Transition Path Theory

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The problem of rare events

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- ❑ Why the study of rare events is difficult

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- ❑ Why the study of rare events is difficult
- ❑ Prior to TPT: TST, TPS, ...

Overdamped Langevin dynamics

Overdamped Langevin regime

$$\gamma_i \dot{x}_i(t) = -\frac{\partial V(x(t))}{\partial x_i} + \sqrt{2k_B T \gamma_i}\,\eta_i(t)$$

$$\langle \eta_i(t) \rangle = 0 \qquad \langle \eta_i(t)\eta_j(t+\tau) \rangle = \delta_{ij}\delta(\tau)$$

Mathematically:

stochastic differential equations

Overdamped Langevin regime

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Mathematically:

stochastic differential equations

Numerically:

Euler-Maruyama scheme

$$dx_i = f_i(x(t))dt + g_i dW_i(t)$$

$$x_i^{(k+1)} = x_i^{(k)} + f_i(x^{(k)})\Delta t + g_i \Delta W_i^{(k)}$$

Theoretical background

Transition Path Theory: assumptions

- If overdamped regime is assumed: Only ***configuration space*** degrees of freedom matter

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- Dynamics satisfies the ***Markov assumption***
- ***Ergodic assumption***

First aimed object: Transition Path Density

It is the probability density function $m(x|TP) =: m_T(x)$

➔ Implicitly defined exploiting ergodicity

Find an expression for the TPD

We already know:

$$m(x) = \frac{1}{Z} e^{-\beta V(x)}$$

The Gibbs distribution

Find an expression for the TPD

We can obtain: $$\mathbb{P}(TP|x) =: P_{\mathcal{R}}(x)$$

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Central quantity: the ***committor function*** $q(x)$

$$P_{\mathcal{R}}(x) = q(x)(1 - q(x))$$

Find an expression for the TPD

Can apply Bayes' theorem to find:

