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ABSTRACT

Rare event sampling algorithms are essential for understanding processes that occur infrequently on the molecular scale, yet they are important for the long-time dynamics of complex molecular systems. One of these algorithms, transition path sampling (TPS), has become a standard technique to study such rare processes since no prior knowledge on the transition region is required. Most TPS methods generate new trajectories from old trajectories by selecting a point along the old trajectory, modifying its momentum in some way, and then "shooting" a new trajectory by integrating forward and backward in time. In some procedures, the shooting point is selected independently for each trial move, but in others, the shooting point evolves from one path to the next so that successive shooting points are related to each other. To account for this memory effect, we introduce a theoretical framework based on an extended ensemble that includes both paths and shooting indices. We derive appropriate acceptance rules for various path sampling algorithms in this extended formalism, ensuring the correct sampling of the transition path ensemble. Our framework reveals the need for amended acceptance criteria in the flexible-length aimless shooting and spring shooting methods.

I. INTRODUCTION

Transition path sampling (TPS) is a simulation method that yields unbiased insights into the mechanisms and kinetics of rare events occurring in complex molecular systems. It is applicable to a wide range of processes, including nucleation,[1] biomolecular reorganization,[2,3] and chemical reactions.[4,5] Unlike many enhanced sampling techniques, TPS does not require detailed *a priori* knowledge about the process of interest, other than a definition of the start and end states of the process.[6] TPS samples from a distribution of unbiased dynamical trajectories with start and end points located in these predefined (meta)stable states. This ensemble of transition paths is generated sequentially by employing a Markov chain Monte Carlo framework.[6] At the core of many path sampling schemes is the so-called shooting move, in which a new path is generated by the integration of the equations of motion (forward and backward in time) starting from a preselected configuration taken from an existing transition path, known as the *shooting point*. Valid reactive paths that connect the start and end states are accepted or rejected in a Metropolis step. Standard TPS has successfully been used on a wide variety of systems and processes.[7,8]

Several methods have been proposed to increase the sampling efficiency of TPS by incorporating prior knowledge of the system into the selection of the shooting point using collective variables, such as biased TPS[3,6] or shooting range TPS.[9] Likewise, artificial intelligence-assisted sampling can increase the sampling efficiency significantly[10,11] and enable efficient rate calculations.[12] While methods involving prior knowledge about the reaction are useful in many cases, such knowledge is often not available. For such cases, aimless shooting[13–15] and spring shooting[16] were introduced as system-agnostic, yet efficient, alternatives.[17–20] While the shooting point is selected freshly from the current path for each trial move in most other TPS procedures, in the aimless and spring shooting methods, the new shooting point is chosen based on knowledge of the previous shooting point. As a result, the shooting point evolves in a certain way from one path to the next. A key concept in these methods is that incorporating the memory of the shooting point allows the algorithm to focus automatically on the barrier region, thereby increasing the acceptance probability of pathways.

In this study, we revisit several history-based shooting point Monte Carlo methods, including flexible-length aimless shooting and spring shooting. We find that the particular procedures to select shooting points in these methods lead to violations of detailed balance, resulting in an improperly sampled path ensemble. This issue arises because the generation of the new shooting point depends on information on the previous shooting point.

Our objective here is to develop a general formalism that accounts for the evolving shooting point in order to restore detailed balance and ensure correct sampling of the desired path distribution. This formalism makes use of an extended state space that includes shooting points in addition to trajectories. We develop the general formalism and apply it to the case of the aimless and spring shooting algorithms. In particular, we show that the performance of the fixed-length versions of these methods depends strongly on the total path length. Furthermore, we find a detailed balance-related issue in the original spring shooting method,[16] which we correct in the new formalism. Unfortunately, one of the consequences of treating the algorithms correctly in the extended space formalism is that they are not behaving as efficiently as concluded in the original papers.

The remainder of this paper is organized as follows: First, we introduce the extended space of paths and shooting indices, necessary to capture the evolution of the shooting point. Next, we derive detailed balance relations for Monte Carlo moves in this extended space and apply them to regular TPS, aimless shooting and spring shooting. This formalism leads to corrections of the original flexible-length aimless and spring shooting algorithms, which we then validate by performing path sampling in a one-dimensional test system.

II. THEORY

A. Fixed- and flexible-length path ensembles

Assuming two (meta)stable states A and B, we consider an ensemble of discretized trajectories $X = \{x_1, x_2, \ldots x_L\}$ that connect A and B, where each time slice or frame x contains the coordinates (and possibly momenta) of all particles in the system. We define a probability density in the ensemble of transition paths as $P_{\mathrm{AB}}(X)$. For instance, a path distribution where all paths are of fixed length L can be defined as

$$P_{\mathrm{AB}}(X) = \frac{1}{Z_{\mathrm{AB}}} h_{\mathrm{A}}(x_1) h_{\mathrm{B}}(x_L) \rho(x_1) \prod_{i=1}^{L-1} p(x_i \to x_{i+1}), \tag{1}$$

where $h_{\mathrm{A}}(x)$ and $h_{\mathrm{B}}(x)$ are the characteristic functions of the states A and B (unity when $x \in$ A, B; zero otherwise), $\rho(x_1)$ is the stationary distribution generated by the underlying dynamics (e.g., the Boltzmann distribution), and $p(x_i \to x_{i+1})$ is the short time transition probability from x_i to x_{i+1}. The partition function Z_{AB} normalizes the distribution.

