

Γ -Limit for Transition Paths of Maximal Probability

F.J. Pinski · A.M. Stuart · F. Theil

Received: 31 October 2011 / Accepted: 7 February 2012 / Published online: 22 February 2012
© Springer Science+Business Media, LLC 2012

Abstract Chemical reactions can be modeled via diffusion processes conditioned to make a transition between specified molecular configurations representing the state of the system before and after the chemical reaction. In particular the model of Brownian dynamics—gradient flow subject to additive noise—is frequently used. If the chemical reaction is specified to take place on a given time interval, then the most likely path taken by the system is a minimizer of the Onsager-Machlup functional. The Γ -limit of this functional is determined explicitly in the case where the temperature is small and the transition time scales as the inverse temperature.

Keywords Onsager-Machlup · Gamma-convergence

1 Introduction

In this paper we study the problem of determining the most likely paths taken by a system undergoing a chemical reaction. We employ the model known as *Brownian dynamics* [1]: the atomic positions are assumed to be governed by a gradient flow in an interaction potential, subject to additive thermal noise. The resulting stochastic differential equation is conditioned to make a transition between two different atomic configurations representing the state of the system before and after the chemical reaction [2]. If the chemical reaction is specified to take place on a given time interval, then the most likely path taken by the system is a minimizer of the Onsager-Machlup functional [3, 4]. Minimizers of the Onsager-Machlup functional have received considerable attention in the chemistry literature (see [5])

F.J. Pinski
Physics Department, University of Cincinnati, PO Box 210011, Cincinnati, OH 45221, USA
e-mail: frank.pinski@uc.edu

A.M. Stuart · F. Theil (✉)
Mathematics Institute, Warwick University, Coventry, CV4 7AL, UK
e-mail: f.theil@warwick.ac.uk

A.M. Stuart
e-mail: a.m.stuart@warwick.ac.uk

and [6] and the references therein) and the work in this paper provides a mathematically rigorous explanation for what is observed in these computational studies. In [6] numerical computations are presented which study minimizers of the Onsager-Machlup functional for a variety of model problems in low dimension, together with some higher dimensional problems from physics and chemistry such as vacancy diffusion and the Lennard-Jones cluster of 38 atoms. The minimizers exhibit a number of interesting effects, including multiple pathways between configurations, together with transition paths which concentrate at saddle points of the potential, and not at minima. The computations in [6] were performed at low temperature over fixed long intervals. To gain mathematical insight into these computations, the work in this paper is concerned with determining the Γ -limit (see [7, 8]) of the Onsager-Machlup functional in the case where the temperature is small and the transition time scales as the inverse temperature. The explicit Γ -limit which we exhibit may also be of independent interest. It can be optimized via knowledge of the critical points of the potential, the trace of the Hessian of the potential at the critical points, and certain heteroclinic orbits connecting them. Notably these heteroclinic orbits are in a Hamiltonian system; heteroclinic orbits in the forward or backward gradient flow found from our model at zero temperature are solutions of this Hamiltonian problem but not necessarily vice versa. Regarding the role of the Hessian in the Γ -limit, it is pertinent to mention the paper [9] in which second derivative of the potential plays a role in a large deviations principle for SDEs.

In Sect. 2 we provide a precise mathematical description of the conditioned SDE which forms our mathematical model. We provide an informal derivation of the Onsager-Machlup functional whose minimizers determine most likely transition paths and we explain the sense in which this informal argument can be made rigorous. In Sect. 3 we compute the Γ -limit of the Onsager-Machlup functional building on related analysis in [10, 11]. The paper concludes, in Sect. 4, with an informal characterization of the Γ -limit, together with numerical experiments which illustrate this characterization.

2 Set-Up

Consider the following conditioned SDE for $x \in C([0, T]; \mathbb{R}^N)$ making a transition between two states x^- and x^+ in time T :

$$\begin{aligned} dx &= -DV(x) dt + \sqrt{2\varepsilon} dW, \\ x(0) &= x^- \quad \text{and} \quad x(T) = x^+. \end{aligned} \tag{2.1}$$

Here $V : \mathbb{R}^N \rightarrow \mathbb{R}$ is the potential, W is a standard Brownian motion in \mathbb{R}^N and $\varepsilon \ll 1$. In many applications in physics/chemistry $N = nd$, $d \in \{1, 2, 3\}$ being the physical dimension and n the number of particles. Then ε is the (non-dimensional) temperature and $x \in C([0, T]; \mathbb{R}^N)$ denotes the configurational path of the n atoms making a transition between x^\pm . Throughout we assume that x^\pm are chosen as critical points of V . We will be particularly interested in choosing these critical points to be minima, so that the problem (2.1) describes a chemical reaction; but, in the numerical computations, we will also choose saddle points in order to illustrate certain mathematical phenomena.

Escape from local minima occurs on timescales which are exponentially long in ε^{-1} as this is the typical time required for an escape over the energy barriers. Conditioned on this escape occurring, the remainder of the transition into the next local minimum itself occurs on scales which are logarithmic in ε^{-1} , being governed by the time taken for a heteroclinic orbit to connect small neighborhoods of critical points. We focus interest on an intermediate

timescale between these two regimes, which is ε^{-1} . This timescale is hence long enough to capture a single transition, but not long enough to capture the typical waiting time in a potential minimum. In particular, transition paths calculated in this scaling, and which pass through an intermediate minimum x^0 of V , will not necessarily exhibit the “typical” behavior that would be exhibited if the time to make the transition from x^- to x^+ via x^0 were left free. The behavior of the most likely single transitions in this regime is captured by minimizers of the Freidlin-Wentzell action [12, 13]. Numerical methods to capture multiple such transitions are the subject of active study, and the reader should consult [14], and the references therein, for details. From an applied perspective, our work serves to highlight the potential pitfalls of using the Onsager Machlup approach to compute transition paths, and this point is discussed in detail in [6]. As mentioned above, the work in this paper gives a mathematical explanation for the numerical results observed in [6]. The results may also be of independent interest from the point of view of the calculus of variations. In particular the results show how heteroclinic orbits in a certain Hamiltonian flow form the building block for the construction of the Γ -limit. This fact may also be of interest in applications where attention has focused on heteroclinic orbits in the forward or backward gradient flow found from (2.1) with $\varepsilon = 0$; these form particular instances of heteroclinic orbits in the Hamiltonian flow, but non-gradient connections are also possible, as we will demonstrate.

To explain our focus on the particular scaling of interest in this paper we choose $T = \varepsilon^{-a}$ and demonstrate why the choice of $a = 1$ has a distinguished property for Γ -limits. To this end we rescale time as $t = \varepsilon^{-a}s$, to obtain

$$\begin{aligned} dx &= -\frac{1}{\varepsilon^a}DV(x) ds + \sqrt{2\varepsilon^{1-a}} dW, \\ x(0) &= x^- \quad \text{and} \quad x(1) = x^+. \end{aligned} \tag{2.2}$$

In this scaling we are studying transitions on a unit time-interval, in which the systematic motion of the molecules is large and the thermal noise is small (resp. large) if $a < 1$ (resp. $a > 1$).

Conditioning the diffusion process to hit a point at time 1 is of course a measure zero event with respect to the Brownian motion. However the regular conditional probability measure π governing the stochastic boundary value problem (2.2) exists and may be characterized via its density with respect to the Brownian bridge measure π_0 arising in the case $V \equiv 0$ [15, 16]. To obtain this we first obtain an expression for the law of x , *without* the condition $x(1) = x^+$, which we denote by ν . If ν_0 is the Wiener measure on $[0, 1]$ then the Girsanov formula gives

$$\frac{d\nu}{d\nu_0}(x) \propto \exp\left(-\frac{1}{2} \int_0^1 \frac{1}{2\varepsilon^{1+a}} |DV(x(s))|^2 ds + \frac{1}{\varepsilon} (DV(x(s)), dx(s))\right)$$

with constant of proportionality independent of x and with $|\cdot|$ denoting the Euclidean norm. If we apply the Itô formula to $V(x(s))$ then we obtain

$$\frac{d\nu}{d\nu_0}(x) \propto \exp\left(-\frac{1}{2} \int_0^1 \left(\frac{1}{2\varepsilon^{1+a}} |DV(x(s))|^2 - \frac{1}{\varepsilon^a} \Delta V(x(s))\right) ds\right)$$

where the constant of proportionality now depends on x , but only through the value of $x(1)$. If we now condition on the boundary value $x(1) = x^+$, as in [16], we find that

$$\frac{d\pi}{d\pi_0}(x) \propto \exp\left(-\frac{1}{2\varepsilon^{1+a}} \int_0^1 G(x(s); \varepsilon) ds\right) \tag{2.3}$$

where the *path potential* G is

$$G(x; \varepsilon) = \frac{1}{2} |DV(x)|^2 - \varepsilon \Delta V(x). \tag{2.4}$$

Now the constant of proportionality does not depend on x .

