STATIONARY STATES AND FLUCTUATIONS

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I. STATIONARY STATES

1. In a Stationary State macroscopic (=average) properties of a system do not change with time.

2. Microscopic particle motion continues unabatedly and causes fluctuations around macroscopic (=average) properties.

II. Equilibrium + Fluctuations around it

1. Equilibrium is simplest stationary state.

2. Characterized by T, p, ρ etc.

3. Fluctuations around equilibrium guided by .
   Onsager's Hypothesis

   "The average decay of a fluctuation away from equilibrium back to equilibrium, follows the ordinary macroscopic linear law"

- Thus for an adiabatically insulated system, characterized by the macroscopic properties $A_1, A_2, \ldots, A_n$, with fluctuations from their equilibrium values $a_1, a_2, \ldots a_n$, the average average decay back to equilibrium follows:

- $\overline{\dot{a}_i} = J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, \ldots, n)$

$\overline{\dot{a}_i}$ = average decay of fluctuation away from equilibrium;
J_i = macroscopic current;
L_{ik} = Linear transport coefficient;
X_k = force (gradient);

- The average is taken with the microcanonical ensemble

$$P(a_1 \ldots a_n) \prod_{i=1}^{n} da_i = \frac{\exp(\Delta S/k) \prod_{i=1}^{n} da_i}{\int \exp(\Delta S/k) \prod_{i=1}^{n} da_i}$$

Consequences of Onsager's Hypothesis:

- Onsager's reciprocal relations are between linear transport coefficients L_{ik}: i.e. a linear relation between currents J_i and gradients X_k: $J_i = \sum_k L_{ik} X_k$.

- In a mixture with components $1, .., i, .., k, ..., n$: the Onsager relations are:

$$L_{ik} = L_{ki}$$

They are based on the time reversal invariance of the (microscopic) equations of motion.

- Green-Kubo formulae for linear transport coefficients.

- Fluctuation - Dissipation Relation = relation of equilibrium fluctuations and linear transport coefficients.

Irreversible Thermodynamics:

- Onsager's Hypothesis makes it possible to construct a purely macroscopic theory of irreversible processes.

- That is: generalization of Thermodynamics of systems in equilibrium to a Thermodynamics of Non-equilibrium systems, close to equilibrium, but where irreversible processes take place.

- The system is then still in local equilibrium, where it can be partitioned in "physically infinitesimal" cells, in each of which, i.e. locally, the usual thermodynamic relations of equilibrium hold.

- In particular, in any local cell at position $\vec{\mathbf{r}}$ and at time t, the specific entropy s is the same function of the specific internal energy u and the specific volume $v = 1/\rho$, as in equilibrium:

$$s = s(u, \rho)$$

and

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt}$$

- Here d/dt is the barycentric (or center of mass) time derivative and s, u and $v = 1/\rho$ are all per unit mass.

- Using the hydrodynamic equations for du/dt and $d\rho/dt$ - which are based on local equilibrium, the conservation laws and the linear transport laws - gives a local form of the Second Law as an
entropy balance equation:

$$\rho\frac{ds}{dt} = -div J_s + \sigma$$

with $\sigma = \sum_i J_i X_i$ and $J_i = \sum_k L_{ik} X_k$

- Here ρ is the mass density, J_s the (baricentric) entropy flow per unit area and time and $\sigma > 0$ the entropy production per unit volume and time.

- These equations together with Onsager's Hypothesis form the basis of Irreversible Thermodynamics.

ons from “fluctuating
ıamics” by adding (Landau-Lifshitz)
ıg terms to the hydrodynamical
s.

•

rms are due to spontaneously
d (random) local stresses and heat
the fluid, not related to the
ɔpic gradients (linear laws) in the
ɔpic hydrodynamic equations, but
e microscopic motion of the fluid

(Fluctuating) Hydrodynamic Equations

$$\frac{d\rho}{dt} = -\rho\nabla\cdot\vec{v} \quad \text{(continuity equation)}$$

$$\rho\frac{d\vec{v}}{dt} = \nabla\cdot\vec{\vec{P}} \quad \text{(equation of motion)}$$

$$\rho\frac{du}{dt} = -\nabla\cdot\vec{J}_q - p\nabla\cdot\vec{v} - \left(\vec{\vec{P}} - p\vec{\vec{U}}\right) : \nabla\vec{v}$$

(energy equation)

- $\vec{\vec{P}}$= Stress Tensor + $\tilde{\vec{\vec{P}}}$; $\tilde{\vec{\vec{P}}} \rightarrow \vec{\vec{s}}$
- $\vec{J}_q$= Heat current + $\tilde{\vec{J}}_q$; $\tilde{\vec{J}}_q \rightarrow \vec{g}$
- p= pressure
- ρ= mass density
- $\vec{\vec{U}}$= unit tensor
- : tensor product

Conditions: 1. Local Equilibrium

2. Conservation Laws

3. Linear Transport Laws.

Hydrodynamic Fluctuations

| Liftshitz:

; between the components of the
:t flux:

$$\overline{(\vec{r_2}, t_2)} = 2\kappa T^2 \delta_{ik} \delta(t_1 - t_2) \delta(\vec{r_1} - \vec{r_2})$$

:an similarly obtain formulae for the
)etween the components of the •
ss tensor:

$$\overline{{}_n(\vec{r_2}, t_2)} = 2T[\eta(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl}) + (\zeta - \frac{2}{3}\eta)\delta_{ik}\delta_{lm}] \times \delta(t_1 - t_2)\delta(\vec{r_1} - \vec{r_2})$$

Non-Eq. Stationary States "far" from Equil.

- These states cannot be characterized by local equilibrium quantities, like $\boldsymbol{T}, \boldsymbol{u}, \boldsymbol{\rho}$, alone, but also by stationary currents of mass, momentum and energy, which, in general, will not obey linear relations between currents and gradients of $\boldsymbol{T}, \boldsymbol{u}, \boldsymbol{\rho}$.

