Microscopic Chaos, Fractals and Transport in Nonequilibrium Statistical Mechanics

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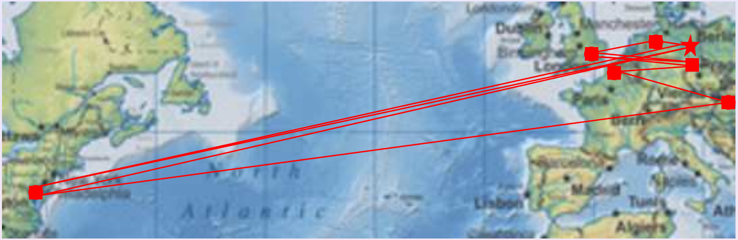
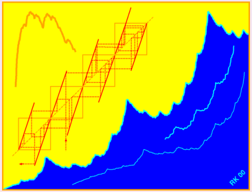
Outline

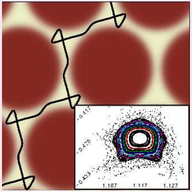
1. **Motivation:** microscopic chaos and transport; Brownian motion, dissipation and thermalization
2. the **thermostated dynamical systems approach** to nonequilibrium steady states and its surprising (fractal) properties
3. **generalized Hamiltonian dynamics** and universalities?

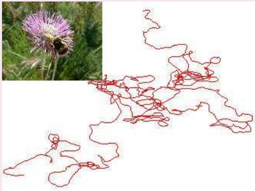
My scientific movements and research interests



my scientific foraging; and my food sources:







chaos, complexity and nonequilibrium statistical physics with applications to small systems and biology

Why this topic?

$$\cancel{\hbar}$$

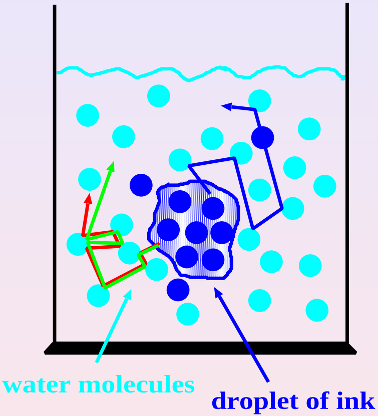
(sorry!)

but: R.F. Werner (U. Hannover)

Generally observed features of the theory, like, e.g., the **approach of equilibrium** *in macroscopic systems, deserve a general explanation don't they?*

point of this talk: There is a cross-link.

Microscopic chaos in a glass of water?



- dispersion of a droplet of ink by *diffusion*
- assumption: *chaotic collisions* between billiard balls

microscopic chaos
$\Updownarrow$
macroscopic transport

- relaxation to *equilibrium*

J.Ingenhousz (1785), R.Brown (1827), L.Boltzmann (1872), P.Gaspard et al. (Nature, 1998)

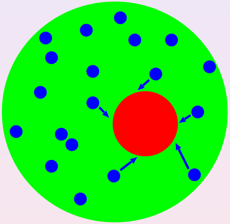
Simple theory of Brownian motion

for a single **big** tracer particle of velocity **v** immersed in a fluid:

$$\boxed{\dot{\mathbf{v}} = -\kappa\mathbf{v} + \sqrt{\zeta}\,\xi(t)}$$ **Langevin equation** (1908)

'Newton's law of stochastic physics'

force decomposed into
viscous damping
and
random kicks of surrounding particles



- models the interaction of a subsystem (tracer particle) with a thermal reservoir (fluid) in $(\mathbf{r}, \mathbf{v})$-space
- two aspects: fluctuations and dissipation; replace the tracer particle by a bottle of beer: thermalization problem in $\mathbf{v}$-space

