Path integral formulation of stochastic processes:

non-equilibrium reaction pathways, hyperdynamics, and enhanced sampling

Steve Fitzgerald

$$P(x_1, t_1) = \int \mathcal{D}x \, \mathrm{e}^{-\mathcal{S}[x]/4kT}$$

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New Mathematics for the Exascale: Applications to Materials Science

Department of Applied Mathematics

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Overview

- Introduction to path integral formulation
- Path integral hyperdynamics
  - Celia Reina, S Huang, I Graham, R Riggleman, P Arriata
- Finite-time transitions
  - Andy Archer, Amanda Hass, Grisell Díaz Leines
- Outlook and future directions

Research funded by EPSRC *fellowship*

Engineering and Physical Sciences Research Council

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Modelling stochastic processes

- Interplay between thermal fluctuations and mechanical forces controls many things*

- Two main mathematical modelling approaches:
  - Langevin (SDE)
  - Fokker-Planck (PDE)

$$\cancel{m\ddot{q}}(t) + \Gamma \dot{q}(t) = -V'(q) + \xi(t)$$

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q}\left(V'P + D\frac{\partial P}{\partial q}\right)$$

- Third way: *path integral*

$$\text{Prob.}(q_0 \to q; t) = \int_{\text{paths from } q_0 \to q;\, t} \text{d(paths) Prob.(path)}$$

*Pretty much everything!

Langevin equation

$$\boxed{\cancel{m\ddot{q}}(t) + \Gamma\dot{q}(t) = -V'(q) + \xi(t)}$$

- $q(t)$ is the position of the particle
- Inertial term neglected (reaches terminal velocity instantaneously, "overdamped")
- Γ is friction, $V(q)$ is potential, ξ is *noise*
- Simplest option is uncorrelated Gaussian white noise

$$\boxed{\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')}$$

- D is the noise strength; $\boxed{D = k_{\mathrm{B}}T/\Gamma}$ by fluctuation-dissipation theorem

$$\mathrm{d}Q_t = -V'(Q_t)\mathrm{d}t + \mathrm{d}\xi_t$$

maths

$$\dot{q}(t) + V'(q) = \xi(t)$$

physics

Fokker-Planck-Smoluchowski equation

$$\boxed{\frac{\partial P}{\partial t} = \frac{\partial}{\partial q}\left(V'P + D\frac{\partial P}{\partial q}\right)}$$

set $\Gamma = 1$

- $P(q,t)$ is the probability density
- No $\ddot{P}$ or velocity terms – still overdamped, no memory, *Markovian*
- Velocity dependence integrated out
- Initial condition $\boxed{P(q, t=0) = \delta(q - q_0)}$
- Returns to usual diffusion equation when $V = 0$

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Simulating stochastic processes

- MD: assign random initial velocities according to Boltzmann; evolve deterministic Hamiltonian dynamics *non-equilibrium constant energy*

  NVE

- Langevin dynamics: change the particle velocity at each timestep according to a specified thermostat *non-equilibrium constant temperature*

  NVT

- kinetic Monte Carlo: evolve system from state to state with probabilities according to rates…
  - *Much* longer timescales accessible, but:
  - Rates are based on equilibration at each state
  - Problems when rates for different transitions vary widely
  - Rates look like $Ae^{-\Delta V/kT}$, nonlinearity means this is common
  - May be OK at one temperature but not at another
  - *Discards all finite time information for average transition rate*

Many tricks available to accelerate, AMD, metadynamics, path integral hyperdynamics

See Danny Perez talk this morning!

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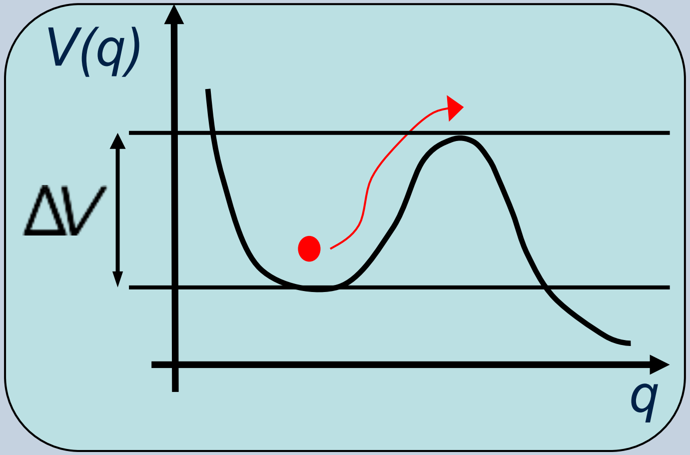
Transition rates

$$\dot{q}(t) = -V'(q) + \xi(t) \rightarrow Ae^{-\Delta V/kT}$$



- Particle moving in potential *V(q)*
- Friction scaled to 1 so $D = kT$

- Usual method: solve Fokker-Planck approximately for flux over barrier in long-time, weak-noise limit, get Kramers' rate / Arrhenius function

$$\text{rate} \quad \sim \mathrm{e}^{-\Delta V/kT} \qquad \Delta V \ll k_\mathrm{B} T$$

- *Discards all finite time information for average transition rate*

- Finite time Green function / propagator would be desirable

- *Would allow cool stuff like first passage MC with nontrivial V*

Bulatov et al PRL 2006

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- Alternative is to use *path integral* (cf. Feynman-Kac formula)

- Noise distribution functional

$$\mathcal{P}[\xi(t)] \sim \exp -\frac{1}{4kT}\int_{t_0}^{t_1} \xi(t)^2 \mathrm{d}t$$

  - Gives probability of a particular realization of $\xi(t), \;\; t \in (t_0, t_1)$

- Substitute for ξ in Langevin equation to get probability of trajectory *q(t)*

$$\dot{q}(t) + V'(q) = \xi(t)$$

$$\mathcal{P}[q(t)] \sim \exp -\frac{1}{4kT}\int_{t_0}^{t_1} (\dot{q} + V')^2 \, \mathrm{d}t$$

Like a change of measure, Girsanov theorem

Wiener 1920s, Onsager & Machlup 1953, Stratonovich 1971, Graham 1970s

- Then write transition probability as:

$$\boxed{\mathrm{Prob.}(q_0 \to q;\, t) = \underset{\text{paths from } q_0 \to q;\, t}{\int \mathrm{d(paths)}\ \mathrm{Prob.(path)}} = \underset{\text{paths from } q_0 \to q;\, t}{\int \mathrm{d(paths)}}\ \exp -\frac{1}{4kT}\int_{t_0}^{t_1} (\dot{q} + V')^2\, \mathrm{d}t}$$

- where the integral *Dq* is over functions (paths) *q(t)* satisfying b.c.s

$$q(t_0) = q_0;\ \ q(t_1) = q_1$$

- this defines an *action*:

$$\boxed{\mathcal{S}[q(t)] = \int_{t_0}^{t_1} (\dot{q} + V')^2\, \mathrm{d}t}$$

- *S*[*q*] quantifies by how much the trajectory *q(t)* fails to satisfy the deterministic equation of motion $\dot{q} = -V'$
  - i.e. how large the fluctuations that are required to realize *q(t)* are

More recently Ikonen et al JCP2010, PRE2011; Chen & Yin 1999…

Much work Graham, McKane, book by Wio, …

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$$P(q_1, t_1 | q_0, t_0) = \int \mathcal{D}q \exp -\frac{1}{4kT} \int_{t_0}^{t_1} (\dot{q} + V')^2 \, \mathrm{d}t$$

$$\mathcal{S}[q(t)] = \int_{t_0}^{t_1} (\dot{q} + V')^2 \, \mathrm{d}t$$

- Min. $S[q]$ is the large deviation rate function in the $kT \to 0$ limit

$$\lim_{kT \to 0} -4kT \log P(q_1, t_1 | q_0, t0) = \min_{\text{paths } q(t)} \mathcal{S}[q(t)]$$