Another commonly used definition is the flexible-length ensemble, in which pathways have different lengths $L(X)$. These paths are required to have the start and end points in A and B, respectively, while all other points in between should lie outside of A and B,

$$P_{\mathrm{AB}}(X) \propto H_{\mathrm{AB}}(X) \rho(x_1) \prod_{i=1}^{L(X)-1} p(x_i \to x_{i+1}). \tag{2}$$

Here, $H_{\mathrm{AB}}(X)$ is unity if the path X fulfills all requirements to be considered reactive and zero otherwise, as specified below, i.e., $x_1 \in$ A, $x_L \in$ B.

B. Extended space of paths and shooting indices

In path sampling methods, such as aimless shooting and spring shooting, information on the previous shooting point is used to generate the new shooting point. To take this information into account, we denote with k the index of a (configuration) point x_k on the path X. Depending on the sampling scheme, this point can either be a shooting point directly or a point that is used to generate the next shooting point. The exact interpretation of k will become clear later when we discuss several path sampling algorithms (see, for example, Secs. II E–II H). We refer to k as the *shooting index* in both cases since, even in the second case, the move is initiated from k. Common for both cases is that the index k, in some form or another, evolves from trial to trial.

To track the evolution of X and k at the same time in a Monte Carlo procedure while preserving the Markovianity of the process, we define an extended space that includes both the paths and the shooting indices. Each point Y in this extended space is composed of a path X and a shooting index k,

$$Y = (X, k). \tag{3}$$

In each step of the Monte Carlo procedure, a new path X^{n} is generated together with a new shooting index k^{n},

$$(X^{\mathrm{o}}, k^{\mathrm{o}}) \to (X^{\mathrm{n}}, k^{\mathrm{n}}), \tag{4}$$

with a particular generation probability,

$$p_{\mathrm{gen}}\left[(X^{\mathrm{o}}, k^{\mathrm{o}}) \to (X^{\mathrm{n}}, k^{\mathrm{n}})\right], \tag{5}$$

that depends on the details of the generation algorithm. The new path and shooting index are then accepted with acceptance probability $p_{\mathrm{acc}}\left[(X^{\mathrm{o}}, k^{\mathrm{o}}) \to (X^{\mathrm{n}}, k^{\mathrm{n}})\right]$. If $(X^{\mathrm{n}}, k^{\mathrm{n}})$ is rejected, the old path and shooting index are counted again in the path or index ensembles and the corresponding averages.

To derive an acceptance probability for the Monte Carlo move, the joint probability density $P_{\mathrm{AB}}(X, k)$ must be specified. Since our goal is to sample the transition path ensemble $P_{\mathrm{AB}}(X)$, we require that marginalizing $P_{\mathrm{AB}}(X, k)$ with respect to k yields $P_{\mathrm{AB}}(X)$,

$$\sum_k P_{\mathrm{AB}}(X, k) = P_{\mathrm{AB}}(X). \tag{6}$$

This condition is naturally fulfilled by defining $P_{AB}(X,k)$ via the conditional probability $p(k|X)$, which has been described previously in the context of auxiliary variable methods,[21]

$$P_{AB}(X,k) = P_{AB}(X)p(k|X). \tag{7}$$

Due to the normalization of the conditional probability, $\sum_k p(k|X) = 1$, the sum over all k is guaranteed to lead to $P_{AB}(X)$ as marginal distribution. Apart from this condition, there is total freedom in setting the concrete form of $p(k|X)$, the target distribution for the shooting index k.

C. Shooting point Monte Carlo

The goal is now to construct a Markov chain Monte Carlo procedure for sampling the joint probability $P_{AB}(X,k) = P_{AB}(X)p(k|X)$. In the subspace of the trajectories X, this procedure then samples the desired transition path ensemble $P_{AB}(X)$. Imposing detailed balance

$$\begin{aligned} P_{AB}(X^o)p(k^o|X^o)p_{gen}\big[(X^o,k^o)\to(X^n,k^n)\big] \\ \times p_{acc}\big[(X^o,k^o)\to(X^n,k^n)\big] \\ = P_{AB}(X^n)p(k^n|X^n)p_{gen}\big[(X^n,k^n)\to(X^o,k^o)\big] \\ \times p_{acc}\big[(X^n,k^n)\to(X^o,k^o)\big] \end{aligned} \tag{8}$$

