# Langevin equation for slow degrees of freedom of Hamiltonian systems

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$$m\frac{d^2x}{dt^2} = -6\pi\mu a\frac{dx}{dt} + X.$$

- Sur la théorie du mouvement brownien, Comptes Rendus Acad Sci Paris 146 (1908) 530-3

# Outline

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7. Kinetics out of chemical equilibrium
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# 1. Introduction

- Suppose a Hamiltonian system consists 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).
- Derive a Langevin equation for the slow degrees of freedom (i.e. an effective Hamiltonian + damping + noise).
- Precursors: Ford,Kac&Mazur; Zwanzig; Mori&Zwanzig, van Kampen, Ottinger; 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 $(M,\omega)$, dim $M = 2m$
- Hamiltonian $H$, vector field $X(H)$, $i_X\omega=dH$, flow $\varphi_t$
- 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" $\mu$ on $H_Z^{-1}(E)$ def by $\mu\wedge dH=\Omega$.
- $V_j=\{Z_j\pi,H\}$ are slow compared to $X(H_Z)$.
- $X(H_Z)$ is mixing Anosov on $H_Z^{-1}(E)$; in particular, autocorrelation of deviation $v$ of $V$ from its mean decays on short time $\varepsilon$ compared to significant change in $Z$
- Size of $v$ is of order $\varepsilon^{-1/2}$ on slow timescale.
- Fast system has bounded specific heat.

# 3. Aim

Show the distribution of paths $\pi\varphi_t(Y)$ for random Y wrt $\mu$ 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, $\beta$ = 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" [see next]
- 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.

# Proof

The following calculation shows that

$$\lambda(V) = J\nabla f. \tag{5}$$

Firstly, $W_Z(f(Z)) = w_0$, so $\nabla W + W'\nabla f = 0$, i.e.

$$\nabla f = -\frac{1}{W'}\nabla W. \tag{6}$$

Thus $(J\nabla f)_j = \{Z_j, f\} = -\frac{1}{W'}\{Z_j, W\}$. Next, the flow $\chi_u$ of $X_{Z_j\circ\pi}$ preserves $\Omega$ (because it is Hamiltonian) and the fibration $\pi$ (because $\pi$ is Poisson). Thus the change of $W_Z(E) = \int_{\{H\leq E\}}\Omega$ from $Z(0)$ to $Z(u)$ along the flow $\chi_u$ is the $\Omega$-measure of the band in $\pi^{-1}(Z(u))$ between $H^{-1}(E)$ and $\chi_u((H,Z)^{-1}(E,Z(0))$. The rate of change of $H$ along the flow $\chi_u$ is $\{H, Z_j\circ\pi\}$ and we can write $\Omega = \mu\wedge dH$ in a fibre, so

$$\{W, Z_j\} = -\int_{H^{-1}(E)}\{H, Z_j\circ\pi\}\mu.$$

Finally, $\lambda(V_j) = \frac{1}{W'}\int_{H^{-1}(E)}\{Z_j\circ\pi, H\}\mu$.

# (b) Fluctuations

- The fluctuations $v(t)$ from the mean can be approximated by a multidimensional white noise $\sigma\, dW/dt$ with covariance

  $\sigma\sigma^T = \int ds\, \lambda(v(t)v(s)) = D+D^T$.

- Proofs at various levels, e.g. Green-Kubo for the weakest [see next], Melbourne&Nicol vector-valued almost sure invariance principle for the strongest.
- Refinement of $\pi$ to make correlations decay as rapidly as possible could be useful to increase accuracy.

# Proof

The simplest version is to let $z(t) = \int_0^t v(s)\, ds$ (I denote it by $z$ rather than $Z$ because this expression does not include the mean velocity of $Z$ nor the fact that the distribution of $v$ changes as $Z$ moves) and prove that

$$\lambda(z_i(t)z_j(t))/t \to R_{ij}$$

as $t \to +\infty$ (Green-Kubo formula).