Minimum action method, MAM, Ren & van den Eijnden CPAM 2004

- Large deviations isn't the whole story, however…

See also Kikuchi and Cates PRR 2020

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$$P(q_1, t_1 | q_0, t_0) = \int \mathcal{D}q \exp - \frac{1}{4kT} \int_{t_0}^{t_1} (\dot{q} + V')^2 \, \mathrm{d}t$$

- Looks a lot like the QM path integral

$$\langle q_1, t_t | q_0, t_0 \rangle = \int \mathcal{D}q \exp \frac{i}{\hbar} \int_{t_0}^{t_1} \left(\frac{m}{2} \dot{q}^2 - V(q) \right) \mathrm{d}t$$

- but
  - real, no *i* *this is a good thing!*
  - Noise strength plays role of $\hbar$
  - No mass (actually it’s 2x the friction squared, which I set = 1)
  - “All-squared” form for “Lagrangian”
  - $+V'^2$ instead of $-V$ *Effective potential $F = -V'^2$*
  - cross term

Lagrangian *L* = *K.E. – P.E.*

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$$\dot{q}(t) + V'(q) = \xi(t)$$

- Cross term in stochastic action is a total derivative, pulls out a $2\Delta V$

$$\boxed{\int 2\dot{q}V'(q)\mathrm{d}t = \int 2V'\mathrm{d}q = 2\Delta V}$$

Path-independent

$$\boxed{\mathcal{S} = \int_{t_0}^{t_1} (\dot{q} + V')^2 \,\mathrm{d}t = 2\left(V(q_1) - V(q_0)\right) + \int_{t_0}^{t_1} \left(\dot{q}^2 + V'^2\right) \mathrm{d}t}$$

$$P(q_1, t_1|q_0, t_0) = \exp\left(-\frac{\Delta V}{2kT}\right) \int \mathcal{D}q \exp - \frac{1}{4kT} \int_{t_0}^{t_1} \left(\dot{q}^2 + V'^2\right) \mathrm{d}t$$

$$\equiv \exp\left(-\frac{\Delta V}{2kT}\right) f(q_1, t_1|q_0, t_0)$$

defining f

- *Substitute this into Fokker-Planck…*

See book by H Wio 2013, also Ge & Qian 2012, many papers of Hanggi, Marchesoni , Bray, McKane et al PR 1990s
SPF 2016; SPF 2022, 2023

- **Also:** can actually keep inertial term from Langevin eq. too:
- Works in d > 1, fairly general *V*

$$\boxed{P(\underset{\dot{q}_1,\,\dot{q}_0}{q_1, t_1 | q_0, t_0}) = \int \mathcal{D}q \exp -\frac{1}{4k_\mathrm{B}T}\int_{t_0}^{t_1} \left|m\ddot{q} + \Gamma\dot{q} + \nabla V(q)\right|^2 \mathrm{d}t,}$$

- Expanding the square in "Lagrangian" gives total derivative:

$$\boxed{\mathcal{L} = 2\Gamma\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{2}m\dot{q}^2 + V\right) + \Gamma^2\dot{q}^2 + (m\ddot{q} + \nabla V)^2}$$

- Instead of ΔV coming out from the total derivative, get ΔE

$$\boxed{\Delta E = \left[\frac{1}{2}m\dot{q}^2 + V\right]_{\text{initial}}^{\text{final}}}$$

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$$P(q_1, t_1 | q_0, t_0)$$

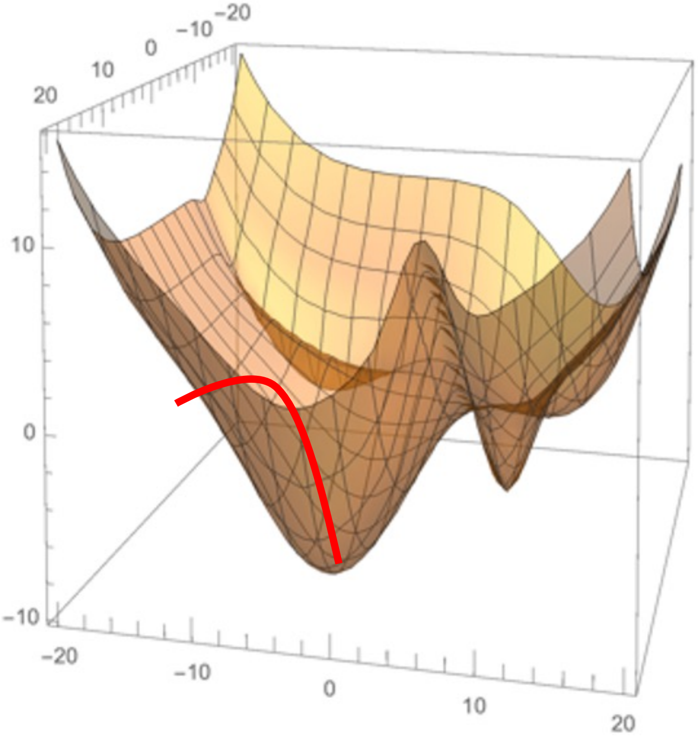
$$\dot{q}_1, \dot{q}_0 = \left(\exp -\frac{\Delta E}{2k_B T}\right) \int \mathcal{D}q \exp -\frac{1}{4k_\mathrm{B} T} \int_{t_0}^{t_1} \left(\Gamma^2 \dot{q}^2 + (m\ddot{q} + \nabla V)^2\right) \mathrm{d}t$$

- Consider a trajectory in phase space and its time reversal
    - ΔE flips sign
    - other terms in S are time reversal invariant
- Path integrals cancel exactly, so get

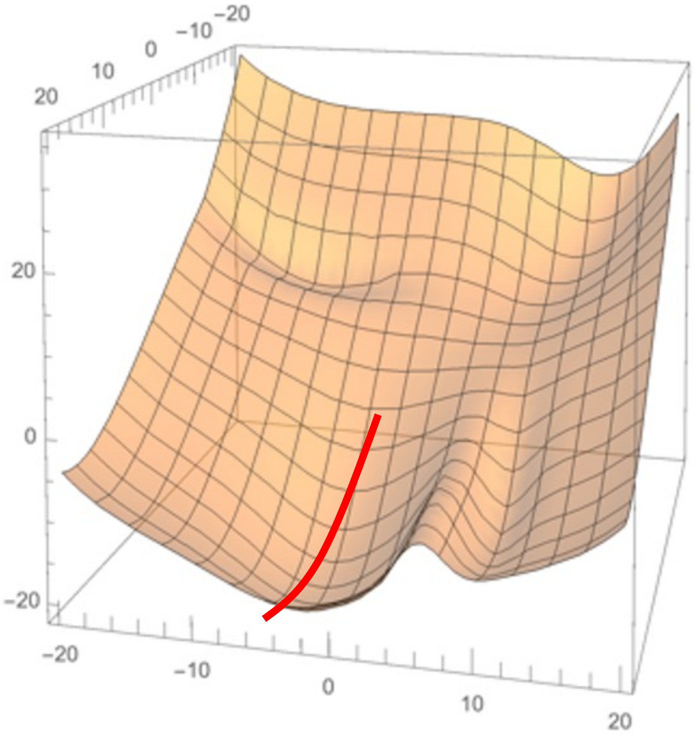
$$\frac{P(\nearrow)}{P(\swarrow)} = \exp -\frac{\Delta E}{k_B T}$$

- Trajectory with positive ΔE is *exponentially less likely than its reverse*
- a Crooks-like theorem – *exact* for arbitrary temperature, arbitrary damping, arbitrarily far from equilibrium

This leads to a remarkable relation between trajectories through different potentials…



V(x,y)



U = *V(x,y)* – 0.5 *x*, say

Exact trajectory-by-trajectory

Suppose you want to simulate rare escapes from a deep well in *V*. Simulate common "escapes" in *U* instead…

