Thermostats, entropy and chaotic hypothesis

nonequilibrium system: mechanical sys. & non conserv. forces: is there a "Thermodynamics?". Key points:

(a) realization that the analogue of equilibrium statistical mechanics should be the study of *stationary states*, or *steady states*

(b) simulations on steady states performed in the 80's after the essential role played by *finite thermostats* was fully realized.

Steady State $\stackrel{def}{=}$ probability dist. μ: used $\Rightarrow$ *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

General model: thermostats "external" to $\mathcal{C}_0$. Particles mutually interacting and through portions $\partial_i \mathcal{C}_0$ of the surface of $\mathcal{C}_0$, with $\mathcal{C}_i$: constraint that the N_i particles in i-th thermostat have K.E. $K_i = \frac{m}{2}\dot{\mathbf{X}}_i^2 = \frac{3}{2} N_i k_B T_i$.

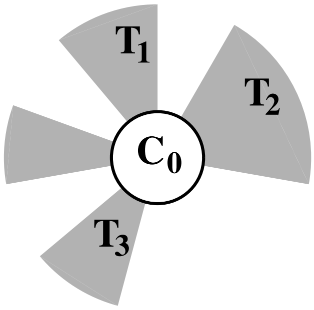

Fig1

Particles in $\mathcal{C}_0$ ("system") interact with $\mathcal{C}_i$ shaded ("thermostats") constrained fixed total K.E.

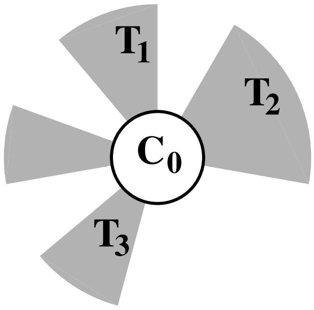

Fig1

The equations of motion will be

$$
\begin{aligned}
m\ddot{\mathbf{X}}_0 =& -\partial_{\mathbf{X}_0}\Big(U_0(\mathbf{X}_0)+\sum_{j>0}W_{0,j}(\mathbf{X}_0,\mathbf{X}_j)\Big)+\mathbf{E}(\mathbf{X}_0),\\
m\ddot{\mathbf{X}}_i =& -\partial_{\mathbf{X}_i}\Big(U_i(\mathbf{X}_i)+W_{0,i}(\mathbf{X}_i,\mathbf{X}_j)\Big)-\alpha_i\dot{\mathbf{X}}_i
\end{aligned}
$$

with α_i s.t. K_i constant. $W_{0,i}$ inter. potential $\mathcal{C}_i$-$\mathcal{C}_0$, U_0, U_i intern. energ. I.e.

$$
\alpha_i \equiv \frac{Q_i - \dot{U}_i}{3N_i k_B T_i} \qquad \Rightarrow \qquad K_i \equiv const \stackrel{def}{=} \frac{3}{2} N_i k_B T_i
$$

where $Q_i \stackrel{def}{=} -\dot{\mathbf{X}}_i \cdot \partial_{\mathbf{X}_i} W_{0,i}(\mathbf{X}_0,\mathbf{X}_i)$ = work of $\mathcal{C}_0$ on i-th thermostat

$Q_i \stackrel{def}{=} -\partial_{\mathbf{X}_i} W_{0,i}(\mathbf{X}_0, \mathbf{X}_i) \cdot \dot{\mathbf{X}}_i$
is **interpreted** as "amount of heat Q_i entering" thermostat $\mathcal{C}_i$.

Main features
a) thermostats are *external to system proper*
b) *time reversible*: *i.e.* if $I(\mathbf{X}, \dot{\mathbf{X}}) \stackrel{def}{=} (\mathbf{X}, -\dot{\mathbf{X}})$ is the *time reversal* then if $S_t(\mathbf{X}, \dot{\mathbf{X}})$ denotes the solution then

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

Unphysical? infinite thermostats? (with Gibbs states at temperatures T_i at ∞)
$\rightarrow$ BUT progress through simulations made possible by finite thermostats.

First question is which will be the steady state distribution μ describinng steady statistics? from an initial $(\dot{\mathbf{X}}, \mathbf{X})$

Statistical properties **are** the ones of randomly chosen data with distribution with density over the volume on phase space (fact?).

Is there a privileged invariant distribution? in equilibrium yes: Liouville!

