Program on « NONEQUILIBRIUM STEADY STATES »
Institut Henri Poincaré
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1) TRANSPORT AND THE ESCAPE RATE FORMALISM

2) HYDRODYNAMIC MODES AND NONEQUILIBRIUM STEADY STATES

3) *AB INITIO* DERIVATION OF ENTROPY PRODUCTION

4) TIME ASYMMETRY IN NONEQUILIBRIUM STATISTICAL MECHANICS

TRANSPORT AND THE ESCAPE RATE FORMALISM

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J. R. Dorfman, *College Park*

G. Nicolis, *Brussels*

S. A. Rice, *Chicago*

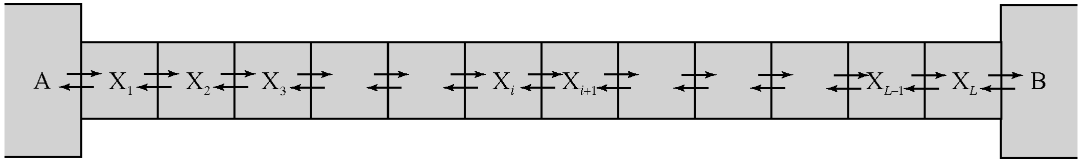
F. Baras, *Dijon*

- **INTRODUCTION: IRREVERSIBLE PROCESSES AND THE BREAKING OF TIME-REVERSAL SYMMETRY**
- **TRANSPORT COEFFICIENTS & THEIR HELFAND MOMENT**
- **ESCAPE OF HELFAND MOMENTS & FRACTAL REPELLER**
- **CHAOS-TRANSPORT FORMULAE**
- **CONCLUSIONS**

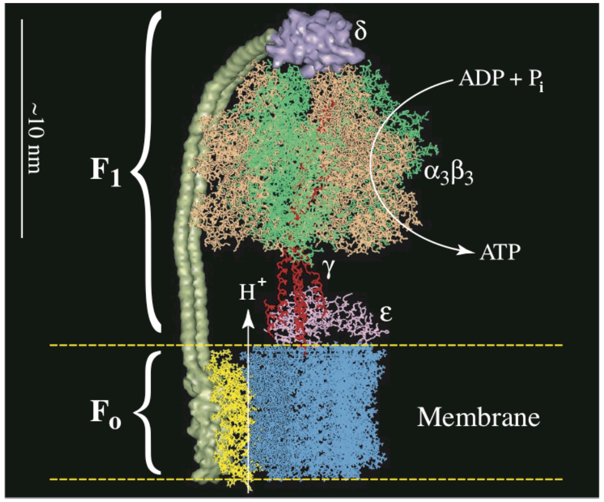
NONEQUILIBRIUM SYSTEMS

diffusion
electric conduction

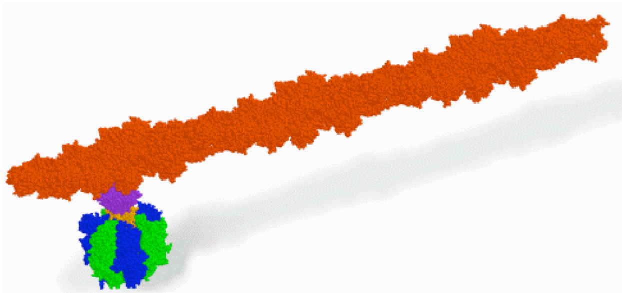
between two reservoirs

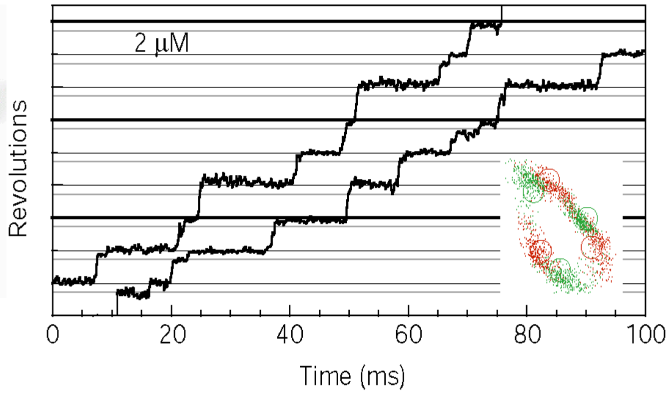


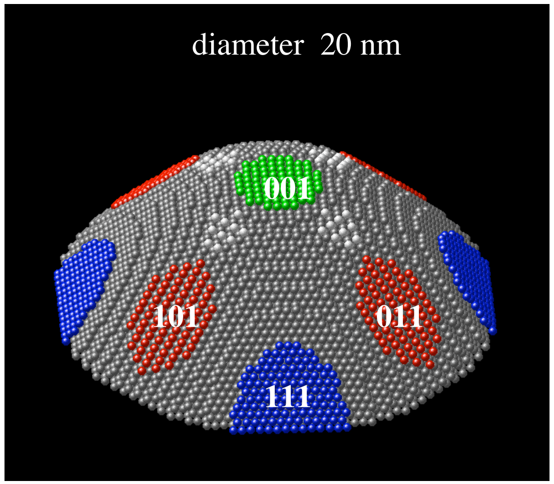
molecular motor: F_oF_1-ATPase



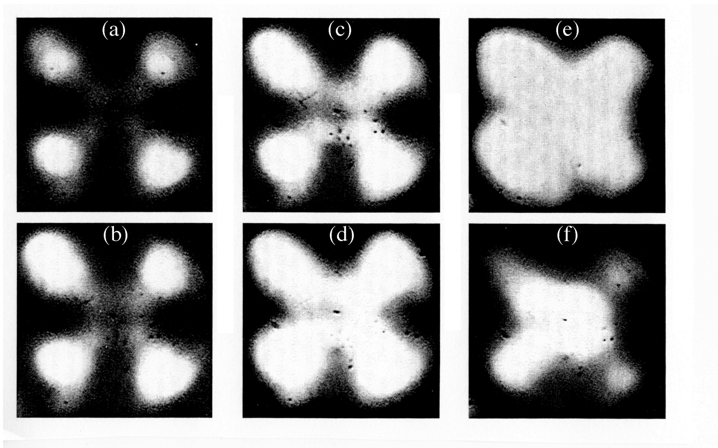
K. Kinosita and coworkers (2001): F_1-ATPase + filament/bead

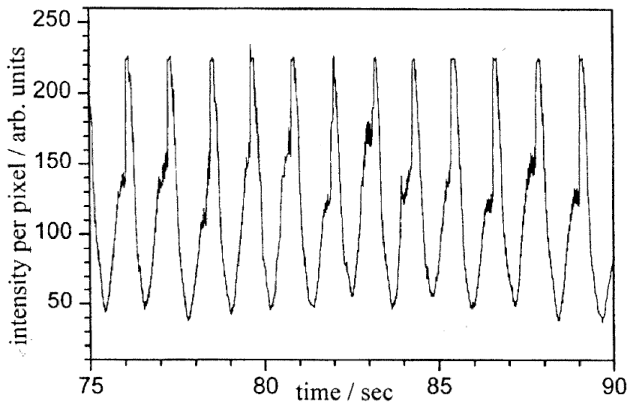






C. Voss and N. Kruse (1996): $NO_2/H_2/Pt$ reaction





IRREVERSIBLE PROCESSES

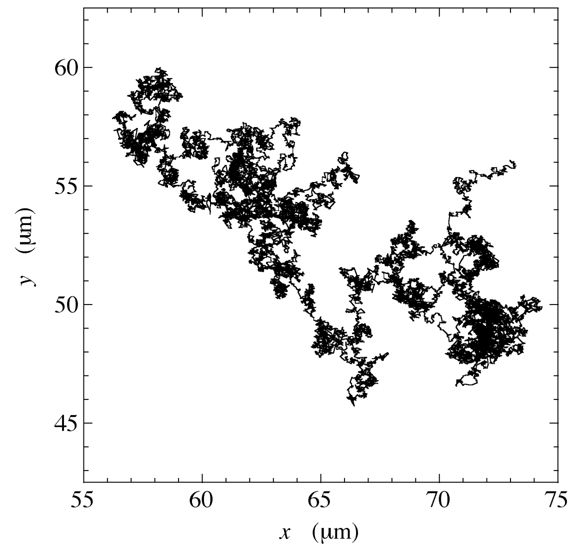
viscosity, heat conductivity, electric conductivity,…

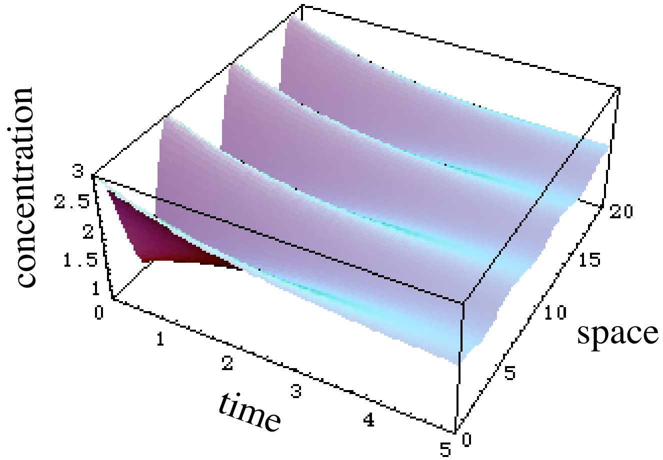
Example: diffusion   density of particles: n

diffusion equation: $\partial_t n = \mathcal{D} \nabla^2 n$

diffusion coefficient: Green-Kubo formula

$$\mathcal{D} = \int_0^\infty \langle v_x(0) v_x(t) \rangle \, dt$$





entropy density: $s = n \ln (n^0/n)$

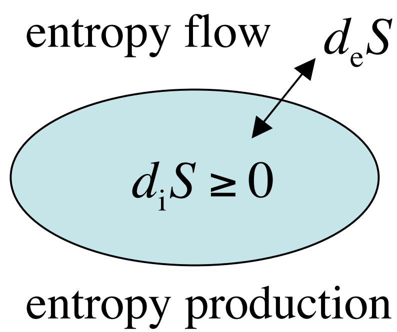
entropy current: $\boldsymbol{j}_s = -\mathcal{D}(\nabla n) \ln (n^0/en)$

entropy source: $\sigma_s = \mathcal{D}(\nabla n)^2/n \geq 0$

balance equation for entropy: $\partial_t s + \nabla \cdot \boldsymbol{j}_s = \sigma_s \geq 0$

Second law of thermodynamics: entropy $S = \int s \, d\mathbf{r}$

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} \quad \text{with} \quad \frac{d_i S}{dt} \geq 0$$