yields

$$\frac{p_{acc}[(X^o,k^o)\to(X^n,k^n)]}{p_{acc}[(X^n,k^n)\to(X^o,k^o)]} = \frac{P_{AB}(X^n)p(k^n|X^n)p_{gen}[(X^n,k^n)\to(X^o,k^o)]}{P_{AB}(X^o)p(k^o|X^o)p_{gen}[(X^o,k^o)\to(X^n,k^n)]}, \tag{9}$$

which can be satisfied with the Metropolis–Hastings criterion. The generation probability can be further factorized as

$$p_{gen}\big[(X^o,k^o)\to(X^n,k^n)\big] = p_{gen}(X^n|X^o,k^o)p_{gen}(k^n|X^n,X^o,k^o), \tag{10}$$

to separate the generation probabilities of the new path from the generation probabilities of the new shooting index. This factorization implies that first, a new path is generated according to $p_{gen}(X^n|X^o,k^o)$ based on the old path and the old shooting index. This probability includes all factors resulting from the propagation rules of the underlying dynamics.[6,22] Then, the new shooting index is generated according to $p_{gen}(k^n|X^n,X^o,k^o)$ based on the old shooting index as well as the old and new paths. This factor describes the probability to select the new shooting index k^n. Another possibility, corresponding to a different factorization, is to first generate the new shooting index and then the new path or further factorize the shooting index generation process.

To further simplify the acceptance probability, we assume that all pathways are generated using shooting moves based on the underlying dynamics, which conserves the equilibrium distribution. Furthermore, we assume that momenta of the shooting point are either unchanged or independently redrawn from the Maxwell–Boltzmann distribution.[22] This leads to a cancellation of the path probabilities $P_{AB}(X)$ and the respective generation probabilities, where we factorize p_{gen} as in Eq. (10).[22] For the flexible-length path ensemble, this leads to

$$\frac{p_{acc}[(X^o,k^o)\to(X^n,k^n)]}{p_{acc}[(X^n,k^n)\to(X^o,k^o)]} = H_{AB}(X^n)\frac{p(k^n|X^n)p_{gen}(k^o|X^o,X^n,k^n)}{p(k^o|X^o)p_{gen}(k^n|X^n,X^o,k^o)}. \tag{11}$$

Equation (11) can be satisfied by applying the Metropolis–Hastings criterion,

$$p_{acc}\big[(X^o,k^o)\to(X^n,k^n)\big] = H_{AB}(X^n)\min\left[1,\frac{p(k^n|X^n)p_{gen}(k^o|X^o,X^n,k^n)}{p(k^o|X^o)p_{gen}(k^n|X^n,X^o,k^o)}\right]. \tag{12}$$

Below, we will use this equation to derive appropriate acceptance rules for different TPS-algorithms.

D. Shooting point densities

To assess the convergence of a path sampling scheme and further understand its inner workings, it is useful to examine the distribution of points on transition paths, denoted by $\rho(x|\mathrm{TP})$, and the distribution of points from which shooting moves are initiated, denoted by $\rho(x|\mathrm{SP})$. For pathways distributed according to $P_{AB}(X)$, $\rho(x|\mathrm{TP})$ is given by

$$\begin{aligned}\rho(x|\mathrm{TP}) &= \frac{\int \mathrm{d}X\, P_{AB}(X)\sum_{i=1}^{L(X)}\delta(x-x_i)}{\int dx\int \mathrm{d}X\, P_{AB}(X)\sum_{i=1}^{L(X)}\delta(x-x_i)} \\ &= \frac{\int \mathrm{d}X\, P_{AB}(X)\sum_{i=1}^{L(X)}\delta(x-x_i)}{\int \mathrm{d}X\, P_{AB}(X)L(X)} \\ &= \frac{1}{\langle L(X)\rangle_{\mathrm{TP}}}\int \mathrm{d}X\, P_{AB}(X)\sum_{i=1}^{L(X)}\delta(x-x_i), \end{aligned} \tag{13}$$

where the delta function probes the occurrence of x at position x_i on a transition path X. In the above equation, the notation $\langle\cdots\rangle_{\mathrm{TP}}$ implies an average over the transition path ensemble $P_{AB}(X)$. Hence, $\langle L(X)\rangle_{\mathrm{TP}}$ is the average length of transition pathways. Note that shorter paths contribute fewer points to the distribution $\rho(x|\mathrm{TP})$ defined in Eq. (13). For low-dimensional systems, this density can be computed numerically in a TPS simulation by histogramming points on the sampled transition pathways. In higher dimensions, it is more practical to consider the distribution $\rho(r|\mathrm{TP})$ of a collective variable $r(x)$ for points on transition pathways. In either case, the distribution is a key indicator for the correct convergence of a path sampling scheme.