BUT equations of motion do not conserve phase space volume and will contract it, at least in average: important exception is equilibrium, modeled by Hamiltonian eq. *Ergodic Hypothesis.* **Idea: extend the ergodic hypothesis**

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

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

μ is the *SRB distribution*, ie statistics of a.a. motions.

Properties: (for instance) given observables F_i, smooth and with nonzero time average $F_{i,+} = \int F_i \, d\mu \neq 0$, one can consider their *finite time averages*

$$f_i = \frac{1}{\tau} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{F_i(S_t(\mathbf{X}, \dot{\mathbf{X}}))}{F_{i,+}} \, dt$$

then $\exists$ a convex open set C and SRB-probability that $\mathbf{f} = (f_1, \ldots, f_n) \in \boldsymbol{\Delta} \subset C$

$$prob_\mu(\mathbf{f} \in \boldsymbol{\Delta}) \;=\; const\, e^{\tau \, \max_{\mathbf{f}\in\boldsymbol{\Delta}} \zeta_{\mathbf{F}}(\mathbf{f}) + O(1)}$$

where $\zeta_{\mathbf{F}}(\mathbf{f})$ is analytic and convex in C and is $-\infty$ for $f \notin \overline{C}$.

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f_i has *by its definition* average $1 \Rightarrow \mathbf{1} = (1, \ldots, 1) \in \overline{C}$.

Hence $\zeta_{\mathbf{F}}(\mathbf{f})$ has maximum at $\mathbf{f} = \mathbf{1}$

A *large deviations rule* with “rate $\zeta_{\mathbf{F}}(\mathbf{f})$”.

If $\mathbf{1} \in C$ and $D^{-1} \stackrel{def}{=} \zeta''_{\mathbf{F}}(\mathbf{1}) > 0 \Rightarrow$ "central limit theorem" for $\boldsymbol{\varphi} \stackrel{def}{=} \sqrt{\tau}\,(\mathbf{f}-\mathbf{1})$, *i.e.*

$$prob_\mu(\boldsymbol{\varphi} \in \Gamma) \xrightarrow[\tau\to\infty]{} \int_\Gamma e^{-(\mathbf{c},(2D)^{-1}\mathbf{c})} \frac{d\mathbf{c}}{\sqrt{2\pi \det D}}$$

but $\zeta(\mathbf{f})$ informs on the *very large fluctuations* too,
where $\mathbf{f} = (f_1, \ldots, f_n)$ attains size $O(\sqrt{\tau})$.

If F_i are odd under time reversal then C is *symmetric around* $\mathbf{O}$.

Fluctuation Theorem: [GC95] If $F_1 = \sigma(\mathbf{X}, \dot{\mathbf{X}})$ then set $p \equiv f_1$ and $\sigma_+ \equiv F_{1,+}$ (hence $p = \frac{1}{\tau}\int_0^\tau \frac{\sigma(S_\tau(\dot{\mathbf{X}},\mathbf{X}))}{\sigma_+}\,d\tau$)

$$\zeta_\sigma(-p) = \zeta_\sigma(p) - p\sigma_+, \qquad\qquad \text{for all } |p| < p^*$$

More general: if F_i are odd under time reversal $\zeta_{\mathbf{F}}(\mathbf{f}) = \zeta_{\mathbf{F}}(-\mathbf{f}) - p\,\sigma_+$

Application: divergence is $\sigma(\dot{\mathbf{X}}, \mathbf{X}) = \varepsilon(\dot{\mathbf{X}}, \mathbf{X}) + \dot{R}(\mathbf{X})$ is, remarkably, *observable*

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

and can be interpreted as the *entropy creation rate*, because of the meaning of $Q_i \stackrel{def}{=} -\dot{\mathbf{X}}_i \cdot \partial_{\mathbf{X}_i} W_{0,i}(\mathbf{X}_0, \mathbf{X}_i)$, while $R(\mathbf{X}) = \sum_{j>0} \frac{U_j}{k_B T_j}$.

$\Rightarrow$ 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

$$p = \frac{1}{\sigma_+ \tau} \int_0^\tau \sigma(S_t(\dot{\mathbf{X}}, \mathbf{X}))dt \equiv \frac{1}{\varepsilon_+ \tau} \int_0^\tau \varepsilon(S_t(\dot{\mathbf{X}}, \mathbf{X}))dt + \frac{R(\tau) - R(0)}{\sigma_+ \tau}$$

the latter is measurable as it concerns heat exchanges (calorimeters).