$$m_T(x) = \frac{1}{\mathcal{Z}_T} m(x) q(x)(1 - q(x))$$

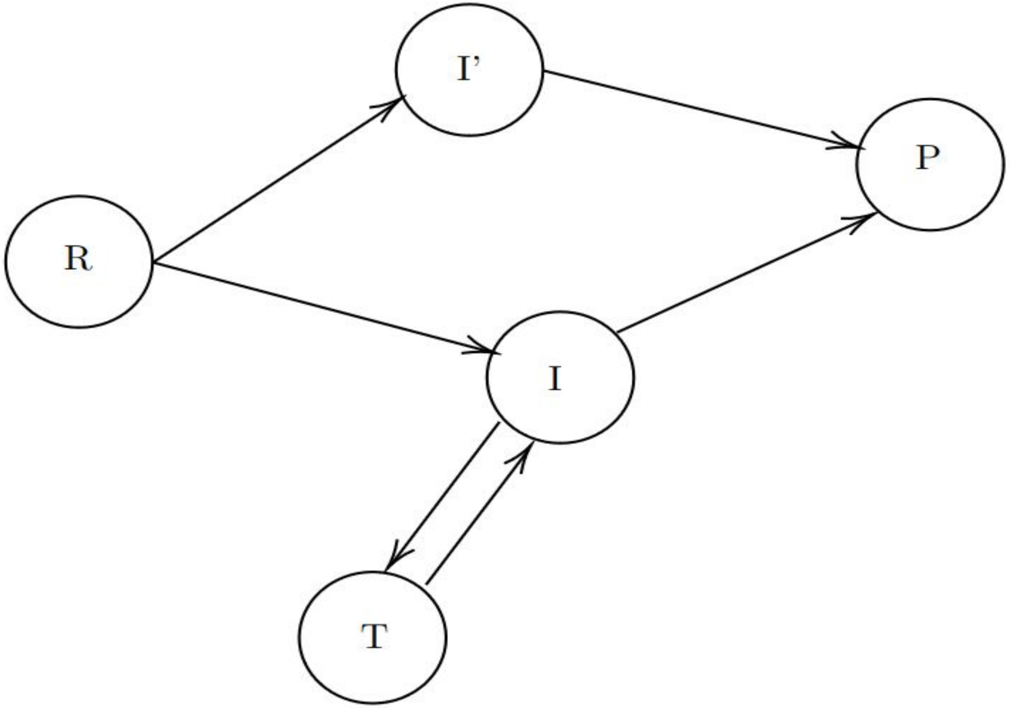
Find an expression for the TPD

It is all reduced in solving the ***backward Kolmogorov eq.***

$$(\nabla^2 - \beta \nabla V \cdot \nabla) q(x) = 0$$

$$q^+(x)|_{\partial R} = 0 \quad q^+(x)|_{\partial P} = 1$$
$$q^-(x)|_{\partial R} = 1 \quad q^-(x)|_{\partial P} = 0$$

Why the TPD is not enough: kinetic traps



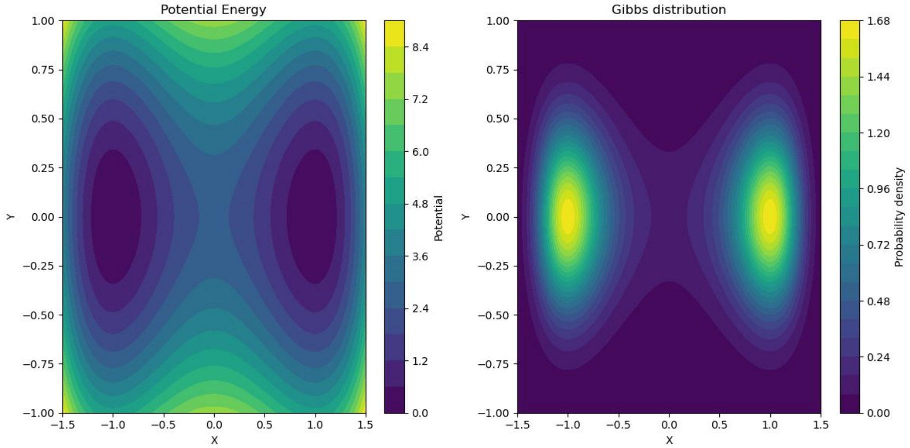
Second aimed object: Transition Path Current

$$J_T(x) = D\nabla q(x)\frac{e^{-\beta V(x)}}{Z}$$

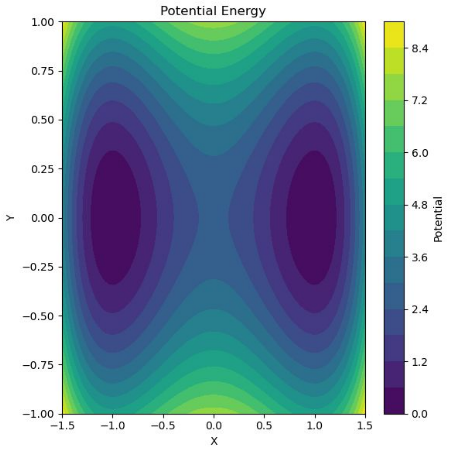
- ➢ Transition rate calculation
- ➢ Reaction tubes

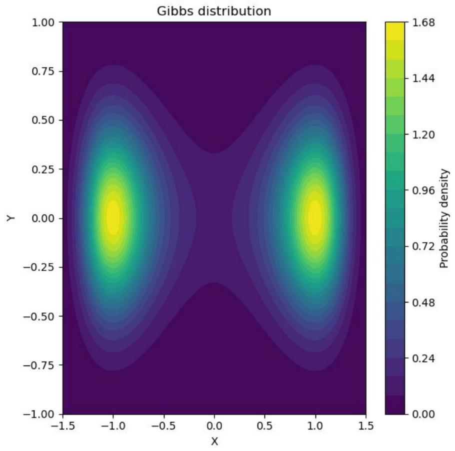
First case study:
the symmetric double well