Another distribution that is important to discuss is the distribution of attempted shooting points, given that one follows the Monte Carlo scheme described in Sec. II C. In contrast to $\rho(x|\mathrm{TP})$, which is fully defined by specifying the transition path ensemble $P_{AB}(X)$, this distribution also depends on the specific protocol employed in the TPS simulation. To obtain a general expression for the distribution of attempted shooting points, we need to take into account that k does not necessarily need to be the shooting index directly but may instead be used to generate an index $\hat{k}$, from which the shooting move is initiated. Denoting with $p_{sel}(\hat{k}|X,k)$ the probability to select

$\hat{k}$ given the current index k, the (protocol-dependent) shooting point distribution is given by

$$\rho(x|\mathrm{SP}) = \int \mathrm{d}X\, P_{\mathrm{AB}}(X) \sum_{k=1}^{L(X)} \left[p(k|X) \sum_{\hat{k}=1}^{L(X)} p_{\mathrm{sel}}(\hat{k}|X,k)\delta(x - x_{\hat{k}}) \right]. \tag{14}$$

Note that the shooting point distribution depends both on the imposed distribution $p(k|X)$ of shooting indices and on the specific shooting algorithm as encoded in the selection probability $p_{\mathrm{sel}}(\hat{k}|X,k)$ [and, of course, also on $P_{\mathrm{AB}}(X)$].

For path sampling schemes that do not evolve the shooting index from trial to trial, each new shooting index can be generated independently by directly drawing it from $p(k|X)$, implying that $p_{\mathrm{sel}}(\hat{k}|X,k) = p(\hat{k}|X)$. In this case, the above expression reduces to

$$\rho(x|\mathrm{SP}) = \int \mathrm{d}X\, P_{\mathrm{AB}}(X) \sum_{k=1}^{L(X)} \left[p(k|X) \sum_{\hat{k}=1}^{L(X)} p(\hat{k}|X)\delta(x - x_{\hat{k}}) \right], \tag{15}$$

where the sum over k cancels and, renaming $\hat{k}$ as k, we arrive at

$$\rho(x|\mathrm{SP}) = \int \mathrm{d}X\, P_{\mathrm{AB}}(X) \sum_{k=1}^{L(X)} p(k|X)\delta(x - x_k). \tag{16}$$

For a uniform shooting index distribution, $p(k|X) = 1/L(X)$, with independent drawing of shooting indices, as is done in standard TPS, we obtain the shooting point distribution

$$\rho(x|\mathrm{SP}) = \int \mathrm{d}X\, P_{\mathrm{AB}}(X) \frac{1}{L(X)} \sum_{k=1}^{L(X)} \delta(x - x_k). \tag{17}$$

This distribution is very similar to the distribution $\rho(x|\mathrm{TP})$ of points on transition pathways, but it differs from it by a weight factor proportional to $L(X)$. This factor arises because each transition path X contributes $L(X)$ points to the distribution $\rho(x|\mathrm{TP})$, but only one point to the shooting point distribution $\rho(x|\mathrm{SP})$.

We can then relate the attempted shooting point distributions in Eqs. (14), (16), and (17) to the extended space ensemble $P_{\mathrm{AB}}(X,k)$. For that, we determine the distribution of shooting points, not attempted, but as obtained from $P_{\mathrm{AB}}(X,k)$ by integrating/summing over pathways X and shooting indices k,

$$\begin{aligned} \rho_{\mathrm{ens}}(x) &= \int \mathrm{d}X \sum_{k=1}^{L(X)} P_{\mathrm{AB}}(X,k)\delta(x - x_k) \\ &= \int \mathrm{d}X \sum_{k=1}^{L(X)} P_{\mathrm{AB}}(X)p(k|X)\delta(x - x_k) \\ &= \int \mathrm{d}X\, P_{\mathrm{AB}}(X) \sum_{k=1}^{L(X)} p(k|X)\delta(x - x_k). \end{aligned} \tag{18}$$

This means that $\rho_{\mathrm{ens}}(x)$, the distribution of points after summing over k, is the same as the distribution of attempted shooting points [Eq. (16)] one would obtain if shooting was performed by freshly drawing k each trial from $p(k|X)$. Since $\rho_{\mathrm{ens}}(x)$ is independent of the specific shooting scheme yet depends on $p(k|X)$, we use it to assess the convergence of shooting schemes in the extended space (X,k) as shown in Figs. 5 and 6.

E. One-way and two-way TPS

We will next cast various TPS algorithms in the extended space formalism, starting with regular one-way and two-way shooting. In fixed- or flexible-length regular TPS, one draws the shooting index k freshly at each round. As a result, there is no dependence of the picked shooting index on the previous shooting index k^{o}. In fact, since regular TPS is carried out in trajectory space only, the acceptance rules derived for the extended space do not directly apply to this case. Vice versa, casting the algorithm without modification to the extended space leads to irreversibility of the move (Fig. 1). However, we can construct an alternative TPS scheme that is reversible in the extended space and closely resembles the original two-way shooting algorithm.