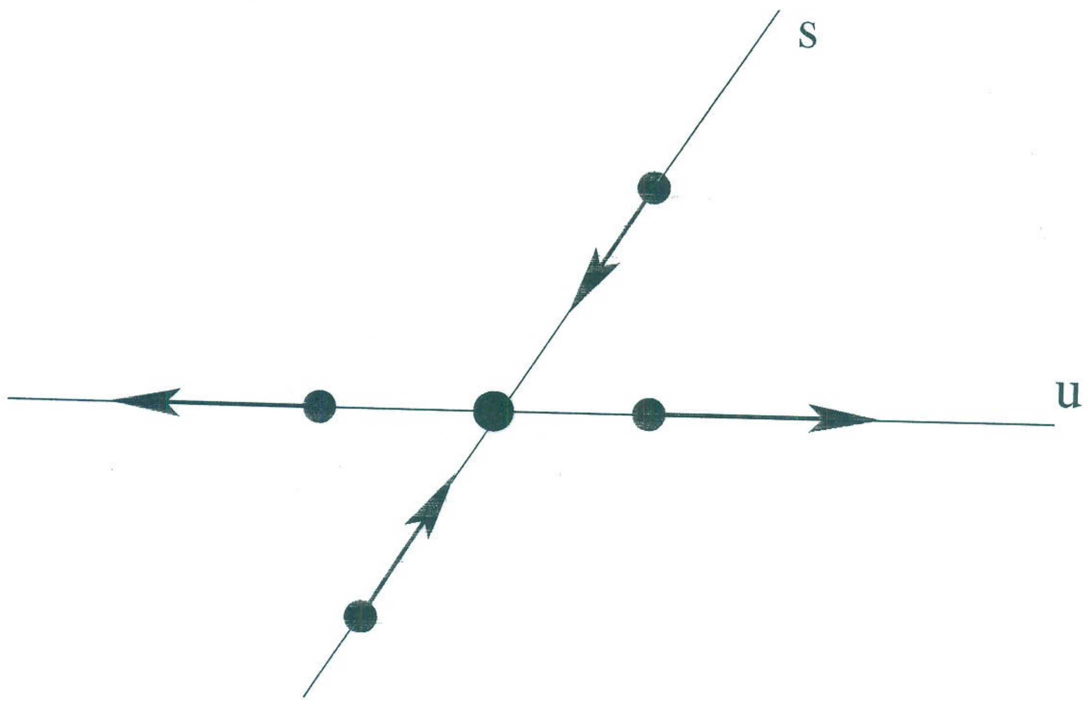
- Their probability distribution is not described by a modified (static) Gibbs ensemble, but by a (dynamic) Sinai-Ruelle-Bowen (SRB) distribution, at least if the system is smooth and very chaotic (Anosov-like).

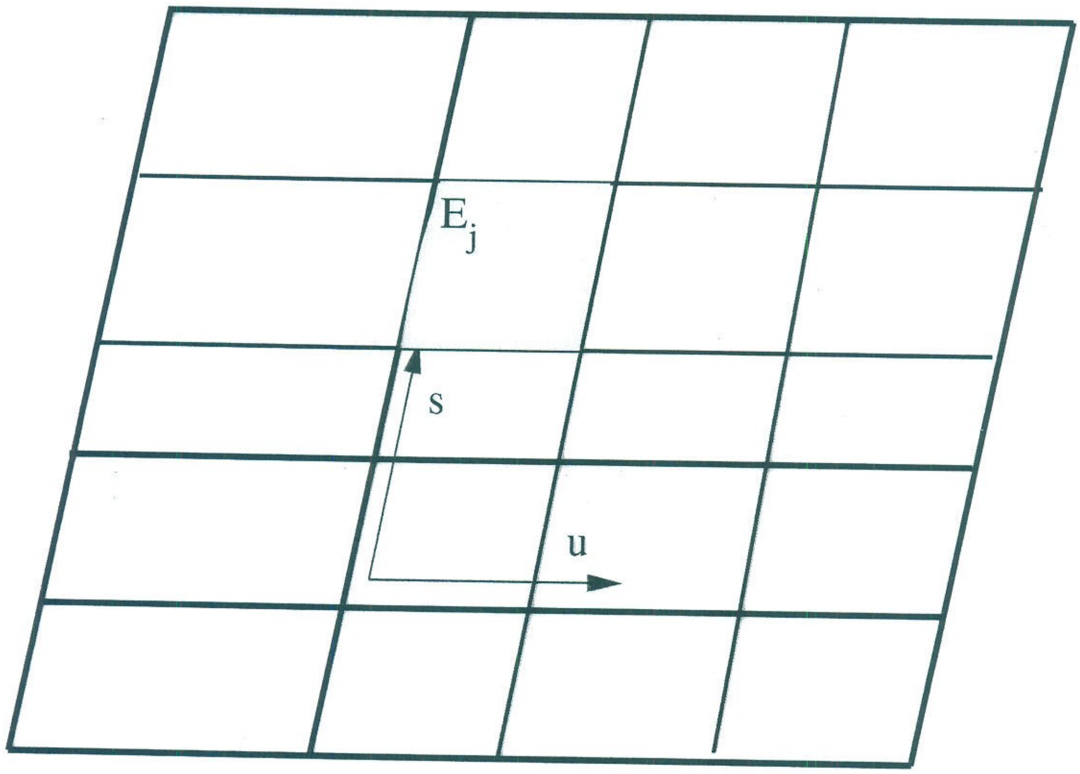
cription of Obtaining SRB Distr.

oticity of the system is based on the icity of the points representing the n phase space.

ch point in phase space has two s, on one of which two separated oints near a fixed phase point tially approach each other, while on manifold two such points will tially separate from each other.

n of all the first manifolds is called e manifold (s), while that of the latter stable manifold (u), in phase space.


s
u


E_j
s
u

3 distribution can be obtained by a
partition of the phase space of the
n "parallelograms", $\{E_j\}$, based on
rbolicity of the phase space.

"horizontal sides" of the cells or
grams form the unstable manifold,
tical sides" form the stable

of the cells is determined by a
er T, so that for $T \to \infty$ their size
ero

- Now each cell $\boldsymbol{E}_j$ in phase space is given a statistical weight equal to the inverse of a characteristic phase space volume expansion rate (along the unstable (expanding) manifold) $\bar{\Lambda}^{-1}_{u,\tau}(\boldsymbol{x}_j)$ associated with this cell.

