Transition paths of maximal probability

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Setup

$x \in \mathbb{R}^N$ is the state, $V \in C^2(\mathbb{R}^N)$ is associated potential energy. We assume

- The set of stationary points $\{x \ : \ \nabla V(x) = 0\}$ is finite or countable and
- The stationary points are non-degenerate, i.e.

$$\det(\nabla^2 V(x)) \neq 0 \text{ if } \nabla V(x) = 0.$$

Metastability

Transitions in the overdamped regime:

$$\mathrm{d}x = -\nabla V(x)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W,$$
$$x(0) = x^-.$$

Transition state theory: The 'most likely path' can be constructed by joining solutions of the the gradient flow

$$\dot{x} = \pm\nabla V(x)$$

and the transition rate is $\propto \exp\left(\varepsilon^{-1}(V(x^-) - V(x^{\mathrm{saddle}}))\right)$.

Objective: Characterize the implications of action-minimization (variational analysis).

The Onsager-Machlup functional

Step 1: Girsanov's theorem implies that the density of the path measure π with respect to rescaled Brownian motion μ_ε can be written as

$$\frac{\mathrm{d}\pi_\varepsilon}{\mathrm{d}\mu_\varepsilon}(z) \sim \exp\left(-\frac{1}{2\varepsilon}\int_0^T |\nabla V(z(t))|^2 \,\mathrm{d}t + \frac{1}{\varepsilon}\int \nabla V(z)\,\mathrm{d}z\right).$$

Ito's lemma:

$$\nabla V(z)\cdot \mathrm{d}z = \mathrm{d}V - \frac{\varepsilon}{2}\Delta V(z)\,\mathrm{d}t,$$

and thus

$$\frac{\mathrm{d}\pi_\varepsilon}{\mathrm{d}\mu_\varepsilon}(z) \sim \exp\left(-\frac{1}{2\varepsilon}L_\varepsilon(z)\right),$$

with

$$L_\varepsilon(x) = \int_0^T \left(|\nabla V(z(t))|^2 - \varepsilon\Delta V(z)\right)\mathrm{d}t + 2(V(z(T)) - V(z(0))).$$

The Onsager-Machlup functional (continued)

Step 2: Replace reference measure. Watanabe-Ikeda:

$$\lim_{\delta \to 0} \frac{\pi_\varepsilon\left(\{\|x - z_1\| \le \delta\}\right)}{\pi_\varepsilon\left(\{\|x - z_2\| \le \delta\}\right)} = \exp\left(\frac{1}{2\varepsilon}\left(I_\varepsilon(z_2(T\cdot) - I_\varepsilon(z_1(T\cdot))\right)\right),$$

with

$$\begin{aligned} & I_\varepsilon(\zeta) - 2\left\{V(\zeta(1)) - V(\zeta(0))\right\} \\ = & \int_0^1 \left(\frac{1}{T}|\dot{\zeta}|^2 + T|\nabla V(\zeta(s))|^2 - T\varepsilon\,\Delta V(\zeta(s))\right)\,\mathrm{d}s \\ = & \int_0^T \left(|\dot{z}|^2 + |\nabla V(z(t))|^2 - \varepsilon\,\Delta V(z(t))\right)\,\mathrm{d}t. \end{aligned}$$

The blue functional is the time-rescaled Onsager-Machlup functional

Asymptotic behavior of I_ε as $\varepsilon \to 0$

- Choose $T \sim \varepsilon^{-1}$, unphysical scaling! Physical scaling:

$$\log(T) \sim \varepsilon^{-1}(V(x_{\text{saddle}}) - V(x_{\text{min}})).$$

- Variants of the functional I_ε are studied in Calculus of Variations.
- The Ito-term decouples from the other terms.
- Minimizer of I_ε is the MAP-estimator (maximum a-posterior estimator) in Bayesian statistics: the mode of the posterior distribution.
- Minimum value of I_ε depends on the number of transitions:

$$\inf\{I_\varepsilon(z) \ : z(0) = x^-, z(1) = x^+\}$$
$$= \sum \text{ individual transition energies}$$

Related work: Anrich-Mielke-Peletier-Savaré-Veneroni '12

The marginal $\rho_\varepsilon(s,x) = \pi_\varepsilon(z(s) = x)$ satisfies the Fokker-Planck equation

$$\frac{1}{T}\frac{\partial}{\partial s}\rho_\varepsilon = \mathrm{div}(\rho \nabla V(x)) + \varepsilon \Delta \rho.$$

Theorem. *If* $T = \exp(k/\varepsilon)$, $k = \max_{-1 \le x \le 1}(V(x) - V(0))$, $N = 1$, $V(-1) = V(1) = \min_{x\in\mathbb{R}} V(x)$*. Then*

$$\lim_{\varepsilon\to 0} u_\varepsilon(s,x) = \sum_{\{x\,:\,V'(x)=0\}} \lambda_x(s)\,\delta(\cdot - x)$$

in the weak- sense, and* λ *satisfies the ode*

$$\dot{\lambda}_{\pm 1} = \pm k(\lambda_{-1} - \lambda_1).$$

Previous results: Bovier et al. 2004 (using potential theory).