HAMILTONIAN DYNAMICS

A system of particles evolves in time according to Hamilton's equations:

$$\frac{d\mathbf{r}_a}{dt} = +\frac{\partial H}{\partial \mathbf{p}_a} \qquad \frac{d\mathbf{p}_a}{dt} = -\frac{\partial H}{\partial \mathbf{r}_a}$$

Hamiltonian function: $$H = \sum_{a=1}^{N} \frac{\mathbf{p}_a^2}{2m_a} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

Time-reversal symmetry: $$\Theta(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots, \mathbf{r}_N, \mathbf{p}_N) = (\mathbf{r}_1, -\mathbf{p}_1, \mathbf{r}_2, -\mathbf{p}_2, \ldots, \mathbf{r}_N, -\mathbf{p}_N)$$

Determinism: Cauchy's theorem asserts the unicity of the trajectory issued from initial conditions in the phase space $\mathcal{M}$ of the positions $\mathbf{r}_a$ and momenta $\mathbf{p}_a$ of the particles:

$$\Gamma = (\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots, \mathbf{r}_N, \mathbf{p}_N) \in \mathcal{M} \qquad \dim \mathcal{M} = 2Nd$$

Flow: one-dimensional Abelian group of time evolution: $\Gamma = \Phi^t(\Gamma_0) \in \mathcal{M}$

Liouville's theorem: Hamiltonian dynamics preserves the phase-space volumes:

$$d\Gamma = d\mathbf{r}_1\, d\mathbf{p}_1\, d\mathbf{r}_2\, d\mathbf{p}_2 \ldots d\mathbf{r}_N\, d\mathbf{p}_N$$

LIOUVILLE'S EQUATION: STATISTICAL ENSEMBLES

Liouville's equation: time evolution of the probability density $p(\Gamma,t)$

local conservation of probability in the phase space: continuity equation

$$\partial_t p + \mathrm{div}(\dot{\Gamma} p) = 0$$

Liouville's equation for Hamiltonian systems: Liouville's theorem

$$\partial_t p = -\mathrm{div}(\dot{\Gamma} p) = -p \underbrace{\mathrm{div}(\dot{\Gamma})}_{=0} - \dot{\Gamma} \cdot \mathrm{grad}\, p = \{H, p\} \equiv \hat{L} p$$

Liouvillian operator: $$\hat{L} \equiv \{H, \cdot\} = \sum_{a=1}^{N} \left(\frac{\partial H}{\partial \mathbf{r}_a} \cdot \frac{\partial}{\partial \mathbf{p}_a} - \frac{\partial H}{\partial \mathbf{p}_a} \cdot \frac{\partial}{\partial \mathbf{r}_a} \right)$$

Time-independent systems: $$p_t = \mathrm{e}^{\hat{L}\, t} p_0 = \hat{P}^t p_0$$

Frobenius-Perron operator: $$p_t(\Gamma) = \hat{P}^t p_0(\Gamma) \equiv p_0\left(\Phi^{-t}\Gamma\right)$$

Statistical average of a physical observable $A(\Gamma)$:

$$\langle A \rangle_t = \int A(\Phi^t \Gamma_0)\, p_0(\Gamma_0)\, d\Gamma_0 = \int A(\Gamma)\, p_0\left(\Phi^{-t}\Gamma\right) d\Gamma \equiv \int A(\Gamma)\, p_t(\Gamma)\, d\Gamma$$

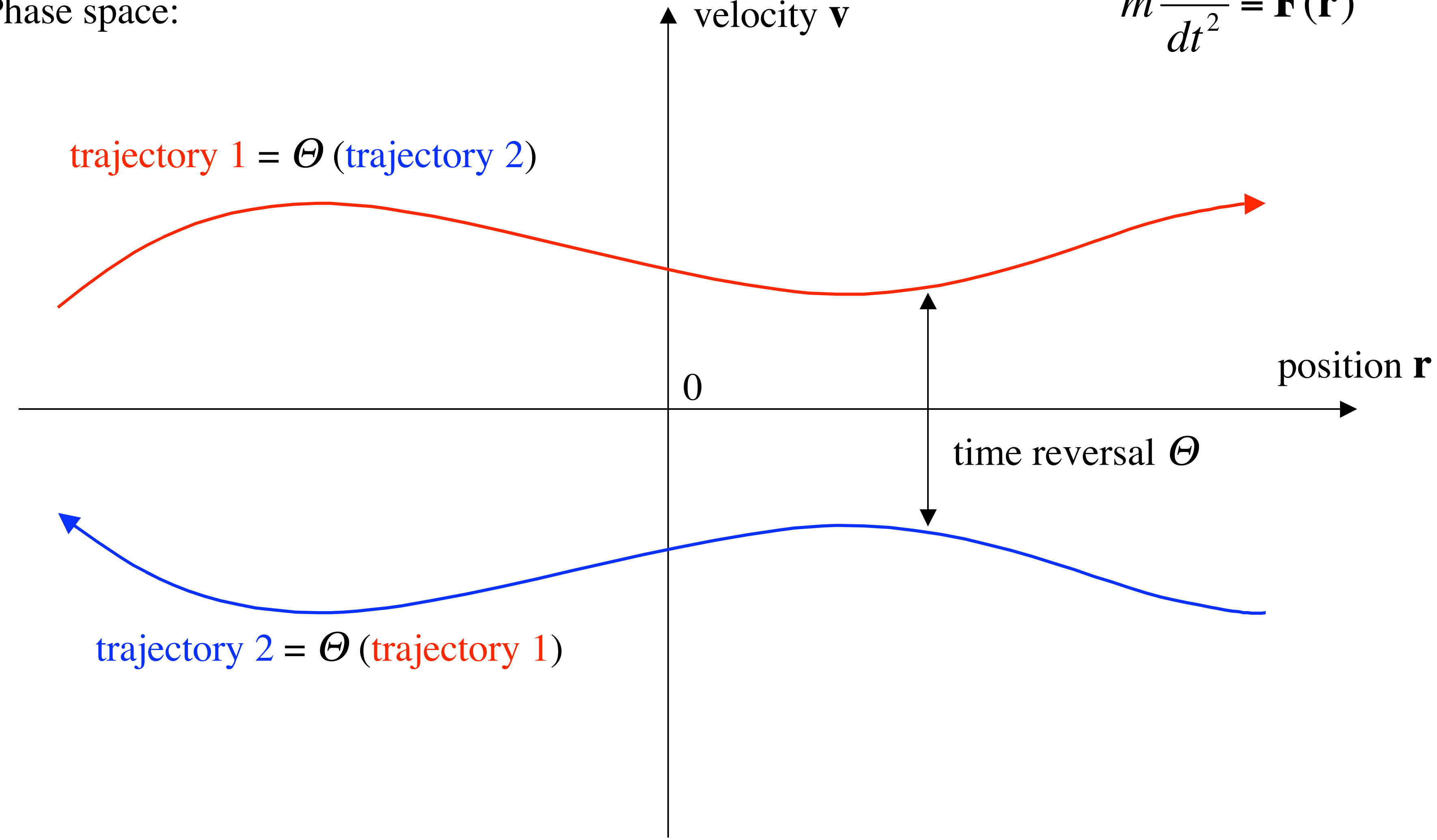
Time-reversal symmetry: induced by the symmetry of Hamiltonian dynamics

TIME-REVERSAL SYMMETRY $\Theta(\mathbf{r},\mathbf{v}) = (\mathbf{r},-\mathbf{v})$

Newton's fundamental equation of motion for atoms or molecules composing matter is time-reversal symmetric.

$$m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r})$$

Phase space:

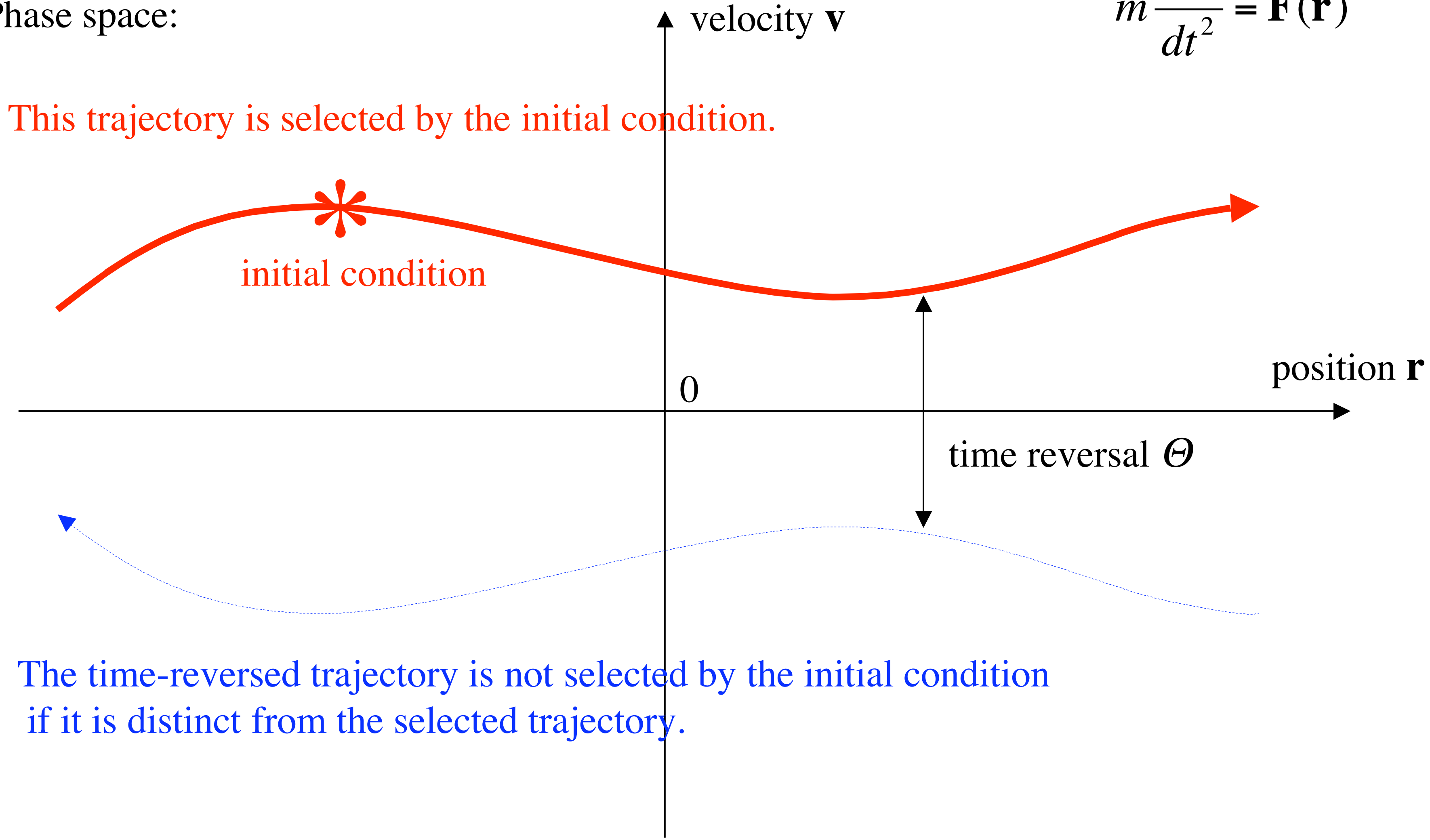


BREAKING OF TIME-REVERSAL SYMMETRY

Selecting the initial condition typically breaks the time-reversal symmetry.