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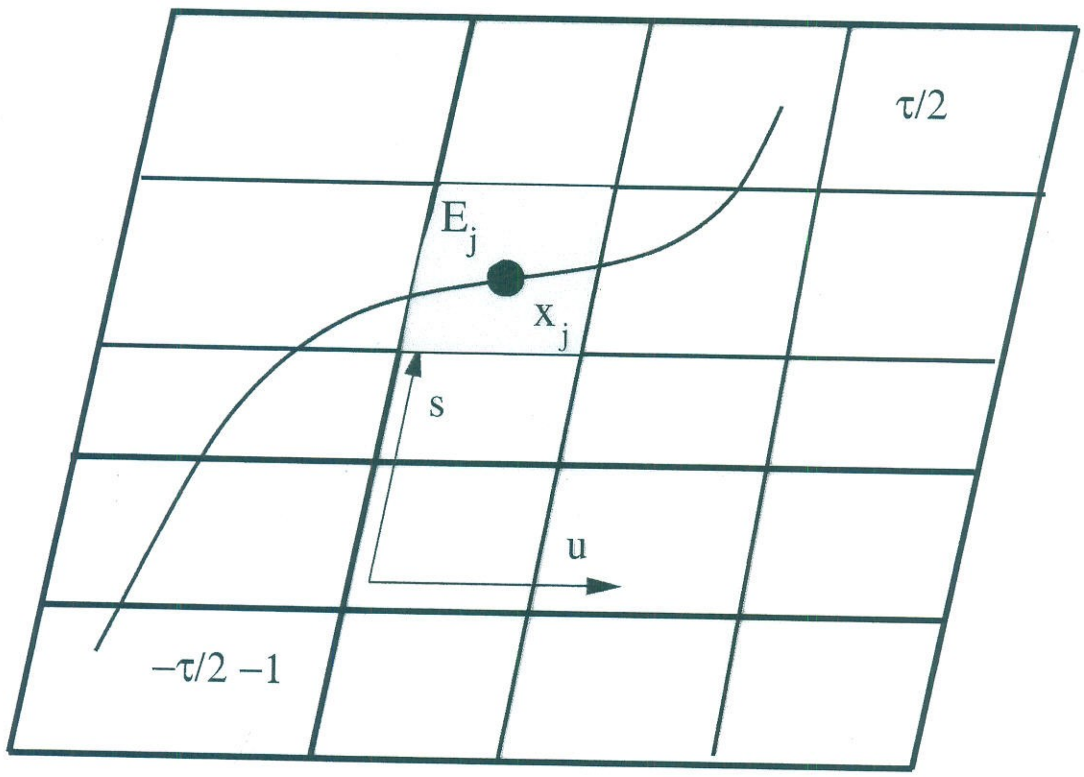
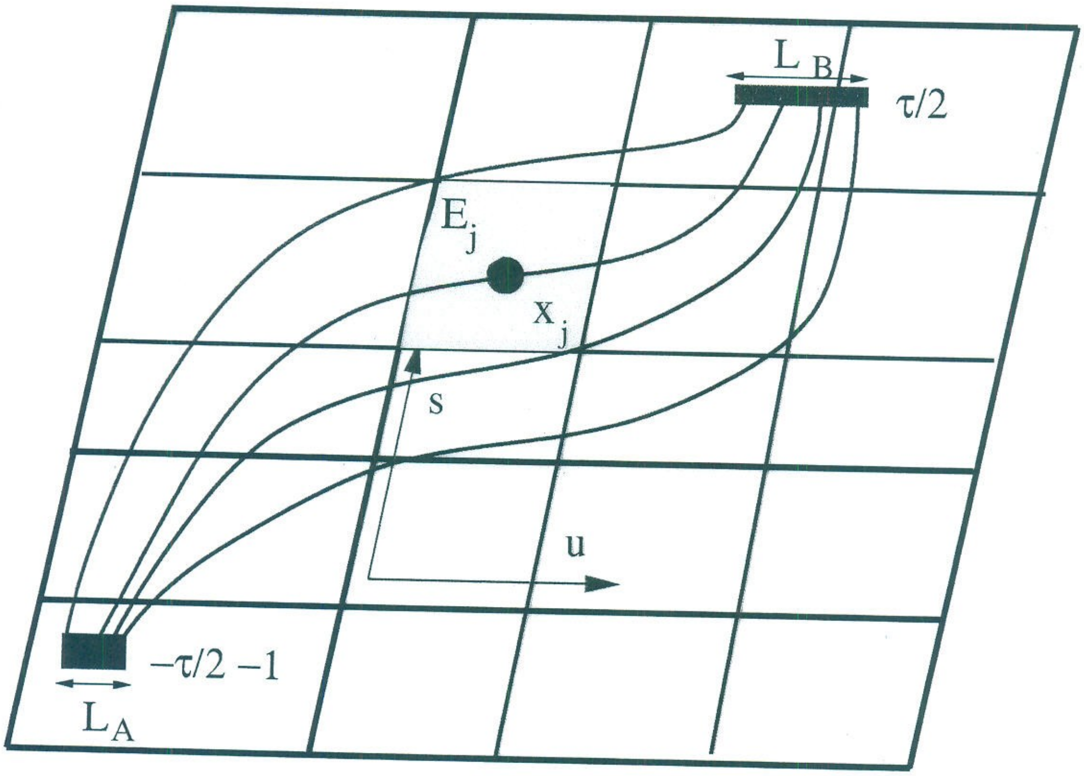
- Consider thereto a phase point moving during a discrete time τ along a phase space trajectory from $-\tau/2-1$ to $\tau/2$, which goes through the center $\boldsymbol{x}_j$ of the cell $\boldsymbol{E}_j$.


τ/2
E_j
x_j
s
u
−τ/2 −1

- Considering a small phase space volume A around the initial point at $-\tau/2-1$, all points in A will go via phase space trajectories to corresponding points in the phase space volume B around the final point at $+\tau/2$.

