Oak Ridge National Laboratory

April 2008

Nonlinear response theory, chaos and the fluctuation theorem.

Lecture I:

Chaos, Lyapunov Exponents and Transport Coefficients

By

Denis J. Evans Research School of Chemistry, Australian National University Canberra, ACT 2601, Australia

Abstract

We very briefly describe the historical development of nonequilibrium statistical mechanics and computer simulation. We describe how algorithms were developed and how they were proved to be correct. We also describe the impact that the mathematical study of chaos has had on nonequilibrium statistical mechanics. We briefly describe new mathematical relationships between transport processes, the Second Law of Thermodynamics and chaotic measures.



Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008 Liouville Equation for N-particle distribution function

The Liouville equation is analogous to the mass continuity equation in fluid mechanics. The "mass" is the number of ensemble members. This quanitity is conserved (like mass). The mass density can change in time either at a fixed position in phase space:

$$\frac{\partial f(\Gamma, t)}{\partial t} = -\frac{\partial}{\partial \Gamma} \bullet [\dot{\Gamma} f(\Gamma, t)] \equiv -iLf(\Gamma, t)$$

or for thermostatted systems, as a function of time, along a streamline in phase space:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = [\frac{\partial}{\partial t} + \dot{\Gamma} \bullet \frac{\partial}{\partial \Gamma}]f = -f\Lambda$$

 Λ is called the *phase space compression factor*, and

$$\mathrm{iL}=\dot{\Gamma}\bullet\frac{\partial}{\partial\Gamma}...,\quad\mathrm{iL}=\frac{\partial}{\partial\Gamma}\bullet\dot{\Gamma}...,\quad\mathrm{iL}-\mathrm{iL}=\frac{\partial}{\partial\Gamma}\bullet\dot{\Gamma}\equiv\Lambda(\Gamma)$$

Equation of motion of phase function

$$\frac{\mathrm{dA}(\Gamma)}{\mathrm{dt}} = \dot{\Gamma} \bullet \frac{\partial \mathrm{A}(\Gamma)}{\partial \Gamma} \equiv \mathrm{iLA}(\Gamma)$$

Thermostats

Deterministic, time reversible, homogeneous thermostats were simultaneously but independently proposed by Hoover and Evans in 1982. Later they realised that the equations of motion could be derived from Gauss' Principle of Least Constraint (Evans, Hoover, Failor, Moran & Ladd (1983)).

The form of the equations of motion is

$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \alpha \mathbf{p}_{i}$$

 α can be chosen such that the energy is constant or such that the kinetic energy is constant. In the latter case the equilibrium, field free distribution function can be proved to be the isokinetic distribution, $f(\Gamma) \sim \delta(\sum p_i^2 / 2m - 3Nk_BT/2)\exp[-\Phi(q)/k_BT]$.

In 1984 Nosé showed that if α is determined as the time dependent solution of the equation

$$\frac{d\alpha}{dt} = \left[\left(\sum p_i^2 / 2m \right) / \left(3Nk_BT / 2 \right) - 1 \right] / \tau^2$$

then $\forall \tau$, in an ergodic system the equilibrium distribution is canonical $f(\Gamma) \sim \exp[-H_0(\Gamma)/k_BT]$.

Thermostatted Response theory

Assume system is canonical at t=0.

$$f(\Gamma, 0) = \frac{\exp[-\beta H_0(\Gamma)]}{\int d\Gamma \exp[-\beta H_0(\Gamma)]}$$

$$f(\Gamma, t) = \exp[-(iL + \Lambda)t]f(\Gamma, 0)$$

Using a *Dyson decomposition* (and some operator algebra) gives,

$$f(\Gamma, t) = \exp[-\int_0^t ds \Lambda(s)] \exp[-\beta H_0(-t)]$$

For the equations of motion,

$$\begin{split} \dot{\mathbf{q}}_{i} &= \frac{\mathbf{p}_{i}}{m} + \mathbf{C}_{i} \cdot \mathbf{F}_{e} \\ \dot{\mathbf{p}}_{i} &= \mathbf{F}_{i} + \mathbf{D}_{i} \cdot \mathbf{F}_{e} - \alpha \mathbf{p}_{i} \end{split}$$

Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008 From equations of motion,

$$\frac{dH_0}{dt} = \frac{dH_0}{dt}^{ad} + \frac{dH_0}{dt}^{therm}$$
$$= -\mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e - 2\mathbf{K}\alpha$$
$$= 0, \quad \dot{H}_0 = 0$$
$$= \dot{\Phi}, \quad \dot{K} = 0.$$

but

$$\Lambda = 3N\alpha + O(1) .$$

This leads in the isokinetic case, to the so-called *Kawasaki* expression for the nonequilibrium distribution function, (Evans & Morriss (1984)).

 $f(\mathbf{\Gamma},t) = \exp[-\beta \int_0^t ds \ \mathbf{J}(-s) \bullet \mathbf{F}_e] f(\mathbf{\Gamma},0)$

We can use this to compute averages,

$$< \mathbf{B}(t) >= \int d\mathbf{\Gamma} f(\mathbf{\Gamma}, t) \mathbf{B}(\mathbf{\Gamma})$$
$$= \int d\mathbf{\Gamma} \mathbf{B}(\mathbf{\Gamma}) \exp[-\beta \int_{0}^{t} ds \mathbf{J}(-s) \cdot \mathbf{F}_{e}] f(\mathbf{\Gamma}, 0)$$

Since

$$d < B(t) > /dt = -\beta \int d\Gamma B(\Gamma) \mathbf{J}(-t) \cdot \mathbf{F}_{e} f(\Gamma, t)$$
$$= -\beta \int d\Gamma B(t) \mathbf{J}(0) \cdot \mathbf{F}_{e} f(\Gamma, 0)$$

We can write averages in terms of the *Transient Time Correlation Function*, (Evans & Morriss, (1984)).

$$< \mathbf{B}(t) > = -\beta \mathbf{F}_{e} \bullet \int_{0}^{t} ds < \mathbf{J}(0) \mathbf{B}(s) >$$

In the weak field limit we can linearise both Kawasaki and TTCF giving, the *Linear Response Green-Kubo formula*

$$\lim_{F_e \to 0} \langle B(t) \rangle = -\beta \mathbf{F}_e \cdot \int_0^t ds \langle \mathbf{J}(0) B(s) \rangle_{eq}$$

NB All dynamics is thermostatted and <...> has the external field applied.

Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008 **Further observations concerning thermostats**

• If
$$\mathbf{J}(\Gamma), \mathbf{B}(\Gamma) = O(1)$$
, then $\langle \mathbf{J}(0)\mathbf{B}(t_{\text{Newton}}) \rangle_{eq} = O(1/N)$ and,

$$< \mathbf{J}(0)\mathbf{B}(\mathbf{t}_{\text{Newton}}) >_{\text{eq}} - < \mathbf{J}(0)\mathbf{B}(\mathbf{t}_{\text{thermo}}) >_{\text{eq}} = O(1/N^2)$$

• For the infinite family of μ -thermostats,

 $\dot{p}_{i\beta} = F_{i\beta} - \alpha Sgn(p_{i\beta}) \mid p \mid_{i\beta}^{\mu}, \quad \beta = x, y, z$

Only μ =1 generates an equilibrium state.

Green-Kubo Relations for linear thermal (Navier Stokes) Transport Coefficients

1 Self Diffusion coefficient

$$D = \frac{1}{3} \int_0^\infty ds < \mathbf{v}_i(0) \cdot \mathbf{v}_i(s) >_{eq}$$

2 Thermal Conductivity

$$\lambda = \frac{V}{3k_{B}T^{2}} \int_{0}^{\infty} ds < \mathbf{J}_{Q}(0) \cdot \mathbf{J}_{Q}(s) >_{eq}$$

3 Shear Viscosity

$$\eta = \frac{V}{k_{\rm B}T} \int_0^\infty ds < P_{\rm xy}(0) P_{\rm xy}(s) >_{\rm eq}$$

4 Bulk Viscosity

$$\eta_{V} = \frac{1}{Vk_{B}T} \int_{0}^{\infty} ds < [p(0)V(0) - < pV >][p(s)V(s) - < pV >]_{eq}$$

NEMD Algorithms for Navier-Stokes transport coefficients.

