The thermostated dynamical systems approach to nonequilibrium steady states

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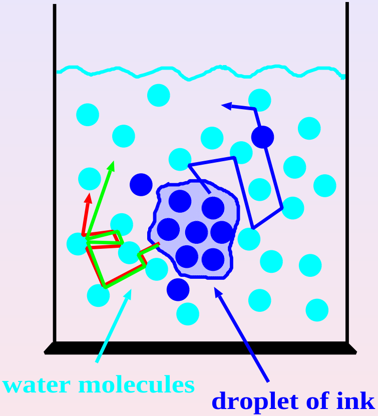
Queen Mary University of London

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?

Microscopic chaos in a glass of water?



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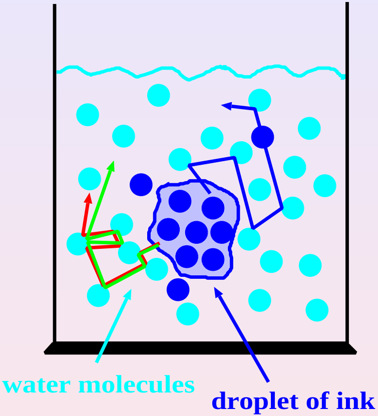

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microscopic chaos
⇕
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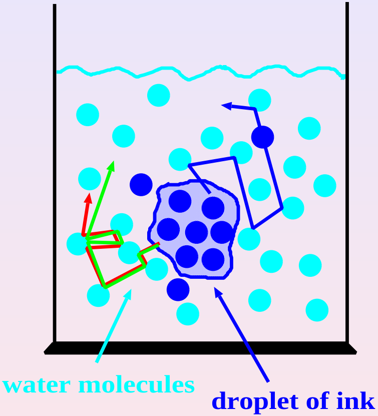

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J.Ingenhousz (1785), R.Brown (1827), L.Boltzmann (1872), P.Gaspard et al. (Nature, 1998)

Simple theory of Brownian motion

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

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

Langevin equation (1908)

‘Newton’s law of stochastic physics’

force decomposed into
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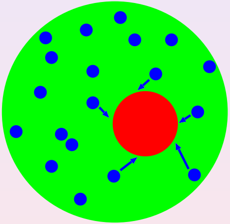

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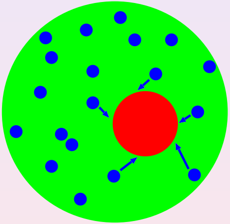

- models the interaction of a subsystem (tracer particle) with a thermal reservoir (fluid) in $(\mathbf{r}, \mathbf{v})$-space
- two aspects: diffusion and dissipation

Langevin dynamics

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basic properties:

stochastic

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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:

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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

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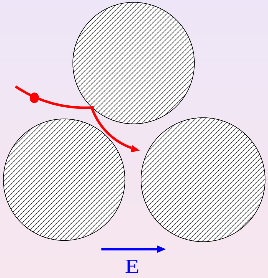
- follows from *Gauss' principle of least constraints*
- generates a *microcanonical velocity distribution*
- total *internal energy* can also be kept constant

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



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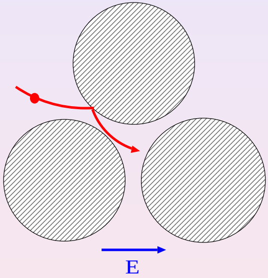
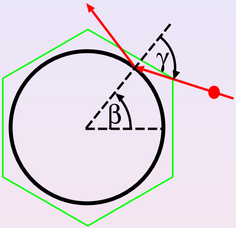


Galton (1877), Lorentz (1905)

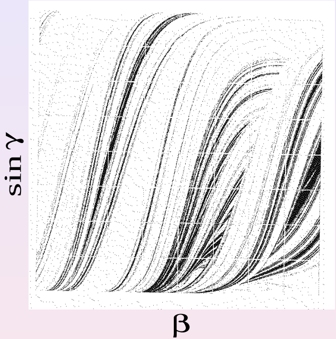
couple it to a Gaussian thermostat - **surprise:** dynamics is **deterministic, chaotic, time reversible, dissipative, ergodic**

Hoover/Evans/Morriss/Posch (1983ff)

Gaussian dynamics: first basic property



Hoover, Moran (1989)



reversible equations of motion

⇕

fractal attractors in phase space

⇕

irreversible transport

Second basic property

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

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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)

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mobility in terms of **Lyapunov exponents**

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

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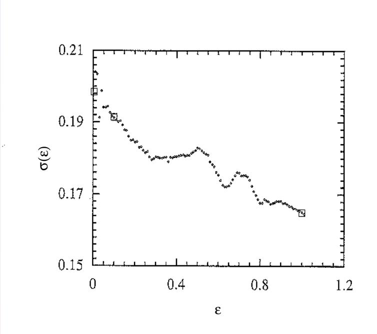
similar relations for Hamiltonian dynamics and other transport coefficients from a *very different* (escape rate) theory

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

(more details on this in my talk next Wednesday)

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

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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

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

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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

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

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put the above equations into the Liouville equation

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

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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

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

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matching the 1st eq. to physical coordinates suggests the 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

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- fractal attractors
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- formula for transport coefficients in terms of Lyapunov exponents

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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:

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

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counterexample 2:

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

- same results as above

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$\oplus$ 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

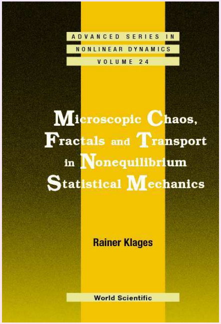
small nonlinear systems

Acknowledgements and literature

counterexamples developed with:

K.Rateitschak (PhD thesis 2002, now Rostock), Chr.Wagner (postdoc in Brussels 2002/3), G.Nicolis (Brussels)

literature:



for the rigorous maths: D. Ruelle, JSP **95**, 393 (1999)!