$$m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{F}(\mathbf{r})$$

Phase space:

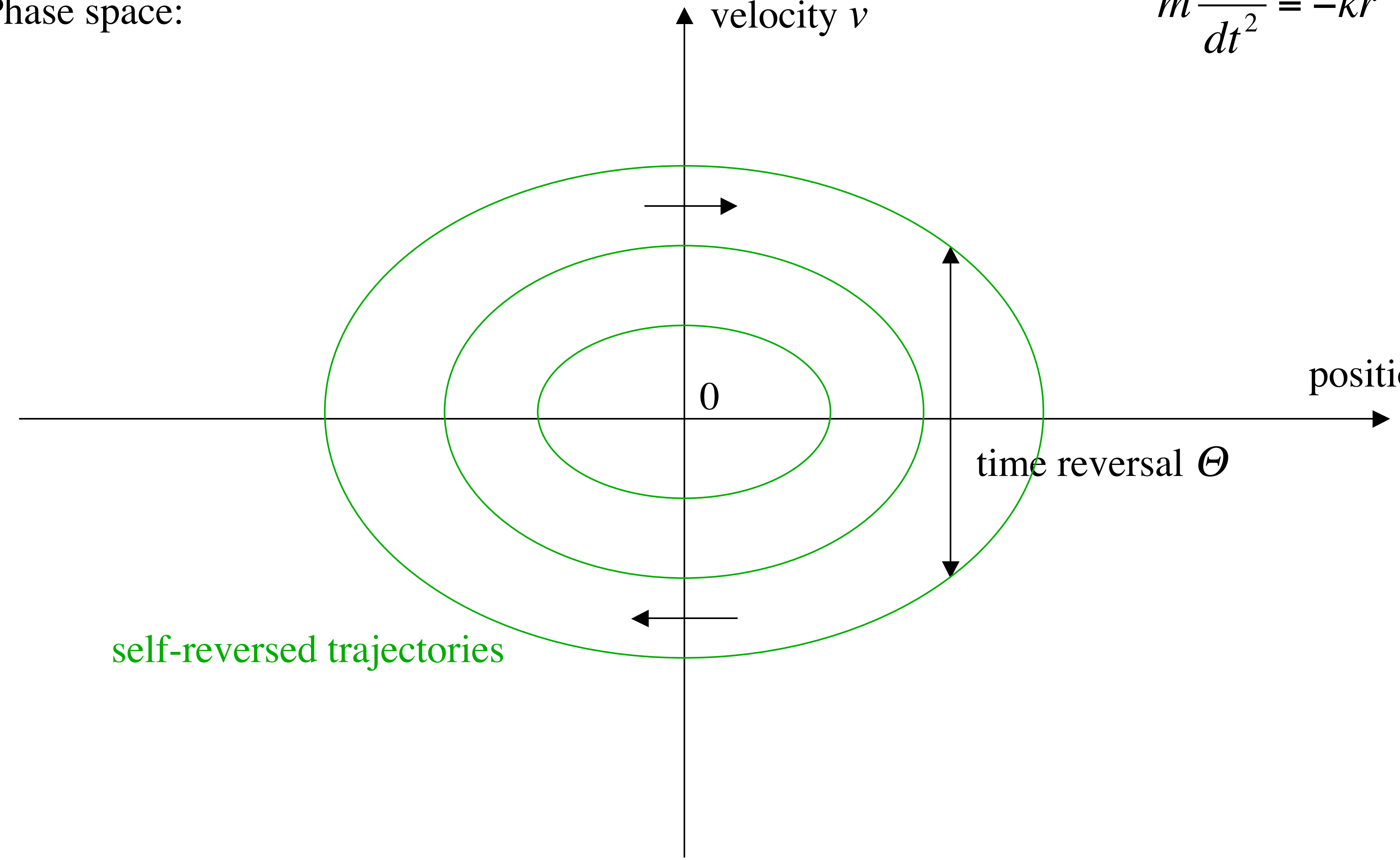


HARMONIC OSCILLATOR

All the trajectories are time-reversal symmetric in the harmonic oscillator.

$$m\frac{d^2r}{dt^2} = -kr$$

Phase space:

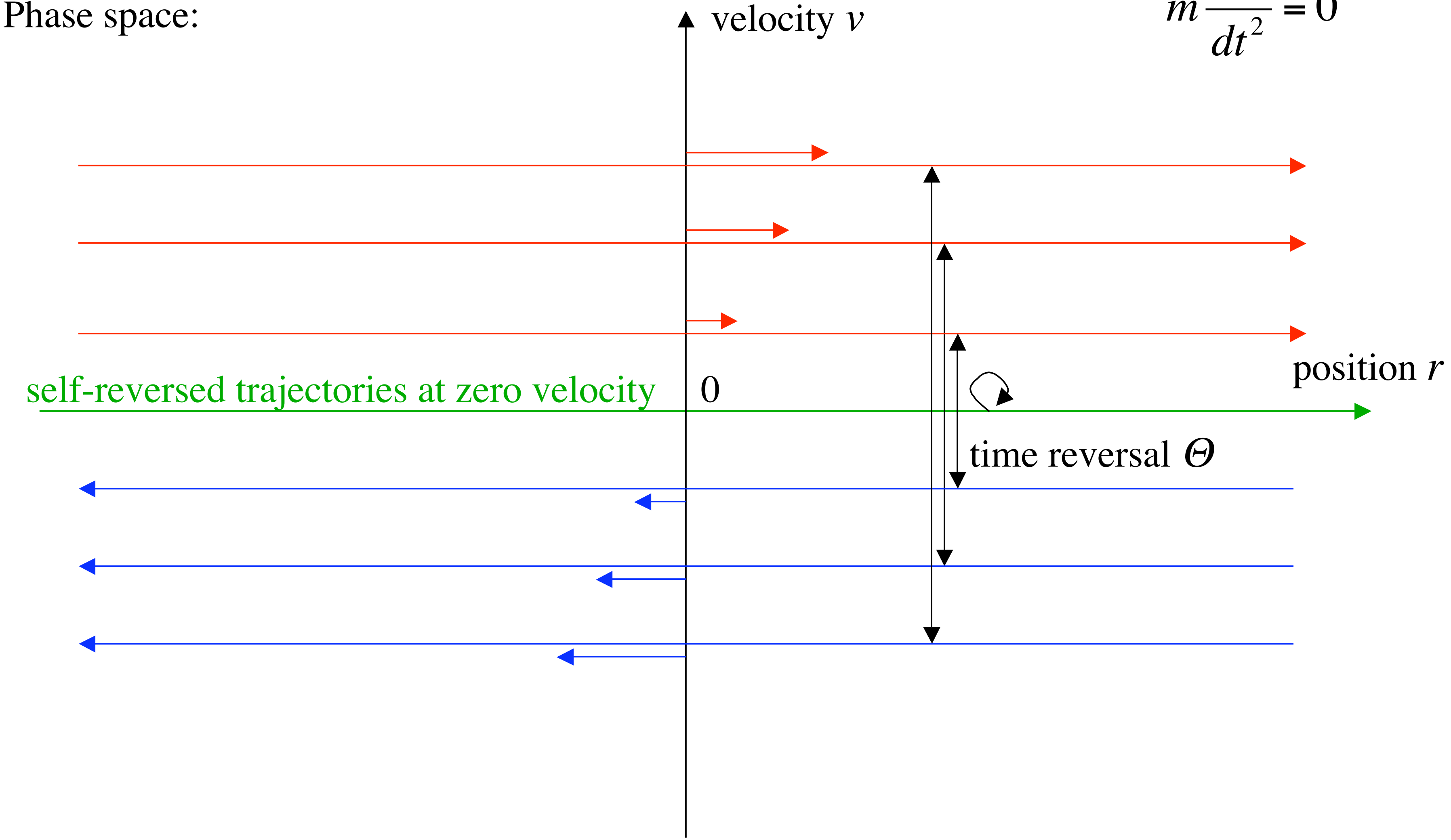


FREE PARTICLE

Almost all of the trajectories are distinct from their time reversal.

Phase space:

$$m\frac{d^2r}{dt^2}=0$$

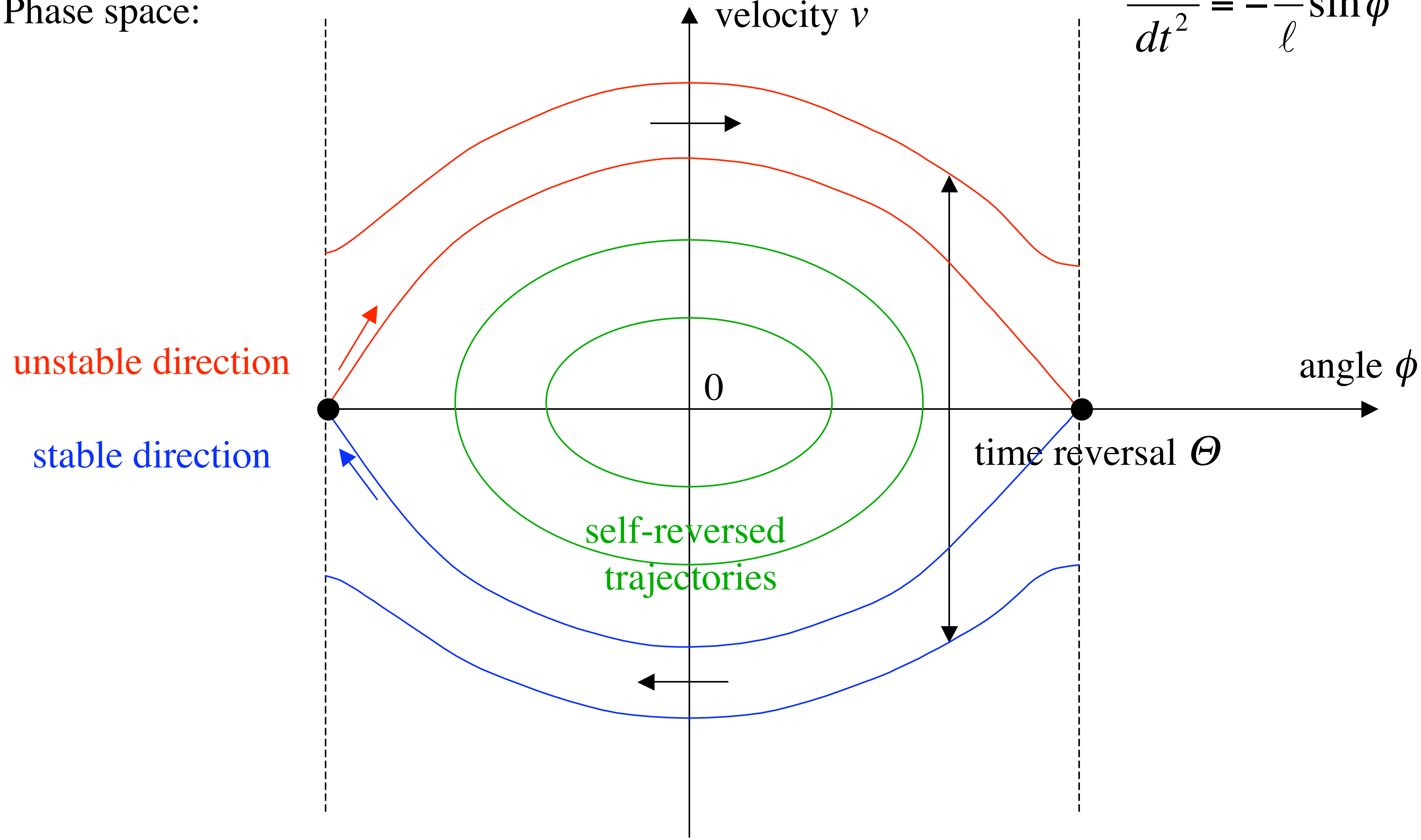


PENDULUM

The oscillating trajectories are time-reversal symmetric
while the rotating trajectories are not.

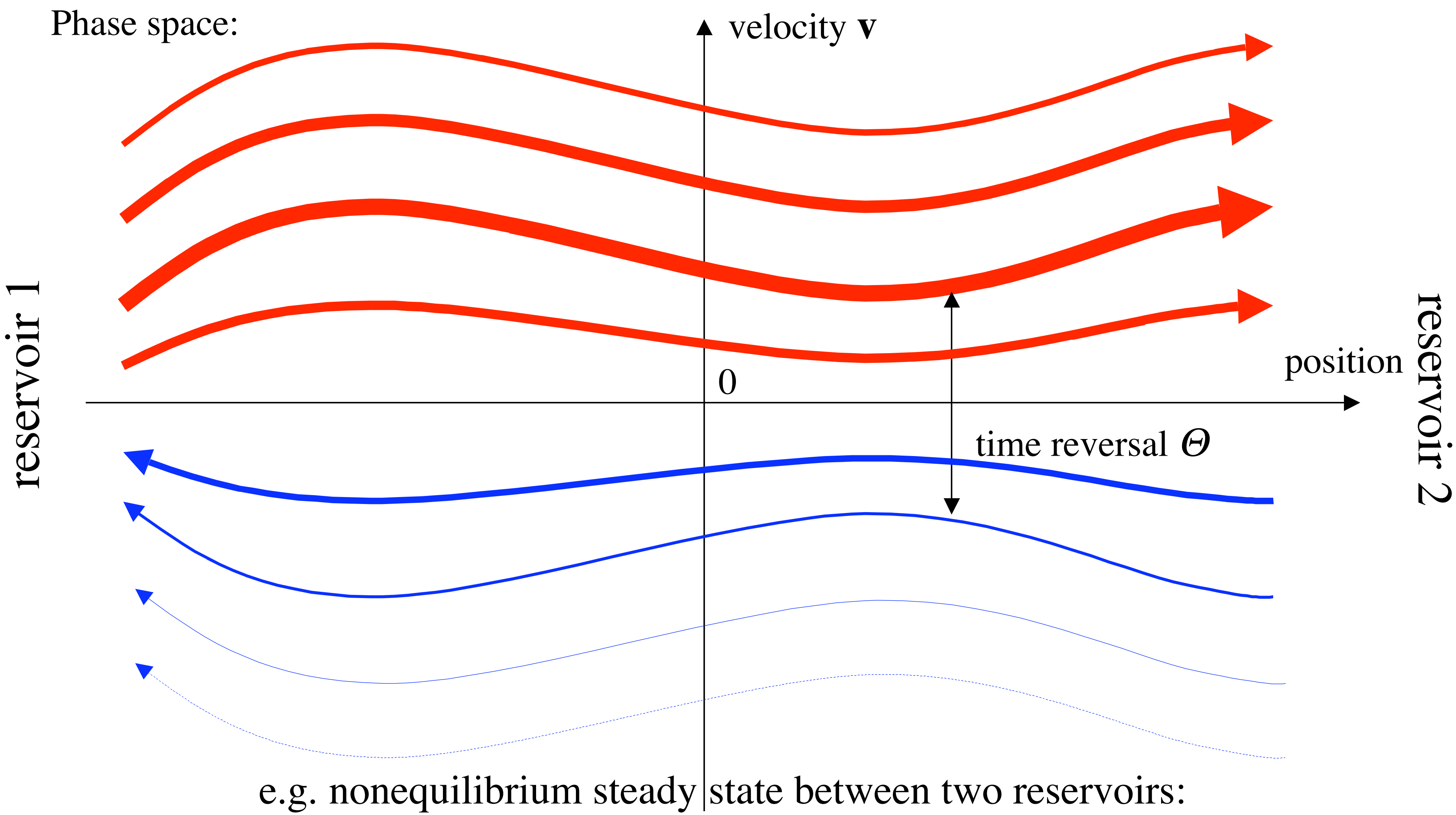
$$\frac{d^2\phi}{dt^2} = -\frac{g}{\ell}\sin\phi$$

Phase space:



STATISTICAL MECHANICS

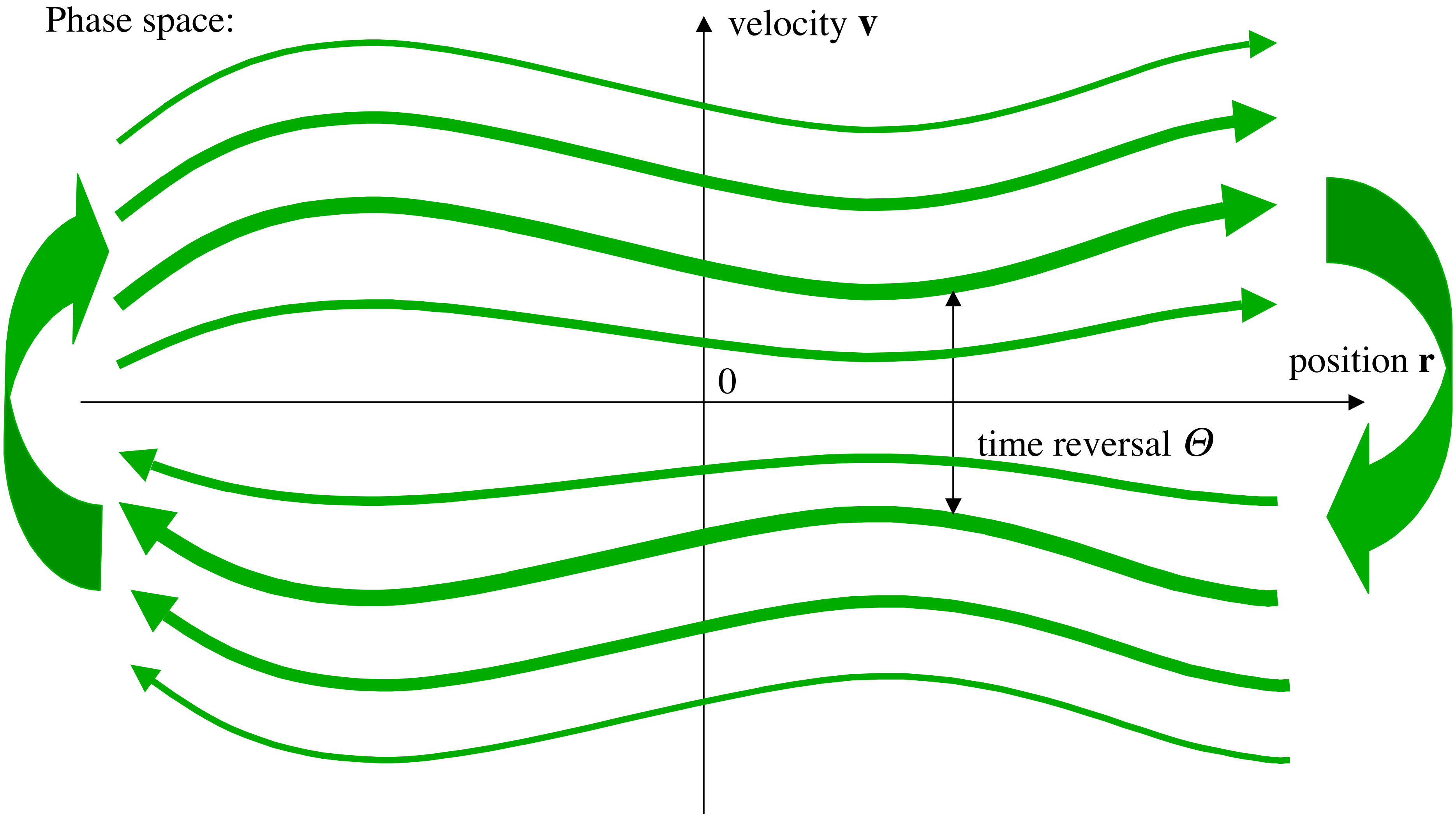
weighting each trajectory with a probability
-> invariant probability distribution



e.g. nonequilibrium steady state between two reservoirs:
breaking of time-reversal symmetry.

STATISTICAL EQUILIBRIUM

The time-reversal symmetry is restored
e.g. by ergodicity (detailed balance).



BREAKING OF TIME-REVERSAL SYMMETRY $\Theta(\mathbf{r},\mathbf{v}) = (\mathbf{r},-\mathbf{v})$

Newton's equation of mechanics is time-reversal symmetric
if the Hamiltonian H is even in the momenta.