Dolls Tensor algorithm for flow, $H = H_0 + \sum q_i p_i : (\nabla u(t))^T$

$$\begin{split} \dot{\mathbf{q}}_{i} &= \frac{\mathbf{p}_{i}}{m} + \mathbf{q}_{i} \cdot \nabla \mathbf{u} \\ \dot{\mathbf{p}}_{i} &= \mathbf{F}_{i} - \nabla \mathbf{u} \cdot \mathbf{p}_{i} - \alpha \mathbf{p}_{i} \end{split}$$

(Hoover, Evans, Hickman, Ladd, Ashurst, Moran (1980)).

Evans Heat Flow algorithm

$$\dot{\mathbf{q}}_{i} = \frac{\mathbf{p}_{i}}{m}$$
$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - (\mathbf{E}_{i} - \overline{\mathbf{E}})\mathbf{F}$$
$$-\frac{1}{2}\sum_{j=1}^{N}\mathbf{F}_{ij}\mathbf{q}_{ij}\cdot\mathbf{F} + \frac{1}{2N}\sum_{j,k=1}^{N}\mathbf{F}_{jk}\mathbf{q}_{jk}\cdot\mathbf{F} - \alpha\mathbf{p}_{i}$$

where (Evans, (1982)).

$$\overline{E} = \{\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j}^{N} \Phi_{ij}\} / N$$

Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008 *Colour Conductivity* algorithm for self diffusion

$$\dot{\mathbf{q}}_{i} = \frac{\mathbf{p}_{i}}{m}$$
$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \mathbf{i}\mathbf{c}_{i}\mathbf{F}_{c} - \alpha(\mathbf{p}_{i} - \mathbf{i}\mathbf{c}_{i}\mathbf{J}_{x} / \rho)$$

where

$$J_{x} = \frac{1}{V} \sum_{i=1}^{N} c_{i} \dot{x}_{i} \text{ and } \sum_{i=1}^{N} (\mathbf{p}_{i} - ic_{i} J_{x} / \rho)^{2} / m = 3Nk_{B}T$$

(Evans and Morriss (1983)).

Sllod algorithm for shear viscosity is exact for adiabatic planar shear flow

$$\dot{\mathbf{q}}_{i} = \frac{\mathbf{p}_{i}}{m} + \mathbf{q}_{i} \cdot \nabla \mathbf{u}$$
, which is equivalent to: $\ddot{\mathbf{q}}_{i} = \frac{\mathbf{F}_{i}}{m} + \mathbf{i}\gamma\delta(t)y_{i}$

(Evans and Morriss (1984)).

The shear flow algorithms must be accompanied by appropriate periodic boundary conditions - (Lees, Edwards (1972)).

For each algorithm, the Navier-Stokes transport coefficient, L, is evaluated as

$$L(0) = \lim_{F \to 0} \lim_{t \to \infty} \frac{1}{F_e t} \int_0^t ds J(s)$$

Note: NEMD algorithms and Green Kubo relations are also known for thermal and mutual diffusion (Soret and Dufour effects) in nonideal binary mixtures, and for the 12 or so viscosity coefficients of nematic liquid crystals.

Advantages of NEMD over Green-Kubo:

- Nonlinear transport can be studied. GK is solely for linear transport.
- Can study structural changes induced in systems by the nonequilium fluxes and forces.
- Is usually more efficient than GK.



Newton's Constitutive Relation for Shear Flow

Lees-Edwards periodic boundary conditions for shear flow



Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008

The Sllod equations of motion are equivalent to Newton's equations for $t > 0^+$, with a linear shift applied to the initial x-velocities of the particles.