Functions are infinite dimensional and there is no Lebesgue measure in infinite dimensions. Nonetheless, it is instructive to think heuristically of the Brownian bridge obtained from (2.2) with $V \equiv 0$ as having a probability density (with respect to Lebesgue measure) of the form [17]

$$\exp\left(-\frac{1}{4\varepsilon^{1-a}} \int_0^1 \left|\frac{dx}{ds}\right|^2 ds\right). \tag{2.5}$$

(This is the formal limit obtained from the probability density function for a discretized Brownian bridge.) Let $H_{\pm}^1((0, 1))$ denote the subset of $H^1((0, 1); \mathbb{R}^N)$ comprised of functions satisfying $x(0) = x^-$ and $x(1) = x^+$. Then, combining (2.3) and (2.5), we may think of the probability density for π as being proportional to $\exp(-\frac{1}{2\varepsilon} I_{\varepsilon}(x))$ where the Onsager-Machlup functional $I_{\varepsilon} : H_{\pm}^1((0, 1)) \rightarrow \mathbb{R}$ is defined by

$$I_{\varepsilon}(x) := \int_0^1 \left(\frac{\varepsilon^a}{2} \left|\frac{dx}{ds}\right|^2 + \frac{1}{\varepsilon^a} G(x; \varepsilon) \right) ds.$$

In this form it may be seen that for all $a \in (0, 1)$ the term ΔV in G in (2.4) disappears in the limit $\varepsilon \rightarrow 0$. If $a = 1$ it contributes to the Γ -limit of I_{ε} at the same order, namely $\mathcal{O}(1)$, as the other two terms. If $a > 1$ the Γ -limit of I_{ε} is more complex, this case is beyond the scope of this article.

We will concentrate on the choice $a = 1$ from now on, the cases $a \in (0, 1)$ give the same results without the Ito-term ΔV . This leads to the Onsager-Machlup functional in the following form:

$$I_{\varepsilon}(x) := \int_0^1 \left(\frac{\varepsilon}{2} \left|\frac{dx}{ds}\right|^2 + \frac{1}{\varepsilon} G(x; \varepsilon) \right) ds. \tag{2.6}$$

The remainder of the paper is devoted to studying this problem from the point of view of the calculus of variations.

This intuitive definition of $I_{\varepsilon}(x)$, via the logarithm of the pathspace probability density function, suggests that minimizers of I_{ε} are related to paths of maximal probability. It is, however, derived from the heuristic (2.5). Nonetheless, the idea of paths of maximal probability can be formulated precisely as follows [3, 4]. Let $B^{\delta}(z)$ denote a ball of radius δ in $C([0, 1]; \mathbb{R}^N)$ centered on $z \in H_{\pm}^1((0, 1))$. Then, for any $z_1, z_2 \in H_{\pm}^1((0, 1))$,

$$\lim_{\delta \rightarrow 0} \frac{\pi(B^{\delta}(z_1))}{\pi(B^{\delta}(z_2))} = \exp\left(\frac{1}{2\varepsilon} (I_{\varepsilon}(z_2) - I_{\varepsilon}(z_1))\right).$$

Thus, for small ball radius δ , the logarithm of the ratio of the probabilities of the two balls is equal to the difference in I_{ε} evaluated at the ball centers. For this reason we are interested in minimizers of I_{ε} .

The following notation will be useful. We define

$$\begin{aligned}
 J_\varepsilon(x) &= \int_0^1 \left(\frac{\varepsilon}{2} \left| \frac{dx}{ds} \right|^2 + \frac{1}{2\varepsilon} |DV(x)|^2 \right) ds, \\
 J(x) &= \int_{-\infty}^\infty \left(\frac{1}{2} \left| \frac{dx}{ds} \right|^2 + \frac{1}{2} |DV(x)|^2 \right) ds.
 \end{aligned}
 \tag{2.7}$$

Then

$$I_\varepsilon(x) = J_\varepsilon(x) - \int_0^1 \Delta V(x(s)) ds.
 \tag{2.8}$$

Our goal in what follows is to demonstrate that the Γ -limit of I_ε is finite only when evaluated on the set of BV functions supported on the critical points of V . And, furthermore, that on this set the value of the Γ -limit is determined by (suitably rescaled) minima of J , subject to end-point conditions, together with the integral of $\Delta V(x)$. Thus we conclude this section with some observations concerning minima of J .

The Euler-Lagrange equations for the functional J are

$$\frac{d^2x}{ds^2} - D^2V(x)DV(x) = 0,
 \tag{2.9}$$

where D^2V denotes the Hessian of V . These equations are Hamiltonian and conserve the energy

$$E = \frac{1}{2} \left| \frac{dx}{ds} \right|^2 - \frac{1}{2} |DV(x)|^2.$$

Thus heteroclinic orbits connecting critical points of V via (2.9), for which E is necessarily zero, satisfy

$$\left| \frac{dx}{ds} \right| = |DV(x)|.
 \tag{2.10}$$

Hence, if there is a heteroclinic orbit connecting critical points of V under either of the forward or backward gradient flows

$$\frac{dx}{ds} = \pm DV(x)
 \tag{2.11}$$

then this will also determine a heteroclinic orbit in the Hamiltonian system. However, the converse is not necessarily the case: there are heteroclinic orbits in the Hamiltonian flow which are not heteroclinic orbits in the gradient dynamics.

We say that a potential $V : \mathbb{R}^N \rightarrow \mathbb{R}$ is *admissible* if $V \in C^3(\mathbb{R}^N, \mathbb{R})$ and

1. the set of critical points

$$\mathcal{E} = \{x \in \mathbb{R}^N \mid DV(x) = 0\}$$

is finite;

2. the Hessian $D^2V(x)$ has no zero eigenvalues for every $x \in \mathcal{E}$;
3. the weak coercivity condition

$$\exists R > 0 \quad \text{such that} \quad \inf_{|x| > R} |DV(x)| > 0
 \tag{2.12}$$

is satisfied.

Admissibility implies, in particular, that all critical points for the gradient flows (2.11) are hyperbolic.

For each pair $x^-, x^+ \in \mathcal{E}$ the set of *transition paths* is defined as

$$X(x^-, x^+) = \left\{ y \in BV(\mathbb{R}) \mid \lim_{t \rightarrow \pm\infty} y(t) = x^\pm \text{ and } \dot{y} \in L^2(\mathbb{R}) \right\}.$$

Lemma 2.1 *For any $x \in X(x^-, x^+)$*

$$J(x) \geq |V(x^+) - V(x^-)|. \tag{2.13}$$

Furthermore, if the infimum of J over $X(x^-, x^+)$ is attained at $x^ \in X(x^-, x^+)$, then $x^* \in C^2(\mathbb{R})$ satisfies the Euler-Lagrange equation (2.9) and has the property*

$$J(x^*) = \int_{-\infty}^{\infty} |DV(x^*(s))|^2 ds. \tag{2.14}$$

Assume that the potential is admissible. If either x^- or x^+ is a local minimum or maximum and there exists a heteroclinic orbit x^ connecting x^- and x^+ under the Hamiltonian dynamics (2.9), then x^* solves (2.11) and*

$$J(x^*) = |V(x^+) - V(x^-)|. \tag{2.15}$$

In particular x^ is a minimizer of J which attains the lower bound the lower bound (2.13).*

Proof Clearly

$$\begin{aligned} J(x) &\geq \int_{-\infty}^{\infty} \left| \frac{dx}{ds} \right| |DV(x)| ds \\ &\geq \int_{-\infty}^{\infty} \left| \frac{d}{ds} (V(x)) \right| ds \\ &\geq \left| \int_{-\infty}^{\infty} \frac{d}{ds} (V(x)) ds \right|. \end{aligned}$$

Integrating and using the end point conditions gives the first result. Standard regularity results imply that minimizers x of J are $C^2(\mathbb{R})$ and satisfy the Euler-Lagrange equation (2.9). Equation (2.14) then follows from (2.10).