Liouville equation of statistical mechanics,
ruling the time evolution of the probability density p
is also time-reversal symmetric.

$$\frac{\partial p}{\partial t} + \frac{\partial(\dot{\mathbf{r}}p)}{\partial \mathbf{r}} + \frac{\partial(\dot{\mathbf{v}}p)}{\partial \mathbf{v}} = 0$$

$$\frac{\partial p}{\partial t} = \{H, p\} = \hat{L}p$$

The solution of an equation may have a lower symmetry than the equation itself
(spontaneous symmetry breaking).

Typical Newtonian trajectories $\mathcal{T}$ are different from their time-reversal image $\Theta\,\mathcal{T}$:

$$\Theta\,\mathcal{T} \neq \mathcal{T}$$

Irreversible behavior is obtained by weighting differently
the trajectories $\mathcal{T}$ and their time-reversal image $\Theta\,\mathcal{T}$ with a probability measure.

Spontaneous symmetry breaking: *relaxation modes of an autonomous system*

Explicit symmetry breaking: *nonequilibrium steady state by the boundary conditions*

DYNAMICAL INSTABILITY

The possibility to predict the future of the system depends on the stability or instability of the trajectories of Hamilton's equations.

Most systems are not integrable and presents the property of **sensitivity to initial conditions** according to which two nearby trajectories tend to separate at an exponential rate.

Lyapunov exponents: $$\lambda_i = \lim_{t\to\infty} \frac{1}{t} \ln \frac{\|\delta\Gamma_i(t)\|}{\|\delta\Gamma_i(0)\|}$$

Spectrum of Lyapunov exponents: $$\lambda_1 = \lambda_{\max} \geq \lambda_2 \geq \lambda_3 \geq \ldots \geq 0 \geq \ldots \geq \lambda_{2f-1} \geq \lambda_{2f}$$

Pairing rule for Hamiltonian systems (symplectic character): $\{+\lambda_i, -\lambda_i\}_{i=1}^{f}$

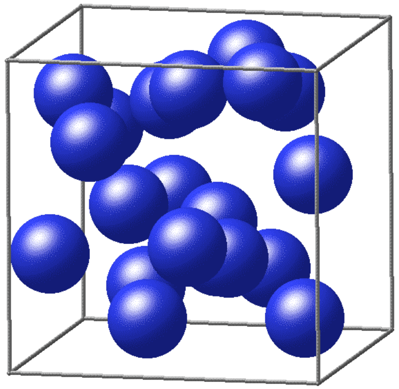
Liouville's theorem: $\sum_{i=1}^{2f} \lambda_i = 0$

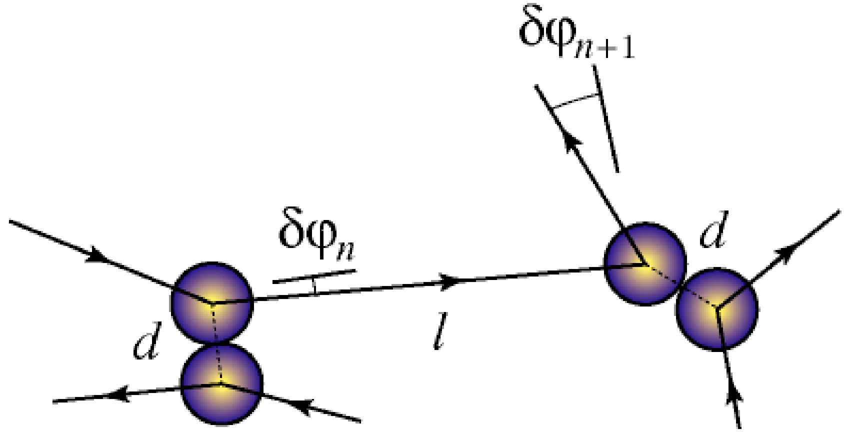
Prediction limited by the Lyapunov time: $$t < t_{\text{Lyap}} \approx \frac{1}{\lambda_{\max}} \ln \frac{\varepsilon_{\text{final}}}{\varepsilon_{\text{initial}}}$$

A statistical description is required beyond the Lyapunov time.

CHAOTIC BEHAVIOR IN MOLECULAR DYNAMICS

Hard-sphere gas:





intercollisional time τ diameter d mean free path l

Perturbation on the velocity angle:

$$\delta\varphi_n \approx \delta\varphi_0 \left(\frac{l}{d}\right)^n \approx \delta\varphi_0\, \mathrm{e}^{\lambda t} \qquad t \approx n\tau$$

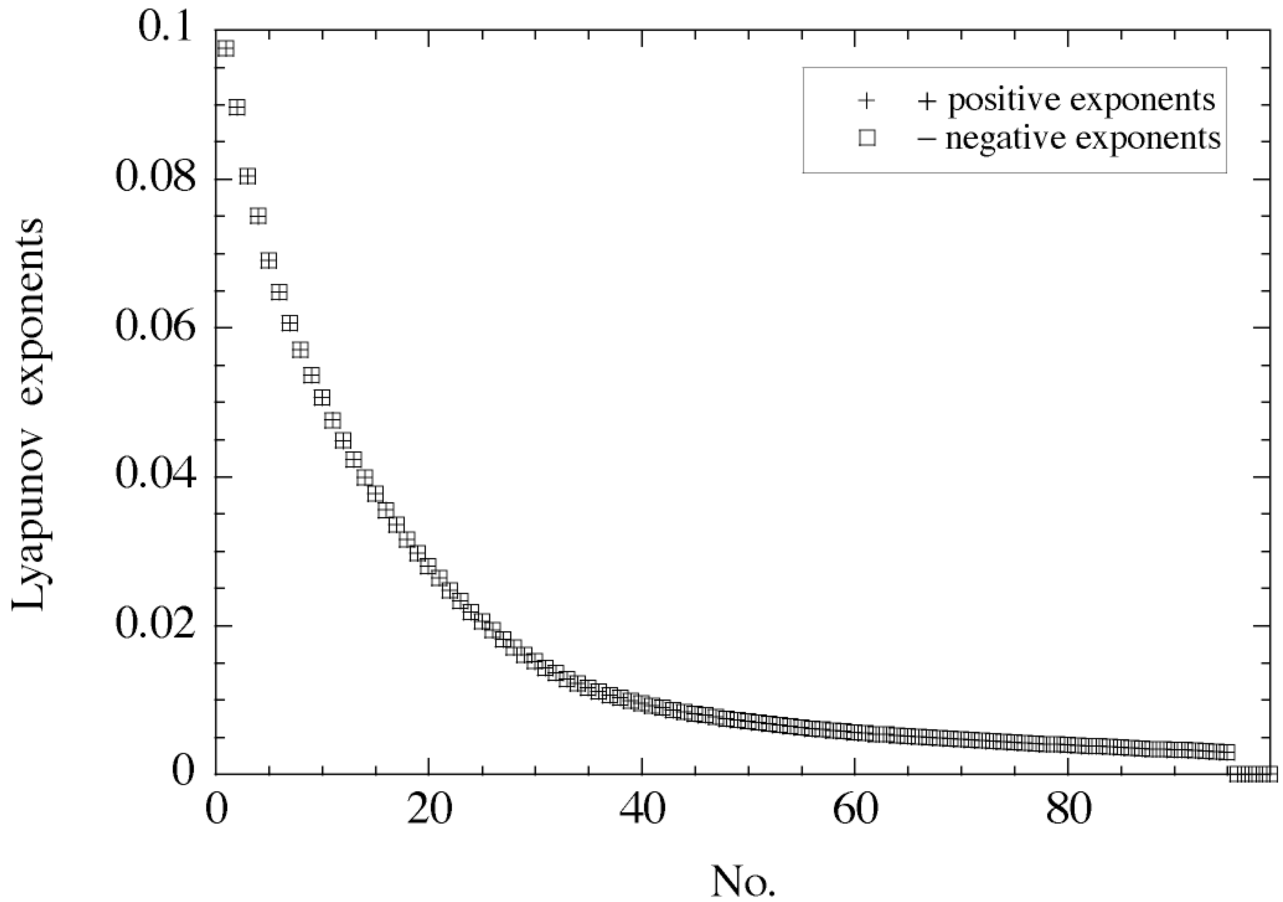
Estimation of the largest Lyapunov exponent: (Krylov 1940's)

$$\lambda \approx \frac{1}{\tau} \ln\frac{l}{d} \approx 10^{10} \text{ sec}^{-1} \quad \text{(air in the room)}$$

CHAOTIC BEHAVIOR IN MOLECULAR DYNAMICS (cont'd)

Hard-sphere gas: spectrum of Lyapunov exponents

(dynamical system of 33 hard spheres of unit diameter and mass at unit temperature and density 0.001)



STATISTICAL AVERAGE: PROBABILITY MEASURE

Ergodicity (Boltzmann 1871, 1884): time average = phase-space average

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T A(\Phi^t \Gamma_0)\, dt = \int A(\Gamma)\, \Psi_0(\Gamma)\, d\Gamma = \langle A \rangle = \langle A | \Psi_0 \rangle$$

Ψ_0 stationary probability density representing the invariant probability measure μ

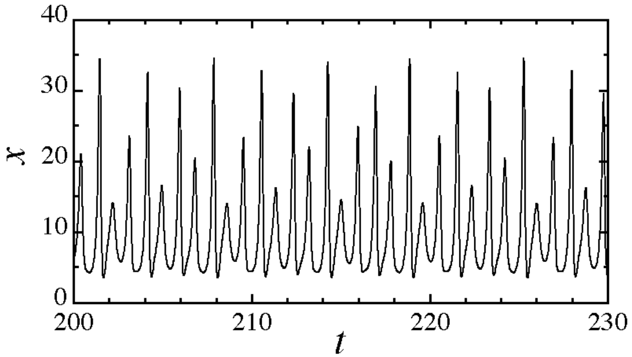
Spectrum of unitary time evolution: $p_t = \hat{U}^t p_0 = \mathrm{e}^{i\hat{G}\,t} p_0$ $\qquad \hat{G} = i\hat{L}$

Ergodicity:

The stationary probability density is unique: $\hat{G}\Psi_0 = 0$

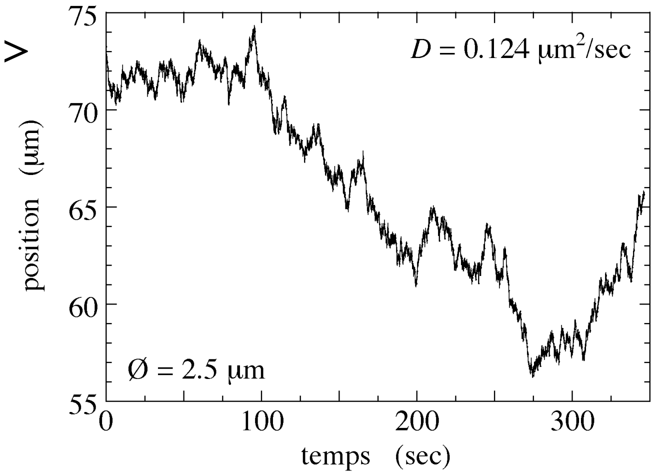
The eigenvalue $z = 0$ is non-degenerate.