Here is a proof. From the definitions of $z$ and $C$, $\lambda(z_i(t)z_j(t)) = \int_{-t}^t (t - |u|)C_{ij}(u)\, du$. So

$$\lambda(z_i(t)z_j(t))/t = \int_{-t}^t (1 - \frac{|u|}{t})C_{ij}(u)\, du.$$

Tackle the positive and negative ranges of $u$ separately. Convergence of the integral for $R$ implies that given $\varepsilon > 0$ there is a $t_0$ such that $|\int_u^t C(v)\, dv| \le \varepsilon$ for all $t \ge u \ge t_0$. Then for $t \ge t_0$,

$$\int_0^\infty C(u)\, du - \int_0^t (1 - \frac{u}{t})C(u)\, du = \int_t^\infty C(u)\, du + \frac{1}{t}\int_0^{t_0} uC(u)\, du + \frac{1}{t}\int_0^t \int_{\max(u,t_0)}^t C(v)\, dv\, du.$$

The first and third terms are each at most $\varepsilon$ in absolute value. The second is at most $\varepsilon$ as soon as $t \ge \frac{1}{\varepsilon}\int_0^{t_0} uC(u)\, du$. Hence $\int_0^t (1 - \frac{u}{t})C(u)\, du \to \int_0^\infty C(u)\, du$ as $t \to \infty$. Similarly for $u < 0$ and hence the result. Note that in contrast to a statement in [Ga] it is not necessary to assume $\frac{1}{T}\int_{-T}^T |t|C(t)\, dt \to 0$ as $T \to \infty$: it follows automatically from $\int_{-\infty}^\infty C(t)\, dt < \infty$.

# (c) Correction to $\lambda$

- If $Z(t)$ is varied slowly, the measure on $\pi^{-1}(Z(t))$ starting with $\lambda$ for given $w_0$ at $t=-\infty$ (Stosszahlansatz) 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 ($\varphi_{ts}$= 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

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

# Proof

Let us calculate the change in the mean of $V$ due to slow motion of $Z$. For $X_t$ we use $X_{H_{Z(t)}}$ and for the ensemble average we use $\lambda_{Z(t),E}$. Any motion of $Z$ can be specified as the result of a (possibly time-dependent) Hamiltonian flow on $N$, with some Hamiltonian $G$, so $\dot{Z} = J\nabla G$. The function $G$ lifts to $G \circ \pi$ on $M$ and so induces a fibre-preserving flow $\chi$ on $M$, which we can use to identify points of different fibres. In particular for $X_s$ in Ruelle's formula we can use $\chi^*_{ts} X_{H_{Z(s)}}$, which can be written as $X_{(H\circ\chi_{st})_{Z(t)}}$. Then

$$d(V_j \circ \psi_{ts})X_s = \{V_j \circ \psi_{ts}, H \circ \chi_{st}\}_{Z(t)}, \tag{9}$$

where $\{,\}_Z$ is the Poisson bracket on $\pi^{-1}(Z)$, defined via the restriction of the symplectic form to the fibre. Thus Ruelle's formula gives a time-integral of an energy-level average of a Poisson bracket on a fibre.

**Lemma**: For symplectic manifold $K$ with volume form $\Omega$, Hamiltonian $H$, energy level $E$, normalised energy level volume $\lambda_E$ and any smooth functions $F, G : K \to \mathbb{R}$ for which the required integrals converge,

$$\int \{F, G\}\, d\lambda_E = \frac{1}{W'(E)} \frac{\partial}{\partial E}\left(W'(E) \int \{F, H\} G\, d\lambda_E\right). \tag{10}$$

**Proof**: For any smooth functions $F, U : K \to \mathbb{R}$ for which the integral converges,

$$\int \{F, U\}\, d\Omega = \int dF(X_U)\, d\Omega = 0,$$

because it is the integral of the rate of change of $F$ along orbits of $X_U$ with respect to an invariant measure. Apply this to a product $U = GA$ and use Leibniz' rule and antisymmetry for Poisson brackets to deduce that

$$\int A\{F, G\}\, d\Omega = \int \{A, F\} G\, d\Omega. \tag{11}$$

Now take $A$ to be (a sequence of smooth approximations to) $\delta(E - H)$:

$$\int \delta(E-H)\{F,G\}\, d\Omega = \int \{\delta(E-H), F\} G\, d\Omega = -\int \delta'(E-H)\{H,F\} G\, d\Omega, \tag{12}$$

since $\{., F\}$ is a derivation. The right hand side can be written as

$$\frac{\partial}{\partial E} \int \delta(E-H)\{F,H\} G\, d\Omega.$$

All that remains is to write $\delta(E-H)\, d\Omega = W'(E)\, d\lambda$ on both sides. $\square$