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*: namely

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

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: thermostats as infinite systems. However $\cdots\cdots$!

Consider quantum $\mathcal{C}_0$. Let H on $L_2(\mathcal{C}_0^{3N_0})$, space of symm./antisym. $\Psi(\mathbf{X}_0)$,

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

its spectrum consists of $E_n = E_n(\{\mathbf{X}_j\}_{j>0})$, for $\mathbf{X}_j$ fixed.

System–reservoirs: *dynamical system* on the space of $\big(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0}\big)$ def.

$$-i\hbar\dot\Psi(\mathbf{X}_0) = \, (H(\{\mathbf{X}_j\}_{j>0})\Psi)(\mathbf{X}_0), \qquad\qquad \text{and for } j>0$$

$$\ddot{\mathbf{X}}_j = -\Big(\partial_j U_j(\mathbf{X}_j) + \langle\partial_j U_j(\mathbf{X}_0, \mathbf{X}_j)\rangle_\Psi\Big) - \alpha_j \dot{\mathbf{X}}_j$$

$$\alpha_j \stackrel{def}{=} \frac{\langle W_j\rangle_\Psi - \dot U_j}{2K_j}, \qquad W_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_j U_{0j}(\mathbf{X}_0, \mathbf{X}_j)$$

Evolution maintains the $K_j \equiv \frac{1}{2}\dot{\mathbf{X}}_j^2$ exactly $K_j = \frac{3}{2}k_B T_j N_j$, as classical case.

"Formal volume element" $\mu_0(\{d\Psi\}) \times \nu(d\mathbf{X}\, d\dot{\mathbf{X}})$ with

$$\delta\Big(||\Psi||^2 - 1\Big)\,\Big(\prod_{\mathbf{X}_0} d\Psi(\mathbf{X}_0)\Big) \times \prod_{j>0}\Big(d\mathbf{X}_j\, d\dot{\mathbf{X}}_j\, \delta(\dot{\mathbf{X}}_j^2 - 3N_j k_B T_j)\Big)$$

conserved, by unitarity, *up to thermostats volume contraction* σ

$$\sigma = \sum_j \frac{Q_j}{k_B T_j} + \dot{R} \qquad \text{with} \qquad Q_j = \langle W_j \rangle_\Psi$$

with $Q_j = \langle -\dot{\mathbf{X}}_j \cdot \partial_{\mathbf{X}_j} W_j(\mathbf{X}_0, \mathbf{X}_j)\rangle_\Psi$, as classical.

Chaotic Hyp. $\Rightarrow$ dynamics selects invariant distribution μ, the SRB

and reversibility will imply fluctuation relation for $\sigma = \sum_j \frac{Q_j}{k_B T_j} + \dot{R}$

Measurable by calorimetry.

A check? only one thermostat T_1, no forces. **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 $\varphi_n \in [0, 2\pi]$ is a phase, $E_n = E_n(\mathbf{X}_1) = n$-th level of $H(\mathbf{X}_1)$ with $\Psi_n(\mathbf{X}_1)$ eigenfunction.

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.

However not invariant. Difficult to find explicit inv. distribution.

Nevertheless under *adiabatic approximation* eigenstates of H at time 0 follow ariations of $H(\mathbf{X}(t))$ due to the motion of $\mathbf{X}$ without changing quantum numbers

In *adiabatic limit* (classical motion of thermostat particles on a time scale much slower than the quantum evolution) $\Rightarrow$ *invariant*: variation of the energy levels is compensated by the therm. phase space contraction.

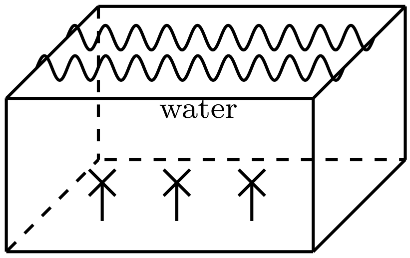
Under evolution $\mathbf{X}_1$ at time $t > 0$ becomes $\mathbf{X}_1 + t\dot{\mathbf{X}}_1 + O(t^2)$ and, if non degeneracy, $E_n(\mathbf{X}_1)$ changes, by perturbation analysis, into $E_n + t\,e_n + O(t^2)$ with