- The larger the phase space volume expansion $\Lambda_{u,\tau}(x_j)$ in the direction of the unstable manifold u is in time τ, i.e. the larger L_B/L_A, the more the phase space trajectories will tend to avoid (bypass) the point x_j.

- The inverse of this ratio $\sim L_A/L_B \sim \Lambda_{u,\tau}^{-1}(x_j)$ will therefore be a measure of the "eagerness" or frequency of the phase space trajectories to be near x_j, i.e. that the system will visit the cell E_j.


L B
τ/2
E j
x j
s
u
−τ/2 −1
L A

- This inverse expansion rate is a measure of the stability of the trajectories near x_j.

- Weighing the Markov partitions in phase space this way, one obtains in a dynamical fashion the probability to find the system anywhere in phase.

- The average of a smooth function $F(x)$, where x is a point in phase space, is then given by the following SRB measure:

$$\int_{\mathcal{C}} \mu_{SRB}(dx) F(x) = \lim_{T \geq \tau/2 \to \infty} \frac{\sum_j \bar{\Lambda}_{u,\tau}^{-1}(x_j) F(x_j)}{\sum_j \bar{\Lambda}_{u,\tau}^{-1}(x_j)}$$

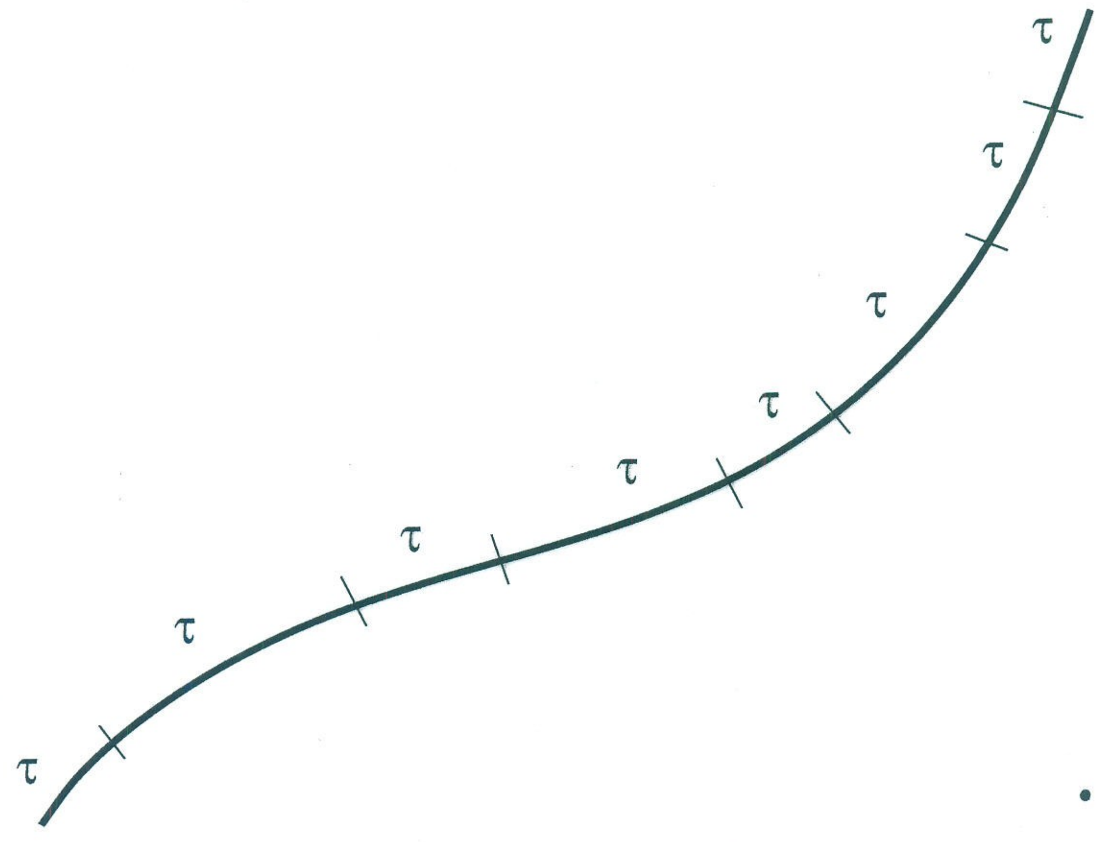
- $\mu_{SRB} = \mu_{microcan.}$ in equilibrium.

- Here $\int_{\mathcal{C}}$ is an integral over phase space and the phase space weight $\bar{\Lambda}_{u,\tau}^{-1}(\boldsymbol{x}_j)$ is $\ln \, \det |\partial \boldsymbol{S}_\tau(\boldsymbol{x})_u|$ i.e. the logarithm of the determinant of the Jacobian matrix of the map $\partial \boldsymbol{S}_\tau(\boldsymbol{x})_u$, giving the expansion rate over a time τ along the unstable manifold, where $\boldsymbol{S}_\tau$ represents the dynamics of the system over a time τ.

Fluctuations Far From Equilibr. (The CFT)

- A Fluctuation theorem has been derived based on the SRB distribution, for the heat fluctuations of a reversible, very chaotic, smooth (Anosov-like) many particle system in a non-equilibrium stationary state.

- To understand this Conventional Fluctuation Theorem (CFT), one considers a long trajectory in the phase space of the system in a non-equilibrium stationary state.