We split the shooting move into three substeps as illustrated in Fig. 2. In the first part, the *index shift*, the shooting index is redrawn shifting the old shooting index k^{o} to the point $\hat{k}^{\mathrm{o}}$. In the second step, the shooting move itself is carried out from the point at $\hat{k}^{\mathrm{o}}$, leading to the new path X^{n}. As the shooting move in most cases leads to a renumbering of points, we then define $\hat{k}^{\mathrm{n}}$ as the index of the shooting point on the new path. As a last step, the shooting index is redrawn once again to ensure reversibility of the move. The whole shooting move results in a new path and shooting index $(X^{\mathrm{n}}, k^{\mathrm{n}})$.

Since we now work in the extended space, we need to specify the target shooting index probability $p(k|X)$ in order to obtain the full joint probability $P_{\mathrm{AB}}(X,k)$. To enforce a uniform shooting index distribution, we define $p(k|X)$ as

$$p(k|X) = \frac{1}{L(X)} \quad \text{for } 1 \le k \le L. \tag{19}$$

For both index shift moves [steps (2) and (4) in Fig. 2], we draw the shooting index from the uniform distribution to simplify the

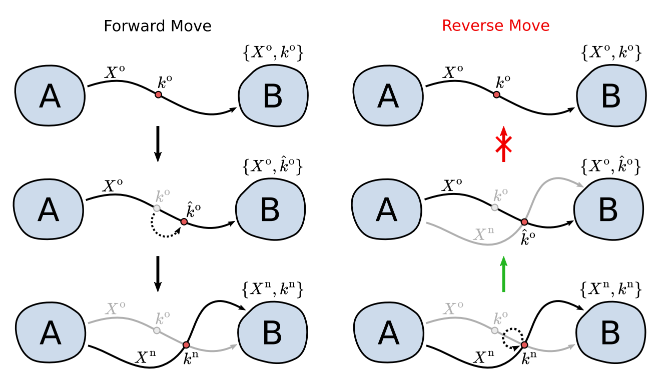

FIG. 1. The standard shooting move is irreversible in the extended space framework. Starting from a path X^{o} and previous shooting index k^{o} (left), the shooting move is usually divided into two steps: first, a new index $\hat{k}^{\mathrm{o}}$ is picked and, second, the new path X^{n} is generated from the selected point. On the new path, the used shooting point has the index k^{n}. Although the reverse move (right) can recover the old path by selecting the same shooting index k^{n} again, it is not possible to recover the old shooting index (indicated by the red arrow).

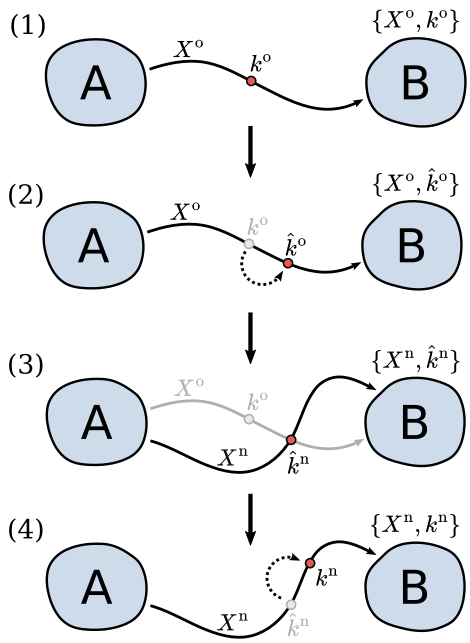

FIG. 2. General scheme of a reversible shooting move in the extended space. The shooting index is shifted, and the equations of motion are integrated. After that, the new shooting index is shifted a second time to ensure reversibility.

acceptance and keep the algorithm close to standard TPS such that

$$p_{\text{sel}}(\hat{k}^{\text{o}}|X^{\text{o}}) = \frac{1}{L(X^{\text{o}})} \quad \text{for } 1 \le k \le L(X^{\text{o}}),$$
$$p_{\text{sel}}(k^{\text{n}}|X^{\text{n}}) = \frac{1}{L(X^{\text{n}})} \quad \text{for } 1 \le k \le L(X^{\text{n}}). \tag{20}$$

Combining both selection probabilities leads to a symmetric index generation probability for the forward and reverse moves, $p_{\text{gen}}^{\text{fw}} = p_{\text{gen}}^{\text{rv}} = p_{\text{sel}}(\hat{k}^{\text{o}}|X^{\text{o}})p_{\text{sel}}(k^{\text{n}}|X^{\text{n}})$. Therefore, the acceptance probability based on Eqs. (12) and (19) is then given by

$$p_{\text{acc}}\big[(X^{\text{o}}, k^{\text{o}}) \to (X^{\text{n}}, k^{\text{n}})\big] = H_{\text{AB}}(X^{\text{n}}) \min\left[1, \frac{p(k^{\text{n}}|X^{\text{n}})}{p(k^{\text{o}}|X^{\text{o}})}\right]$$
$$= H_{\text{AB}}(X^{\text{n}}) \min\left[1, \frac{L(X^{\text{o}})}{L(X^{\text{n}})}\right], \tag{21}$$

which is identical to the acceptance criterion derived previously.[3,22] Note that for this algorithm, the distribution of shooting points $\rho(x|\text{SP})$ follows Eq. (17).