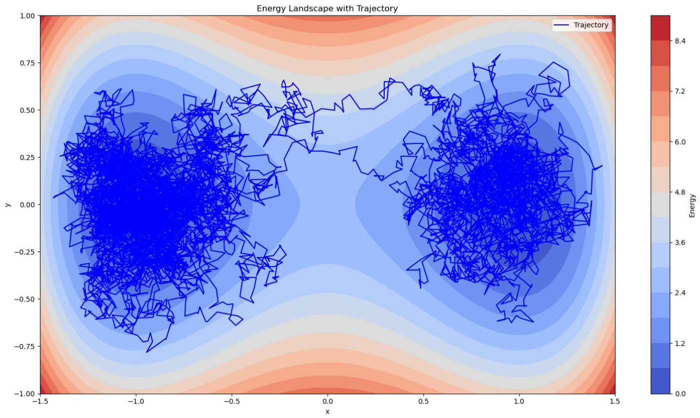
The symmetric double well



The symmetric double well







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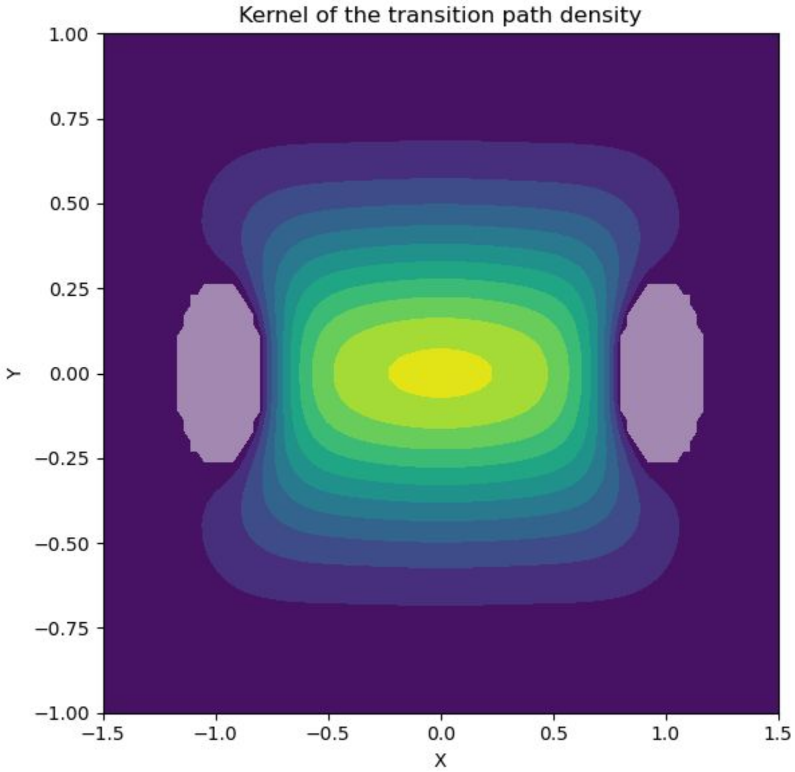