Sllod algorithm for shear viscosity

$$\dot{\mathbf{q}}_{i} = \frac{\mathbf{p}_{i}}{m} + \mathbf{i}\gamma y_{i}$$

 $\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \mathbf{i}\gamma p_{yi} - \alpha \mathbf{p}_{i}$, which is equivalent to: $\ddot{\mathbf{q}}_{i} = \frac{\mathbf{F}_{i}}{m} + \mathbf{i}\gamma\delta(t)y_{i}$



Therefore Sllod is exact arbitrarily far from equilibrium.



We compare the results of direct NEMD simulation against Kawasaki and TTCF for 2-particle colour conductivity.



Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008
Instability of Phase Space Trajectories



The deformation of a small initial phase space volume element, $\delta V_{\Gamma(0)}$ around $\Gamma(0)$ to an evolved volume element $\delta V_{\Gamma(t)}$. Both volume elements contain the same number of ensemble members.



The mother and first daughter trajectories $\Gamma_0(t)$, $\Gamma_1(t)$ evolve according to the natural dynamics of the system. The first daughter is infinitesmally close to mother $|\Gamma_0(t) - \Gamma_1(t)| \rightarrow 0$. The largest lyapunov exponent λ_1 is defined,

 $\lim_{t\to\infty} |\Gamma_1(t) - \Gamma_0(t)| = |\Gamma_1(0) - \Gamma_0(0)| e^{\lambda_1 t}$

If we now choose a second infinitesmally nearby daughter trajectory, $\Gamma_2(t)$, such that,

Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008

$$(\Gamma_1(t) - \Gamma_0(t)) \cdot (\Gamma_2(t) - \Gamma_0(t)) = 0, \forall t,$$

then the second largest Lyapunov exponent is defined as,

 $\lim_{t\to\infty} |\Gamma_2(t) - \Gamma_0(t)| = |\Gamma_2(0) - \Gamma_0(0)| e^{\lambda_2 t}.$

There are 6N Lyapunov exponents $\{\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4,\}$. The 6N dimensional phase space volume evolves as,

$$\lim_{t \to \infty} \lim_{\delta V(\mathbf{\Gamma}, 0) \to 0} \delta V(\mathbf{\Gamma}(t), t) = \delta V(\mathbf{\Gamma}, 0) \exp\left[\sum_{i=1}^{6N} \lambda_i t\right]$$

The Liouville equation states that, $(1/f)df/dt = 3N\alpha$. We can see that the accessible volume of phase space, V~1/f, decreases to zero.

$$\lim_{t \to \infty} \overline{\int d\Gamma f(\Gamma, t) \frac{d \ln[f(\Gamma, t)]}{dt}} = -\left\langle \frac{d \ln \delta V(\Gamma(t))}{dt} \right\rangle_{F_e} = -\sum_{i=1}^{6N} \lambda_i = 3N \langle \alpha \rangle_{F_e}$$

If $\dot{H}_0 = 0 = -P_{xy}\gamma V - \alpha \sum p_i^2 / m$ then for **isoenergetic** shear flow in a nonequilibrium steady state

$$\eta(\gamma) = \frac{-k_{\rm B}T}{V\gamma^2} \sum_{i=1}^{6N} \lambda_i(\gamma)$$

We this the Lyapunov Sum Rule for shear viscosity (Posch and Hoover (1988)).

Conjugate Pairing Rule

:

For Hamiltonian systems, or more precisely *symplectic* systems that are thermostatted by a homogeneous Gaussian thermostat, ergostat or Nose-Hoover thermostat, the Lyapunov exponents occur in conjugate pairs, λ_i , λ_i' .

$$\lambda_i + \lambda_{i'} = - < \alpha > = 2\overline{\lambda}$$

This relationship is referred to as the *Conjugate Pairing Rule*, (Evans Cohen and Morriss (1990)).



Lyapunov spectrum for colour conductivity.

3

2

1



ă ^ă ă

×

X

×□

ъъ^ъ

Lyapunov spectrum for thermostatted shear flow.