τ
τ
τ
τ
τ
τ
τ
τ
τ

1. One cuts this trajectory in many segments, on each of which the system spends an equal time τ.

2. One determines the heat produced Q_τ or absorbed $-Q_\tau$ on each segment and makes a histogram of them.

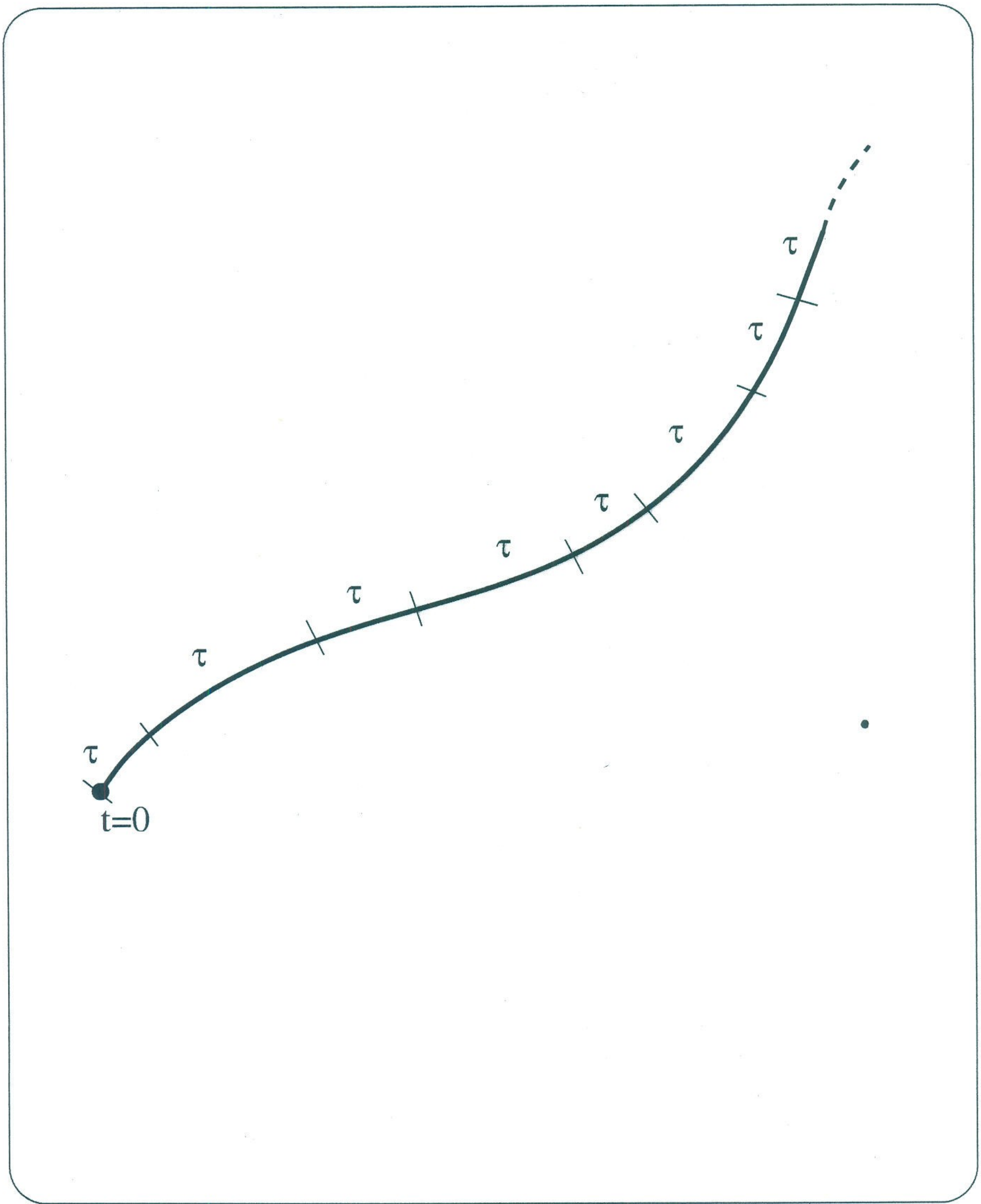
3. This leads to a probability distribution $P(Q_\tau)$ for the heat production or absorption on a trajectory segment of duration τ.

- This has led to the following (CFT):
  Conventional Heat Fluctuation Theorem
  for smooth potentials when $\tau \to \infty$:

$$\frac{P(Q_\tau)}{P(-Q_\tau)} = \exp[\beta Q_\tau] \text{ for } Q_\tau < p^* \overline{Q}_\tau$$

- Here $\overline{Q}_\tau$ is the average heat produced in the stationary state over all segments τ, for positive times t.

- Extension of Second Law of Thermodynamics.


τ
τ
τ
τ
τ
τ
τ
τ
t=0

- In terms of a scaled Q_τ: $\boxed{p = Q_\tau/\bar{Q}_\tau}$, the CFT reads then for smooth potentials and $\tau \longrightarrow \infty$:

$$\frac{\pi_\tau(p)}{\pi_\tau(-p)} = \exp[p\tau\sigma_+] \text{ for } p < p^*$$

- Here p^* is a limiting magnitude of p related to the dynamics of the system and $\sigma_+ = \beta\overline{Q}_\tau/\tau$, the average entropy production rate ($\beta = 1/k_B T$).

