Langevin equations for slow degrees of freedom of Hamiltonian systems

R.S.MacKay

University of Warwick

Outline

1. Introduction
2. Assumptions
3. Aim
4. Strategy
5. Overdamped case
6. Quantum degrees of freedom
7. Kinetics out of chemical equilibrium
8. Conclusion/Comments

1. Introduction

- Suppose a Hamiltonian system consisting of some slow degrees of freedom coupled to a high-dimensional chaotic system (e.g. conformations of a biomolecule coupled to vibrations, water movement etc).
- Would like to derive a Langevin equation for the slow degrees of freedom (i.e. an effective Hamiltonian + damping + noise).
- Precursors: Ford,Kac&Mazur; Zwanzig;

  Ott; Wilkinson; Berry&Robbins; Jarzynski…

2. Assumptions

- Gallavotti-Cohen “chaotic hypothesis”: chaotic Hamiltonian systems can be treated as if mixing Anosov on each energy level.
- Anosov condition is unlikely to hold, but it allows some nice theory, aspects of which are likely to hold more generally.
- A low-dimensional mechanical example:

The triple linkage

Assumptions in detail

- Symplectic manifold (M,ω), dim $M = 2m$
- Hamiltonian H, vector field $X(H)$, flow φ_t
- Poisson map $\pi: M \to N = R^{2n}$ locally, $n << m$
- for each Z in N, $\pi^{-1}(Z)$ is a symplectic submanifold of M; then the restriction H_Z of H to $\pi^{-1}(Z)$ defines constrained dynamics $X(H_Z)$ preserving volume $\Omega=\omega^{\wedge(m-n)}$, value of H, and “ergode” μ on $H_Z^{-1}(E)$ def by $\mu \wedge dH=\Omega$.
- $V_j=\{H,Z_j\pi\}$ are slow compared to $X(H_Z)$.
- $X(H_Z)$ is mixing Anosov on $H_Z^{-1}(E)$; in particular, autocorrelation of deviation ζ of V from its mean decays on short time ε compared to significant change in Z
- Size of ζ is of order $\varepsilon^{-1/2}$ on slow timescale.

3. Aim

to show the distribution of paths $\pi\varphi_t(Y)$ for random Y wrt μ on $(\pi x H)^{-1}(Z_0,E_0)$ is close to that for the solutions of a stochastic ODE

$$dZ = (J-\beta D)\ \nabla F\ dt + \sigma\ dW,\ Z(0)=Z_0,$$

with J representing the Poisson bracket on N, F = free energy function on N, β = inverse temperature, W a multidimensional Wiener process, Einstein-Sutherland relation $D+D^T = \sigma\sigma^T$, and Klimontovich interpretation.

4. Strategy: (a) Zeroth order mean velocity

- Let $W_Z(E) = \int_{H\leq E} \Omega$ on $\pi^{-1}(Z)$
- Anosov-Kasuga adiabatic invariant for slow Z when $H^{-1}(E)$ ergodic: $W_{Z(t)}(E(t)) \approx w_0$.
- Let $\lambda = \mu/W_Z'(E)$, normalised ergode
- $\lambda(V) = J\,\nabla f$, where $f(Z) = W_Z^{-1}(w_0)$, “microcanonical free energy”.
- Alternatively, start in canonical ensemble $d\nu = e^{-\beta(H-F)}\,\Omega(dY)$ on $\pi^{-1}(Z)$ (“monode”) and find $\nu(V) = J\nabla F$, but not obvious how to continue.

(b) Fluctuations

- The fluctuations $\zeta(t)$ from the mean can be approximated by a multidimensional white noise σ dW/dt with covariance
  $\sigma\sigma^T = \int ds\ \lambda(\zeta(t)\zeta(s)) = D+D^T$.
- Proofs at various levels, e.g. Melbourne&Nicol for the strongest.
- Refinement of π to make correlations decay as rapidly as possible could be useful to increase accuracy.

(c) Correction to λ

- If Z(t) is varied slowly, the measure on $\pi^{-1}(Z(t))$ starting with λ for given w_0 at $t=-\infty$ lags behind that for t.
- Ruelle's formula for 1st order change in SRB for t-dependent mixing Anosov system:

  $\delta\langle O(t)\rangle = \int^t ds \langle d(O\varphi_{ts})\delta X_s\rangle$

  for any observable O (φ_{ts}= flow from s to t).
- In particular (assuming w_0 conserved), find

  $\delta\langle V\rangle = (W'D)'/W' \, J \, dZ/dt \approx -\beta D\nabla F$, with

  $D_{ij} = \int^t ds \, \lambda(\zeta_i(s)\zeta_j(t))$, $\zeta = V-\lambda(V)$ along constrained orbits, $\beta = (\log W')' = 1/T$.

(d) Put together

- Adding the preceding ingredients yields

  $V = (J-\beta D)\,\nabla f + \sigma\, dW/dt$

  to first order.
- Now remove constraint of externally imposed Z(t): hope to get

  $dZ/dt = V = (J-\beta D)\,\nabla f + \sigma\, dW/dt$,

  but have to examine correlations.

(e) Micro to canonical

- For m large, $f \approx F + cst$, canonical free energy, because

$\nabla F = \int e^{-\beta E} W_Z'(E)\, \nabla f\, dE \,/ \int e^{-\beta E} W_Z'(E)\, dE$

and $e^{-\beta E} W_Z'(E)$ is sharply peaked around E_0 for which $(\log W')' = \beta$ (large deviation theory)

- If σ depends on Z, Klimontovich interpretation is necessary to make $e^{-\beta F}\, \omega^{\wedge n}$ stationary

5. Overdamped case

- If $N=T^*L$, $H(Q,P,z) = P^T M^{-1} P/2 + h(Q,z)$ then $F(Q,P) = P^T M^{-1} P/2 + G(Q)$ and D has PP-block only and indpt of P
- If motion of Q is slow on time $T|MD^{-1}|$ then P relaxes onto a slow manifold and get further reduction to

  $dQ = -TD^{-1}\nabla G\, dt + 2T\sigma^{-T}\, dW$ on L

6. Quantum DoF

- Quantum Mechanics is Hamiltonian: for Hermitian operator h on complex Hilbert space U, take M = P(U) with Fubini-Study form, and $H(\psi) = <\psi|h\psi>/<\psi|\psi>$; gives Schrodinger evolution $i\, d\psi/dt = h\psi$.
- Or take M = (dual of) Lie algebra of Hermitian operators on U with inner product $<A,B> = \mathrm{Tr}\, AB$ and its Lie-Poisson bracket, and $H(A) = \mathrm{Tr}\, hA$; gives von Neumann $dA/dt = -i\,[h,A]$.
- So can incorporate quantum DoF, e.g. electrons in rhodopsin conformation change.
- Not Anosov, but maybe not really required.

7. Kinetics out of chemical equilibrium

- N can be a covering space, e.g. base= conformation of myosin, decks differ by number of ATP
- Need to adapt for constant pressure

8. Conclusion/Comments

- Mathematical justification of the Langevin equation looks possible.
- Can probably extend to some non-Anosov fast dynamics, e.g. partial hyperbolicity + accessibility may suffice for Ruelle formula.
- Main interest may be ways in which the above program can fail, e.g. no gap in spectrum of timescales.