Using the Conjugate Pairing Rule the shear viscosity can be related to the maximal Lyapunov exponents,

X

X

M

ď

$$\eta(\gamma) = \frac{-3nk_{B}T}{\gamma^{2}} [\lambda_{max}(\gamma) + \lambda_{min}(\gamma)],$$

In order to calculate λ_{min} , normally an **extraordinarily** difficult task; we calculate the largest Lyapunov exponent for the time reversed *anti-steady state*:



 λ_{\min} (steady state) = $-\lambda_{\max}$ (anti steady state)

Observation: Anti steady states are less stable than the usual steady state but that is **NOT** why entropy production is positive.



The figure above compares the shear viscosity computed directly using NEMD with the value obtained using the Conjugate Pairing Rule.

Three lectures on NonEquilibrium Stat Mech at ORNL, April 2008 **Transport Coefficients and the Kaplan-Yorke Dimension**

The Kaplan-Yorke dimension of a nonequilibrium steady state is defined as,

$$D_{KY} = N_{KY} + \sum_{i=1}^{N_{KY}} \lambda_i / \lambda_{N_{KY}+1}$$

 N_{KY} is the largest integer for which $\sum_{i=1}^{N_{KY}} \lambda_i > 0$



Then from this definition one can derive an exact formula for the linear transport coefficient (Evans, Cohen, Searles & Bonetto (2000)).

$$L(0) = \lim_{F_{e} \to 0} \frac{(2dN - f - D_{KY}(F_{e}))\lambda_{max}(F_{e} = 0)nk_{B}T}{NF_{e}^{2}}$$

This equation has a status that is equivalent to that of a Green-Kubo relation for transport coefficients.

The corresponding expression for the Kaplan-Yorke dimension of the steady state attractor is,

$$D_{KY}(F_e) = 2dN - f - \frac{L(0)F_e^2V}{\lambda_{max}(F_e = 0)k_BT} + O(F_e^4)$$

In practice the dimensional reduction in real non turbulent Navier-Stokes fluids is tiny $O(1/N_A)$!!

Summary: Exact formulae for transport coefficients

Constitutive Equation - definition:

$$J(F_e) \equiv -L(F_e)F_e$$

Green-Kubo relation:

$$\lim_{F_e \to 0} \langle \mathbf{J}(t) \rangle = -\beta V \int_0^t ds \langle \mathbf{J}(0) \mathbf{J}(s) \rangle_{eq} \bullet \mathbf{F}_e \equiv L(0) \mathbf{F}_e$$

Kaplan-Yorke relation:

$$L(0) = \lim_{F_{e} \to 0} \frac{(2dN - f - D_{KY}(F_{e}))\lambda_{max}(F_{e} = 0)nk_{B}T}{NF_{e}^{2}}$$

Transient Time Correlation Function:

$$< \mathbf{J}(t) >= -\beta V \int_0^t ds < \mathbf{J}(0) \mathbf{J}(s) > \mathbf{\bullet} \mathbf{F}_e \equiv L(\mathbf{F}_e) \mathbf{F}_e$$

Kawasaki:

$$\langle \mathbf{J}(t) \rangle = \left\langle \mathbf{J}(0) \exp[-\beta \int_0^t \mathrm{ds} \, \mathbf{J}(-s) \bullet \mathbf{F}_e] \right\rangle \equiv L(\mathbf{F}_e) \mathbf{F}_e$$

Conjugate Pairing Rule:

$$L(F_{e}) = \frac{-3nk_{B}T}{F_{e}^{2}} [\lambda_{max}(F_{e}) + \lambda_{min}(F_{e})],$$

REFERENCES

Nonlinear Response Theory: D. J. Evans and G. P. Morriss, Statistical Mechanics of NonEquilibrium Liquids (Academic Press, London, 1990).

Proof of Conjugate Pairing Rule: D. J. Evans, E. G. D. Cohen and G. P. Morriss, Phys. Rev., A42 (1990) 5990.

Numerical Tests of Conjugate Pairing Rule: S. Sarman, D.J. Evans, and G. P. Morriss, Phys. Rev., A45 (1992) 2233.