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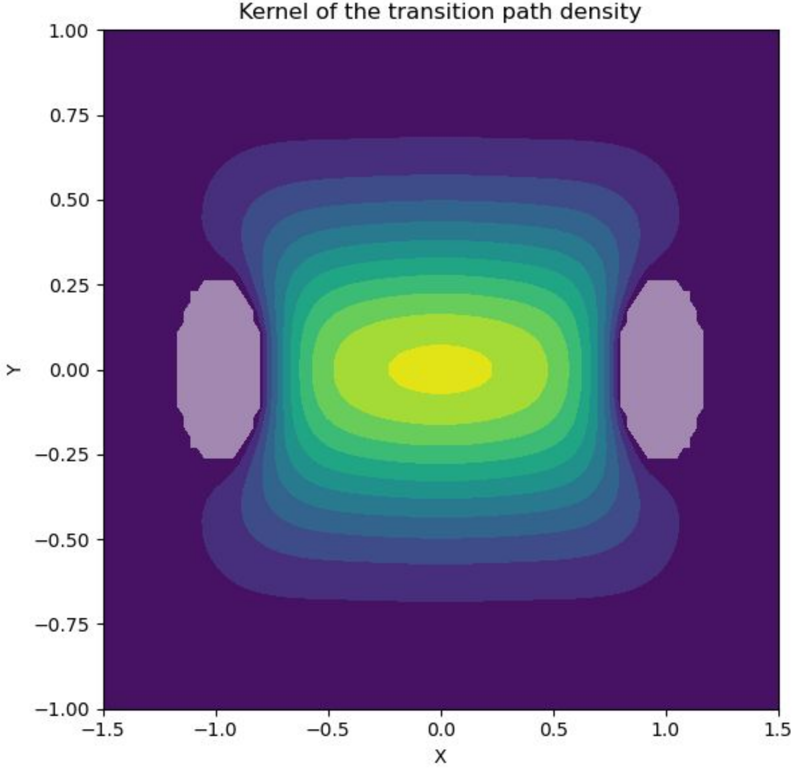
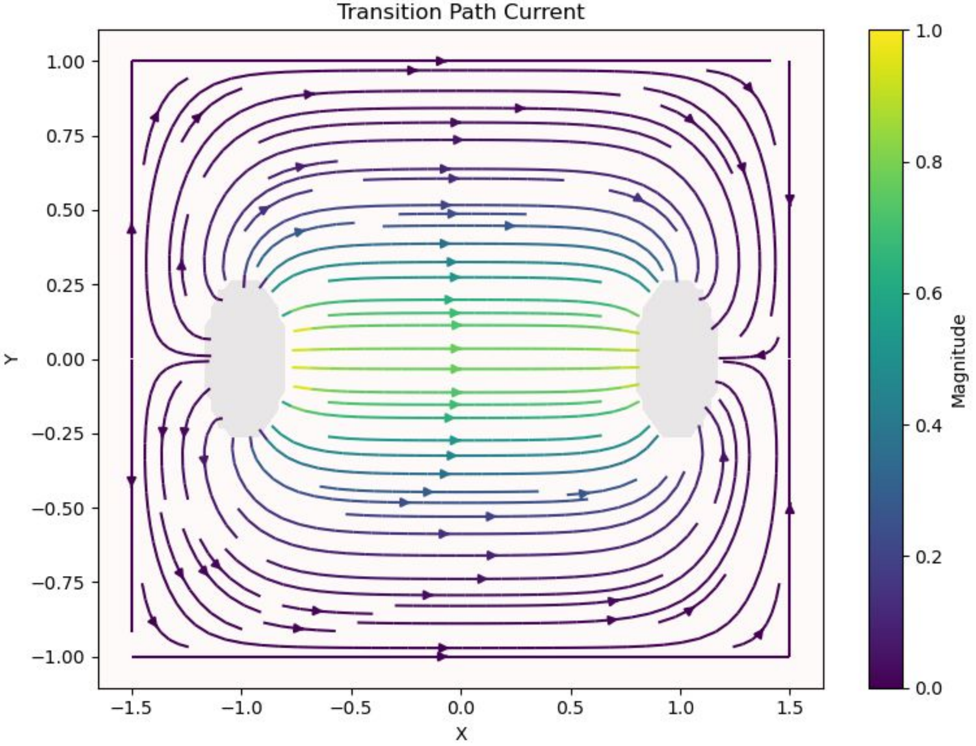
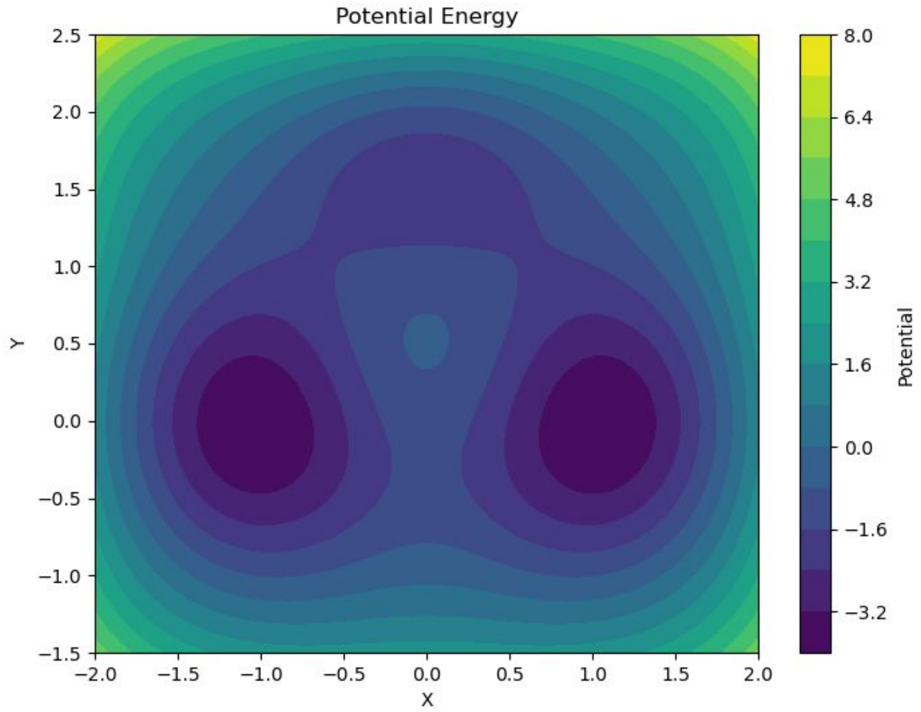