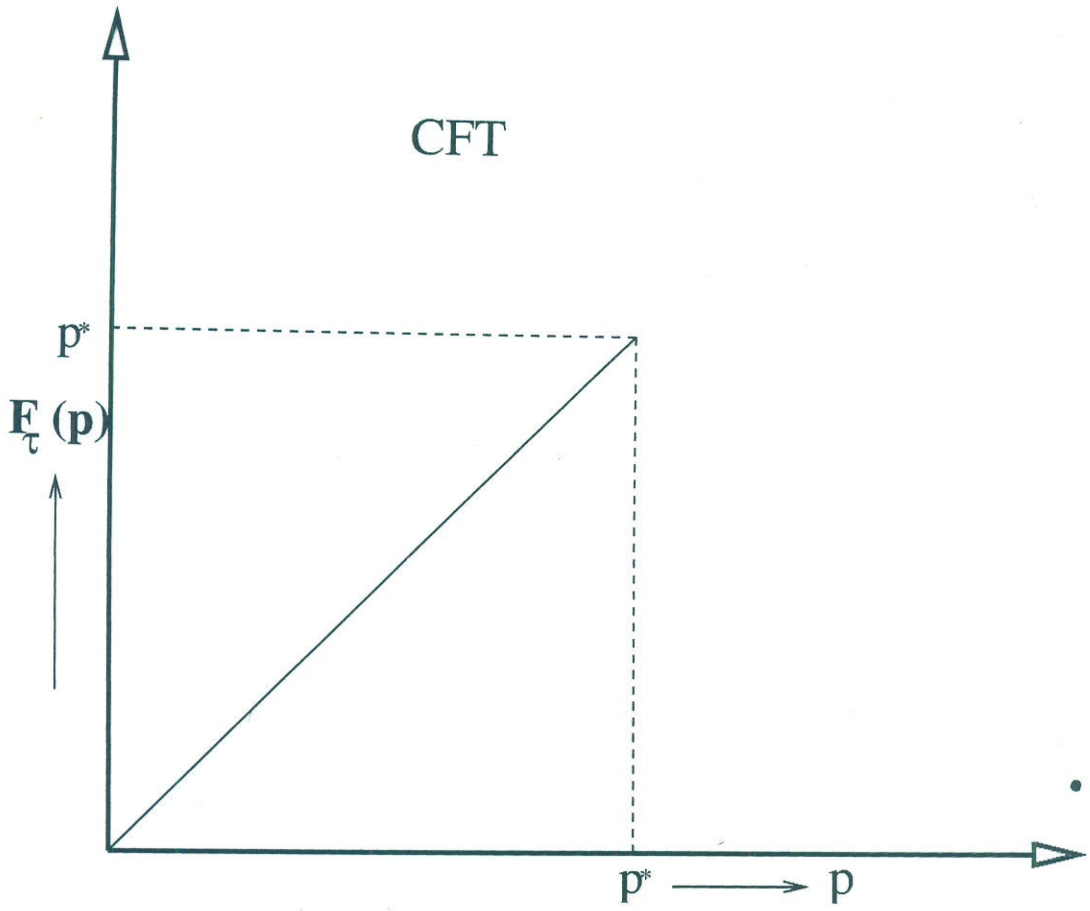
- Introducing a Fluctuation Function, $F_\tau(p)$, the CFT can be written for $\tau \longrightarrow \infty$ as:

$$F_\tau(p) \equiv \frac{1}{\beta \bar{Q}_\tau} \ln \frac{\pi_\tau(p)}{\pi_\tau(-p)} = p < p^*$$

i.e. $F_\tau(p)$ is a straight line with slope 1 as a function of p.

- Gallovotti and Ruelle derived the Onsager and GK relations from the CFT, if the system is near equilibrium, in agreement with IT.

- In this form the CFT has been confirmed both by laboratory and computer experiments.


CFT
p*
F_τ (p)
p*
p

Extended Heat Fluc. Theorem. (EFT)

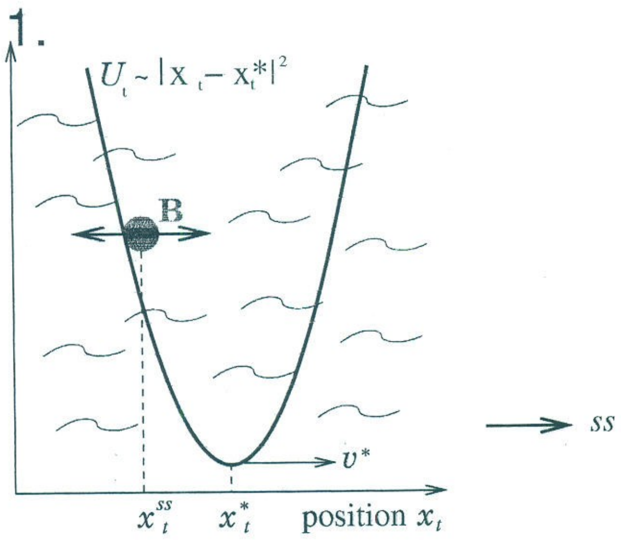
- Very recently the CFT has been extended, from smooth Anosov-like systems, using the SRB distribution, to systems of particles interacting with singular potentials e.g. with singularities as for the LJ potential at $r = 0$ or for the harmonic potential for $x \to \infty$.

- This has led formally to an Extended FT (EFT) that goes beyond the CFT and holds for fluctuations: $p = Q_\tau/\bar{Q}_\tau \le p^{**}$.

- The EFT has been obtained explicitly for a Brownian particle system. It is identical to that of a parallel electric circuit, for which a laboratory verification of the EFT has been obtained.

Brownian particle Fluctuations

1.



2. Energy Conservation:

$$W_\tau = Q_\tau + \Delta U_\tau$$

$$\text{or } Q_\tau = W_\tau - \Delta U_\tau$$

3. W_τ = total work done on system in time τ

Q_τ = heat = friction energy dissipated by B into water in time τ (stochastic)

$\Delta U_\tau = U_{\tau+t} - U_t$ = potential energy difference of the particle in time τ (deterministic)

Brownian particle Fluctuations

- Based on overdamped (m=0) Langevin equation:

$$0 = \underbrace{-\alpha\dot{\vec{x}}_t}_{\substack{\uparrow \\ \text{Friction} \\ \text{dissipative}}} \quad \underbrace{-\kappa(\vec{x}_t - \vec{x}^*_t)}_{\substack{\uparrow \\ \text{linear force} \\ \text{deterministic}}} \quad + \quad \underbrace{\vec{\zeta}_t}_{\substack{\uparrow \\ \text{fluctuations} \\ \text{stochastic}}}$$

- Harmonic potential: $U_t = \frac{\kappa}{2}|\vec{x}_t - \vec{x}^*_t|^2$; $\vec{x}^*_t = \vec{v}^* t$=position of the pot. min.