- Wish to sample rare event dynamics in *V*
- Instead, simulate $\boxed{m\ddot{q}(t) + \Gamma\dot{q}(t) = -\nabla V(q) + F + \xi(t)}$
- with a helpful bias force *F*

$$\begin{aligned} \mathcal{S}[q] &= \int_{t_0}^{t_1} |m\ddot{q} + \Gamma\dot{q} + \nabla V - F + F|^2 \, \mathrm{d}t \\ &= \int_{t_0}^{t_1} |m\ddot{q} + \Gamma\dot{q} + \nabla V - F|^2 \, \mathrm{d}t + \int_{t_0}^{t_1} F \cdot (F + 2\xi) \, \mathrm{d}t \end{aligned}$$

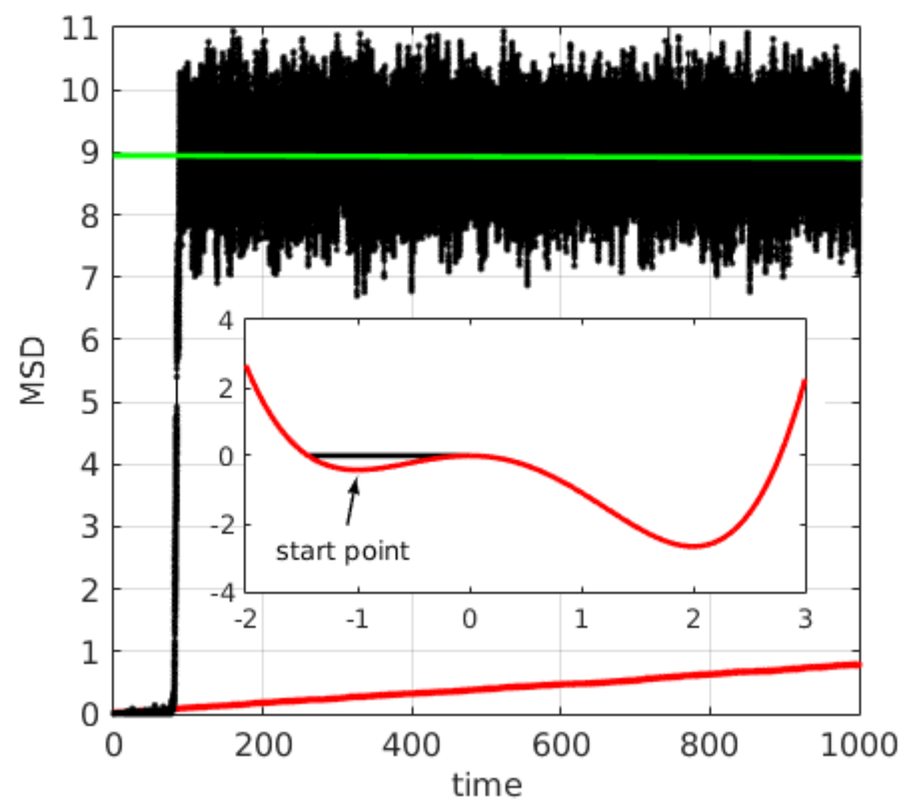
- so

$$\underbrace{P[q]_V}_{\text{What you want to know}} = \underbrace{P[q]_U}_{\text{Fast to sample}} \, \underbrace{\mathrm{e}^{-\int_{t_0}^{t_1} F\cdot(F+2\xi)\mathrm{d}t/4kT}}_{\text{Easy to calculate}}$$

Chen and Horing, J Chem Phys 2007

Nummela and Andricioaei, Biophys J 2007

- *F* need not be conservative
- *F* can be different for each path sampled
- *F* can depend on time
- Works for entropic as well as energetic barriers, no transition state required
- *BUT* too big an *F* destroys your statistics
- Depending on what you want to know, this may or may not be a problem



5000 particles escaping from metastable well driven by weak noise. MSD → ~ 9 as $t \to \infty$

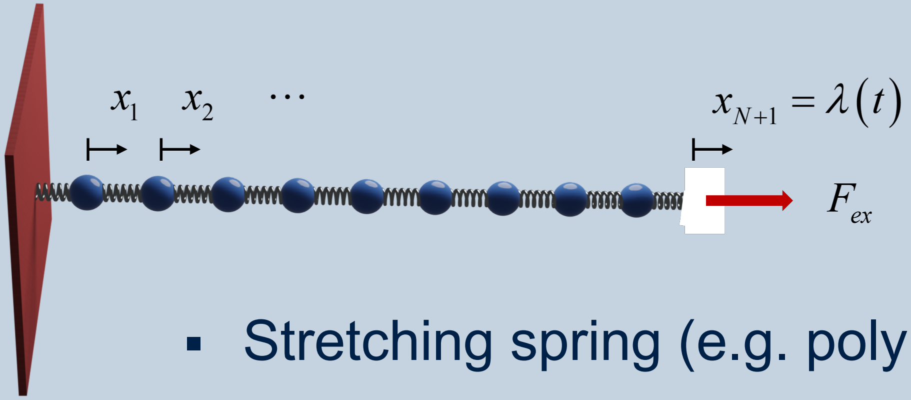
No bias; full bias *cf AMD*

- You can't get something for nothing!
- The bigger the bias, the smaller the path weights, the more runs are needed to compute ensemble averages
- This can be quantified with the Kullback-Leibler divergence:

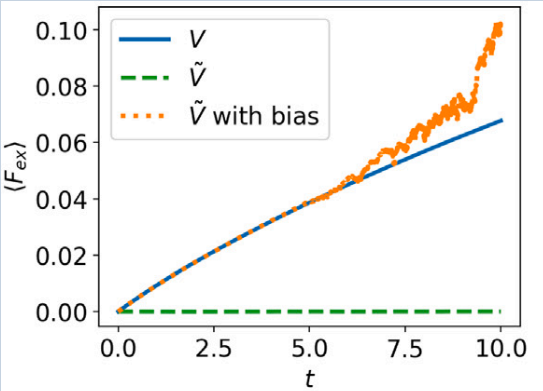
$$\mathcal{D}_{KL}(\mathcal{P}_U||\mathcal{P}_V) = \left\langle \log \frac{\mathcal{P}_U}{\mathcal{P}_V} \right\rangle = \frac{1}{kT} \left\langle \int_{t_0}^{t_1} F \cdot (F + 2\xi)\, \mathrm{d}t \right\rangle$$

- *When the averages are taken wrt the biased density* this is zero
- So, need to keep sampling until this gets sufficiently small
- The bigger the bias and the longer the simulation time, the worse this gets
- But at least it's quantifiable

Example



- Stretching spring (e.g. polymer toy model)
- Go from equilibrium ($\lambda = 0$) simulations to non-equilibrium predictions

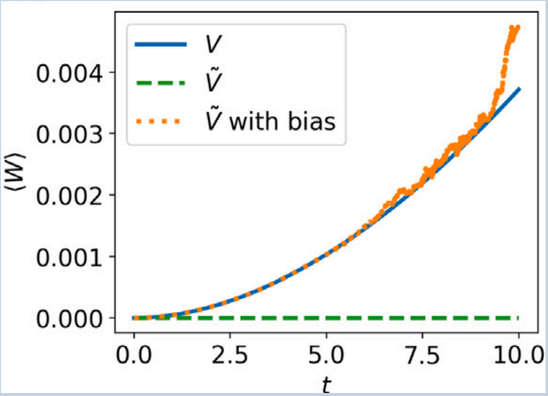


External force vs time

- - - equilib.