Langevin dynamics

$$\dot{\mathbf{v}} = -\kappa\mathbf{v} + \sqrt{\zeta}\,\boldsymbol{\xi}(t)$$

basic properties:

stochastic

dissipative

not time reversible

$\Rightarrow$ **not Hamiltonian**

however:

see, e.g., Zwanzig's (1973) derivation of the Langevin equation from a heat bath of harmonic oscillators

non-Hamiltonian dynamics arises from eliminating the reservoir degrees of freedom by starting from a purely Hamiltonian system

Summary I

setting the scene:

- microscopic chaos and transport
- Brownian motion, dissipation and thermalization
- **Langevin dynamics:** stochastic, dissipative, not time reversible, not Hamiltonian

now to come:

the **deterministically thermostated dynamical systems approach** to nonequilibrium steady states

Nonequilibrium and the Gaussian thermostat

- Langevin equation with an electric field

$$\dot{\mathbf{v}} = \mathbf{E} - \kappa \mathbf{v} + \sqrt{\zeta}\, \xi(t)$$

generates a **nonequilibrium steady state**: physical macro-scale quantities are constant in time
numerical inconvenience: slow relaxation

- alternative method via velocity-dependent friction coefficient

$$\dot{\mathbf{v}} = \mathbf{E} - \alpha(\mathbf{v}) \cdot \mathbf{v}$$

(for free flight); keep kinetic energy constant, $d\mathbf{v}^2/dt = 0$:

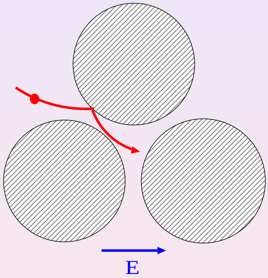
$$\boxed{\alpha(\mathbf{v}) = \frac{\mathbf{E} \cdot \mathbf{v}}{v^2}}$$

Gaussian (isokinetic) **thermostat**
Evans/Hoover (1983)

- follows from *Gauss' principle of least constraints*
- generates a *microcanonical velocity distribution*
- total *internal energy* can also be kept constant

The Lorentz Gas

free flight is a bit boring: consider the periodic Lorentz gas as a microscopic toy model for a conductor in an electric field

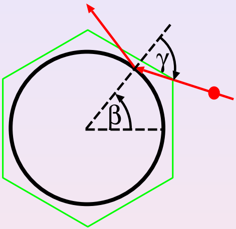


Galton (1877), Lorentz (1905)

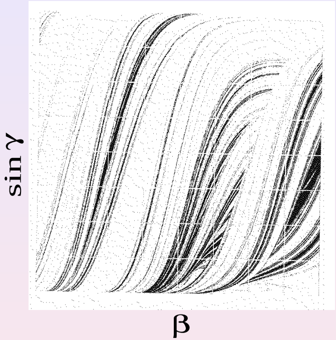
couple it to a Gaussian thermostat - **surprise:** dynamics is **deterministic, chaotic, time reversible, dissipative, ergodic**

Hoover/Evans/Morriss/Posch (1983ff)

Gaussian dynamics: first basic property



Hoover, Moran (1989)



reversible equations of motion

$\Updownarrow$

fractal attractors in phase space

$\Updownarrow$

irreversible transport

Second basic property

- use equipartitioning of energy: $v^2/2 = T/2$
- consider ensemble averages: $\boxed{<\alpha>= \frac{\mathbf{E}\cdot <\mathbf{v}>}{T}}$

absolute value of average **rate of phase space contraction** = thermodynamic (Clausius) **entropy production**

that is:

entropy production is due to **contraction onto fractal attractor** in nonequilibrium steady states

more generally: identity between Gibbs entropy production and phase space contraction (Gerlich, 1973 and Andrey, 1985)