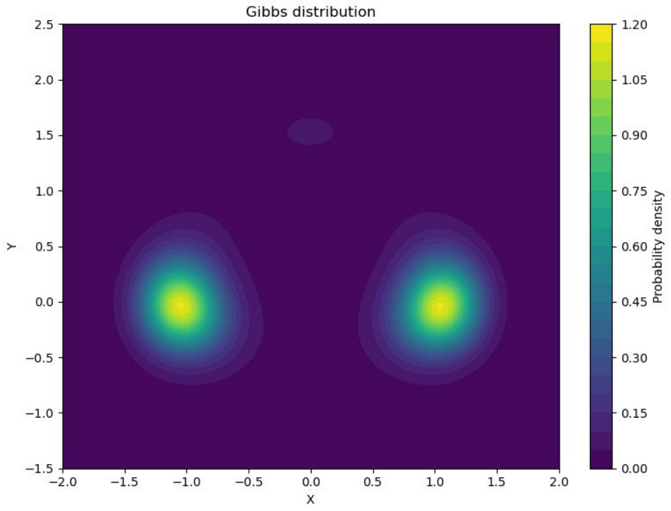


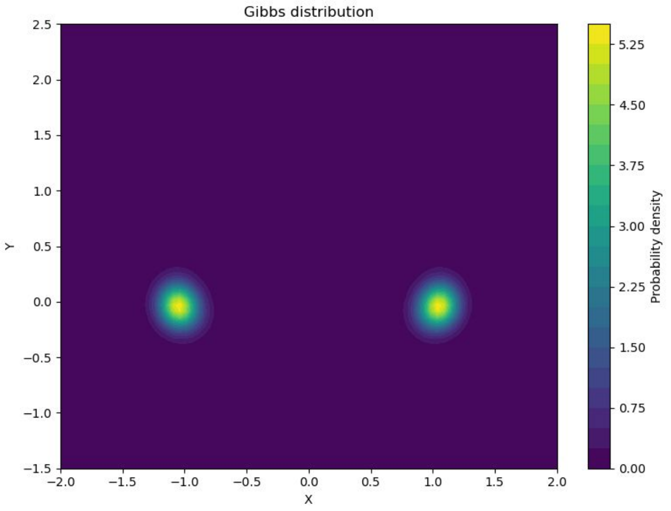
Second case study:
Entropic switching in a triple well