To prove the final result we first note that the linearization of (2.9) at a critical point $x_c \in \mathcal{E}$ is given by

$$\frac{d^2y}{ds^2} - D^2V(x_c)^2y = 0, \tag{2.16}$$

whilst the forward gradient flow, given by (2.11) with a minus sign, has linearization

$$\frac{dy}{ds} + D^2V(x_c)y = 0. \tag{2.17}$$

If V is admissible, and x_c is a critical point of V , then $(x_c, 0)$ is hyperbolic for the Hamiltonian flow and, from (2.16), has stable and unstable manifolds both of dimension N .

We assume next that x^+ is a local minimum of V . Let \mathcal{M} be the N -dimensional manifold defined by

$$\mathcal{M} = \{(x, -DV(x)) \mid x \in \mathbb{R}^N\} \subset \mathbb{R}^{2N}.$$

Differentiating (2.11) with respect to t shows that \mathcal{M} is invariant under the flow of (2.9). Since $D^2V(x^+)$ is positive definite there exists $\varepsilon > 0$ such that all solutions $y(t)$ of (2.9) with the properties $|y(0) - x^+| < \varepsilon$ and $\dot{y}(0) = -DV(y(0))$ converge to x^+ as t tends to infinity. Define next the stable manifold

$$\mathcal{M}(x^+) = \{(x, v) \in \mathbb{R}^{2N} \mid \lim_{t \rightarrow \infty} y(t) = x^+\},$$

where y solves (2.9) and satisfies the initial condition $y(0) = x, \dot{y}(0) = v$. Since the dimension of $\mathcal{M}(x^+)$ is N the sets $\mathcal{M}(x^+) \cap \{|x - x^+| < \varepsilon\}$ and $\mathcal{M} \cap \{|x - x^+| < \varepsilon\}$ coincide. Thanks to the invariance of \mathcal{M} it follows that $\mathcal{M}(x^+) \subset \mathcal{M}$. As a result one obtains that

$$J(x^*) = - \int_{-\infty}^{\infty} DV(x^*(t))x^* = V(x^-) - V(x^+) \geq 0,$$

where the last inequality holds because (2.11) implies that V is a decreasing Lyapunov function along the trajectory x^* . Thus, formula (2.15) has been proven under the assumption that x^+ is a local minimum. The remaining three cases (x^+ is a local maximum, x^- is a local minimum/maximum) can be dealt with in an analogous fashion. □

The result shows that only saddle-saddle connections can give rise to heteroclinic orbits in the Hamiltonian system (2.9) which cannot be found by in one of the gradient flows (2.11). As a closing remark in this section we observe that the existence of heteroclinic orbit in (2.9) is a generic property of non-degenerate systems. For the Hamiltonian flow the effective dimension of the space is $2N - 1$, because it is constrained to a level set of the Hamiltonian. Since the stable and unstable manifolds for the Hamiltonian system are both of dimension N (cf. (2.16)) we expect that, generically, there will be a 1 dimensional manifold connecting any pair of equilibria under the Hamiltonian flow.

3 The Γ -Limit

We now determine the Γ -limit for the Onsager-Machlup function (2.6). A thorough introduction to Γ -convergence can be found in [8] and [7]. Problems closely related to ours are studied using Γ -convergence in [10, 11].

We start with some basic definitions and propositions which serve to explain the form of the Γ -limit. The key result is contained in Proposition 3.2 which demonstrates that every transition is achieved via a *finite* collection of intermediate transitions. The limit Theorem 3.4 is then stated and proved, building on a number of lemmas which follow it.

Recall the definition of admissible potential V , as well as that of a transition path.

Proposition 3.1 *Let V be admissible and define for each pair $x^-, x^+ \in \mathcal{E}$ the function $\Phi(x^-, x^+)$ by*

$$\Phi(x^-, x^+) = \inf\{J(y) \mid y \in X(x^-, x^+)\}.$$

Then there exists $c > 0$ such that $\Phi(x^-, x^+) > c$ for all pairs $x^\pm \in \mathcal{E}$ with $x^- \neq x^+$.

We can establish a direct representation of the transition energy Φ which involves only minima and avoids the usage of infima.

Proposition 3.2 *Let V be admissible and $x^\pm \in \mathcal{E}$ be two critical points of V . Then there exists a finite sequence $\{x_i\}_{i=0}^k \in \mathcal{E}$ such that $x_0 = x^-$, $x_k = x^+$ and*

$$\Phi(x^-, x^+) = \sum_{i=1}^k \min\{J(y) \mid y \in X(x_{i-1}, x_i)\}.$$

A straight-forward refinement of the analysis shows that the sequence x_i is injective. Now we state the definition of Γ -convergence.

Definition 3.3 Let X be a Banach-space, $\varepsilon > 0$ a parameter and $I_\varepsilon : X \rightarrow \mathbb{R}$ a family of functionals. The functional $I_0 : X \rightarrow \mathbb{R} \cup \{+\infty\}$ is the Γ -limit of I_ε as $\varepsilon \rightarrow 0$ if for all $x \in X$ and all sequences $x_\varepsilon \in X$ which converge weak- $*$ to x as ε tends to 0 the liminf-inequality

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

holds, and for all $z \in X$, there exists a recovery sequence $z_\varepsilon \in X$ which converges weak- $*$ to z and satisfies

$$\limsup_{\varepsilon \rightarrow 0} I_\varepsilon(z_\varepsilon) \leq I_0(z).$$

Theorem 3.4 *Let V be an admissible potential. Then the Γ -limit of the functional I_ε as ε tends to 0 is*

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

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 .

Proposition 3.2 shows that the infimum Φ can be written as a finite sum of minima. These minima are obtained from evaluation of (2.14), where x^* solves (2.9) subject to $x^*(t) \rightarrow x_{i-1}/x_i$ as $t \rightarrow \pm\infty$. Furthermore, if either x_{i-1} or x_i is a local extremum of V , then x^* is also a heteroclinic orbit in one of the gradient flows (2.11), then the minimum is given by (2.15). Thus Theorem 3.4 shows that the Γ -limit of I_ε can be computed through knowledge of the critical points of V and the set of (Hamiltonian or gradient) heteroclinic orbits connecting them.

We start the proof of Theorem 3.4 by proving a lemma which delivers a lower bound for the amount of energy needed to reach one of the stationary points $x \in \mathcal{E}$ when starting nearby. We will often write x^\pm as a shorthand for $\{x^-, x^+\}$.

Lemma 3.5 *Let V be an admissible potential. There exists numbers $C, \varepsilon_0 > 0$ such that for and all $\varepsilon \in [0, \varepsilon_0]$, $x^\pm \in \mathcal{E}$ and all paths $y \in X(x^-, x^+)$ with $\text{dist}(y(0), x^\pm) \geq \varepsilon$ the estimate*

$$J(y) \geq \frac{1}{2C} \varepsilon^2$$

holds.

Proof We first show that there exist numbers $\delta, C > 0$ such that, for all $x, y \in \mathbb{R}^N$ with $x \in \mathcal{E}$ and with the property $|y - x| < \delta$, the estimates

$$\frac{1}{C}|y - x|^2 \leq |DV(y)|^2 \leq C|y - x|^2. \tag{3.1}$$

Indeed, thanks to the smoothness of V and nondegeneracy condition $\det(D^2V(x)) \neq 0$ for $x \in \mathcal{E}$, for sufficiently small ε and large \tilde{C}

$$\begin{aligned} |DV(y) - D^2V(x) \cdot (y - x)| &\leq \tilde{C}|y - x|^2, \\ |z| &\leq \tilde{C}|D^2V(x) \cdot z| \quad \forall z \in \mathbb{R}^N \end{aligned}$$

hold. Thus

$$\begin{aligned} |DV(y)| &\geq |D^2V(x) \cdot (y - x)| - \tilde{C}|y - x|^2 \\ &\geq \frac{1}{\tilde{C}}|y - x| - \tilde{C}|y - x|^2 \geq \frac{1}{2\tilde{C}}|y - x| \end{aligned}$$

if $|y - x| \leq \min\{\delta, \frac{1}{2\tilde{C}^2}\}$. This shows that the first inequality in (3.1) holds. The second inequality is obtained in a similar way.