Third basic property

- define conductivity σ by $<\mathbf{v}>=: \sigma\mathbf{E}$; into previous eq. yields

$$\sigma = \frac{T}{E^2} < \alpha >$$

- combine with identity $-<\alpha>= \lambda_+ + \lambda_-$ for Lyapunov exponents $\lambda_{+/-}$:

$$\boxed{\sigma = -\frac{T}{E^2}(\lambda_+ + \lambda_-)}$$

conductivity in terms of **Lyapunov exponents**

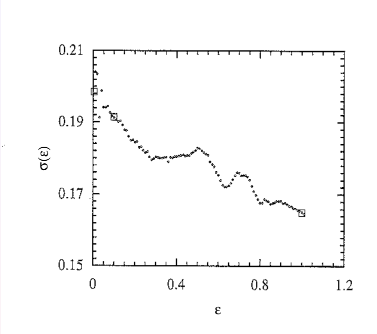
Posch, Hoover (1988); Evans et al. (1990)

similar relations for Hamiltonian dynamics and other transport coefficients from a different theory

Gaspard, Dorfman (1995)

Side remark: electrical conductivity

field-dependent electrical conductivity from NEMD computer simulations:



Lloyd et al. (1995)

• mathematical proof that there exists Ohm's Law for small enough (?) field strength (Chernov et al., 1993)

• but irregular parameter dependence of $\sigma(E)$ in simulations (cf. book by RK, Part 1 on fractal transport coefficients)

Summary II

- **thermal reservoirs** needed to create steady states in nonequilibrium
- **Gaussian thermostat** as a deterministic alternative to Langevin dynamics
- Gaussian dynamics for **Lorentz gas** yields nonequilibrium steady states with very interesting dynamical properties

recall that Gaussian dynamics is *microcanonical*

last part:
construct a deterministic thermostat that generates a *canonical* distribution

The (dissipative) Liouville equation

Let $(\dot{\mathbf{r}}, \dot{\mathbf{v}})^* = \mathbf{F}(\mathbf{r}, \mathbf{v})$ be the equations of motion for a point particle and $\rho = \rho(t, \mathbf{r}, \mathbf{v})$ the probability density for the corresponding Gibbs ensemble

balance equation for conserving the number of points in phase space:

$$\boxed{\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{F} = 0}$$

Liouville equation (1838)

For Hamiltonian dynamics there is no phase space contraction, $\nabla \cdot \mathbf{F} = 0$, and Liouville's theorem is recovered:

$$\frac{d\rho}{dt} = 0$$

The Nosé-Hoover thermostat

Let $(\dot{\mathbf{r}}, \dot{\mathbf{v}}, \dot{\alpha})^* = \mathbf{F}(\mathbf{r}, \mathbf{v}, \alpha)$ with $\dot{\mathbf{r}} = \mathbf{v}$, $\dot{\mathbf{v}} = \mathbf{E} - \alpha(\mathbf{v})\mathbf{v}$ be the equations of motion for a point particle with friction variable α

problem: derive an equation for α that generates the canonical distribution

$$\rho(t, \mathbf{r}, \mathbf{v}, \alpha) \sim \exp\left[-\frac{v^2}{2T} - (\tau\alpha)^2\right]$$

put the above equations into the Liouville equation

$$\frac{\partial \rho}{\partial t} + \dot{\mathbf{r}}\frac{\partial \rho}{\partial \mathbf{r}} + \dot{\mathbf{v}}\frac{\partial \rho}{\partial \mathbf{v}} + \dot{\alpha}\frac{\partial \rho}{\partial \alpha} + \rho\left[\frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}} + \frac{\partial \dot{\mathbf{v}}}{\partial \mathbf{v}} + \frac{\partial \dot{\alpha}}{\partial \alpha}\right] = 0$$

restricting to $\partial\dot{\alpha}/\partial\alpha = 0$ yields the **Nosé-Hoover thermostat**

$$\boxed{\dot{\alpha} = \frac{v^2 - 2T}{\tau^2 2T}}$$

Nosé (1984), Hoover (1985)

widely used in NEMD computer simulations

Generalized Hamiltonian formalism for Nosé-Hoover

Dettmann, Morriss (1997): use the Hamiltonian

$$H(\mathbf{Q},\mathbf{P},Q_0,P_0) := e^{-Q_0}E(\mathbf{P},P_0) + e^{Q_0}U(\mathbf{Q},Q_0)$$

where $E(\mathbf{P},P_0) = \mathbf{P}^2/(2m) + P_0^2/(2M)$ is the kinetic and $U(\mathbf{Q},Q_0) = u(\mathbf{Q}) + 2TQ_0$ the potential energy of particle plus reservoir for generalized position and momentum coordinates

