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Brownian dynamics

Recall again the Langevin equations for a single particle in a potential:

$$\begin{cases} \dot{q} = \dfrac{p}{m} = v \\ \dot{p} = -\dfrac{\partial V}{\partial q}(q) - \gamma v + \sqrt{2\gamma kT}\, W(t) \end{cases}$$

The velocity relaxes to equilibrium (Maxwell - Boltzmann) distribution at a time scale $\tau = m/\gamma$. In the limit $\tau \to 0$ diffusion of position will be much slower: <u>overdamped</u>

In the <u>overdamped</u> or <u>Brownian dynamics</u> limit, we want to coarse-grain by eliminati[ng] v (p) as a fast variable and only keep q. We expect a stochastic ODE of the diffusive type for q, but what is it?

Let's switch to differential notation

B ≡ Brownian motion

$$\begin{cases} dq = v\,dt \\ dv = -\dfrac{\gamma(q)}{m}\underbrace{(v\,dt)}_{=\,dq} + \dfrac{F}{m}(q)\,dt + \sqrt{\dfrac{2kT\gamma(q)}{m^2}}\cdot dB \end{cases}$$

and then solve for dq

$$dq = -\frac{m}{\gamma}\,dv + \frac{F}{\gamma}\,dt + \sqrt{\frac{2kT}{\gamma}}\,dB$$

The tricky term is $\gamma^{-1}dv$, since v is a fast variable. Use that

$$\gamma^{-1}dv = d(\gamma^{-1}v) - \left[\frac{d}{dx}(\gamma^{-1})\,dx\right]\cdot v$$

$$= d(\gamma^{-1}v) - (\gamma^{-1})'\cdot v^2\,dt$$

Taking expectation values over $\underline{\underline{\text{fast}}}$ var

$$\langle \gamma^{-1}dv\rangle_v = -(\gamma^{-1})'\cdot\langle v^2\rangle\,dt$$

$\frac{kT}{m}$ Maxwell-Boltzmann distributi

Due to equipartition

Therefore

$$\left\langle -\frac{m}{\gamma}\, dv \right\rangle_{\text{fast } v} = (k_B T)\frac{d}{dx}\left(\gamma^{-1}\right)\, dt$$

Denote

$$\begin{cases} D = \dfrac{kT}{\gamma} \leftarrow \text{diffusion coefficient} \\ \quad = kT \cdot M(x) \leftarrow \underline{\text{mobility}} \text{ (inverse friction)} \end{cases}$$

$$dq = \left[M \cdot F + (kT)\frac{dM}{dx} \right] dt + \sqrt{2kTM} \cdot dB$$

In the multivariable case

$$\dot{q} = -M\left[\nabla_q V(q)\right] + (kT)\left(\nabla_q \cdot M\right) + \left(2kT \cdot M\right)^{1/2} W($$

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This calculation showed that the SODE that describes the dynamics of the position of the Brownian particle is the overdamped Langevin eq:

ITO form:

$$\boxed{\dot{q} = -M \cdot \nabla_q V + (kT)(\nabla_q \cdot M) + \sqrt{2kT} \cdot \tilde{M} \cdot \mathcal{W}(t)}$$

where $\tilde{M}\tilde{M}^* = M$ is the stochastic forcing covariance

fluctuation-dissipation balance

Observe that this is an Ito equation but the (spurious) drift $(kT)(\nabla_q \cdot M)$ would disappear if anti-Ito

The Fokker-Planck equation corresponding to the overdamped Langevin equation is an <u>advection-diffusion</u> equation in phase space:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial \mathbf{q}} \cdot \left\{ \left[-M \nabla_q V + (kT)(\nabla_q \cdot M) \right] P \right\}$$

$$+ \frac{\partial^2}{\partial q^2} : \left[(kT) M P \right]$$

combine terms

$$\boxed{\frac{\partial P}{\partial t} = \frac{\partial}{\partial q} \cdot \left[(M \nabla_q V) P + (kT) M \frac{\partial P}{\partial q} \right]}$$

advective flux

diffusive flux

How do we check if this is a reasonable FPE? Note that at the level of FPE there is no ambiguity ala Ito / Stratonovich.