Let $y \in X(x^-, x^+)$ and recall that by Sobolev’s imbedding theorem y is continuous. For each $\varepsilon \in (0, \min\{\delta, \frac{1}{2\tilde{C}^2}\})$ we define

$$t^+(\varepsilon) = \min\{s \in \mathbb{R} \mid |y(t') - x^+| < \varepsilon \text{ for all } t' > s\}, \tag{3.2}$$

and t^- analogous. Then we obtain

$$\begin{aligned} J(y) &\geq \int_{t^+(\varepsilon)}^\infty |DV(y(s))| |\dot{y}(s)| ds \geq \frac{1}{2C} \int_{t^+(\varepsilon)}^\infty (x^+ - y) \cdot \dot{y}(s) ds \\ &= \frac{1}{4C} |y(t^+(\varepsilon)) - x^+|^2 = \frac{1}{4C} \varepsilon^2. \end{aligned}$$

The claim follows since we can derive the same estimate with t^- instead of t^+ . □

Proof of Proposition 3.1 Let $r > 0$ be the separation of the stationary points of V , i.e.

$$r = \min\{|x - x'| \mid x, x' \in \mathcal{E}, x \neq x'\},$$

and let $y_l \in X(x^-, x^+)$ be such that $\lim_{l \rightarrow \infty} J(y_l) = \Phi(x^-, x^+)$. There exists a sequence $t_l \in \mathbb{R}$ such that $\text{dist}(y_l(t_l), \mathcal{E}) \geq r/2$ and thus Lemma 3.5 applied to the translated sequence $y_l(\cdot - t_l)$ implies that $\inf_l J(y_l) \geq c$, with $c = \frac{1}{2C} \min\{r/2, \varepsilon_0\}^2$. □

The proof of Proposition 3.2, showing the existence of minimizing connecting orbits, is established with the direct method of the calculus of variations, with the aid of the following lemma.

Lemma 3.6 *Let $x^\pm \in \mathcal{E}$. If there exists a minimizing sequence $\{y_l\}_{l \in \mathbb{N}} \in X(x^-, x^+)$ such that the density $\rho_l(t) = \frac{1}{2}(|\dot{y}_l(t)|^2 + |DV(y_l(t))|^2)$ is tight in $L^1(\mathbb{R})$, then there exists a minimizer $y^\pm \in X(x^-, x^+)$ such that $J(y^\pm) = \Phi(x^-, x^+)$.*

Proof First we show that the boundary conditions are not lost during the passage to the limit. The tightness of ρ_l implies that for each $\varepsilon > 0$ there exists $\tau^\pm(\varepsilon) \in \mathbb{R}$ with $\tau^-(\varepsilon) < \tau^+(\varepsilon)$ and the property that, for all l ,

$$\limsup_{l \rightarrow \infty} \frac{1}{2} \int_{\mathbb{R} \setminus (\tau^-, \tau^+)} (|\dot{y}_l|^2 + |DV(y_l(s))|^2) ds \leq \frac{1}{4C} \varepsilon^2, \tag{3.3}$$

where C is the constant in Lemma 3.5. Let

$$t_l^+(\varepsilon) = \min\{s \in \mathbb{R} \mid |y_l(t') - x^+| < \varepsilon \text{ for all } t' > s\},$$

and t_l^- analogously. Without loss of generality we assume that $t^-(\varepsilon) \leq 0 \leq t_l^+(\varepsilon)$ and $|y_l(0) - x^\pm| \geq \varepsilon$. Then Lemma 3.5 implies that

$$\limsup_{l \rightarrow \infty} \frac{1}{2} \int_{t_l^+}^\infty (|\dot{y}_l|^2 + |DV(y_l(s))|^2) ds \geq \frac{1}{4C} \varepsilon^2.$$

Together with inequality (3.3) we obtain that $\limsup_{l \rightarrow \infty} t_l^+(\varepsilon) \leq \tau^+(\varepsilon)$. Another application of this argument with t^+ replaced by t^- delivers the desired result concerning the boundary conditions: for each $\varepsilon > 0$ there exists $-\infty < \tau^-(\varepsilon) < \tau^+(\varepsilon) < \infty$ such that

$$\begin{cases} \limsup_{l \rightarrow \infty} \sup_{s \geq \tau^+} |y_l(s) - x^+| \leq \varepsilon, \\ \limsup_{l \rightarrow \infty} \sup_{s \leq \tau^-} |y_l(s) - x^-| \leq \varepsilon. \end{cases} \tag{3.4}$$

From the bound on \dot{y}_l in $L^2(\tau^-(\varepsilon), \tau^+(\varepsilon))$ we deduce that the length of the vector $y_l(0) \in \mathbb{R}^N$ is bounded. Since $J(y_l)$ is bounded the sequence \dot{y}_l is bounded in $L^2(\mathbb{R})$. We extract a subsequence y_l (not relabeled) such that \dot{y}_l converges weakly to $\eta \in L^2(\mathbb{R})$ and $y_l(0)$ converges to $z \in \mathbb{R}^d$.

We define the limiting path y^\pm by

$$y^\pm(t) = z + \int_0^t \eta(s) ds.$$

Equation (3.4) implies that $\lim_{s \rightarrow \pm\infty} y^\pm(s) = x^\pm$, i.e. the boundary conditions are satisfied.

Next we demonstrate that y^\pm is a minimizer, i.e.

$$\lim_{l \rightarrow \infty} J(y_l) = J(y^\pm).$$

Note that J is weakly lower semicontinuous: the first term is weakly lower semicontinuous because it is convex whilst the second term is weakly continuous. To see the weak continuity note that

$$\begin{aligned} \int_{\mathbb{R}} |DV(y^\pm(s))| ds &= \lim_{R \rightarrow \infty} \int_{-R}^R |DV(y^\pm(s))| ds \\ &= \lim_{R \rightarrow \infty} \lim_{l \rightarrow \infty} \int_{-R}^R |DV(y_l(s))| ds = \lim_{l \rightarrow \infty} \int_{-\infty}^\infty |DV(y_l(s))| ds. \end{aligned}$$

The last equation is again due to the tightness of $J(y_l)$, the second but last equation holds because of Sobolev’s embedding theorem. The weak lower semicontinuity of J , coupled with the fact that $\{y_l\}$ is a minimizing sequence, shows that $J(y^\pm) = \lim_{l \rightarrow \infty} J(y_l)$.

Finally we show that $\dot{y}^\pm \in L^1(\mathbb{R})$, which entails the claim $y^\pm \in X(x^-, x^+)$. Define the functional

$$G_t(y) = \frac{1}{2} \int_t^\infty (|\dot{y}(s)|^2 + |DV(y(s))|^2) ds,$$

and the function $g(t) = G_t(y^\pm)$. Note that g is monotonically decreasing with t and $(y^\pm(s))_{s \geq t}$ minimizes $G_t(y)$ for every t , subject to the boundary condition $y(t) = y^\pm(t)$. Testing $G_t(\cdot)$ with a function which is affine on $[t, t + 1]$ and assumes the value x^+ for all $s \geq t + 1$ together with estimate (3.1) delivers the bound

$$g(t) \leq \frac{1}{2} |y^\pm(t) - x^+|^2 \int_0^1 (1 + Cs^2) ds = \frac{1}{2} \left(1 + \frac{C}{3}\right) |y^\pm(t) - x^+|^2. \tag{3.5}$$

Recall that $\lim_{t \rightarrow \infty} y^\pm(t) = x^+$ and choose $t^+ > 0$ such that $|y(t) - x^+| < \varepsilon_0$ for all $t > t^+$, where ε_0 is defined in Lemma 3.5. The function g satisfies for all $t > t^+$ the differential inequality

$$-\frac{dg}{dt}(t) \geq \frac{1}{2} |DV(y^\pm(t))|^2 \geq \frac{1}{2C} |y^\pm(t) - x^+|^2 \geq \mu g(t),$$

with $\mu = \frac{3}{(3+C)C}$. The last inequality is (3.5), the penultimate inequality is due to (3.1). Gronwall’s inequality implies the exponential decay bound $g(t) \leq \varepsilon_0 e^{-\mu(t-t^+)}$, and Lemma 3.5 delivers that $y^\pm(t)$ converges exponentially fast to x^+ as t tends to infinity. Since y^\pm satisfies the Euler-Lagrange equation (2.9) we obtain that $\dot{y}^\pm(t)$ converges exponentially fast to 0 and in particular $\dot{y}^\pm \in L^1([t^+, \infty))$. The same argument also shows that $\dot{y}^\pm \in L^1((-\infty, t^-])$ for some t^- , and thus $\dot{y}^\pm \in L^1(\mathbb{R})$. \square

The proof of Proposition 3.2 also relies on Lions’ concentration compactness lemma which we state here for completeness.