Hamilton's equations by imposing $H(\mathbf{Q},\mathbf{P},Q_0,P_0) = 0$:

$$\dot{\mathbf{Q}} = e^{-Q_0}\frac{\mathbf{P}}{m}\ ,\ \dot{\mathbf{P}} = -e^{Q_0}\frac{\partial u}{\partial \mathbf{Q}}$$

$$\dot{Q}_0 = e^{-Q_0}\frac{P_0}{M}\ ,\ \dot{P}_0 = 2(e^{-Q_0}E(\mathbf{P},P_0) - e^{Q_0}T)$$

uncoupled equations for $Q_0 = 0$ suggest relation between physical and generalized coordinates

$$\mathbf{Q} = \mathbf{q}\ ,\ \mathbf{P} = e^{Q_0}\mathbf{p}\ ,\ Q_0 = q_0\ ,\ P_0 = e^{Q_0}p_0$$

for $M = 2T\tau^2$, $\alpha = p_0/M$, $m = 1$ Nosé-Hoover recovered

note: the above transformation is **noncanonical**!

Nosé-Hoover dynamics

summary:

Nosé-Hoover thermostat constructed both from Liouville equation and from generalized Hamiltonian formalism

properties:

- fractal attractors
- identity between phase space contraction and entropy production
- formula for transport coefficients in terms of Lyapunov exponents

that is, we have the same class as Gaussian dynamics

basic question:

Are these properties universal for deterministic dynamical systems in nonequilibrium steady states altogether?

Non-ideal and boundary thermostats

counterexample 1:
increase the coupling for the Gaussian thermostat parallel to the field by making the friction field-dependent:

$$\dot{v}_x = E_x - \alpha(1+E_x)v_x \ , \ \dot{v}_y = -\alpha v_y$$

• breaks the identity between phase space contraction and entropy production and the conductivity-Lyapunov exponent formula

• fractal attractors seem to persist

• non-ideal Nosé-Hoover thermostat constructed analogously

counterexample 2:
a time-reversible deterministic boundary thermostat generalizing stochastic boundaries (RK et al., 2000)

• same results as above

Universality of Gaussian and Nosé-Hoover dynamics?

$\ominus$ in general **no identity** between *phase space contraction and entropy production*

$\ominus$ consequently, relations between *transport coefficients and Lyapunov exponents* in thermostated systems are **not universal**

$\oplus$ existence of *fractal attractors* confirmed (stochastic reservoirs: open question)

(possible way out: need to take a closer look at first problem...)

Outlook: the big picture

nonequilibrium conditions

		equilibrium	**nonequilibrium steady states**	**nonequilibrium non-steady states**
microscopic	**dynamical systems**	ergodic hypothesis	**microscopic chaos** strong	weak
	statistical mechanics	Gibbs ensembles	**complexity** fractal SRB measures	infinite measures
macroscopic	**thermodynamics**	thermodynamic properties	**deterministic transport** normal	anomalous

theory of nonequilibrium statistical physics starting from microscopic chaos?

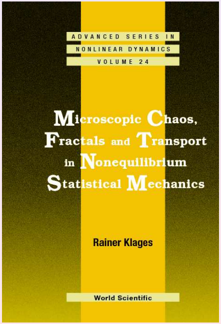
approach should be particularly useful for
small nonlinear systems

Acknowledgements and literature

counterexamples developed with:

K.Rateitschak (PhD thesis in Brussels, 1997-2002),
Chr.Wagner (postdoc in Brussels, 1998-2000), G.Nicolis

literature:



(Part 2)