$$e_n \stackrel{def}{=} t\langle \dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_{01} \rangle_{\Psi_n} + t\dot{\mathbf{X}}_1 \cdot \partial_{\mathbf{X}_1} U_1 \equiv -t(Q_1 + \dot{U}_1)$$

while phase space contracts by $e^{t\frac{3N_1 e_n}{2K_1}}$. *Therefore if* β *chosen* $\beta = (k_B T_1)^{-1}$ *the Boltzmann factor changes by* $e^{-\beta t e_n}$ *and exactly compensates the contraction*

$$\frac{3N_1}{2K_1} = \beta \qquad \Rightarrow \qquad e^{-\beta t e_n} \times e^{t\frac{3N_1 e_n}{2K_1}} = 1$$

$\rightarrow$ *distribution stationary.*



Lagrangian flow *on a 2D surface*
$\dot{\mathbf{x}} = \mathbf{u}(\mathbf{x}, t)$
with $\mathbf{u}$ turbulent
"Kraichnan flow"

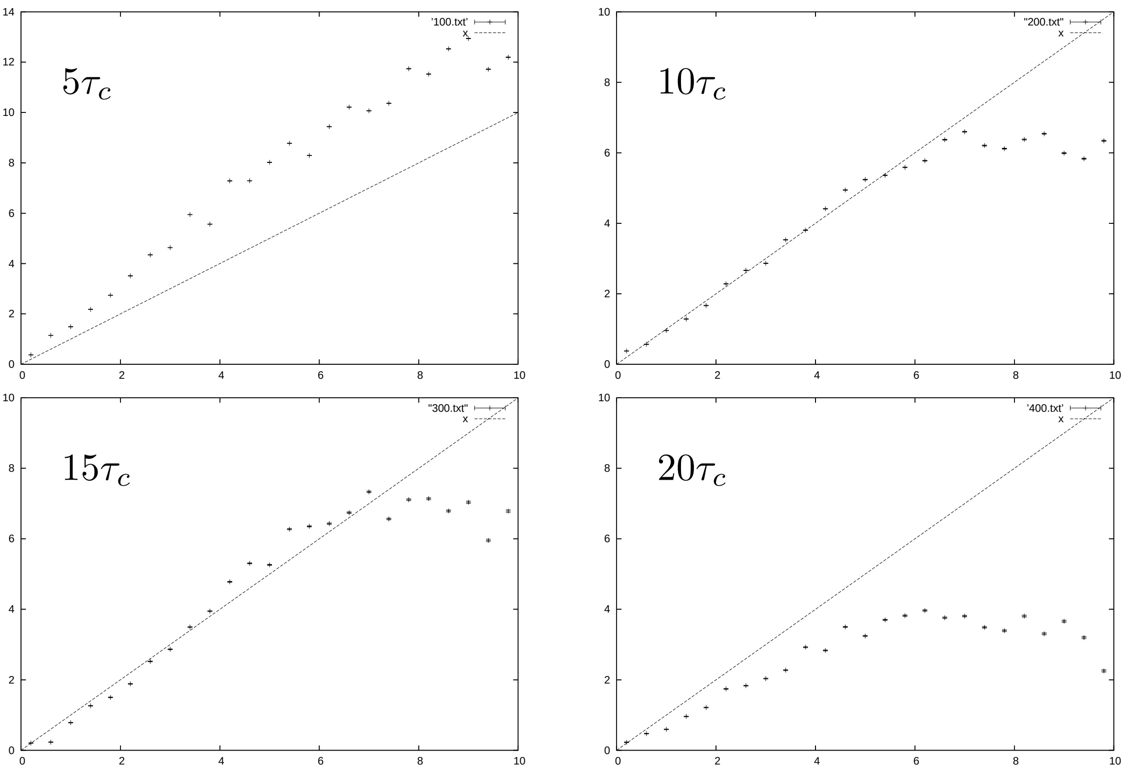
The water in a container of $1m \times 1m \times 0.3m$ size is set into a turbulent state. generate the "lagrangian trajectories" of the surface flow, solutions of the equations

$$\dot{\mathbf{x}} = \mathbf{u}(\mathbf{x}, t)$$

$\sigma(\mathbf{x}(t), t) = -\mathrm{div}\mathbf{u}(\mathbf{x}(t), t)$ whose time av. is exper. measured to be $\sigma_+ = \Omega > 0$.