DYNAMICAL RANDOMNESS / TEMPORAL DISORDER



< deterministic chaos by Rössler

Brownian motion >



How random is a fluctuating process?

A process is random if there are many possible paths. Ex: coin tossing

The longer the time interval, the larger the number of possible paths.
Typically, they multiple exponentially in time: tree of possible paths: ($\omega = 0$ or 1)

…	…
$t = 4\Delta t$	0000, 0001, 0010, 0011, 0100, 0101, 0110, 0111, 1000, 1001, 1010, 1011, 1100, 1101, 1110, 1111
$t = 3\Delta t$	000, 001, 010, 011, 100, 101, 110, 111
$t = 2\Delta t$	00, 01, 10, 11
$t = \Delta t$	0, 1

Hence, the path probabilities decay exponentially:

$$\mu(\omega_0\, \omega_1\, \omega_2 \ldots \omega_{n-1}) \sim \exp(-h\, \Delta t\, n)$$

The decay rate h is a measure of dynamical randomness / temporal disorder.
h is the so-called entropy per unit time.

DYNAMICAL RANDOMNESS AND ENTROPIES PER UNIT TIME

Partition of the phase space into domains: coarse-graining $\mathcal{P} = \{C_1, C_2, \ldots, C_M\}$

Stroboscopic observation of the system at sampling time τ:

$$\Phi^{k\tau}\Gamma \in C_\omega \qquad (k = 0,1,2,\ldots,n-1)$$

Path or history: succession of coarse-grained states $\underline{\omega} = \omega_0\omega_1\omega_2\cdots\omega_{n-1}$

Multiple-time probability to observe a given path or history:

$$\mu(\underline{\omega}) = \mu(\omega_0\omega_1\omega_2\cdots\omega_{n-1}) = \mu\left(C_{\omega_0} \cap \Phi^{-\tau}C_{\omega_1} \cap \cdots \cap \Phi^{-(n-1)\tau}C_{\omega_{n-1}}\right)$$

Entropy per unit time:

$$h(\mathcal{P}) = \lim_{n\to\infty} -\frac{1}{n\tau}\sum_{\underline{\omega}}\mu(\underline{\omega}) \ln \mu(\underline{\omega}) = \lim_{n\to\infty} -\frac{1}{n\tau}\sum_{\omega_0\omega_1\omega_2\cdots\omega_{n-1}}\mu(\omega_0\omega_1\omega_2\cdots\omega_{n-1}) \ln \mu(\omega_0\omega_1\omega_2\cdots\omega_{n-1})$$

Kolmogorov-Sinai entropy per unit time: $h_{\mathrm{KS}} = \operatorname*{Sup}_{\mathcal{P}} h(\mathcal{P})$

closed systems: Pesin’s theorem: $h_{\mathrm{KS}} = \sum_{\lambda_i > 0} \lambda_i$

$$\mu(\omega_0\omega_1\omega_2\cdots\omega_{n-1}) \approx \exp(-hn\tau) = \frac{1}{\Lambda(\omega_0\omega_1\omega_2\cdots\omega_{n-1})} \approx \frac{1}{\exp(\sum_{\lambda_i>0}\lambda_i t)}$$

DYNAMICAL RANDOMNESS IN STATISTICAL MECHANICS

Typically a stochastic process such as Brownian motion is much more random than a chaotic system: its Kolmogorov-Sinai entropy per unit time is infinite.

Partition into cells of size ε, sampling time τ

Brownian motion: $h(\varepsilon) \propto \frac{\mathcal{D}}{\varepsilon^2}$

Birth-and-death processes, probabilistic cellular automata: $h(\tau) \propto \ln\frac{1}{\tau}$

Boltzmann-Lorentz equation for a gas of hard spheres of diameter σ and mass *m* at temperature *T* and density *n*:

$$h(\varepsilon) = 4\, n^2\sigma^2\sqrt{\frac{\pi k_B T}{m}}\ln\frac{399 k_B T}{n\sigma^2 m\varepsilon}$$

with $\varepsilon = \Delta t\Delta^3 v\Delta^2\Omega > \varepsilon_* \approx 100\,\frac{\sigma k_B T}{m}$

Deterministic theory (Dorfman & van Beijeren):

$$h_{KS} = \sum_{\lambda_i>0}\lambda_i = 4\, n^2\sigma^2\sqrt{\frac{\pi k_B T}{m}}\ln\frac{3.9}{\pi n\sigma^3}$$

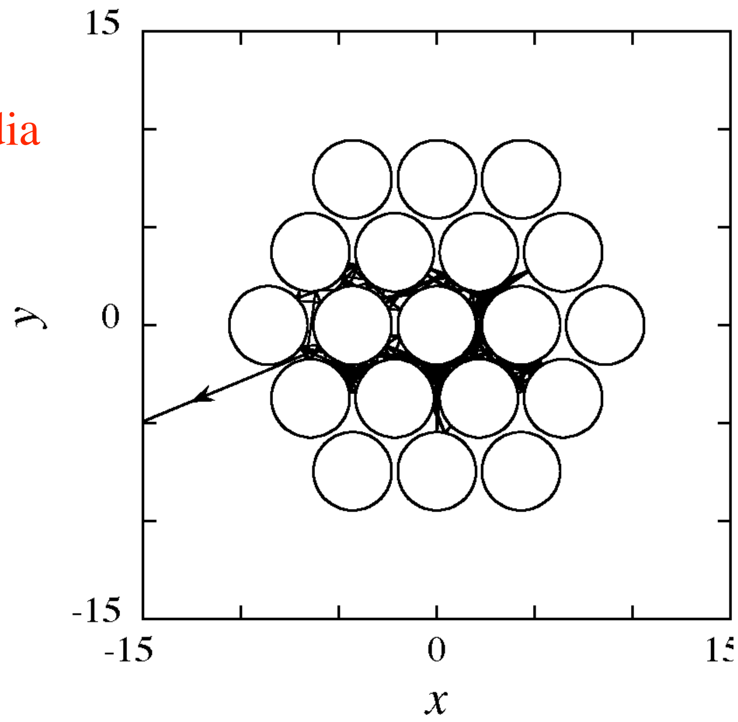
Chaos is a principle of order in nonequilibrium statistical mechanics.

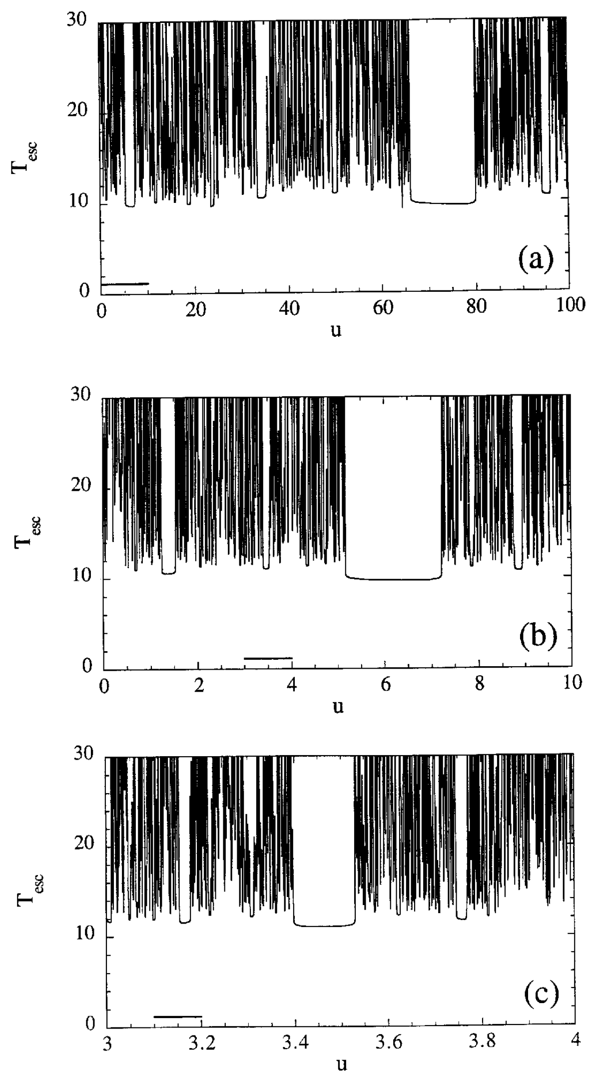
ESCAPE-RATE FORMALISM: DIFFUSION

escape of a particle

out of the diffusive media

Ex: neutron in a reactor





• diffusion coefficient $\mathcal{D} = \lim_{t\to\infty} (1/2t) < (x_t - x_0)^2 >$

diffusion equation: $\partial_t \, p(x, t) \approx \mathcal{D} \, \partial_x^{\,2} \, p(x, t)$

absorbing boundary conditions: $p\,(-L/2,\, t\,) = p\,(+L\,/2,\, t\,) = 0$

solution: $p(x, t) \sim \exp(-\gamma\ t) \cos(\pi\, x \,/\, L\,)$

escape rate: $\gamma \approx \mathcal{D}\,(\pi \,/\, L\,)^2$

P. Gaspard & G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693; P. Gaspard & F. Baras, Phys. Rev. E **51** (1995) 5332

ESCAPE-RATE FORMALISM:
THE TRANSPORT COEFFICIENTS & THEIR HELFAND MOMENT

Transport coefficients:

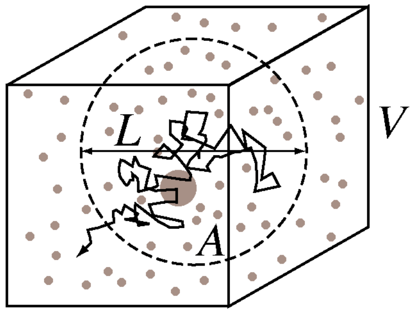
Green-Kubo formula: $\alpha = \int_0^\infty \langle J_0^{(\alpha)} J_t^{(\alpha)} \rangle dt$ microscopic current: $J^{(\alpha)} = \frac{dG^{(\alpha)}}{dt}$