In the analogous way, the shooting range algorithm[9] can be formulated in the extended ensemble. In this case, shooting indices k are accepted according to a weighting function $w(r(x_k))$ along a collective variable $r(x)$, corresponding to a shooting index distribution,

$$p(k|X) = \frac{w(r(x_k))}{\sum_i w(r(x_i))}. \tag{22}$$

In this case, the acceptance criterion becomes

$$p_{\text{acc}}\big[(X^{\text{o}}, k^{\text{o}}) \to (X^{\text{n}}, k^{\text{n}})\big] = H_{\text{AB}}(X^{\text{n}}) \min\left[1, \frac{\sum_i w(r(x_i^{\text{o}}))}{\sum_i w(r(x_i^{\text{n}}))}\right]. \tag{23}$$

Setting $w(r)$ to unity if $a \le r(x) \le b$ with user defined bounds a and b and zero otherwise results in the original shooting range algorithm.[9]

F. Fixed-length aimless shooting

Aimless shooting with fixed path lengths is historically the basis for algorithms that evolve the shooting point from trial to trial. While there are different formulations of the algorithm in the literature, we focus here on the two-point variant described in Ref. 15. Here, we start with an initial path X^{o} of fixed path length L. We assume an even path length in Sec. II F; for odd path lengths, integration steps need to be adjusted accordingly. The shooting index distribution is only nonzero at two points, $L/2 - \Delta k$ and $L/2 + \Delta k$, where Δk is an adjustable parameter. This choice corresponds to the following target shooting index distribution:

$$p(k|X) = \begin{cases} \frac{1}{2} & \text{if } k \in \left\{\frac{L}{2} - \Delta k, \frac{L}{2} + \Delta k\right\}, \\ 0, & \text{otherwise.} \end{cases} \tag{24}$$

The two-point aimless shooting algorithm starts by selecting one of these two indices on the old path as the shooting index $\hat{k}^{\text{o}}$, which corresponds to the first index shift for regular TPS (Fig. 2). For a positive shift, integration is performed in the backward direction by $L/2 + \Delta k - 1$ steps and in the forward direction by $L/2 - \Delta k$ steps to obtain the new path X^{n} (vice versa for a backward shift). This operation produces a new path on which the index of the common point, i.e., the index $\hat{k}^{\text{n}}$ of the point where the old and the new path intersect, can be either at $L/2 - \Delta k$ or at $L/2 + \Delta k$.

In principle, a second shift from $\hat{k}^{\text{n}}$ to k^{n} would now be required to ensure that the move is reversible in the extended space. However, it is important to note that, in *fixed*-length aimless shooting, the shooting index does not evolve, in contrast to its flexible-length counterpart. While there is a chance that the next shooting move is initiated from the same *point* as in the last trial, the shooting *index* is always drawn independently as $L/2 - \Delta k$ or $L/2 + \Delta k$ each trial, effectively erasing the memory of the previous shooting index. In other words, given a certain path X^{o}, determining the new shooting index is always done relative to the center $L/2$ of the path and does not require knowledge of the previous shooting index. As a result, the procedure is Markovian in path space and therefore does not require an extended space formalism with second shift. We introduce a second shift as for standard TPS, which allows us to apply the extended space formalism and infer the distribution of the shooting points from which a shooting is attempted via Eq. (14),

$$\rho(x|\text{SP}) = \int \text{d}X\, P_{\text{AB}}(X)\frac{1}{2}[\delta(x_{L/2-\Delta k} - x) + \delta(x_{L/2+\Delta k} - x)]. \tag{25}$$

This is the distribution of points $\pm\Delta k$ away from the path centers. We validate this result via numerical simulations in Sec. III. As for standard TPS in the extended space, performing both shifts with symmetric probabilities leads to a cancellation in the acceptance probability,

$$p_{\mathrm{acc}}\big[(X^{\mathrm{o}},k^{\mathrm{o}}) \to (X^{\mathrm{n}},k^{\mathrm{n}})\big] = H_{\mathrm{AB}}(X^{\mathrm{n}}) \min\left[1, \frac{p(k^{\mathrm{n}}|X^{\mathrm{n}})}{p(k^{\mathrm{o}}|X^{\mathrm{o}})}\right] = H_{\mathrm{AB}}(X^{\mathrm{n}}). \tag{26}$$

G. Flexible-length aimless shooting

Flexible-length aimless shooting, as proposed by Mullen *et al.*,[14] generalizes the aimless shooting move to a flexible-length scenario, which is particularly useful in systems with diffusive dynamics. Similar to fixed-length aimless shooting, the shooting index for the following trial is chosen from a narrow set of possible indices. Due to the flexible-length setting, these points are no longer defined to lie around the path center as in Eq. (24), but they are close to the previous shooting point. Hence, in aimless shooting with flexible length pathways, there is true memory of the previous shooting point, making the treatment of the algorithm in the extended space formalism necessary. In the following, we will formulate the flexible-length aimless shooting in this formalism and will show that the acceptance probability includes a ratio of path lengths, which was neglected in the original work.[14] As demonstrated below numerically, this factor is necessary to sample the correct transition path ensemble.