Lemma 3.7 [18] *Let $(\rho_l)_{l \geq 1}$ be a sequence in $L^1(\mathbb{R})$ satisfying*

$$\rho_l \geq 0 \text{ in } \mathbb{R} \text{ and } \lim_{l \rightarrow \infty} \int_{\mathbb{R}} \rho_l(t) dt = \lambda,$$

where $\lambda > 0$ is fixed. Then, there exists a subsequence (not relabeled) satisfying one of the following three possibilities:

1. (Compactness) there exists $t_l \in \mathbb{R}$ such that $\rho_l(\cdot - t_l)$ is tight, i.e.

$$\forall \varepsilon > 0, \exists R < \infty \text{ such that } \int_{t_l-R}^{t_l+R} \rho_l(s) ds \geq \lambda - \varepsilon;$$

2. (Vanishing)

$$\lim_{l \rightarrow \infty} \sup_{t \in \mathbb{R}} \int_{t-R}^{t+R} \rho_l(s) ds = 0 \text{ for all } R > 0;$$

3. (Splitting) there exists $0 < \alpha < \lambda$ such that for all $\varepsilon > 0$ there exists $l_0 \geq 1$ and $\rho_l^1, \rho_l^2 \in L^1_{\geq}(\mathbb{R})$ such that for all $l \geq l_0$

$$\begin{cases} \|\rho_l^1 + \rho_l^2 - \rho_l\|_{L^1} + \|\rho_l^1\|_{L^1} - \alpha + \|\rho_l^2\|_{L^1} + \alpha - \lambda \leq \varepsilon, \\ \lim_{l \rightarrow \infty} \text{dist}(\text{supp}(\rho_l^1), \text{supp}(\rho_l^2)) = \infty. \end{cases}$$

Proof of Proposition 3.2 Let $y_l \in X(x^-, x^+)$ be a minimizing sequence of J and define $\rho_l(t)$ as in Lemma 3.6. We now use Lemma 3.7 in the following way: we show that vanishing cannot occur, and that splitting can only occur a finite number of times.

To rule out vanishing we define, for real number ε satisfying

$$\varepsilon \in \left(0, \frac{1}{2} \min\{|x - z| \mid x, z \in \mathcal{E}, x \neq z\} \right),$$

the starting and ending time of the final transition:

$$t_l^+ = \sup\left\{t \in \mathbb{R} \mid \inf_{s \leq t} |y_l(s) - x^+| \geq \varepsilon\right\},$$

$$t_l^- = \sup\left\{t \leq t_l^+ \mid \text{dist}(y_l(t), \mathcal{E} \setminus \{x^+\}) \leq \varepsilon\right\}.$$

By construction $t_l^- \leq t_l^+$ and Jensen’s inequality implies that

$$\begin{aligned} \int_{t_l^-}^{t_l^+} \rho_l(s) \, ds &\geq \frac{1}{2} \int_{t_l^-}^{t_l^+} \left(\frac{\text{dist}(x^+, \mathcal{E} \setminus \{x^+\}) - 2\varepsilon}{t_l^+ - t_l^-} \right)^2 \, ds \\ &= \frac{(\text{dist}(x^+, \mathcal{E} \setminus \{x^+\}) - 2\varepsilon)^2}{2(t_l^+ - t_l^-)}. \end{aligned}$$

Since $\limsup_{l \rightarrow \infty} \int_{\mathbb{R}} \rho_l(s) \, ds < \infty$ this implies that $\liminf_{l \rightarrow \infty} (t_l^+ - t_l^-) > 0$. Furthermore, since V admissible there exists a number $c > 0$ such that $\inf_{s \in [t_l^-, t_l^+]} \rho_l(s) \geq c$ and thus

$$\limsup_{l \rightarrow \infty} (t_l^+ - t_l^-) \leq \frac{1}{c} \limsup_{l \rightarrow \infty} \int_{t_l^-}^{t_l^+} \rho_l(s) \, ds < \infty.$$

This pair of inequalities shows that ρ_l does not vanish.

If the sequence ρ_l splits, then there exist sequences $a_l \leq b_l$ such that $[a_l, b_l] \cap \text{supp}(\rho_l^1 + \rho_l^2) = \emptyset$ and

$$\lim_{l \rightarrow \infty} (a_l - b_l) = \infty, \tag{3.6}$$

$$\liminf_{l \rightarrow \infty} \int_{-\infty}^{a_l} \rho_l(t) \, dt > 0 \quad \text{and} \quad \liminf_{l \rightarrow \infty} \int_{b_l}^{\infty} \rho_l(t) \, dt > 0. \tag{3.7}$$

We claim now that there exists a third sequence $t_l \in [a_l, b_l]$ and a stationary point $x \in \mathcal{E}$ such that $\lim_{l \rightarrow \infty} y_l(t_l) = x$. This is because

$$\limsup_{l \rightarrow \infty} \int_{a_l}^{b_l} \rho_l(t) \, dt < \infty,$$

which together with (3.6) and the weak coercivity assumption (2.12) delivers that

$$\liminf_{l \rightarrow \infty} \{\text{dist}(y_l(t), \mathcal{E}) \mid t \in [a_l, b_l]\} = 0.$$

We define next the sequences $y_l^1 \in X(x^-, x)$ and $y_l^2 \in X(x, x^+)$ as follows:

$$y_l^1(t) = \begin{cases} y_l(t) & \text{if } t \leq t_l, \\ (t_l - t + 1)y_l(t_l) + (t - t_l)x & \text{if } t_l < t < t_l + 1, \\ x & \text{if } t \geq t_l + 1, \end{cases}$$

$$y_l^2(t) = \begin{cases} x & \text{if } t \leq t_l - 1, \\ (t - t_l + 1)y_l(t_l) + (t_l - t)x & \text{if } t_l - 1 < t < t_l, \\ y_l(t) & \text{if } t \geq t_l. \end{cases}$$

Clearly $y_l^1 + y_l^2 - x \in X(x^-, x^+)$ and the convergence $\lim_{l \rightarrow \infty} y_l(t) = x$ implies that

$$\lim_{l \rightarrow \infty} J(y_l^1 + y_l^2 - x) = \lim_{l \rightarrow \infty} (J(y_l^1) + J(y_l^2)) = \lim_{l \rightarrow \infty} J(y_l). \tag{3.8}$$

Moreover, (3.7) implies

$$\liminf_{l \rightarrow \infty} J(y_l^1) > 0 \quad \text{and} \quad \liminf_{l \rightarrow \infty} J(y_l^2) > 0. \tag{3.9}$$

We will show now that $x \notin \{x^\pm\}$. Indeed, if $x = x^-$, then $y_l^2 \in X(x^-, x^+)$ and by (3.8)

$$\liminf_{l \rightarrow \infty} J(y_l^2) \leq \lim_{l \rightarrow \infty} J(y_l) - \liminf_{l \rightarrow \infty} J(y_l^1).$$

Equation (3.9) delivers a contradiction to the assumption that y_l is a minimizing sequence. An analogous argument can be constructed for the case $x = x^+$ and thus $x \in \mathcal{E} \setminus \{x^\pm\}$.

The construction yields the following equation

$$\begin{aligned} \Phi(x^-, x^+) &\geq \lim_{l \rightarrow \infty} J(y_l^1 + y_l^2 - x) \geq \liminf_{l \rightarrow \infty} J(y_l^1) + \liminf_{l \rightarrow \infty} J(y_l^2) \\ &\geq \Phi(x^-, x) + \Phi(x, x^+). \end{aligned}$$

Progressing inductively we obtain a sequence $x_0, x_1, \dots, x_k \in \mathcal{E}$ such that $x_0 = x^-, x_k = x^+, x_{i-1} \neq x_i$ for all $i = 1 \dots k$ and

$$\Phi(x^-, x^+) \geq \sum_{i=1}^k \Phi(x_{i-1}, x_i).$$

Proposition 3.1 implies that $k \leq \Phi(x^-, x^+)/c$, placing a finite bound on the number of splittings possible. The minimizing sequences associated with $X(x_{i-1}, x_i)$ are eventually tight and so achieve their contribution to the infimum at a minimizer of J . □

Proof of Theorem 3.4 Now the representation formula for the Γ -limit will be verified. Let $x \in BV([0, 1], \mathbb{R}^d)$ be a limit path and $x_\varepsilon \in H^1(0, 1)$ such that x_ε converges to x weak-* in $BV([0, 1])$. First we show that the Laplacian can be treated separately. Since weak-* convergence entails boundedness in BV there is a constant $C > 0$ such that $\limsup_{\varepsilon \rightarrow 0} \|x_\varepsilon\|_{L^\infty} \leq C$. Furthermore, thanks to Helly’s theorem we can select a subsequence which converges pointwise for almost every $s \in [0, 1]$ and therefore by dominated convergence

$$\lim_{\varepsilon \rightarrow 0} \int_0^1 \Delta V(x_\varepsilon(s)) \, ds = \int_0^1 \Delta V(x(s)) \, ds.$$

Note that only continuity of ΔV is required for this step. This implies that

$$\liminf_{\varepsilon \rightarrow 0} I_\varepsilon(x_\varepsilon) = \liminf_{\varepsilon \rightarrow 0} J_\varepsilon(x_\varepsilon) - \int_0^1 \Delta V(x(s)) \, ds \tag{3.10}$$

with J_ε as defined in (2.7).