Einstein formula: $\alpha = \lim_{t\to\infty} \frac{1}{2t} \langle (G_t^{(\alpha)} - G_0^{(\alpha)})^2 \rangle$ Helfand moment: $G_t^{(\alpha)} = G_0^{(\alpha)} + \int_0^t J_{t'}^{(\alpha)} dt'$

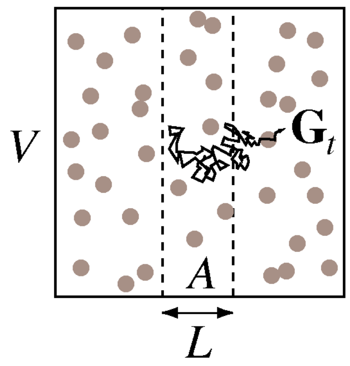
Transport property:	*moment:*
self-diffusion:	$G^{(D)} = x_a$
shear viscosity:	$G^{(\eta)} = \frac{1}{\sqrt{Vk_B T}} \sum_{a=1}^{N} x_a p_{ay}$
bulk viscosity: $\psi = \zeta + \frac{4}{3}\eta$	$G^{(\psi)} = \frac{1}{\sqrt{Vk_B T}} \sum_{a=1}^{N} x_a p_{ax}$
heat conductivity	$G^{(\kappa)} = \frac{1}{\sqrt{Vk_B T^2}} \sum_{a=1}^{N} x_a (E_a - \langle E_a \rangle)$
electric conductivity:	$G^{(\eta)} = \frac{1}{\sqrt{Vk_B T}} \sum_{a=1}^{N} eZ_a x_a$

ESCAPE-RATE FORMALISM:
ESCAPE OF THE HELFAND MOMENT

Diffusion of a Brownian particle



Shear viscosity



$$-\frac{\chi}{2} \leq G_t^{(\alpha)} \leq +\frac{\chi}{2}$$

Einstein formula: $$\alpha = \lim_{t\to\infty} \frac{1}{2t}\left\langle \left(G_t^{(\alpha)} - G_0^{(\alpha)}\right)^2 \right\rangle$$

diffusive equation: $$\frac{\partial p}{\partial t} = \alpha \frac{\partial^2 p}{\partial g^2} \qquad g = G_t^{(\alpha)}$$

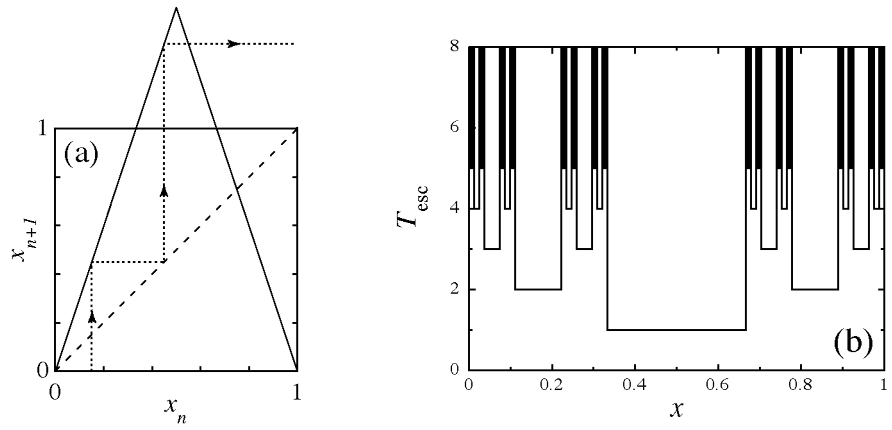
absorbing boundary conditions: $$p(g = \pm\chi/2, t) = 0$$

solution of diffusive equation: $$p(g,t) = \sum_{j=1}^{\infty} a_j \exp\left(-\gamma_j t\right) \sin\left(\frac{j\pi g}{\chi} + \frac{j\pi}{2}\right) \qquad \gamma_j = \alpha\left(\frac{j\pi}{\chi}\right)^2$$

escape rate: $$\gamma = \gamma_1 = \alpha\left(\frac{\pi}{\chi}\right)^2 \qquad \text{for } \chi \to \infty$$

ESCAPE-RATE FORMALISM:
ESCAPE RATE & PROBABILITY MEASURE

stretching factors:



$$\Lambda(\underline{\omega}) = \Lambda(\omega_0\omega_1\omega_2\cdots\omega_{n-1}) = \prod_{k=0}^{n-1}\Lambda_{\omega_k}$$

$$\Lambda_0 = +s \qquad \Lambda_1 = -s$$

escape rate: $$\sum_{\underline{\omega}}\left|\Lambda(\underline{\omega})\right|^{-1} \propto \mathrm{e}^{-\gamma n\tau}$$

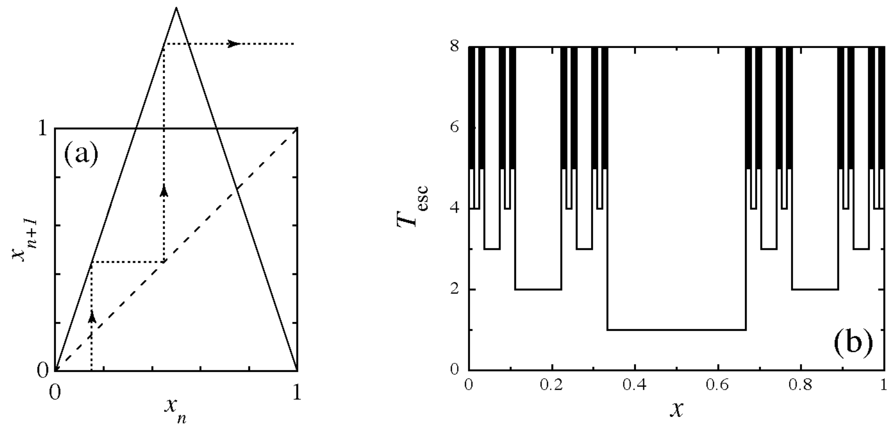
invariant probability measure: $$\mu(\underline{\omega}) \approx \frac{\left|\Lambda(\underline{\omega})\right|^{-1}}{\sum_{\underline{\omega}}\left|\Lambda(\underline{\omega})\right|^{-1}}$$

average Lyapunov exponent: $$\lambda \equiv \lim_{n\to\infty}\frac{1}{n\tau}\sum_{\underline{\omega}}\mu(\underline{\omega})\ \ln\left|\Lambda(\underline{\omega})\right|$$

KS entropy per unit time: $$h \equiv \lim_{n\to\infty} -\frac{1}{n\tau}\sum_{\underline{\omega}}\mu(\underline{\omega})\ \ln\mu(\underline{\omega}) = \lambda - \gamma$$

ESCAPE-RATE FORMALISM:
ESCAPE-RATE FORMULA

stretching factors: $\Lambda(\underline{\omega}) = \Lambda(\omega_0\omega_1\omega_2\cdots\omega_n$



Ruelle topological pressure:

$$P(\beta) \equiv \lim_{n\to\infty} \frac{1}{n\tau} \ln \sum_{\underline{\omega}} \left|\Lambda(\underline{\omega})\right|^{-\beta}$$

escape rate: $\gamma = -P(1)$

Lyapunov exponent: $\lambda = \lambda(1) = -P'(1)$

generalized fractal dimensions:

$$\sum_{\underline{\omega}} \frac{\left|\mu(\underline{\omega})\right|^q}{\ell(\underline{\omega})^{(q-1)d_q}} \propto 1 \qquad \ell(\omega) \propto \left|\Lambda(\underline{\omega})\right|^{-1} \qquad P\left[q + (1-q)\, d_q\right] = -q\,\gamma$$

escape-rate formula ($f = 2$): $\gamma = \lambda - h_{\mathrm{KS}} = \lambda(1 - d_1)$

escape-rate formula ($f > 2$): $\gamma = \sum_{\lambda_i > 0} \lambda_i - h_{\mathrm{KS}} = \sum_{\lambda_i > 0} \lambda_i (1 - d_{1,i})$

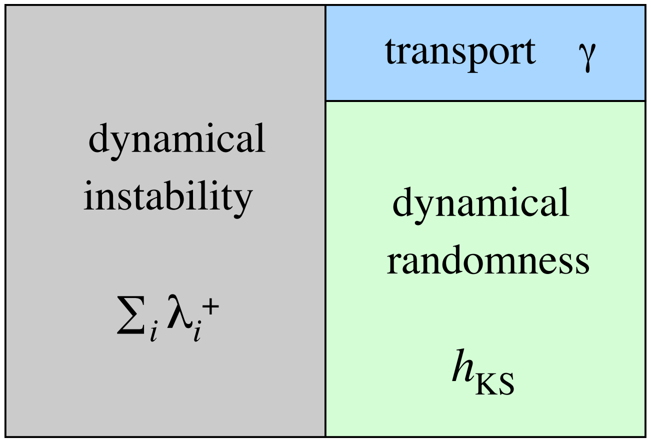
closed system: Pesin’s identity: $h_{\mathrm{KS}} = \sum_{\lambda_i > 0} \lambda_i$

ESCAPE-RATE FORMALISM
CHAOS-TRANSPORT FORMULA

Combining the result from transport theory with
the escape-rate formula from dynamical systems theory,
we obtain the chaos-transport relationship

$$\alpha = \lim_{\chi,V\to\infty}\left(\frac{\chi}{\pi}\right)^2\left(\sum_{\lambda_i>0}\lambda_i - h_{\mathrm{KS}}\right)_\chi = \lim_{\chi,V\to\infty}\left(\frac{\chi}{\pi}\right)^2\sum_{\lambda_i>0}\lambda_i(1-d_i)\bigg|_\chi$$