As mentioned above, there is a crucial difference between the fixed-length and the flexible-length moves. Namely, in the flexible-length algorithm, the new shooting index k^{n} is selected depending on the previous index k^{o} (see Fig. 3). In particular, the two-point variant described in Ref. 14 samples the new shooting index from $\{k^{\mathrm{o}}, k^{\mathrm{o}} + s^{\mathrm{o}}\Delta k\}$, where $s^{\mathrm{o}} \in \{-1, 1\}$ defines whether the second shooting point is on the backward or the forward trajectory segment. Since the sign s is preserved until a next trial is accepted, we include it in the extended ensemble (X, k, s) (see the supplementary material for a detailed balance derivation). To respect reversibility, the generation probability of k^{n} is divided into two steps. We first choose a shooting index $\hat{k}^{\mathrm{o}}$ on the old path according to

$$p_{\mathrm{gen}}(\hat{k}^{\mathrm{o}}|X^{\mathrm{o}},k^{\mathrm{o}},s^{\mathrm{o}}) = \begin{cases} \frac{1}{2} & \text{if } \hat{k}^{\mathrm{o}} \in \{k^{\mathrm{o}}, k^{\mathrm{o}} + s^{\mathrm{o}}\Delta k\}, \\ 0, & \text{else.} \end{cases} \tag{27}$$

If the opposing point, namely $k^{\mathrm{o}} + s^{\mathrm{o}}\Delta k$ is selected, we flip the direction s^{o} such that the two possible shooting indices in the new state are preserved (see Fig. 3, step 2). The new path X^{n} is generated by shooting from $\hat{k}^{\mathrm{o}}$ and integrating the equations of motion until a stable state is reached. We then obtain a new sign $\hat{s}^{\mathrm{n}}$ by drawing from $\{-1, 1\}$ with equal probability. We assume that $p(\hat{s}^{\mathrm{n}}) = p_{\mathrm{gen}}(\hat{s}^{\mathrm{n}}) = \frac{1}{2}$. Denoting $\hat{k}^{\mathrm{n}}$ as the index of the shooting point on X^{n}, the new shooting index k^{n} is generated according to

$$p_{\mathrm{gen}}(k^{\mathrm{n}}|X^{\mathrm{n}},\hat{k}^{\mathrm{n}},\hat{s}^{\mathrm{n}}) = \begin{cases} \frac{1}{2} & \text{if } k^{\mathrm{n}} \in \{\hat{k}^{\mathrm{n}}, \hat{k}^{\mathrm{n}} + \hat{s}^{\mathrm{n}}\Delta k\}, \\ 0, & \text{else.} \end{cases} \tag{28}$$

Again, we obtain s^{n} by flipping $\hat{s}^{\mathrm{n}}$ if the opposing point was selected, or else, we leave it unmodified. In case $\hat{k}^{\mathrm{o}}$ or k^{n} fall outside of the old or new path, respectively, the move is rejected and the old path and shooting index are counted again.

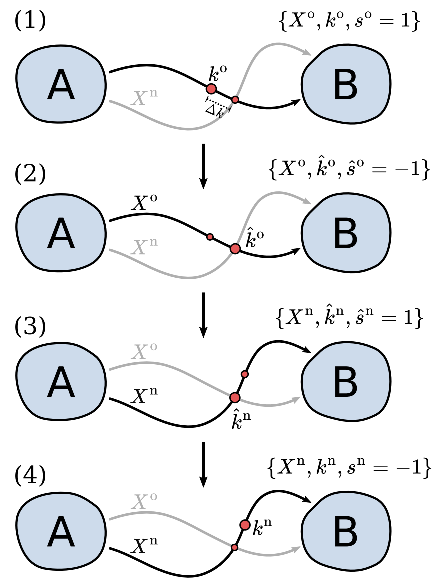

FIG. 3. Two-point aimless shooting move in the extended space of paths X and shooting indices k. (1) The move starts with the current path X^{o}, shooting index k^{o}, and direction s^{o} that determine the position of the valid shooting indices. (2) The first index shift is performed by selecting one of the two potential shooting indices that generate $\hat{k}^{\mathrm{o}}$. The direction $\hat{s}^{\mathrm{o}}$ is flipped as the alternative shooting index is selected. (3) An extended space shooting move generates X^{n} and $\hat{k}^{\mathrm{n}}$. At the same time, a new direction $\hat{s}^{\mathrm{n}}$ is drawn that determines if the second potential shooting point is on the forward or backward segment of the new path. (4) A second index shift is performed, leading to k^{n} with the corresponding direction s^{n}. This shift is required to ensure the reverse move is possible (tracing bottom to top).