Triple well potential



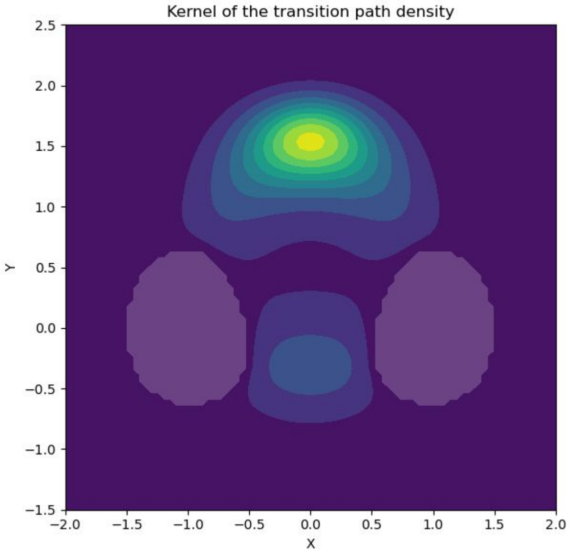
Two different temperatures

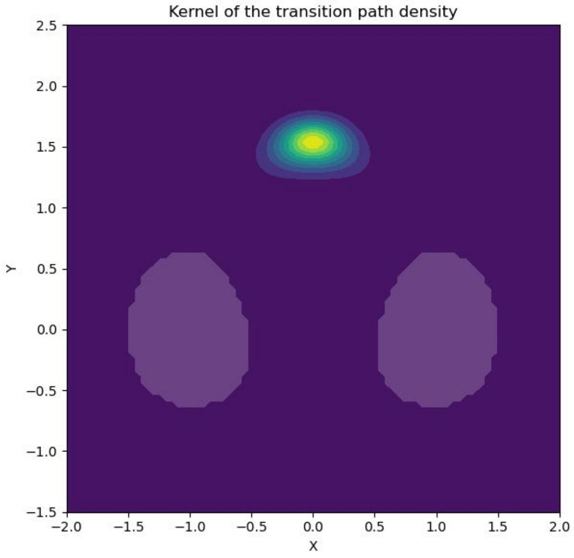




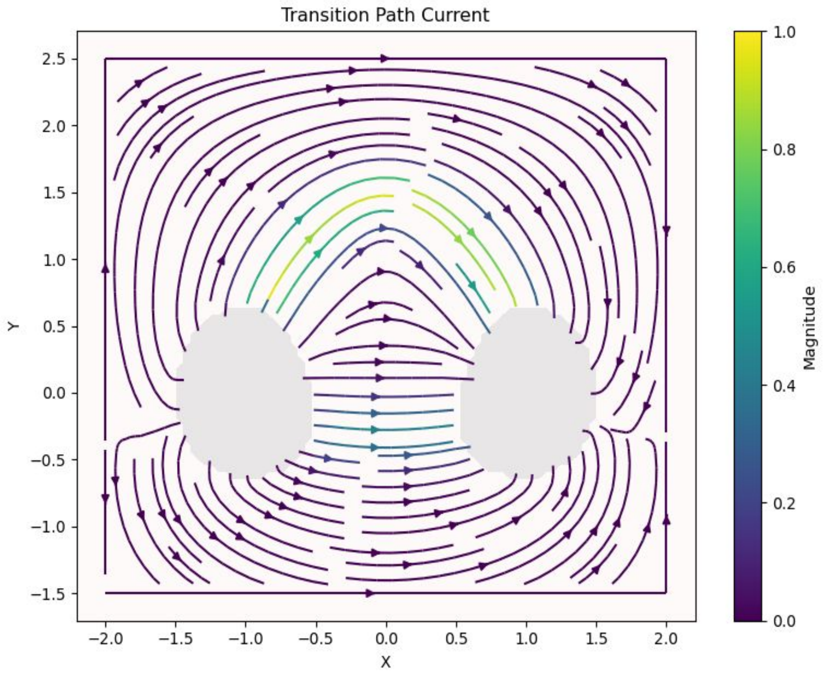
$$\beta_{high} = 1.67 \qquad \beta_{low} = 6.67$$