—— non-equilib. (control)

······ predicted



External work vs time

Need more runs for longer times

al et SPF, C Reina, JMPS 2022

Conclusions I

- Also investigated harmonic to anharmonic springs; caging in Hertzian and L-J colloids (see ref. below)

- Exact relation between stochastic trajectories of two arbitrary systems

- *Ensemble averages* currently feasible for smallish systems, shortish times (1D, laptop; 10 interacting particles in 2D with PBC, workstation)
  - could be more profitably applied to more specific problems
  - extension to coloured noise, non-gradient forces…

- Analytical progress possible in weak noise limit
  - “semiclassical” evaluation of path integral

Celia Reina, S Huang, I Graham, R Riggleman, P Arriata, SPF

J. Mech. Phys. Solids **161** 104779 (2022)

Research funded by EPSRC *fellowship*

Engineering and Physical Sciences
Research Council

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Back to overdamped approx.

$$P = \int \mathcal{D}q \exp -\frac{\mathcal{S}[q]}{4D}$$

- Stochastic action:

$$\mathcal{S} = \int_{t_0}^{t_1} (\dot{q} + V')^2 \, \mathrm{d}t = 2\left(V(q_1) - V(q_0)\right) + \int_{t_0}^{t_1} \left(\dot{q}^2 + V'^2\right) \mathrm{d}t$$

- Can analyze "semi-classically" with kT playing role of $\hbar$

$$D = kT$$

- Path integral dominated by action-minimizing paths as $k_B T \to 0$
- Euler-Lagrange for such a "classical path" most probable path (MPP)

$$\ddot{q} = V'V''; \;\; \dot{q}^2 - V'^2 = H; \;\; \dot{q} = \pm\sqrt{H + V'^2}$$

H is conserved on 'classical' trajectory

See book by H Wio 2013, also Ge & Qian 2012, many papers of Hanggi, Marchesoni , Bray, McKane et al PR 1990s
SPF 2016; SPF in prep

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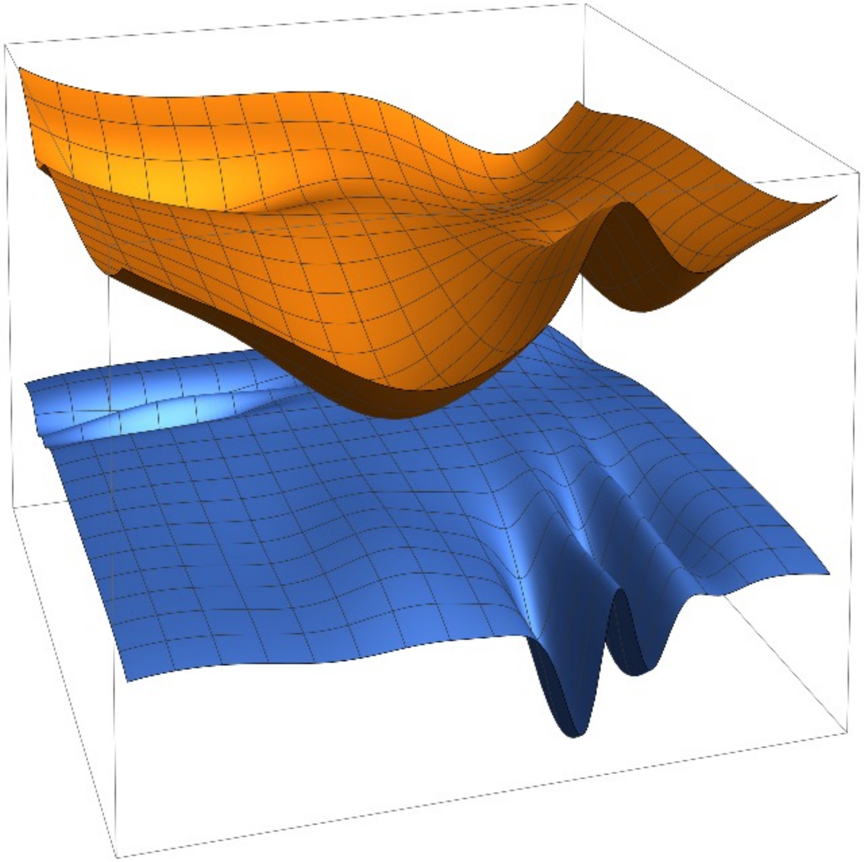
NB smooth paths are measure zero in space of stochastic paths; really we are saying MPPs lie in a tube around smooth path (Stratonovich 1971)



$V(x, y)$

$F(x, y) = -|\nabla V(x, y)|^2$

Most probable stochastic paths in V

↕

Hamiltonian mechanics in F

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$$\mathcal{S} = \int_{t_0}^{t_1} (\dot{q} + V')^2 \,\mathrm{d}t = 2\,(V(q_1) - V(q_0)) + \int_{t_0}^{t_1} (\dot{q}^2 + V'^2)\,\mathrm{d}t$$

- Long-time, zero “energy” solution given by *H = 0*

c.f. QFT instantons
this is the MEP

$$\ddot{q} = V'V'';\; \dot{q}^2 - V'^2 = H \qquad \dot{q} \to \pm V' \qquad \text{as}\;\; H \to 0$$

  - – sign, downhill, no fluctuations required, *S = 0*
  - + sign, uphill,

$$\mathcal{S}[q(t)] = \int_{t_0}^{t_1} 4\dot{q}\,\dot{q}\mathrm{d}t = 4\int_{q_0}^{q_1} V'\mathrm{d}q = 4\Delta V$$

- recover usual rate

$$\exp -\frac{\mathcal{S}}{4kT} = \exp -\frac{\Delta V}{kT}$$

See book by H Wio 2013, also Ge & Qian 2012,
Bray, McKane et al PR 1990s
SPF 2016; SPF 2022, 2023

What about other paths? Can we keep finite time information?

Ge & Qian 2012

- Do other paths with $H \neq 0$ have meaning? Yes! As $kT \to 0$

$$P(q_1, t_1 | q_0, t_0) \to \exp -\frac{1}{4kT}\left(2\Delta V - H(t_1 - t_0) + 2\int_{q_0}^{q_1} \sqrt{H + V'^2} \mathrm{d}q\right)$$

- Find H by extremizing S, $\partial S/\partial H = 0$ leads to

$$t_1 - t_0 = \int_{q_0}^{q_1} \frac{\mathrm{d}q}{\sqrt{H + V'^2}}$$

Or by solving eq. of m.

- Don't need to discard temporal information

- This gives the solution to Fokker-Planck with initial condition

$$\rho(q, 0) = \delta(q - q_0)$$

$$P(q, t | q_0, t_0)$$

- Transition probability / Green function
- for general potential…

What do we mean by the "weak noise limit" in this context?

"Given that the transition $(t_0, q_0) \to (t_1, q_1)$ *occurred, assume it did so via the most probable path"*