Next we consider the case where the set of times s where the limit function $x(s) \in \mathcal{E}$ does not have full measure, so that $I_0(x) = \infty$. Define

$$M = \text{meas}(\{t \in [0, 1] \mid x(t) \notin \mathcal{E}\}).$$

There exists $\delta > 0$ such that

$$\liminf_{\varepsilon > 0} \text{meas}(\{t \in [0, 1] \mid \text{dist}(x(t), \mathcal{E}) > \delta\}) > M/2.$$

Since V satisfies the weak coercivity condition the infimum of $|DV(x)|$ exceeds some $\lambda > 0$, on this set with measure exceeding $M/2$. Thus

$$\liminf_{\varepsilon \rightarrow 0} J_\varepsilon(x_\varepsilon) \geq \liminf_{\varepsilon \rightarrow 0} \frac{1}{2\varepsilon} \int_0^1 |DV(x_\varepsilon(s))|^2 ds \geq \liminf_{\varepsilon \rightarrow 0} \frac{M}{4\varepsilon} \lambda^2 = +\infty.$$

Finally we consider the case where $I_0(x)$ is finite. The proof of the lim inf-inequality follows directly from the definition, as we now show. Since $x \in BV([0, 1])$ and $I_0(x)$ is finite, the set of discontinuity points $\mathcal{D} \subset [0, 1]$ is finite. We assume next that $\mathcal{D} \subset (0, 1)$, i.e. x is continuous at the end-points. If x jumps at one or both end points the same argument can be repeated with obvious modifications of the cut-offs.

Thanks to this assumption for each $\tau \in \mathcal{D}$ the left-sided and right-sided limits $x^\pm(\tau)$ exist. Since x_ε converges weak-* in $BV([0, 1])$ to the piecewise constant function x Helly’s theorem implies that $\lim_{\varepsilon \rightarrow 0} x_\varepsilon(t) = x(t)$ for almost every $t \in [0, 1] \setminus \mathcal{D}$. Choose

$$\delta = \frac{1}{2} \min\{\tau - \tau' \mid \tau, \tau' \in \mathcal{D} \cup \{0, 1\}, \tau < \tau'\}$$

and for each $\tau \in \mathcal{D}$ a pair of such points $t^\pm \in (0, 1)$ such that $\tau - \delta \leq t^- < \tau < t^+ \leq \tau + \delta$ and $\lim_{\varepsilon \rightarrow 0} x_\varepsilon(t^\pm) = x^\pm(\tau)$. Setting $y_\varepsilon(t) = x_\varepsilon(\varepsilon t)$ one obtains

$$\begin{aligned} J_\varepsilon(x_\varepsilon) &= \frac{1}{2} \int_0^1 \left(\varepsilon |\dot{x}(s)|^2 + \frac{1}{\varepsilon} |DV|^2 \right) ds \\ &= \frac{1}{2} \int_0^{1/\varepsilon} (|\dot{y}_\varepsilon(s)|^2 + |DV(y_\varepsilon(s))|^2) ds \\ &\geq \sum_{\tau \in \mathcal{D}} \frac{1}{2} \int_{(t^-(\tau)-\delta)/\varepsilon}^{(t^+(\tau)+\delta)/\varepsilon} (|\dot{y}_\varepsilon(s)|^2 + |DV(y_\varepsilon(s))|^2) ds. \end{aligned}$$

To justify the boundary condition we modify the path segments $y_\varepsilon(t - \tau/\varepsilon)$ in a way such that the energy changes only slightly. Define now the function

$$\bar{y}_\varepsilon^\tau(t) = \begin{cases} x^-(\tau) & \text{if } s \leq \frac{t^-}{\varepsilon} - 1 \\ (\frac{t^-}{\varepsilon} - s)x^-(\tau) + (s - \frac{t^-}{\varepsilon} + 1)x_\varepsilon(t^-) & \text{if } \frac{t^-}{\varepsilon} - 1 < s < \frac{t^-}{\varepsilon} \\ y_\varepsilon(s) & \text{if } \frac{t^-}{\varepsilon} \leq s \leq \frac{t^+}{\varepsilon}, \\ (s - \frac{t^+}{\varepsilon})x^+(\tau) + (\frac{t^+}{\varepsilon} + 1 - s)x_\varepsilon(t^+) & \text{if } \frac{t^+}{\varepsilon} < s < \frac{t^+}{\varepsilon} + 1, \\ x^+(\tau) & \text{if } s \geq \frac{t^+}{\varepsilon} + 1. \end{cases}$$

The construction above implies that $\bar{y}_\varepsilon^\tau \in X(x^-(\tau), x^+(\tau))$ and thus

$$J(\bar{y}_\varepsilon^\tau) \geq \Phi(x^-(\tau), x^-(\tau)).$$

Furthermore, the modification of the function y_ε affects the energy only in a negligible way, i.e.

$$\sum_{\tau \in \mathcal{D}} \frac{1}{2} \int_{(\tau-\delta)/\varepsilon}^{(\tau+\delta)/\varepsilon} (|\dot{y}_\varepsilon(s)|^2 + |DV(y_\varepsilon(s))|^2) ds \geq \sum_{\tau \in \mathcal{D}} J(\bar{y}_\varepsilon^\tau) + o(1).$$

Hence, the liminf-inequality

$$\liminf_{\varepsilon \rightarrow 0} J_\varepsilon(y_\varepsilon) \geq \sum_{\tau \in \mathcal{D}} \Phi(x^-(\tau), x^+(\tau))$$

holds. The same argument also shows that

$$\liminf_{\varepsilon \rightarrow 0} J_\varepsilon(x_\varepsilon) = +\infty,$$

if the set \mathcal{D} is infinite.

To construct a recovery sequence we fix $\delta > 0$. By definition for each $\tau \in \mathcal{D}$ there exists

$$y_\delta^\tau \in X(x^-(\tau), x^+(\tau))$$

such that the support of \dot{y}_δ^τ is compact for all $\tau \in \mathcal{D}$ and $J(y_\delta^\tau) \leq \Phi(x^-(\tau), x^+(\tau)) + \delta$. It can be checked that for fixed $\delta > 0$ the sequence

$$y_{\varepsilon,\delta}(t) = x(0) + \frac{1}{\varepsilon} \sum_{\tau \in \mathcal{D}} \int_0^t \dot{y}_\delta^\tau((s - \tau)/\varepsilon) ds$$

converges weak-* in $BV([0, 1])$ to x as $\varepsilon \rightarrow 0$.

