdot\underline{\partial} T^{-1}\xi^3, \tag{11}$$

if $T_\pm$ are the temperatures at the two bases; therefore summing over E: $k_B\langle\varepsilon\rangle_\mu = \int_{\mathcal{C}_0} \underline{\partial}(\frac{1}{T})\cdot(-\kappa\,\underline{\partial} T)\,d\underline{x}$ which can be written in the more familiar form $\kappa\int_{\mathcal{C}_0}\big(\frac{\underline{\partial} T}{T}\big)^2 d\underline{x}$. Then if $\partial_t T = 0, \Delta T = 0$ and $\underline{u} = \underline{0}$ Eq.(8), hence Eq.(6), follows by partial integration.

More generally in presence of time dependence and non vanishing velocity field there will be an extra amount of energy transfered to elements adjacent to E and due to diffusion across the bases: it can be evaluated in the same way as above to be $\eta \underset{\approx}{\tau}' \cdot \underline{n}\,(\underset{\sim}{u}_+ - \underset{\sim}{u}_-)\xi^2$ if $\underset{\approx}{\tau}'$ is the stress tensor and it changes $\langle\varepsilon\rangle_\mu$ to Eq.(8), hence to Eq.(6) plus $\dot S$ (see Eq.(9)) if account is taken of the fourth of Eq(7).

Finally it is interesting to remark that not only the entropy creation rate but also the phase space contraction can be computed along the above lines. Regarding each volume element E as a thermostated system in a stationary state with a fixed temperature, the phase space contraction is given by $\int_{\mathcal{C}_0} \big(\varepsilon(\underline{x}) - \frac{\dot U(\underline{x})}{k_B T(\underline{x})}\big)\, d\underline{x} - \int_{\partial\mathcal{C}_0} \frac{\dot U_{ext}(\underline{x})}{k_B T(\underline{x})}\, ds_{\underline{x}}$ where $U(\underline{x})$ denotes the energy density and $U_{ext}(\underline{x})$ denotes the potential energy of the thermostats (the kinetic energies do not appear because in this approximation they are supposed to be constant as each volume element is regarded to have a constant kinetic energy, *i.e.* a well defined temperature).

Energy conservation, $\dot U(\underline{x}) = \underset{\approx}{\tau}' \cdot \underline{\partial}\underset{\sim}{u} + \kappa\Delta T$, see (3) in Eq.(7), and partial integration of the contribution $\kappa\big(\frac{\partial T}{T}\big)^2$ to $\varepsilon(\underline{x})$, see Eq.(8), in the integral $\int_{\mathcal{C}_0} \big(\varepsilon(\underline{x}) - \frac{\dot U(\underline{x})}{k_B T(\underline{x})}\big)\, d\underline{x}$ leave us with a boundary term *which is just Eq.(6) minus* $\int_{\partial\mathcal{C}_0} \frac{\dot U_{ext}(\underline{x})}{k_B T(\underline{x})} ds_{\underline{x}}$ as it could be guessed from the expression for σ preceding Eq.(3). Therefore even by regarding the fluid volume elements as thermostated systems in stationary nonequilibrium leads to the expected general relation between entropy creation ε and phase space divergence σ discussed in Sec.1, namely (if x denotes the fields determining the state of the fluid)

$$\sigma(x) = \varepsilon(x) - \int_{\partial\mathcal{C}_0} \frac{\dot U_{ext}(\underline{x})}{k_B T(\underline{x})} ds_{\underline{x}} \qquad (12).$$

Analysis of compressible fluids is unfortunately more difficult and should also be attempted: the first difficulty will be, of course, that it is not clear under which scaling the compressible NS equations should hold as a reasonable approximation.

Acknowledgements: I am indebted to A.Giuliani, F.Zamponi and, in particular, to F.Bonetto for important suggestions.

References

[1] G. Gallavotti. Irreversibility time scale. *Chaos*, 16:023130 (+7), 2006.

[2] F. Bonetto, G. Gallavotti, A. Giuliani, and F. Zamponi. Chaotic Hypothesis, Fluctuation Theorem and Singularities. *Journal of Statistical Physics*, 123:39–54, 2006.

[3] S. de Groot and P. Mazur. *Non equilibrium thermodynamics.* Dover, Mineola, NY, 1984.

[4] G. Gallavotti. *Foundations of Fluid Dynamics.* (second printing) Springer Verlag, Berlin, 2005.

[5] E. Lorenz. Deterministic non periodic flow. *Journal of Atmospheric Science*, 20:130–141, 1963.

e-mail: `giovanni.gallavotti@roma1.infn.it`
web: `http://ipparco.roma1.infn.it`