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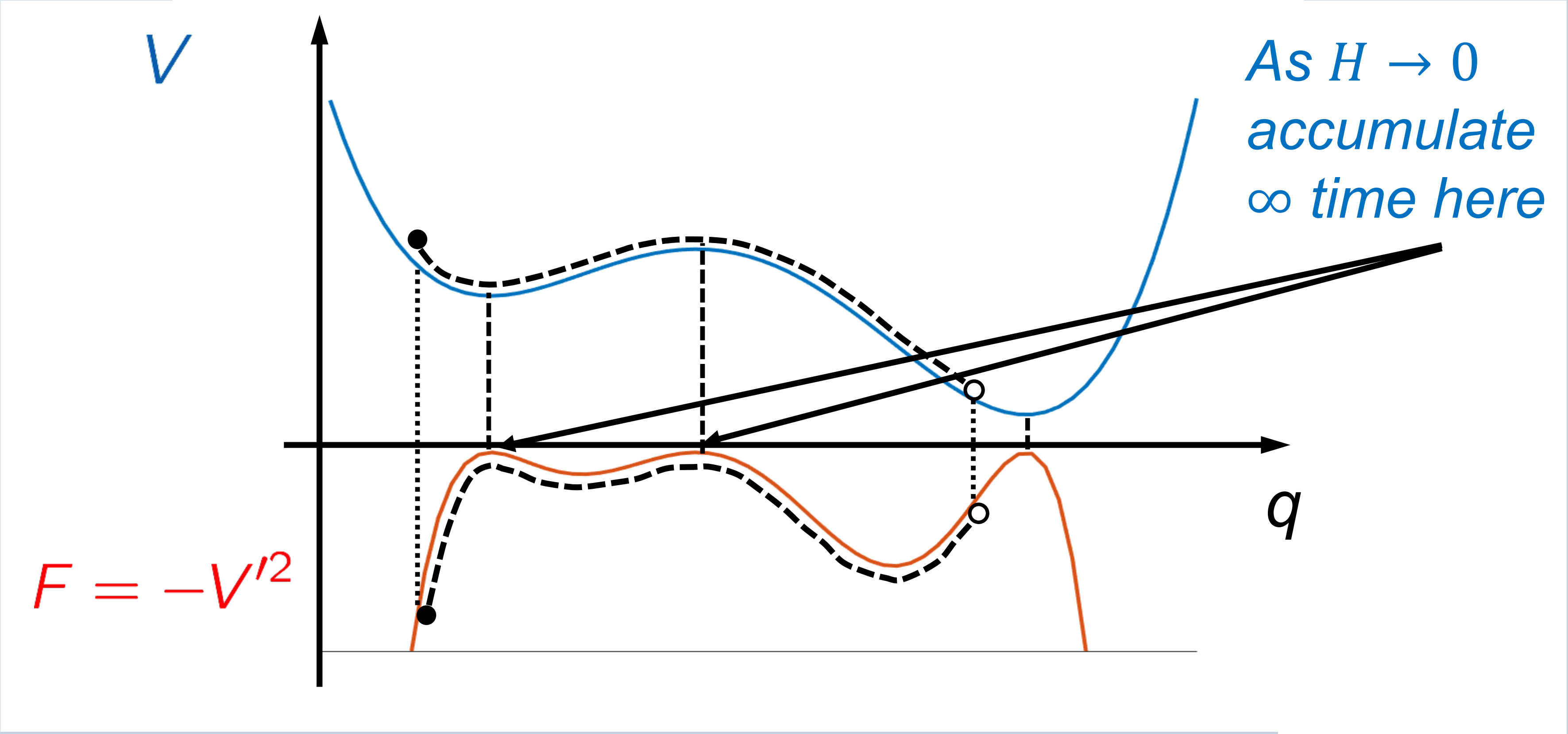
Effective potential $F = -V'^2$



- Euler-Lagrange defines paths satisfying $\ddot{q} = V'V'' = -\left(-V'^2\right)'$
- Dissipative stochastic dynamics in potential *V* correspond to conservative Hamiltonian trajectories in effective potential $F = -V'^2$
- *c.f. inverted potential for QFT instantons*

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What about other paths?

$$P(q_1, t_1 | q_0, t_0) \to \exp -\frac{1}{4kT}\left(2\Delta V - H(t_1 - t_0) + 2\int_{q_0}^{q_1} \sqrt{H + V'^2} \mathrm{d}q\right)$$

$$t_1 - t_0 = \int_{q_0}^{q_1} \frac{\mathrm{d}q}{\sqrt{H + V'^2}}$$

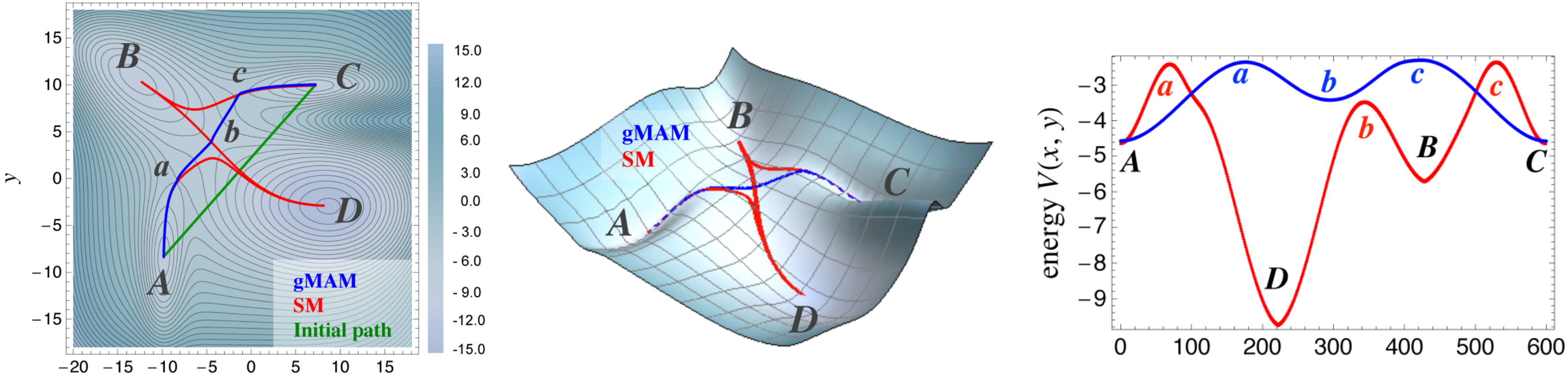
- Find *H* by extremizing *S*, $\frac{\partial S}{\partial H} = 0$ leads to
- Or by solving eq. of m. $\frac{\mathrm{d}q}{\mathrm{d}t} = \pm\sqrt{H + V'(q)^2}$
- If path contains a min/max, *V'* contains a zero, so *H* → 0 corresponds to time → ∞ and recovers Arrhenius rate
- Works exactly for simple potentials, gives WKB-like approximation for more complex ones *in principle!*
- Validity: $\mathcal{S}/4kT > 1$ just like Arrhenius rate validity $\Delta V/kT > 1$

What do we mean by the "weak noise limit" in this context?

"Given that the transition $(t_0, q_0) \to (t_1, q_1)$ *occurred, assume it did so via the most probable path"*

Higher dimensions, geometric min. action method

- Foregoing formalism generalizes to d > 1 *except path unknown*
- Solving the equation of motion is less simple when d > 1
- BVP with fixed start and end points, and time
- gMAM method finds absolute min. action path, $t \to \infty$, $H = 0$
  - *Vanden-Eijnden & Heymann 2008, Díaz Leines & Rogal 2016*
- Better than e.g. string method



From Díaz Leines & Rogal PRE 2016

Finite time paths

- Use geometric method to find finite time $H > 0$ paths

$$S(q_1, q_0, t) = 2\Delta V - Ht + 2\int_\gamma \sqrt{H + |\nabla V|^2}\,\mathrm{d}s$$
$$\equiv 2\Delta V - Ht + 2W$$

- Minimize path-dependent term W over curves γ linking q_0 and q_1

- Parameterize γ using normalized arc length $\alpha \in (0,1)$

$$\phi(\alpha) = (x_1(\alpha), x_2(\alpha), \dots)$$

$$W = 2\int_{\mathrm{start}}^{\mathrm{end}} \sqrt{H + |\nabla V(\phi)|^2}\,|\mathrm{d}\phi| = 2\int_0^1 g(\alpha)\,\phi'^2(\alpha)\,\mathrm{d}\alpha$$