Moreover, there exists a function $\delta(\varepsilon)$ such that $\lim_{\varepsilon \rightarrow 0} \delta(\varepsilon) = o(1)$ and the supports of the functions $\dot{y}_\delta^\tau((\cdot - \tau)/\varepsilon)$, $\tau \in \mathcal{D}$ are disjoint as ε tends to 0. Hence,

$$\begin{aligned} J_\varepsilon(y_{\varepsilon,\delta(\varepsilon)}) &= \sum_{\tau \in \mathcal{D}} J_\varepsilon(y_\delta^\tau((\cdot - \tau)/\varepsilon)) \leq \sum_{\tau \in \mathcal{D}} \Phi(x^-(\tau), x^+(\tau)) + \#\mathcal{D} \delta(\varepsilon) \\ &= \sum_{\tau \in \mathcal{D}} \Phi(x^-(\tau), x^+(\tau)) + o(1) \end{aligned}$$

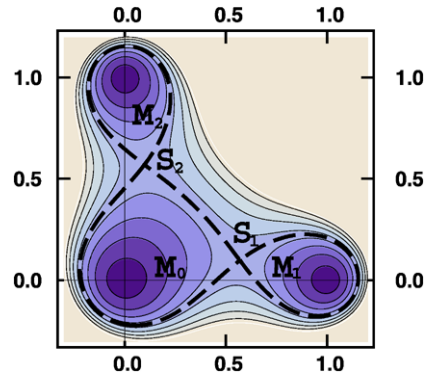
as ε tends to 0. □

4 Numerical Experiments

The aim of these numerical experiments is to illustrate that the Γ -limit derived in Sect. 3 accurately captures the behaviour of the problem of minimizing I_ε given by (2.6) when ε is small. The intuitive picture of the Γ -limit is that it is comprised of minimizers with the following properties:

1. The minimizers are BV functions supported on the set of critical points of V (see Theorem 3.4).
2. The contribution to the limit functional from the jumps in these BV functions (i.e. from J_ε) can be expressed in terms of sums of integrals $\int_{-\infty}^{\infty} |DV(x^*(s))|^2 ds$ where x^* is a heteroclinic orbit for the Hamiltonian equations (2.9) (see Lemma 2.1, (2.14)).

Fig. 1 Contour plot of the potential. The dashed black line is the equipotential contour that connects the saddle points, S_1 and S_2 . The three equal-depth minima are labeled: M_0 , M_1 , and M_2



3. Unless both equilibria x^\pm are saddle points, then these heteroclinic orbits will also be heteroclinic for the gradient system (2.11) and then the contribution to the limit functional from J_ε can be expressed in terms of sums $|V(x^*(\infty)) - V(x^*(-\infty))|$ (see Lemma 2.1, (2.15)).
4. Minimizers x^* will seek to organize the support of the limiting BV function so as to minimize the value of $\int_0^1 \Delta V(x^*)(s) ds$; this is the second contribution to the infimum defined in Theorem 3.4.

A variety of numerical computations, all of which exhibit these phenomena on a range of problems, including high dimensional systems arising in vacancy diffusion and the Lennard-Jones 38 cluster, may be found in the paper [6]. The purpose of this section is to illustrate the four points above on a single low dimensional example and relate the results in an explicit way to the theory developed in earlier sections. We employ the potential $V : \mathbb{R}^2 \rightarrow \mathbb{R}$ given by

$$V(x_1, x_2) = (x_1^2 + x_2^2)((x_1 - 1)^2 + x_2^2)(x_1^2 + (x_2 - 1)^2)$$

which is shown in Fig. 1. The potential has three wells of equal depth, situated at $M_0 = (0, 0)$, $M_1 = (1, 0)$, and $M_2 = (0, 1)$. Saddle points exist at $S_1 = ((2 + \sqrt{2})/6, (2 - \sqrt{2})/6)$ and (by symmetry) at $S_2 = ((2 - \sqrt{2})/6, (2 + \sqrt{2})/6)$. The potential is zero at the minima and attains a value of $2/27$ at the saddles. The Laplacian of V has value zero at the saddle points, 4 at the minimum M_0 and 8 at the minima M_1 and M_2 .

In the following numerical experiments we use gradient descent to minimize I_ε or J_ε given by (2.8) and (2.7). In all the experiments we employ a value of $\varepsilon = 10^{-3}$ which proved to be small enough to exhibit the behaviour of the Γ -limit. We solve the parabolic PDE arising from the L^2 gradient flow for I_ε (resp. J_ε) by means of a linearly implicit method with stepsize chosen to ensure decrease of I_ε (resp. J_ε) at each time-step.

Figure 2 shows heteroclinic orbits for the gradient flow (2.11) (in green) and for the Hamiltonian flow (2.9) (in blue). Figure 3 shows minimizers of J_ε , both connecting M_1 and M_2 . It is instructive to compare this figure with the preceding Fig. 2. The green curve in Fig. 3 connects M_1 to M_2 via M_0 and is comprised of 4 segments each of which has been verified to be approximately given by the gradient heteroclinic orbits (2.11). The blue curve connects M_1 to M_2 via S_1 and S_2 and has been verified to be approximately given by Hamiltonian heteroclinic orbits satisfying (2.9). Furthermore, in the gradient case we have verified that the minimizers obey the sum rule (2.15). This illustrates the connection between minimizers of J_ε and solutions of the Euler Lagrange equations for minimizers of J , and points 2. and 3. in particular.

Fig. 2 (Color online) The *dashed black line* is the equipotential contour that connects the saddle points, S_1 and S_2 . The *green line* is the path that follows the gradient of the potential from M_1 to M_0 via S_1 and then to M_2 via S_2 . The *blue line* is a Hamiltonian minimizer (not a gradient flow) that connects S_1 to S_2

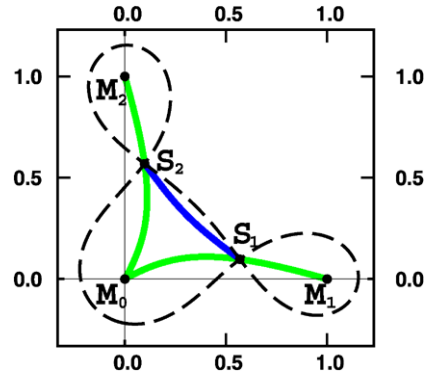


Fig. 3 (Color online) Solutions that minimize J_ε at $\varepsilon = 10^{-3}$. The *dashed black line* is the equipotential contour that connects the saddle points, S_1 and S_2 . The *green line* is the path that starts at M_1 and proceeds to M_2 via M_0 . The *blue line* is the path that starts at M_1 and proceeds to M_2 avoiding M_0

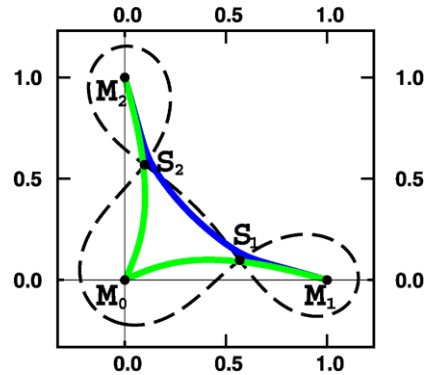


Fig. 4 The x_1 component of the paths that minimize J_ε at $\varepsilon = 10^{-3}$. The paths start at S_1 and are conditioned to end at S_2 . The ending path depends on the nature of the starting path. The results of using three different starting paths are displayed. None of the initial paths approach the origin and thus avoid passing through M_0 . The *black curve* corresponds to a symmetric minimizer. The corresponding minimizers of I_ε are very similar to the minimizers of J_ε

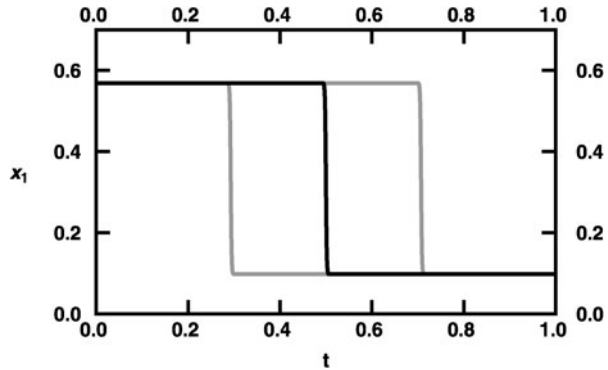


Figure 4 shows minimizers of J_ε which connect the two saddle points S_1 and S_2 . Several approximate minimizers are shown in each case, found from different starting points for the gradient flow. The experiments illustrate point 1, as they show that the solutions concentrate on critical points of V : in this case simply the two saddles. The minimizers of I_ε are indistinguishable from the minimizers of J_ε . This illustrates point 4, as the similarity of the minimizers this is a result of the Laplacian of V being zero at the saddle points.