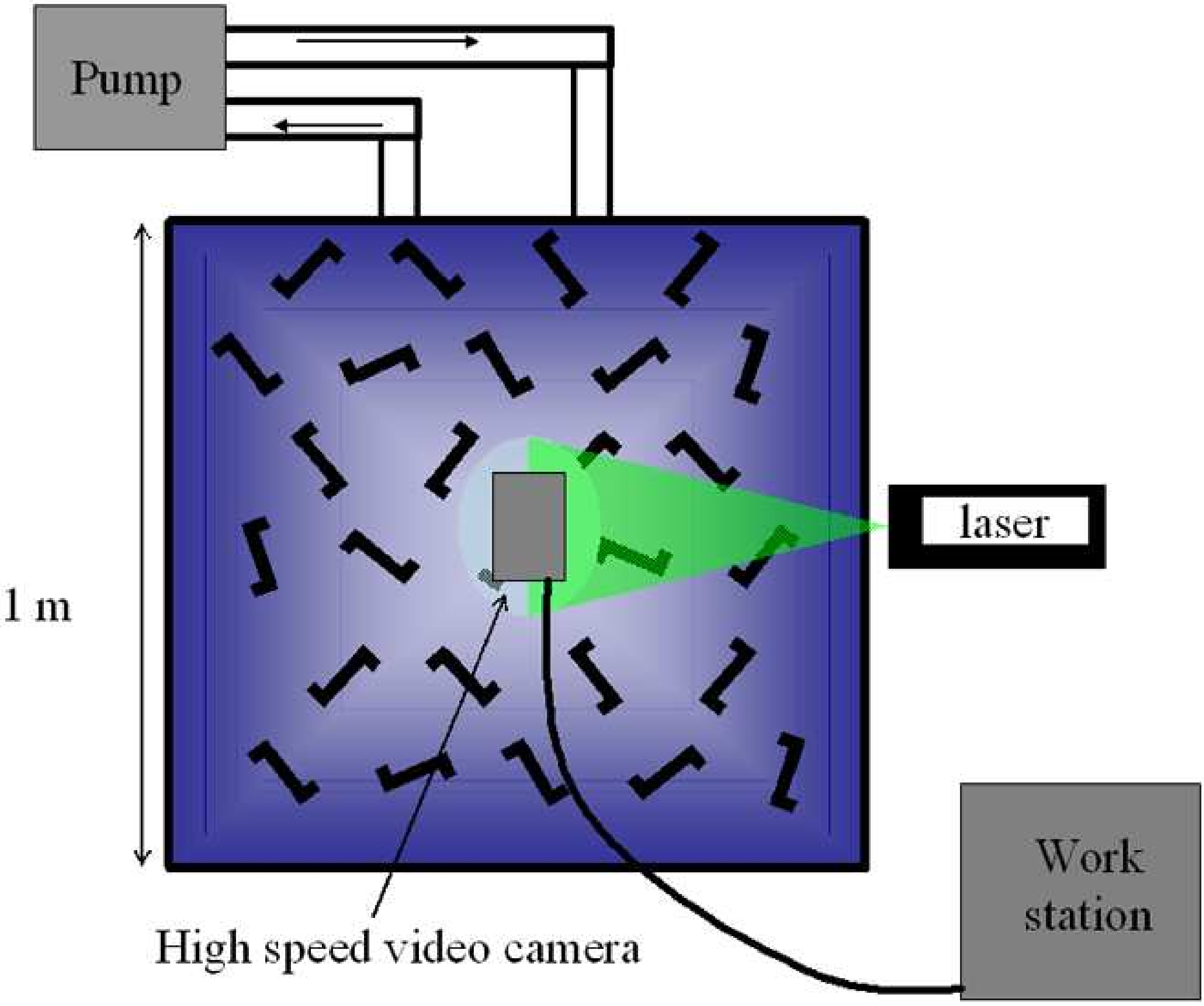
$$p = \frac{1}{\tau} \int_0^\tau \frac{\sigma(\mathbf{x}(t), t)}{\Omega} \, dt$$

for $\tau \gg \tau_c =$ "characteristic time of turbulence evolution".



Results for $\tau = 5, 10, 15, 20$ times τ_c for the turbulent flow ($\sim 20ms$)

`http://ipparco.roma1.infn.it`


Pump
1 m
laser
Work station
High speed video camera