First check: Equilibrium distribution must be Gibbs-Boltzmann:

$$\boxed{P_{eq}(q) = Z^{-1} \exp\left[-V(q)/kT\right]}$$

$$\Rightarrow \frac{\partial P}{\partial q} = -\frac{1}{kT}\left(\frac{\partial V}{\partial q}\right) P \quad \text{denote } \beta = \frac{1}{kT}$$

and

$$\Rightarrow \frac{\partial^2 P}{\partial q^2} = \beta^2 \left(\frac{\partial V}{\partial q}\right)\left(\frac{\partial V}{\partial q}\right)^T P - \beta \frac{\partial^2 V}{\partial q^2} P$$

At equilibrium:

$$\frac{\partial P}{\partial t} = \frac{\partial V}{\partial q} \cdot M \cdot \frac{\partial P}{\partial q} + \left(M : \frac{\partial^2 V}{\partial q^2} \right) P + \left(\frac{\partial}{\partial x} \cdot M \right) \cdot \frac{\partial V}{\partial q} P$$

$$+ \beta^{-1} M : \left(\frac{\partial^2 P}{\partial q^2} \right) + \beta^{-1} \left(\frac{\partial}{\partial x} \cdot M \right) \cdot \frac{\partial P}{\partial q}$$

tenser contraction

$$= P \Bigg[- \beta \left(\frac{\partial V}{\partial q} \cdot M \cdot \frac{\partial V}{\partial q} \right) + \left(M : \frac{\partial^2 V}{\partial q^2} \right) + \left(\frac{\partial}{\partial x} \cdot M \right) \cdot \frac{\partial V}{\partial q}$$

CANCEL

$$+ \beta \left(\frac{\partial V}{\partial q} \cdot M \cdot \frac{\partial V}{\partial q} \right) - \left(M : \frac{\partial^2 V}{\partial q^2} \right) - \left(\frac{\partial}{\partial x} \cdot M \right) \cdot \frac{\partial V}{\partial q} \Bigg]$$

fluctuation-dissipation balance

$$= 0$$ as it should!

A note on matrix expression derivatives: Perhaps the simplest way to make sure you get the order of matrices right is to use the repeated index convention

Notation:

- $\cdot$ $\equiv$ single index contraction (e.g. matrix-vector product)
- $:$ $\equiv$ double contraction
- $\otimes$ $\equiv$ tensor product (outer product)

Consider

$$\frac{\partial}{\partial q}\cdot\left(M\cdot\frac{\partial v}{\partial q}\right) \equiv \frac{\partial}{\partial q_i}\left(M\cdot\frac{\partial v}{\partial q}\right)_i = \frac{\partial}{\partial q_i}\left(M_{ij}\,\frac{\partial v}{\partial q_j}\right)$$

$$= \frac{\partial M_{ij}}{\partial q_i}\,\frac{\partial v}{\partial q_j} + M_{ij}\,\frac{\partial^2 v}{\partial q_i \partial q_j} \equiv \left(\frac{\partial}{\partial q}\cdot M\right)\cdot\frac{\partial v}{\partial q} + M : \frac{\partial^2 v}{\partial q^2}$$

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One can generalize the Langevin description to more general sets of coarse-grained variables x.

For systems in the canonical ensemble i.e. isothermal systems, one considers a coarse-grained Hamiltonian or a free energy that represents the effective Hamiltonian in terms of the chosen variables [see subsequent lectures]

$$\mathcal{H}(x) \equiv F(x)$$

A Markovian stochastic dynamics for x that preserves the <u>equilibrium distribution</u>

$$P_{eq}(x) = Z^{-1} \exp\left[-\beta H(x)\right]$$

is

"reversible" "irreversible" "fluctuations"

$$\begin{cases} \dot{x} = L \cdot \frac{\partial H}{\partial x} - \left(G G^{*}\right) \cdot \frac{\partial H}{\partial x} + (2kT)^{1/2} G \cdot W(t) \\ \quad + kT \frac{\partial}{\partial x} \cdot \left[G G^{*} - L \right] \end{cases}$$

spurious drift

or $G \cdot \left(\frac{\partial}{\partial x} \cdot G\right)$ less generally

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The reversible dynamics is <u>skew-adjoint</u> (just like Hamiltonian dynamics!)

$$\boxed{L^* = -L}$$

which implies "energy" conservation

$$\frac{dH}{dt} = \frac{\partial H}{\partial x} \cdot \frac{\partial x}{\partial t} = \frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial H}{\partial x} = 0$$

For <u>Hamiltonian</u> dynamics $\boxed{\frac{\partial}{\partial x} \cdot L = 0}$

Louiville theorem

but this is <u>not</u> true in general coarse-grained models.