See Kikuchi et al, PRR 2020
for alternative algorithm

$$g(\alpha) = \frac{\sqrt{H + |\nabla V(\phi)|^2}}{|\phi'(\alpha)|}$$

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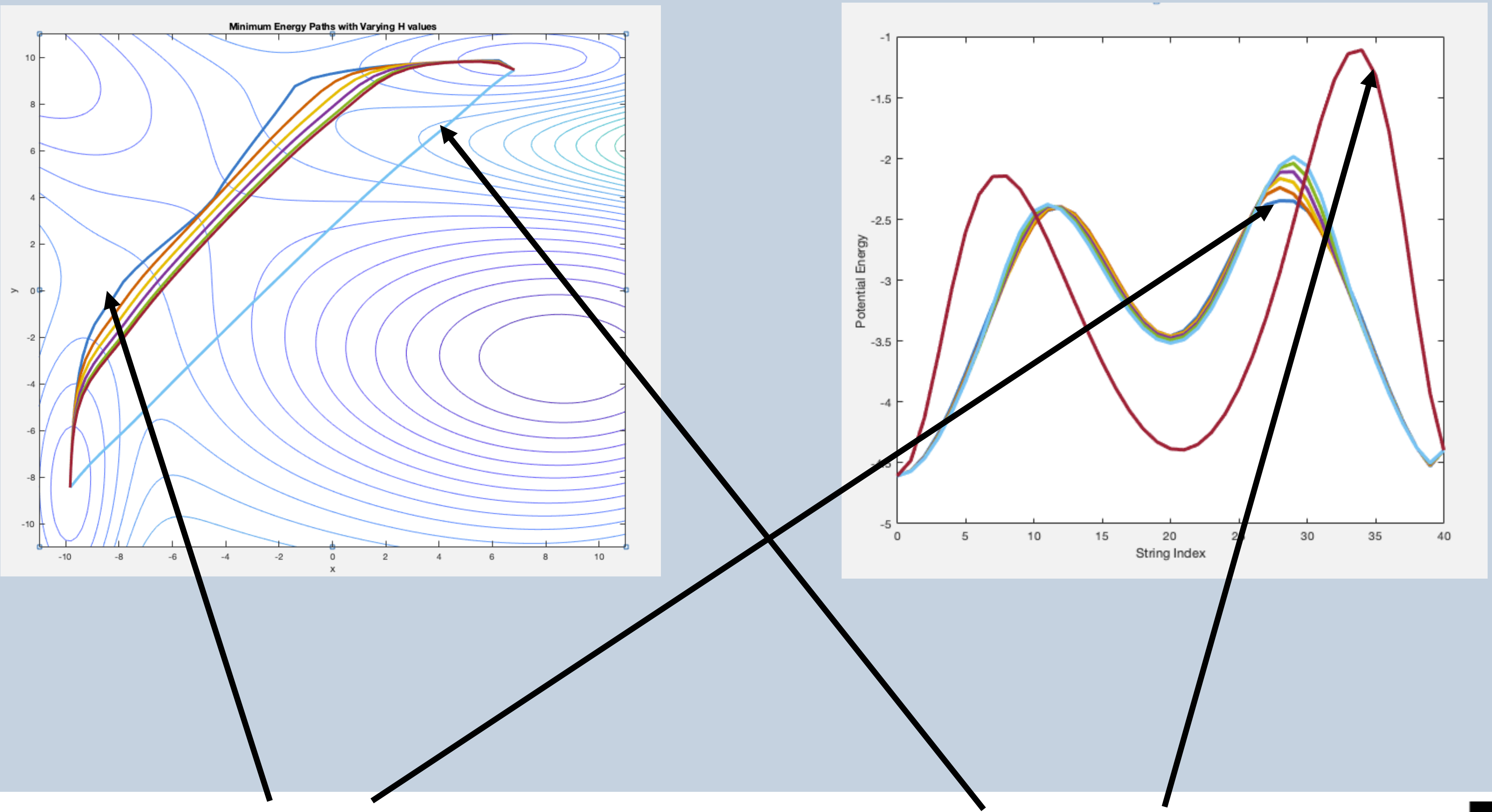
- Start from an initial guess (e.g. straight line $x_0 \to x_1$)
- Evolve path in direction of

$$-\frac{\delta W}{\delta \phi_i} = -\frac{2}{g}(\nabla V)_j (\nabla \nabla V)_{ji} + 2(g\phi_i')'$$



$H = 0$ path

Large H path

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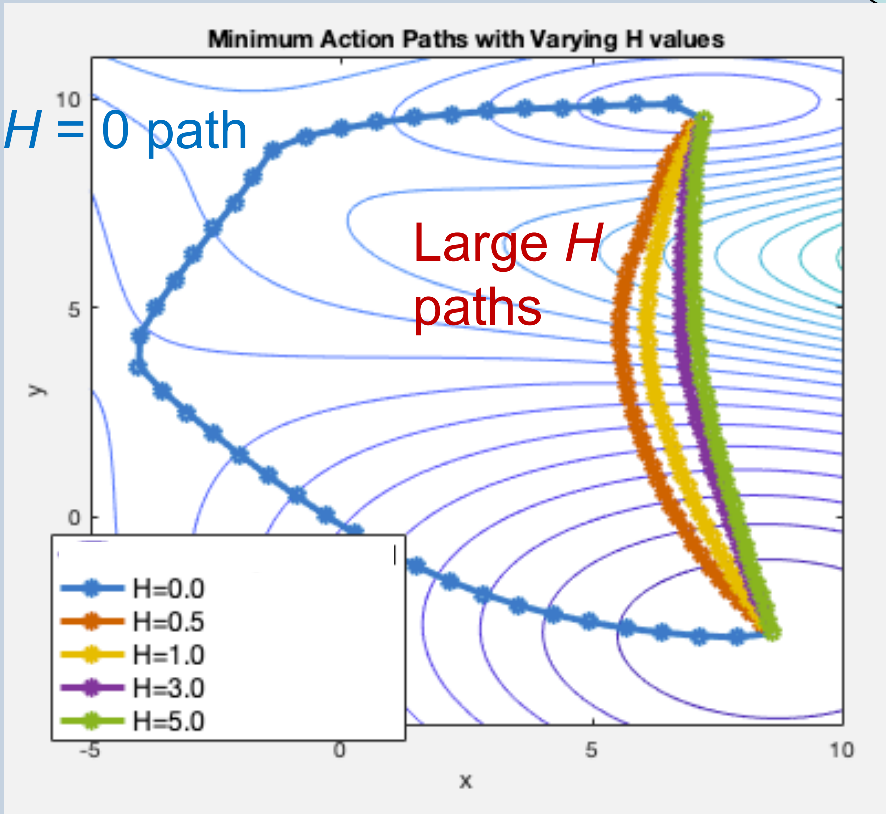
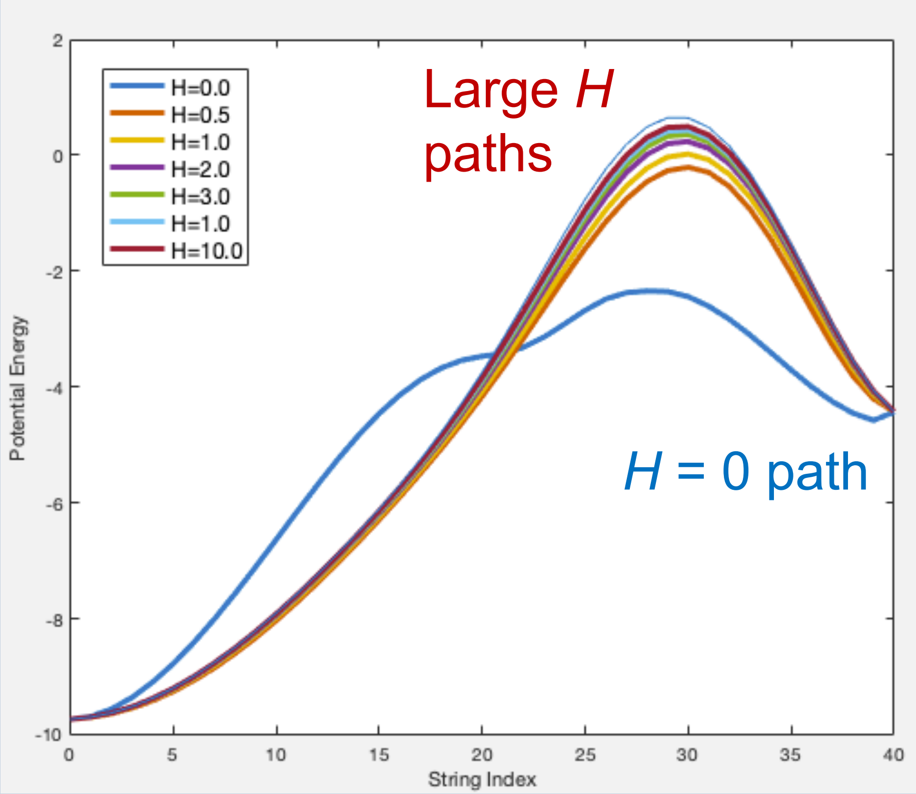
- Start from an initial guess (e.g. straight line $x_0 \rightarrow x_1$)
- Evolve path in direction of

$$-\frac{\delta W}{\delta \phi_i} = -\frac{2}{g}\left(\nabla V\right)_j\left(\nabla\nabla V\right)_{ji} + 2\left(g\phi_i'\right)'$$



