Microscopic Chaos, Fractals and Transport in Nonequilibrium Statistical Mechanics

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Leibniz Universität Hannover, 30 May 2013
Motivation: microscopic chaos and transport; Brownian motion, dissipation and thermalization

the thermostated dynamical systems approach to nonequilibrium steady states and its surprising (fractal) properties

generalized Hamiltonian dynamics and universalities?
Why this talk?

W. and R. Mathis: talks about canonically dissipative systems

(sorry!)

but: R.F. Werner, Generally observed features of the theory, like, e.g., the approach of equilibrium in macroscopic systems, deserve a general explanation don’t they?

main 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

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

\[
\dot{v} = -\kappa v + \sqrt{\zeta} \xi(t)
\]

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 $(r, v)$-space

• two aspects: diffusion and dissipation; replace the tracer particle by a bottle of beer: thermalization problem in $v$-space
Langevin dynamics

\[ \dot{v} = -\kappa v + \sqrt{\zeta} \xi(t) \]

**basic properties:**

- stochastic
- dissipative
- not time reversible

\[ \Rightarrow \text{not Hamiltonian} \]

**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
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
  \[ \dot{v} = E - \kappa v + \sqrt{\zeta} \xi(t) \]
generates a nonequilibrium steady state: physical macro-scale quantities are constant in time
numerical inconvenience: slow relaxation
- alternative method via velocity-dependent friction coefficient
  \[ \dot{v} = E - \alpha(v) \cdot v \]
(for free flight); keep kinetic energy constant, \( dv^2/dt = 0 \):

\[ \alpha(v) = \frac{E \cdot v}{v^2} \]

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

reversible equations of motion

\[\sin \gamma\]

\[\beta\]

fractal attractors in phase space

irreversible transport
Second basic property

- use equipartitioning of energy: $v^2/2 = T/2$

- consider ensemble averages: $\langle \alpha \rangle = \frac{E \cdot \langle v \rangle}{T}$

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 $\sigma$ by $< v > =: \sigma E$; into previous eq. yields
  \[ \sigma = \frac{T}{E^2} < \alpha > \]

• combine with identity $- < \alpha > = \lambda_+ + \lambda_-$ for Lyapunov exponents $\lambda_+/-$:
  \[ \sigma = -\frac{T}{E^2} (\lambda_+ + \lambda_-) \]

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

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

\[
\frac{d\rho}{dt} + \rho \nabla \cdot F = 0
\]

Liouville equation (1838)

For Hamiltonian dynamics there is no phase space contraction, \(\nabla \cdot F = 0\), and Liouville’s theorem is recovered:

\[
\frac{d\rho}{dt} = 0
\]

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The Nosé-Hoover thermostat

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

**Problem:** derive an equation for \(\alpha\) that generates the canonical distribution

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

put the above equations into the Liouville equation

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

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

\[
\dot{\alpha} = \frac{v^2 - 2T}{\tau^2 2T}
\]

Nosé (1984), Hoover (1985)

widely used in NEMD computer simulations
Dettmann, Morriss (1997): use the Hamiltonian

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

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

Hamilton’s equations by imposing \( H(Q, P, Q_0, P_0) = 0 \):

\[ \dot{Q} = e^{-Q_0} \frac{P}{m}, \quad \dot{P} = -e^{Q_0} \frac{\partial u}{\partial Q} \]
\[ \dot{Q}_0 = e^{-Q_0} \frac{P_0}{M}, \quad \dot{P}_0 = 2(e^{-Q_0} E(P, P_0) - e^{Q_0} T) \]

uncoupled equations for \( Q_0 = 0 \) suggest relation between physical and generalized coordinates

\[ Q = q, \quad P = e^{Q_0} p, \quad Q_0 = q_0, \quad P_0 = e^{Q_0} p_0 \]

for \( M = 2T \tau^2, \quad \alpha = p_0 / M, \quad m = 1 \) 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:
\[
\dot{v}_x = E_x - \alpha(1+E_x)v_x, \quad \dot{v}_y = -\alpha v_y
\]
- 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?

- In general, no identity between phase space contraction and entropy production.

- Consequently, relations between transport coefficients and Lyapunov exponents in thermostated systems are not universal.

- Existence of fractal attractors confirmed (stochastic reservoirs: open question).

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

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Approach should be particularly useful for small nonlinear systems.

Theory of nonequilibrium statistical physics starting from microscopic chaos?
counterexamples developed with:

literature:

(Part 2)