In fact, the division of the generator of the Markov process into reversible and irreversible components is somewhat <u>arbitrary</u>: dissipation arises out of the same microscopic dynamics!

Only in the impossible limit $kT \to 0$ can one get away from <u>fluctuations</u> but then <u>dissipation</u> also vanishes! <u>BALANCE</u>

So think of

$$\boxed{\begin{gathered}\dot{x} = -M \cdot \frac{\partial H}{\partial x} + (2kT)^{1/2}\, \tilde{M} \cdot w(t) \quad \text{anti-Ito} \\ \tilde{M}\tilde{M}^{*} = (M+M^{*})/2\end{gathered}}$$

For an isolated system, i.e., the microcanonical ensemble, and assuming the internal energy can be written as a function of coarse-grained variables exactly, $E(x)$, then the GENERIC formalism of Öttinger is appropriate. It also requires expressing the entropy as a function of the coarse-grained variables, $S(x)$

EINSTEIN DISTRIBUTION
$$\boxed{P_{eq}(x) = Z^{-1} \exp\left[S(x) / k_B \right]}$$

$$\dot{x} = L\cdot\frac{\partial E}{\partial x} + M\cdot\frac{\partial S}{\partial x} + \sqrt{2k_BT}\,\tilde{M}\cdot W(t)$$

reversible (conservative)

irreversible (dissipative)

+ DRIFT!

$L^* = L$

(skew-adjoint)

$$\boxed{L\cdot\frac{\partial S}{\partial x} = 0}$$

$M^* = M$

(self-adjoint)

$$\boxed{M\cdot\frac{\partial E}{\partial x} = 0}$$

$$\boxed{\tilde{M}\tilde{M}^* = M}$$

fluctuation-dissipation balance

Fokker-Planck

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\cdot\left\{\left[L\cdot\frac{\partial E}{\partial x} + M\cdot\frac{\partial S}{\partial x}\right]P + k_BT\,M\cdot\frac{\partial}{\partial x}P\right\}$$

which preserves $\exp[S/k_B]$

This formalism can be generalized to <u>infinite-dimensional</u> systems, at least formally, notably, to the case when $X(t)$ includes <u>fields</u> such as density and velocity (fluctuating hydrodynamics). We will come back to this.

But first, it is important to consider numerical schemes for systems of SODE. (e.g., Brownian dynamics, Dissipative Particle Dynamics, Langevin dynamics, etc, Addendum to page 7

Recall SDE: coarse-grained Hamiltonian

$$\begin{cases} \dot{x} = L \cdot \frac{\partial H}{\partial x} - (GG^*) \cdot \frac{\partial H}{\partial x} + \sqrt{2kT} \cdot G \boxdot W(t) & [\text{anti-Ito}] \\ L^* = -L & \text{or } + kT \frac{\partial}{\partial x} \cdot (GG^*) \quad [\text{Ito}] \\ \frac{\partial}{\partial x} \cdot L = 0 & \end{cases}$$

Corresponding FPE (forward Kolmogorov)

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \cdot \left[(GG^*) \cdot \left(\frac{\partial H}{\partial x} P + kT \frac{\partial P}{\partial x} \right) \right] - \frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial P}{\partial x}$$

It is easy to show that

$$P_{eq}(x) = Z^{-1} e^{-H(x)/kT}$$

is the equilibrium distribution since

$$\frac{\partial P_{eq}}{\partial x} = -\frac{1}{(kT)} \frac{\partial H}{\partial x} P_{eq}$$

$$\Rightarrow \quad \frac{\partial H}{\partial x} P_{eq} + kT \frac{\partial P_{eq}}{\partial x} = 0$$

so there is identically no-flux in phase space for any G, if $L = 0$ (think detailed balance versus balance)

Also: $\frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial P_{eq}}{\partial x} \sim \frac{\partial H}{\partial x} \cdot L \cdot \frac{\partial H}{\partial x} = 0$ skew-symmetry