Applying the lemma to (9) produces

$$\delta\langle V_j\rangle = \frac{1}{W'(E)}\frac{\partial}{\partial E}\left(W'(E)\int_{-\infty}^{t} ds\langle\{H, H\circ\chi_{st}\}_Z V_j\circ\psi_{ts}\rangle\right). \tag{13}$$

Now

$$\frac{\partial}{\partial s}H\circ\chi_{st} = -\{H, G\circ\pi\}_M,$$

so for times $s$ out to some decorrelation time, which we supposed to be $\varepsilon \ll 1$, we can write to leading order

$$\{H, H\circ\chi_{st}\} = (t-s)\{H,\{H,G\circ\pi\}_M\}_Z.$$

Specialising to $G = Z_k$ gives $\{H, G\circ\pi\}_M = -V_k$. So the integral in (13) becomes

$$\int_{-\infty}^{t} ds\ (t-s)\langle\{H, V_k\}_Z(s)V_j(t)\rangle.$$

To justify this approximation properly requires some hypothesis on the rate of decay of the correlation function of $v$ (probably $\int_{-\infty}^{0}|tC(t)|\ dt < \infty$ suffices). Now $\{H, V_k\}_Z = -\frac{dV_k}{ds}$ along the flow of $X_{H_Z}$, so integration by parts (with again some assumption about sufficiently rapid convergence of the autocorrelation integral) transforms the integral to

$$-\int_{-\infty}^{t} ds\langle(V_k(s) - \langle V_k\rangle)V_j(t)\rangle = -D_{jk},$$

with $D$ given by (2). Taking $G$ to be an arbitrary linear combination of $Z_k$ yields

$$\delta\langle V(t)\rangle = -\frac{(W'D)'}{W'}J^{-1}\dot{Z}. \tag{14}$$

# (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) and conservation of W: hope to get

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

  need to examine correlations (cf.Kifer).

# (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, assuming specific heat bounded) [see next]
- If $\sigma$ depends on Z, Klimontovich interpretation is necessary to make $e^{-\beta F}\, \omega^{\wedge n}$ stationary (but probably differences are beneath this order of approximation)

# Proof

$$\nabla F = \int e^{-\beta_0 E} W' \nabla f \; dE \; / \int e^{-\beta_0 E} W' \; dE.$$

For large $k = m - n$, assume the heat capacity per degree of freedom $c(\epsilon) = \frac{1}{kT'(k\epsilon)}$ as a function of the energy $\epsilon$ per degree of freedom is positive and bounded uniformly in $k$ (say for simplicity that the limit as $k \to \infty$ exists). It follows by integration that $\beta(E) = 1/T(E)$ is a function of $\epsilon$ nearly independent of $k$, and by another integration the same for $\frac{1}{k} \log W'(E)$; write the latter as $s(\epsilon)$, the entropy per degree of freedom. Then the function $e^{-\beta_0 E} W'(E)$ of $E$ is approximately $e^{-k(\beta_0 \epsilon - s(\epsilon))}$, which is sharply peaked around the $\epsilon_0$ such that $s'(\epsilon_0) = \beta_0$ (because $s''(\epsilon) = -\frac{\beta^2}{c(\epsilon)} < 0$), i.e. $\beta(E_0) = \beta_0$ . Thus $\nabla F$ for $\beta_0$ is approximated by $\nabla f$ for this $E_0$.

# 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

  as used by biochemists.

# 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 $H(\psi) = \langle\psi|h\psi\rangle/\langle\psi|\psi\rangle$; gives Schrodinger evolution $i\, d\psi/dt = h\psi$.
- Or take M = (dual of) Lie algebra of Hermitian operators on U with inner product $\langle A,B\rangle = \mathrm{Tr}\, AB$ 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 (e.g. Eyink et al).
- Main interest may be ways in which the above program can fail, e.g. no gap in spectrum of timescales, heat bath with long-time correlations.
- Reference: RS MacKay, Langevin equation for slow degrees of freedom of Hamiltonian systems, in: ``Nonlinear Dynamics and Chaos'', eds M Theil, J Kurths, MC Romano, G Karolyi, A Moura (Springer, 2010) 89 -102.