Γ-convergence

Tool from Calculus of Variations: Γ-**convergence**.

Definition. A functional I_0 is the Γ-limit of I_ε as $\varepsilon \to 0$ if

$$\liminf_{\varepsilon \to 0} I_\varepsilon(x_\varepsilon) \geq I_0(x)$$

holds for all sequences x_ε which converge weakly to x, and there exists a recovery sequence z_ε which converges weakly to x and satisfies

$$\limsup_{\varepsilon \to 0} I_\varepsilon(z_\varepsilon) \leq I_0(x).$$

Difference between Γ-limit and weak-* limit

Note that the Γ-limit is different from the weak-* limit.

Example

$$p_\varepsilon(x) = \frac{1}{Z_\varepsilon} \exp\left(-\frac{1}{\varepsilon}(x^2-1)^2\right)$$

Clearly p_ε converges to $\frac{1}{2}\delta(\cdot - 1) + \frac{1}{2}\delta(\cdot + 1)$ in the weak-* sense as $\varepsilon \to 0$, i.e.

$$\lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} p_\varepsilon(x)\, \varphi(x)\, \mathrm{d}x = \frac{1}{2}\left(\varphi(1) + \varphi(-1)\right) \text{ for all } \varphi \in C_0(\mathbb{R}).$$

On the other hand, the Γ-limit of $I_\varepsilon(x) = -\log(p_\varepsilon(x)) - \log(Z_\varepsilon) = \frac{1}{\varepsilon}(x^2-1)^2$ is given by

$$I_0(x) = \begin{cases} 0 & \text{if } x \in \{-1, 1\}, \\ +\infty & \text{else.} \end{cases}$$

The Γ-limit is not affected by the width of the wells!

The transition problem

The mathematical core of the minimization problem is to understand

$$\Phi(x^-, x^+) = \inf \left\{ J(z) \;\middle|\; \lim_{s \to \pm\infty} z(s) = x^\pm \right\}$$

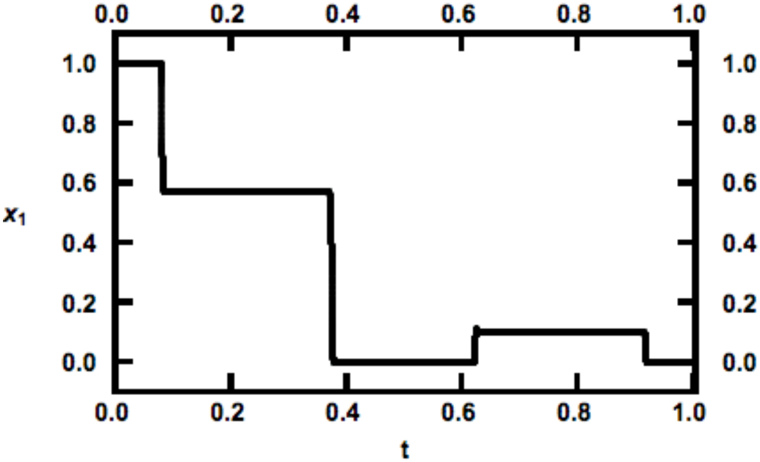
where

$$J(z) = \frac{1}{2} \int_{-\infty}^{\infty} \left(|\dot{z}|^2 + |\nabla V(z)|^2 \right) \, \mathrm{d}t,$$

if $x^\pm$ are stationary points of V, i.e. $\nabla V(x^\pm) = 0$.

- Transition time is order 1.
- Existence of minimizers cannot be expected, because the time interval is infinitely large.

Numerical results for finite T



Connection with coarsening

Consider the solution $u(t,x) \in \mathbb{R}$ of the phase-field equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - u^3 + u, \quad t > 0, x \in \mathbb{R},$$

After some relaxation u is constant on large domains and the movement of the interfaces is exponentially slow with the separation of the interfaces cf. Carr & Pego CPAM '89.

Finite decomposition of transitions

Theorem 1.
Let V be admissible and $x^{\pm}$ be two critical points of V. Then there exists a finite sequence of critical points (transition states) $\{x_i\}_{i=0}^{k}$ such that $x_0 = x^-$, $x_k = x^+$ and

$$\Phi(x^-, x^+) = \sum_{i=1}^{k} \min \left\{ J(z) \;\middle|\; \lim_{s \to -\infty} z(s) = x_{i-1} \;\; \lim_{s \to \infty} z(s) = x_i \right\}.$$

TST: x^- and x^+ are local minima and x_1 is a saddle point between x^- and x^+.