H = 0 path

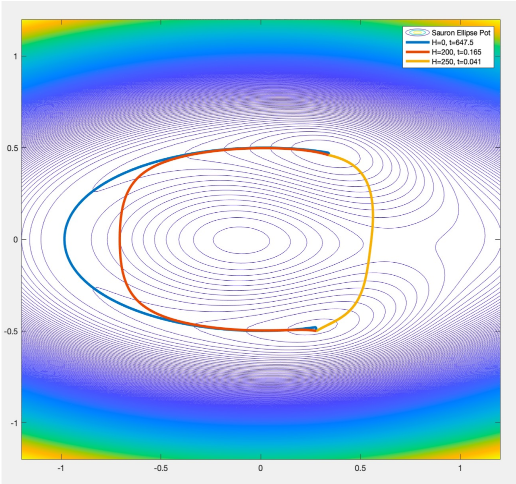
Large H paths



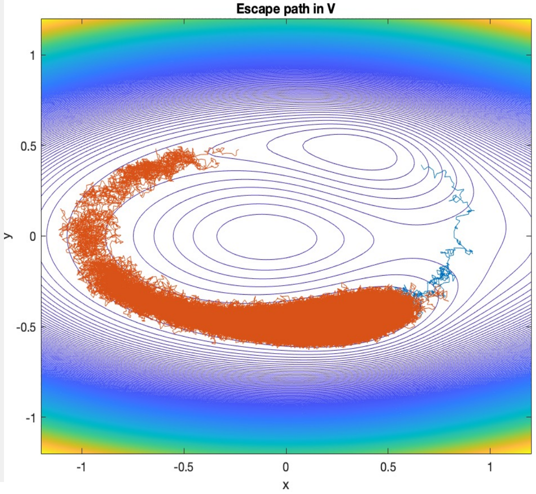
Large H paths

H = 0 path

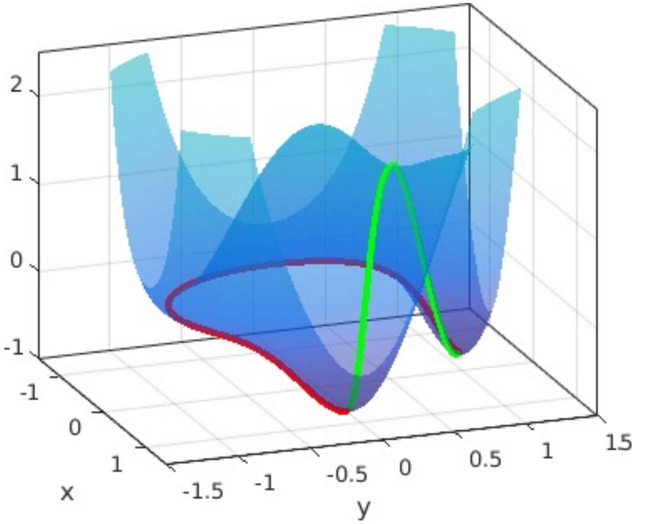
Muller potential



Short, intermediate, and long time paths



Langevin simulations confirm



Different saddles*

Finite time most probable paths can visit different intermediate “states”

**exact saddles only visited by ∞-time paths*

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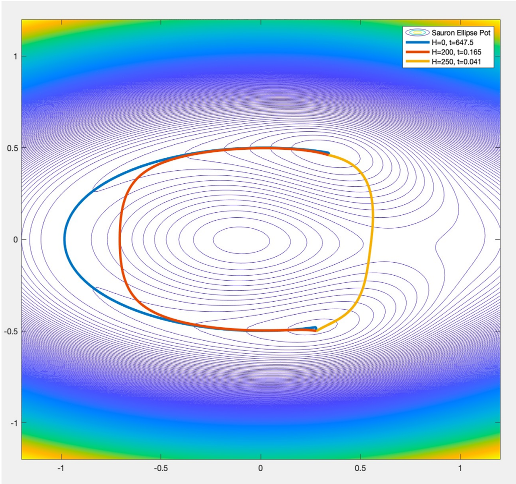

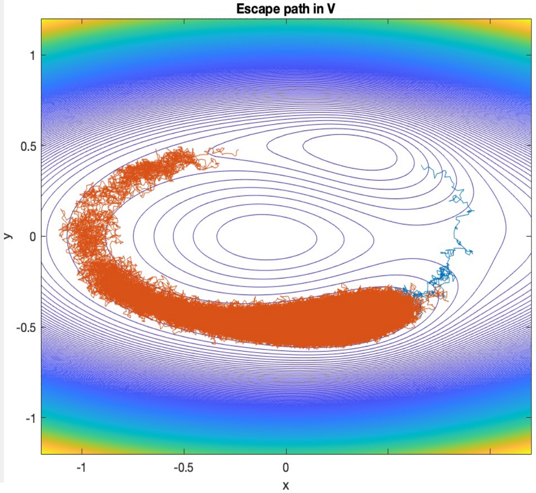

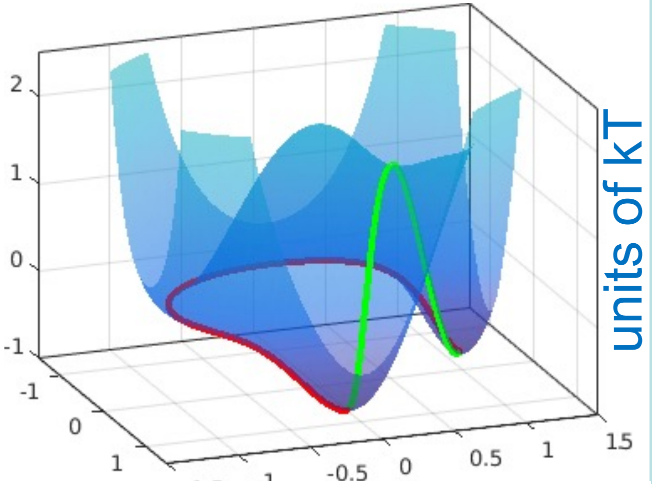

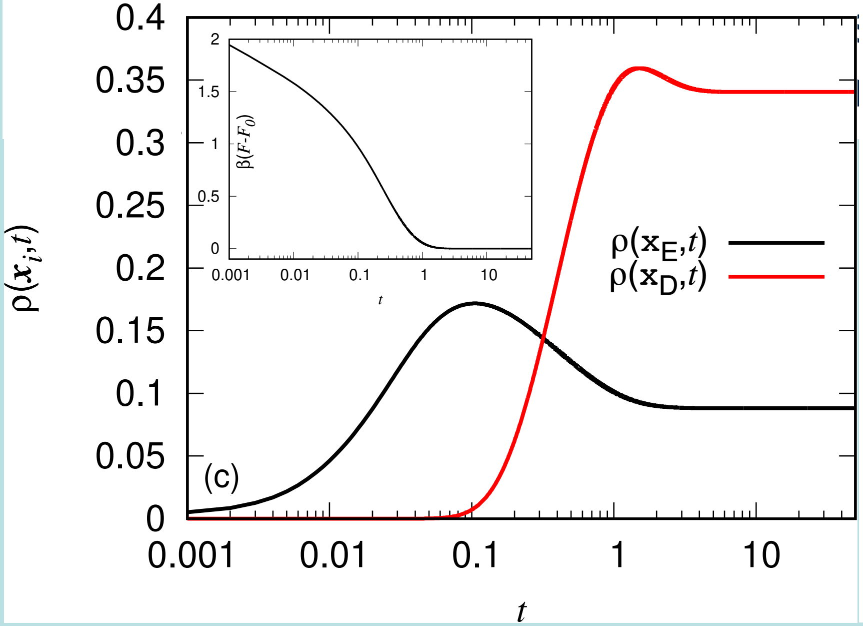

Left: density at upper and lower saddles vs time

Stop simulation/experiment at t = 0.1 and you'd never know about the dominant pathway