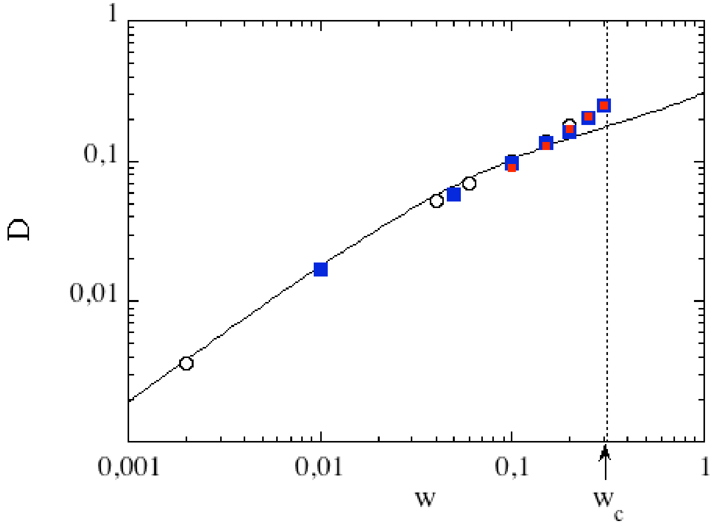
large-deviation dynamical relationship

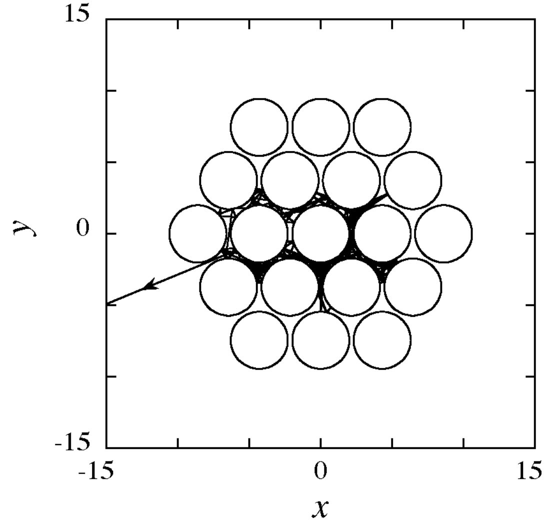


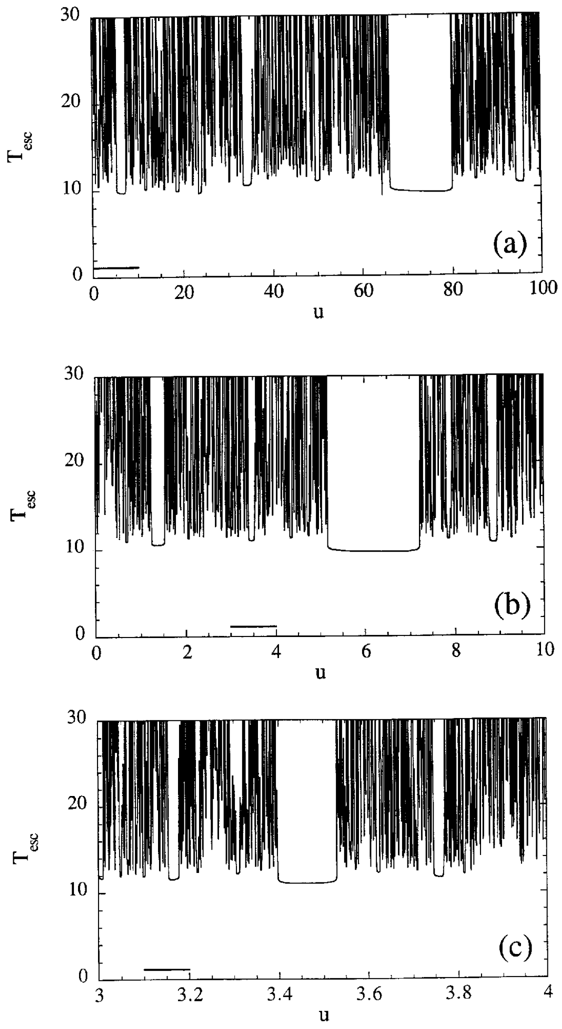
Out of equilibrium, the system has less dynamical randomness
than possible by its dynamical instability.

P. Gaspard & G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693; J. R. Dorfman, & P. Gaspard, Phys. Rev. E **51** (1995) 28

ESCAPE-RATE FORMALISM: DIFFUSION







- Helfand moment for diffusion: $G_t = x_i$

  diffusion coefficient $\eta = \lim_{t\to\infty} (1/2t) < (G_t - G_0)^2 >$

diffusion equation: $\partial_t \, p(x, t) \approx \mathcal{D} \, \partial_x^{\,2} \, p(x, t)$

absorbing boundary conditions: $p\,(-L/2, t\,) = p\,(+L\,/2, t\,) = 0$

solution: $p(x, t) \sim \exp(-\gamma \; t) \cos(\pi \, x \,/\, L\,)$

escape rate: $\gamma \approx \mathcal{D}\,(\pi \,/\, L\,)^2$

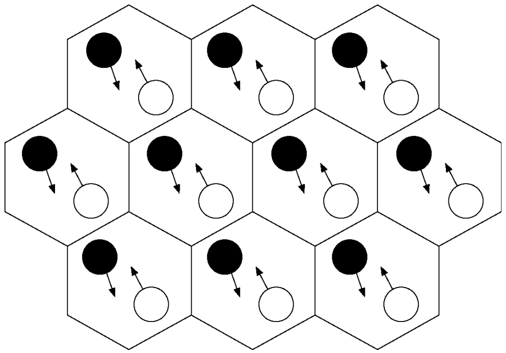
- dynamical systems theory

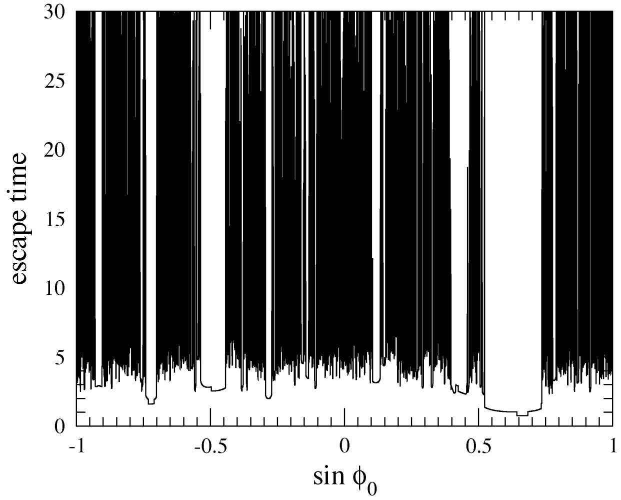
  escape rate (leading Pollicott-Ruelle resonance): $\gamma = \lambda - h_{\mathrm{KS}} = \lambda\,(1 - d_{\mathrm{I}})$

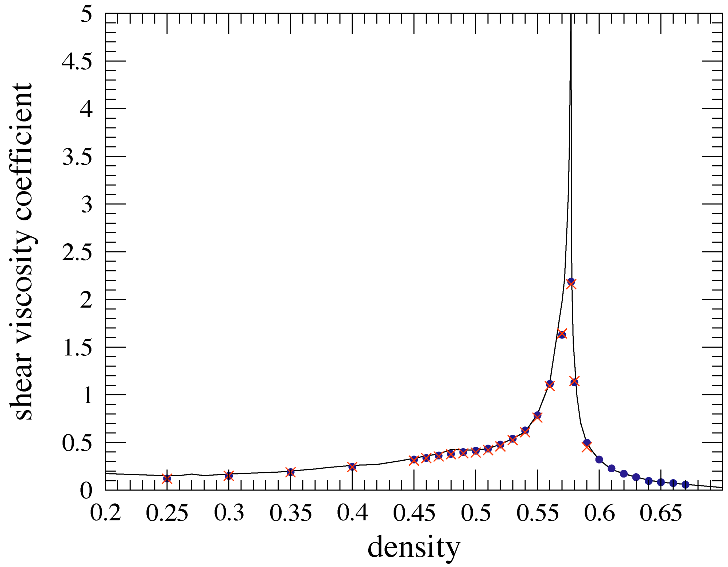
chaos-transport relationship: $\mathcal{D} = \lim_{L\to\infty} (\,L \,/\, \pi\,)^2 \, \lambda \,[1 - d_{\mathrm{I}}\,(L)]$

P. Gaspard & G. Nicolis, Phys. Rev. Lett. **65** (1990) 1693; P. Gaspard & F. Baras, Phys. Rev. E **51** (1995) 5332

ESCAPE-RATE FORMALISM: VISCOSITY







- Helfand moment for viscosity: $G_t = \sum_i x_i\, p_{yi} / (V k_B T)^{1/2}$

  viscosity coefficient $\eta = \lim_{t\to\infty} (1/2t) < (G_t - G_0)^2 >$

  diffusivity equation for the Helfand moment: $\partial_t\, p(g,t) \approx \eta\, \partial_g{}^2\, p(g,t)$

  absorbing boundary conditions: $p(-\chi/2, t) = p(+\chi/2, t) = 0$

  solution: $p(g,t) \sim \exp(-\gamma\, t) \cos(\pi\, g / \chi)$

  escape rate: $\gamma \approx \eta\, (\pi / \chi)^2$

- dynamical systems theory

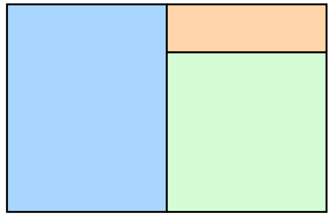
  escape rate (leading Pollicott-Ruelle resonance): $\gamma = \sum_i \lambda_i - h_{KS} = \lambda\,(1 - d_I)$

  chaos-transport relationship: $\eta = \lim_{\chi\to\infty} (\chi / \pi)^2 \left(\sum_i \lambda_i - h_{KS}\right)_\chi$

J. R. Dorfman, & P. Gaspard, Phys. Rev. E **51** (1995) 28; S. Viscardy & P. Gaspard, Phys. Rev. E **68** (2003) 041205.

CONCLUSIONS

Breaking of time-reversal symmetry in the statistical description



Escape-rate formalism: nonequilibrium transients

fractal repeller

diffusion $\mathcal{D}$:

$$\mathcal{D}(\pi/L)^2 \approx \gamma = \left(\sum_{\lambda_i > 0} \lambda_i - h_{\mathrm{KS}} \right)_L$$

(1990)

viscosity η :

$$\eta(\pi/\chi)^2 \approx \gamma = \left(\sum_{\lambda_i > 0} \lambda_i - h_{\mathrm{KS}} \right)_L$$

(1995)

Hamiltonian systems: Liouville theorem: $\sum_{i=1}^{2f} \lambda_i = 0$ $\quad \gamma = \sum_{\lambda_i > 0} \lambda_i - h_{\mathrm{KS}} = -\sum_{\lambda_i < 0} \lambda_i - h_{\mathrm{KS}}$

thermostated systems: no Liouville theorem

volume contraction rate: $\sigma = -\sum_{i=1}^{2f} \lambda_i = -\sum_{\lambda_i < 0} \lambda_i - \sum_{\lambda_i > 0} \lambda_i = -\sum_{\lambda_i < 0} \lambda_i - h_{\mathrm{KS}}$

Pesin's identity on the attractor: $h_{\mathrm{KS}} = \sum_{\lambda_i > 0} \lambda_i$

http://homepages.ulb.ac.be/~gaspard