Figures 5 and 6 also show minimizers of J_ε and I_ε which connect the two saddle points S_1 and S_2 . However the starting points for the gradient flow differ from those used to generate

Fig. 5 The x_1 component of the path that minimize J_ε at $\varepsilon = 10^{-3}$. The path starts at S_1 and is conditioned to end at S_2 . The initial path contains the origin M_0 and thus the ending path spends an arbitrary fraction of the time at M_0 . The ending path depends on the nature of the starting path, in particular where the path crosses the origin. Only the symmetric minimizer is displayed here

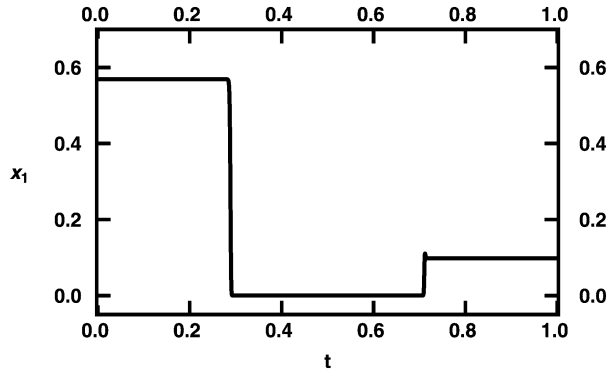


Fig. 6 The x_1 component of the path that minimize I_ε at $\varepsilon = 10^{-3}$. The path starts at S_1 and is conditioned to end at S_2 . The initial path contains the origin M_0 and thus the ending path is dominated by M_0

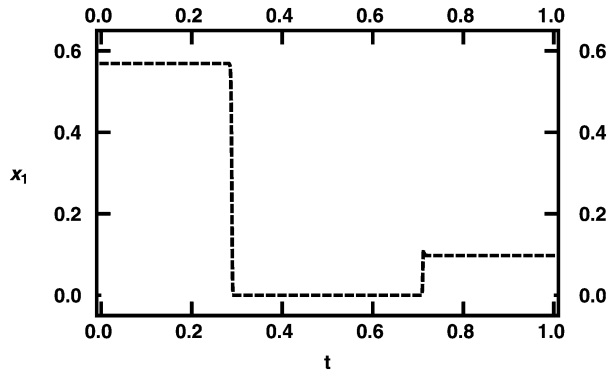


Fig. 4; in particular they are based on a function which passes through the minimum M_0 . As a consequence the minimizers also pass through M_0 . For J_ε there are then multiple approximate minimizers, all supported on S_1 , S_2 and M_0 . However the support can be organized more or less arbitrarily (provided only two transitions occur) to obtain approximately the same value of J_ε ; we show a solution where the support is organized symmetrically. The situation for I_ε is quite different: the effect of the Laplacian of V , which is 4 at M_0 and 0 at S_1 and S_2 , means that minimizers place most of their support at M_0 . The experiments thus again illustrate point 1. as they show that the solutions concentrate on critical points of V . They also illustrate point 4.

Figures 7 and 8 again show minimizers of J_ε and I_ε , now connecting the two minima M_1 and M_2 , and constructed to pass through the other minimum M_0 and the two saddle points S_1 and S_2 . For J_ε there are then multiple approximate minimizers, all supported on the five critical points, one of which is shown in Fig. 7, a solution where the support is organized symmetrically. The situation for I_ε is again very different: the effect of the Laplacian of V , which is 8 at M_1 and M_2 , means that minimizers place most of their support at these two points, as shown in Fig. 8. The single interface in fact contains several transitions, and hence several contributions to the Γ -limit. Furthermore this single interface can be placed arbitrarily; we have shown a symmetric case. The experiments once again illustrate points 1 and 4.

Acknowledgements The authors are grateful to Eric Vanden Eijnden for helpful discussions. AMS is grateful to EPSRC and ERC for financial support.

Fig. 7 The x_1 component of the path that minimize J_ε at $\varepsilon = 10^{-3}$. The path starts at M_1 and is conditioned to end at M_2 . The path breaks into several segments. The initial path contains the origin and thus the “ending” path passes through M_0 . The ending path depends on the nature of the starting path, in particular where the path crosses the origin. Only the symmetric minimizer is displayed here

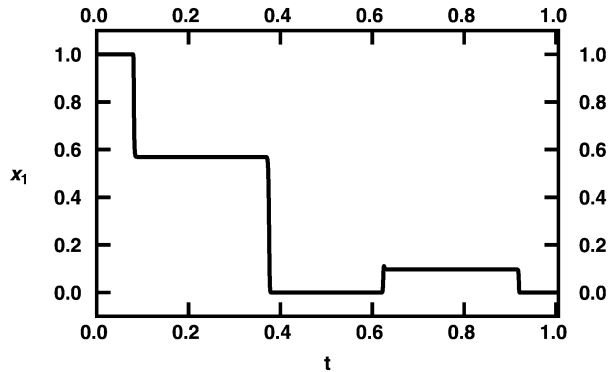
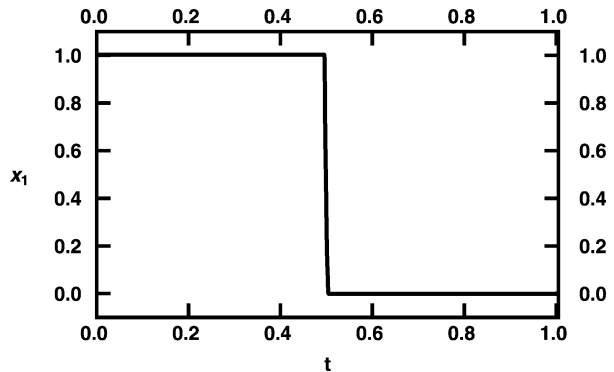


Fig. 8 The x_1 component of the path that minimize I_ε at $\varepsilon = 10^{-1}$. The path starts at M_1 and is conditioned to end at M_2 . The initial path does not approach the origin M_0 and thus the ending path also avoids M_0 . Only the symmetric minimizer is displayed here. Note that all the “activity” is scrunched into a small time interval



References

1. Allen, M.P., Tildesley, D.J.: Computer Simulation of Liquids. Oxford University Press, London (1987)
2. Bolhuis, P., Dellago, C., Geissler, P.L., Chandler, D.: Transition path sampling: throwing ropes over rough mountain passes the dark. *Annu. Rev. Phys. Chem.* **53**, 291–318 (2002)
3. Dürr, D., Bach, A.: The Onsager-Machlup function as Lagrangian for the most probable path of a diffusion process. *Commun. Math. Phys.* **160**, 153–170 (1978)
4. Ikeda, N., Watanabe, S.: Stochastic Differential Equations and Diffusion Processes, 2nd edn. North-Holland, Amsterdam (1989)
5. Olender, R., Elber, R.: Yet another look at the steepest descent path. *J. Mol. Struct., Theochem* **63**, 398–399 (1997)
6. Pinski, F., Stuart, A.M.: Transition paths in molecules: gradient descent in pathspace. *J. Chem. Phys.* **132**, 184104 (2010)
7. Braides, A.: Γ -convergence for Beginners. Oxford Lecture Series in Mathematics and Its Applications, vol. 22. Oxford University Press, Oxford (2002)
8. Dal Maso, G.: An Introduction to Γ -convergence. Birkhäuser, Boston (1993)
9. Voss, J.: Large deviations for one dimensional diffusions with a strong drift. *Electron. J. Probab.* **13**, 1479–1526 (2008)
10. Kohn, R.V., Sternberg, P.: Local minimizers and singular perturbations. *Proc. R. Soc. Edinb.* **111**, 69–84 (1989)
11. Baldo, S.: Minimal interface criterion for phase transitions in mixtures of Cahn-Hilliard fluids. *Ann. Inst. Henri Poincaré* **7**, 67–90 (1990)
12. Freidlin, M.I., Wentzell, A.D.: Random Perturbations of Dynamical Systems. Springer, New York (1984)
13. Ren, W.E.W., Vanden-Eijnden, E.: String method for the study of rare events. *Phys. Rev. B* **66**, 052301 (2002)
14. Ren, W.E.W., Vanden-Eijnden, E.: Transition pathways in complex systems: reaction coordinates, iso-committor surfaces and transition tubes. *Chem. Phys. Lett.* **413**, 242–247 (2005)

15. Reznikoff, E., Vanden Eijnden, E.: Invariant measures of stochastic PDEs. *C.R. Acad. Sci., Paris* **340**, 305–308 (2005)
16. Hairer, M., Stuart, A.M., Voss, A.M.: Analysis of SPDEs arising in path sampling. Part 2: The nonlinear case. *Ann. Appl. Probab.* **340**, 305–308 (2007)
17. Chorin, A.J., Hald, O.H.: *Stochastic Tools in Mathematics and Science. Surveys and Tutorials in the Applied Mathematical Sciences*, vol. 1. Springer, New York (2006)
18. Lions, P.L.: The concentration-compactness principle in the calculus of variations. The locally compact case, Part 1. *Ann. Inst. Henri Poincaré, Anal. Non Linéaire* **1**, 109–145 (1984)