(density obtained from numerical solution of Smoluchowski)

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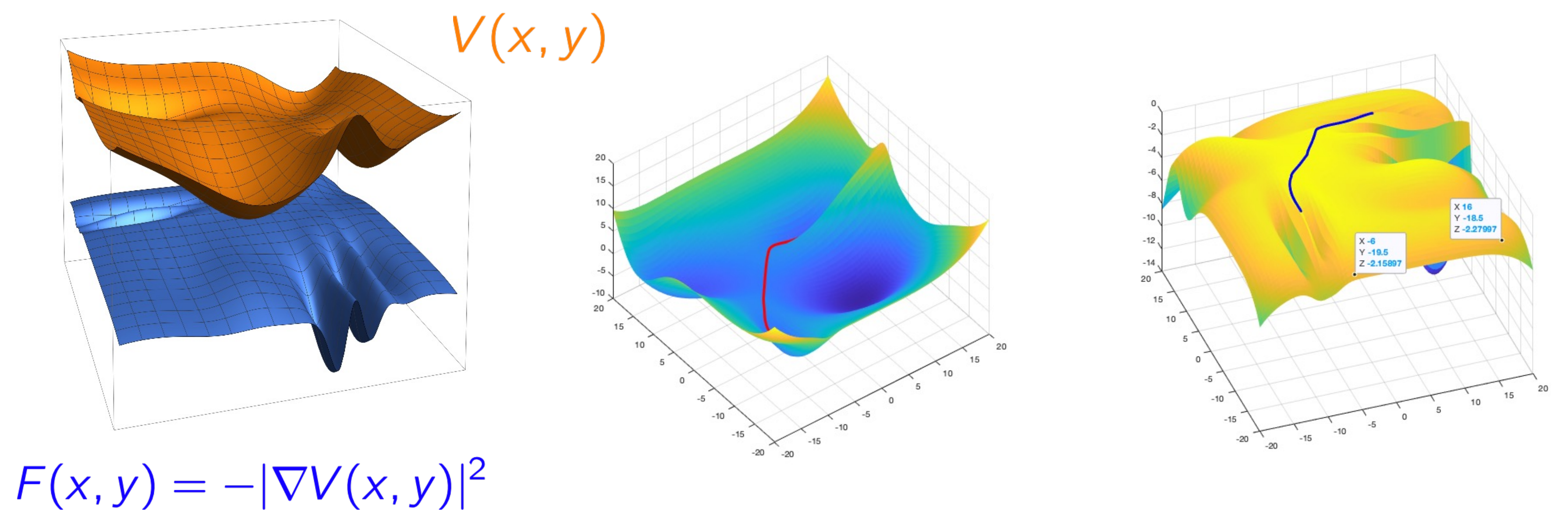


- Most probable paths (MPPs) through *V* correspond to Hamiltonian trajectories in $F = -|\nabla V|^2$

- Finite time paths avoid the saddle, have higher barriers to overcome, *but are still more probable*

- *NB smooth paths are measure zero in space of stochastic paths; really we are saying MPPs lie in a tube around smooth path (Stratonovich 1971)*

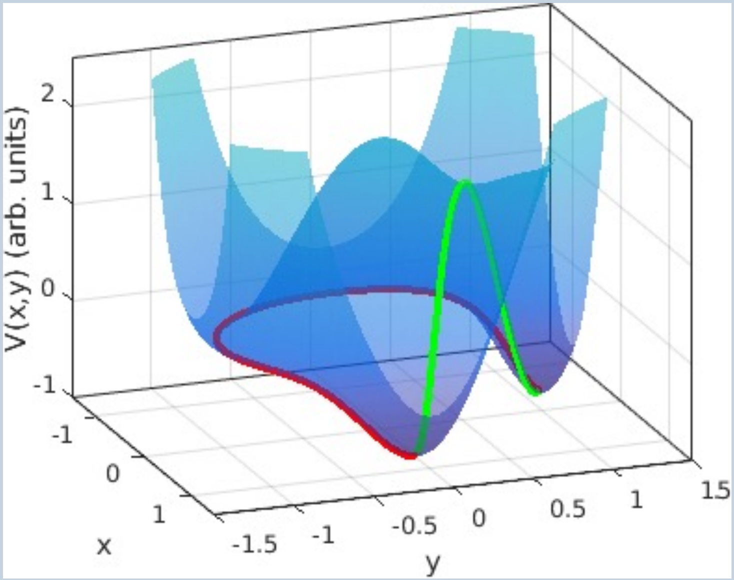
- At short times, higher barrier path may be more probable

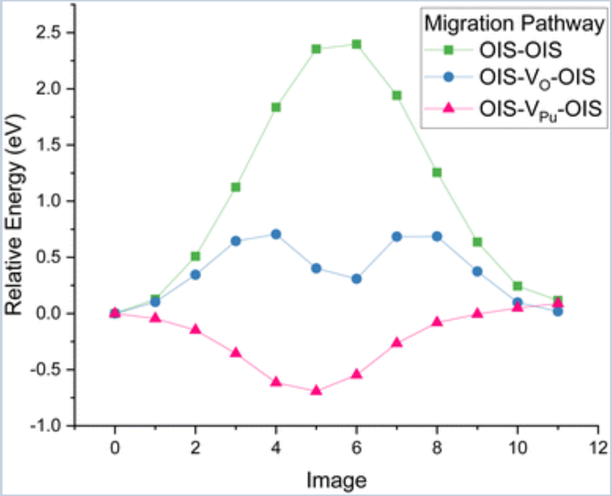
- Murray *et al,* PCCP 2022, He diffusion in PuO_2 :

- *“In a 1 ns time window, 9 out of 12 transitions proceeded via higher barrier pathway”*

- 6.6eV *vs* 2.4eV at 2000K
    - (0.6 + 6 to move O)

- 1 ns not long enough





Murray *et al,* PCCP 2022

Values from Arrhenius fit – at finite time will be fitting S rather than ΔV

Conclusions II

- Finite-time most probable paths are different from the “straight up the hill” MEP

- Whilst nature will take the usual MEP most of the time, simulations or experiments may miss this if their time window is too short
  - Protein chemists call this “kinetic window effect”

- Most important for very rare events eg > ms timescale

- Prefactors are also important
  - not discussed much here; harmonic approx. doable
  - “density of paths” accessible in this limit

SPF, Hass, Díaz Leines, Archer J Chem Phys **158** 124114 (2023)

Conclusions

- Path integrals aren't just for quantum mechanics/QFT
- Provide an intuitive description of classical stochastic processes
- "Semiclassical" (weak noise) limit ($kT \to 0$ rather than $\hbar$) is interesting
- Many extensions possible (inertia, coloured noise, non-gradient forces, fields, first passage times…)
- Thanks to Andy Archer, Celia Reina++, Tom Honour, Amanda Hass, EPSRC
- Please talk to me if you are interested in applications
- I have glossed over technical details; happy to share

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