Sketch of the proof

Concentration compactness In 1984 P.L. Lions characterized all possible ways how a sequence $\rho_l \in L^1(\mathbb{R})$ can fail to be weakly compact.
If $\rho_l \geq 0$ and $\int_{-\infty}^{\infty} \rho_l(s)\,\mathrm{d}s = \lambda > 0$, then there exists a subsequence such that one of the following statements is true:

Compactness ρ_l is tight,

Vanishing $\lim_{l\to\infty} \sup_t \int_{t-R}^{t+R} \rho_l(s)\,\mathrm{d}s = 0$ for all $R > 0$,

Splitting there exists $0 < \alpha < \lambda$ such that for all $\varepsilon > 0$ there exists $\rho_l^1, \rho_l^2 \in L^1(\mathbb{R})$ such that $\lim_{l\to\infty} \mathrm{dist}(\mathrm{s}upp(\rho_l^1), \mathrm{supp}(\rho_l^2)) = \infty$ and

$$\|\rho_l^1 + \rho_l^2 - \rho_l\|_{L^1} + \left|\|\rho_l^1\|_{L^1} - \alpha\right| + \left|\|\rho_l^2\|_{L^1} + \alpha - \lambda\right| \leq \varepsilon.$$

Minimizers of J

If z minimizes $J(z) = \int_{-\infty}^{\infty} \left(|\dot{z}(s)|^2 + |\nabla V(z(s))|^2\right) \mathrm{d}s$ subject to the boundary conditions $\lim_{s \to \pm\infty} z(s) = x^{\pm}$, then y satisfies the Euler-Lagrange equations

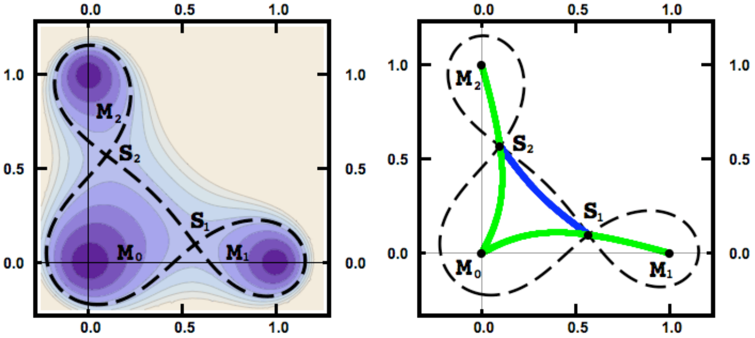
$$\ddot{z} - D^2 V(z) \nabla V(z) = 0. \tag{1}$$

Observation: Solutions of the ode $\dot{z} = \pm \nabla V(z)$ satisfy (1), and the TST formula $J(z) = |V(x^+) - V(x^-)|$ holds.

Theorem 2. *If x^+ or x^- is a local extremum of V, then $\dot{z}^{\pm} = \pm \nabla V(z)$.*

Numerical illustration

$$V(a,b) = \left(a^2 + b^2\right)\left((a-1)^2 + b^2\right)\left(a^2 + (b-1)^2\right).$$



The saddle-saddle connection is not a solution of the gradient-flow as the saddles have the same energy.

The Γ-limit

Theorem. *The Γ-limit of the functional I_ε as ε tends to 0 is*

$$I_0(x) = \begin{cases} \sum_{\tau \in \mathcal{D}} \Phi(x^-(\tau), x^+(\tau)) - \int_0^1 \Delta V(x(s))\,\mathrm{d}s & \text{if } x \in BV([0,1]) \\ & \text{and } x \in \mathcal{E} \text{ a.e} \\ +\infty & \text{else,} \end{cases}$$

where $\mathcal{D}(x)$ is the set of discontinuity points of x and $x^{\pm}(\tau)$ are the left and right-sided limits of x at τ.

Observation: The set of transition times $\mathcal{D}$ is arbitrary, thus the Γ-limit is degenerate.

Conclusions/references

- Minimizers of the Onsager-Machlup functional correspond to the most likely paths.
- The minimizing sequences split into a finite set of individual transitions.
- Transitions which involve at least one local extremum are captured TST transitions, saddle-saddle transitions are not captured by TST.
- The mathematical approach involves a slightly unphysical limit of infinite transition time.

References:

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Outlook

- Characterize the asymptotic behavior of the path measure π_ε as $\varepsilon \to 0$.
  Conjecture: If $T \sim \exp\left(\frac{1}{\varepsilon} \min_{x,x'} \Phi(x, x')\right)$, then π_ε converges to a finite-state, continuous-time Markov process with state space
  $$\mathcal{E} = \left\{ x \in \mathbb{R}^N \; : \; \nabla V(x) = 0 \right\}.$$
- Determine the finite-temperature corrections.