Transition Path Density gives partial information





Transition Path Current to understand the reaction



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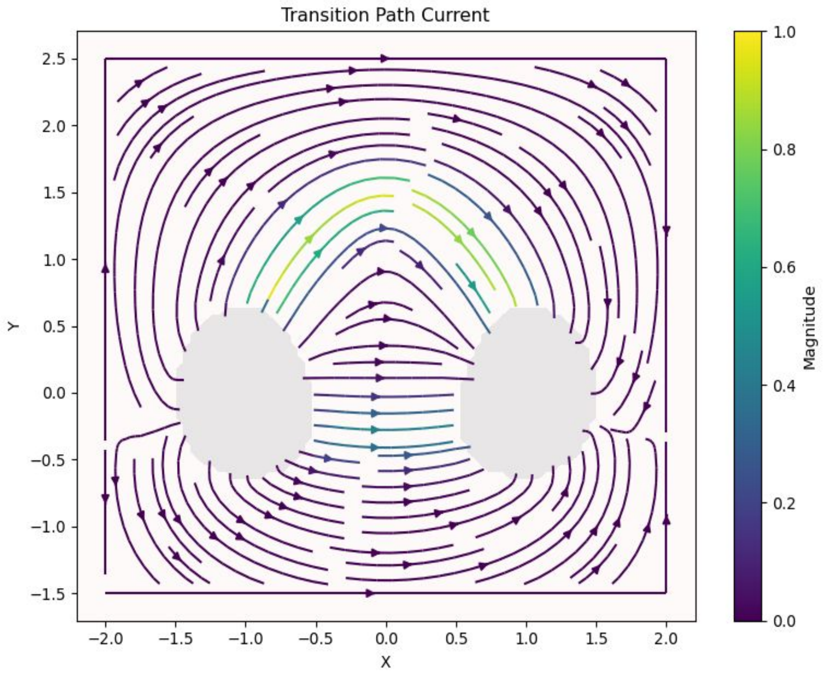

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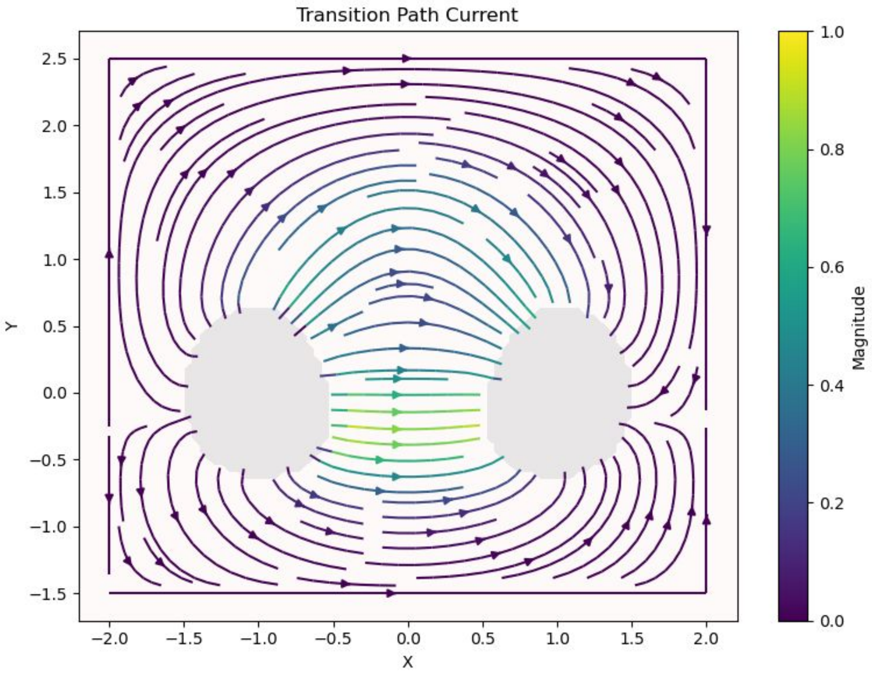

$$\beta_{high} = 1.67$$