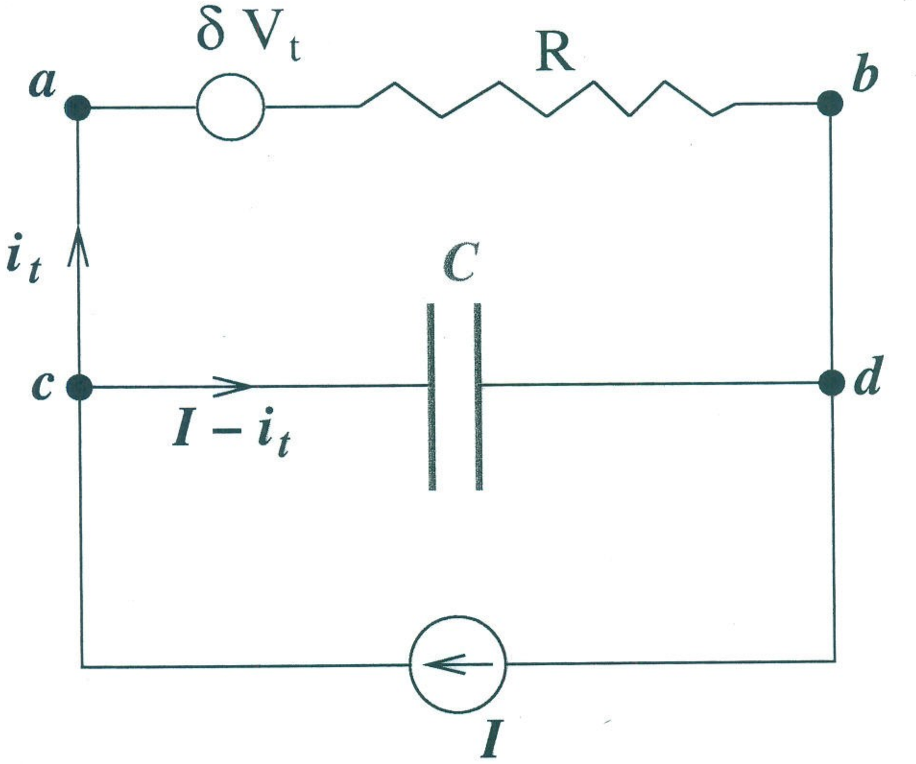
  White noise $\vec{\zeta}_t$: $\overline{\vec{\zeta}_t} = 0$; $\overline{\vec{\zeta}_t\vec{\zeta}_{t'}} = \frac{2\alpha}{\beta}\delta(t-t')\vec{\vec{U}}$

  Relaxation time: $\tau_r = \frac{\alpha}{\kappa}$

- Dimensionless units: $\alpha = \kappa = \beta = 1 \rightarrow \tau_r = 1$

ANALOGY : BROWNIAN MOTION AND ELECTRIC CIRCUITS .

Parallel Circuit



δV_t = Nyquist noise at time t ("stochastic")

R = resistor

i_t = current through R at time t

C = capacitor ("mechanical")

I = current source

a) Brownian motion → Langevin Equation with $m = 0$ and harmonic potential:

$$0 = -\alpha\dot{\vec{x}}_t - \kappa(\vec{x}_t - \vec{v}^* t) + \vec{\zeta}_t$$

b) Parallel circuit → Langevin equation with $L = 0$ and $V_{ab} = V_{cd}$:

$$0 = -R\dot{q}_t - \frac{1}{C}(q_t - It) - \delta V_t$$

c) Analogy:

Brown.	$\vec{x}_t$	$\dot{\vec{x}}_t$	$\vec{v}^*$	$\vec{\zeta}_t$	α	κ
Par. Circuit	q_t	i_t	I	$-\delta V_t$	R	$\frac{1}{C}$

EFT: Extended (Heat) FT (from SPM)

Fluctuation function:

$$F_\tau(p) = \frac{1}{\beta \bar{Q}_\tau} \ln\left[\frac{\pi_\tau(p)}{\pi_\tau(-p)}\right]$$

versus

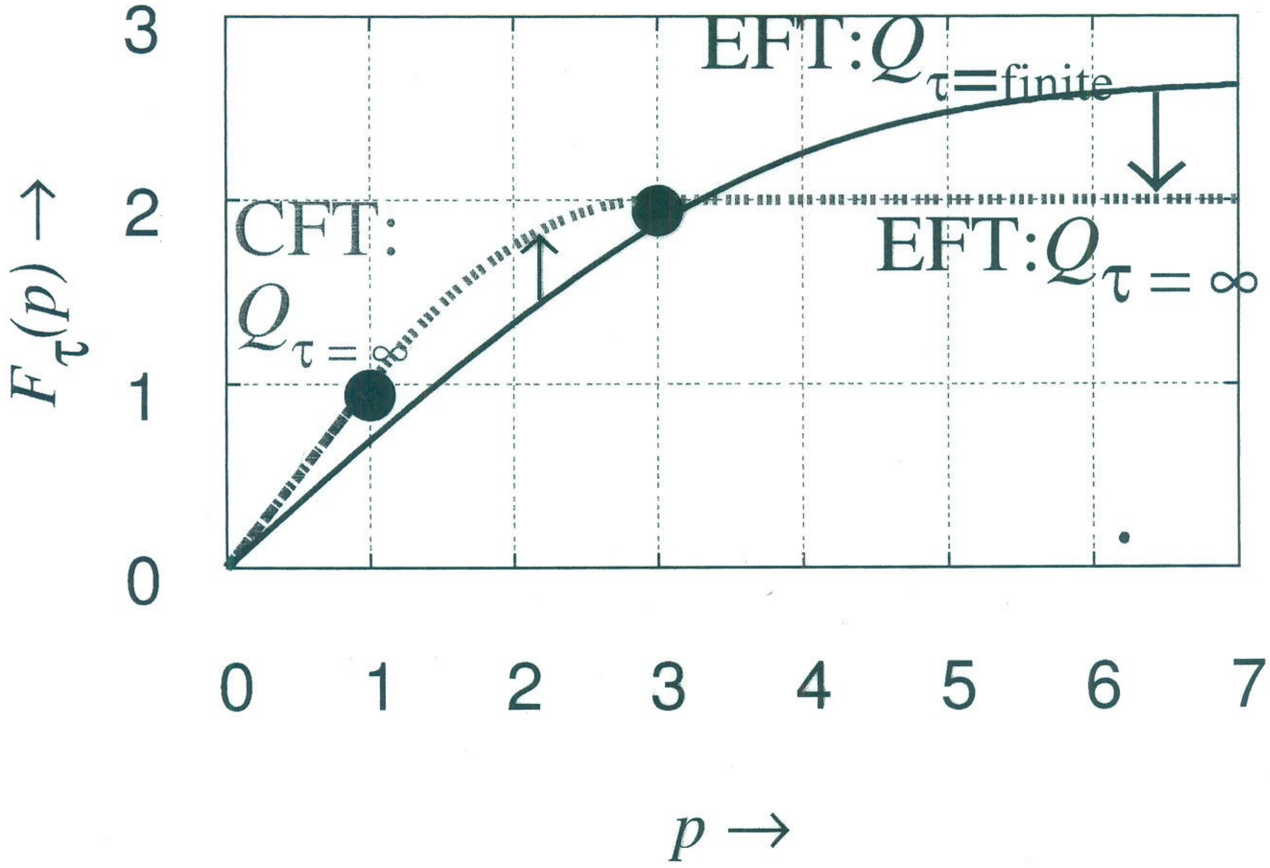
$$p = \frac{Q_\tau}{\bar{Q}_\tau}$$

result:

$$F_\tau(p) = \begin{cases} p + O(\frac{1}{\tau}) & \\ p - \frac{1}{4}(p-1)^2 + O(\frac{1}{\tau}) & \text{for} \\ 2 + \left[\frac{8(p-3)}{\tau}\right]^{\frac{1}{2}} + O(\frac{1}{\tau}) & \end{cases} \begin{cases} 0 < p \leq 1^* \\ 1 < p \leq 3 \\ 3 < p < \infty^{**} \end{cases}$$

* CFT for $\tau \to \infty$ with $p^* = 1$.

** EFT for $\tau \to \infty$ with $p^{**} \to \infty$.


3
2
1
0
EFT:$Q_{\tau=\text{finite}}$
CFT:
$Q_{\tau=\infty}$
EFT:$Q_{\tau=\infty}$
$F_\tau(p) \rightarrow$
0 1 2 3 4 5 6 7
$p \rightarrow$

EFT: EXPERIMENTS FOR PARALLEL ELECTRIC CIRCUITS

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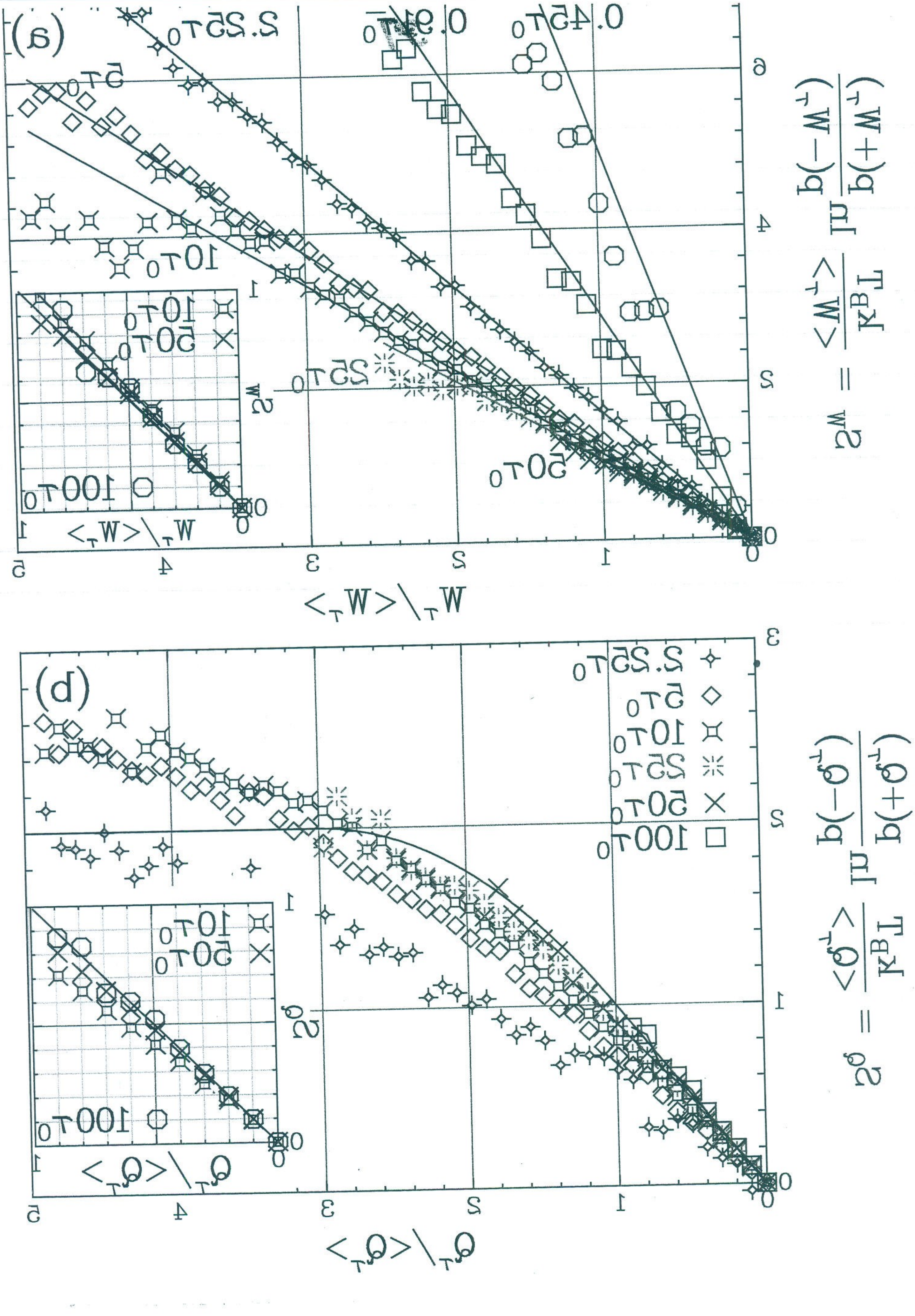
(a)
(b)
$S_W = \frac{\langle W_\tau \rangle}{k_B T} \ln \frac{p(+W_\tau)}{p(-W_\tau)}$
$W_\tau / \langle W_\tau \rangle$
$S_Q = \frac{\langle Q_\tau \rangle}{k_B T} \ln \frac{p(+Q_\tau)}{p(-Q_\tau)}$
$Q_\tau / \langle Q_\tau \rangle$
$0.45\tau_0$
$0.9\tau_0$
$2.25\tau_0$
$5\tau_0$
$10\tau_0$
$25\tau_0$
$50\tau_0$
$100\tau_0$