This two-step procedure ensures that the path X^{o} *and* shooting index k^{o} can be generated from $\{X^{\mathrm{n}}, k^{\mathrm{n}}\}$ in the reverse move. We note that generation probabilities in Eqs. (27) and (28) and $p_{\mathrm{gen}}(s)$ are symmetric with probability $1/2$ and, as a result, they cancel in the acceptance criterion [Eq. (11)]. Hence, given the analogous form of Eq. (11) derived in the supplementary material, we obtain

$$\frac{p_{\mathrm{acc}}\big[(X^{\mathrm{o}},k^{\mathrm{o}}) \to (X^{\mathrm{n}},k^{\mathrm{n}})\big]}{p_{\mathrm{acc}}\big[(X^{\mathrm{n}},k^{\mathrm{n}}) \to (X^{\mathrm{o}},k^{\mathrm{o}})\big]} = H_{\mathrm{AB}}(X^{\mathrm{n}})\frac{p(k^{\mathrm{n}}|X^{\mathrm{n}})}{p(k^{\mathrm{o}}|X^{\mathrm{o}})}. \tag{29}$$

Hence, we are left with the ratio of the shooting index distributions, which are not included in the original algorithm.[14] As a result, accepting a path if $H_{\mathrm{AB}}(X^{\mathrm{n}}) = 1$ in a flexible-length setting violates detailed balance, which is also apparent in the results of numerical simulations (see Sec. III). In the following, we choose a uniform shooting index distribution $p(k|X) = 1/L(X)$ as it requires no prior knowledge of the simulated system, such as an order parameter. In that case, following the described two-step procedure, a properly weighted path ensemble can be obtained even *a posteriori* by assigning each path a statistical weight of $\Omega(X) = 1/L(X)$ in the case of a uniform shooting index distribution (see the supplementary material for derivation).

H. Spring shooting

Inspired by the flexible-length aimless shooting scheme, the spring shooting algorithm of Brotzakis and Bolhuis[16] aimed to achieve a similar efficiency gain in a one-way shooting framework. In this scheme, the displacement Δk from the previous shooting index is chosen according to an exponential distribution, i.e., a Boltzmann distribution based on a linear potential (constant force); hence, the scheme is named spring shooting. We next reformulate the algorithm in the shooting point MC framework (Fig. 4), beginning by selecting the direction of the shooting move and assigning $s = -1$ for a forward shooting and $s = 1$ for a backward shooting. Note that, in this case, s is drawn freshly at the start of every trial, so it does not need to be included in the extended space. The displacement Δk is then sampled according to

$$\pi(\Delta k) = \frac{\min\left[1, \exp\left(s\sigma\Delta k\right)\right]}{\sum_{\tau=-\Delta k_{\max}}^{\Delta k_{\max}} \min\left[1, \exp\left(s\sigma\tau\right)\right]}, \tag{30}$$

where σ is the strength of the spring and $\Delta k_{\max}$ is the maximum displacement. Following the notation of flexible-length aimless shooting, the shooting index $\hat{k}^{\mathrm{o}}$ is set to $k^{\mathrm{o}} + \Delta k$. The generation probability of the new shooting index becomes

$$p_{\mathrm{gen}}\left(\hat{k}^{\mathrm{o}}|X^{\mathrm{o}}, k^{\mathrm{o}}\right) = \begin{cases} \pi\left(\hat{k}^{\mathrm{o}} - k^{\mathrm{o}}\right) & \text{if } |\hat{k}^{\mathrm{o}} - k^{\mathrm{o}}| \le \Delta k_{\max}, \\ 0, & \text{else.} \end{cases} \tag{31}$$

Then, the new path X^{n} is generated starting from the configuration at $\hat{k}^{\mathrm{o}}$. The index of the common point of X^{n} and X^{o} on the new path is denoted as $\hat{k}^{\mathrm{n}}$. As for aimless shooting, we then shift the new shooting index $\hat{k}^{\mathrm{n}}$ a second time by sampling a shift Δk from

$$\tilde{\pi}(\Delta k) = \frac{\min\left[1, \exp\left(-s\sigma\Delta k\right)\right]}{\sum_{\tau=-\Delta k_{\max}}^{\Delta k_{\max}} \min\left[1, \exp\left(-s\sigma\tau\right)\right]}, \tag{32}$$

which corresponds to the following generation probability:

$$p_{\mathrm{gen}}\left(k^{\mathrm{n}}|X^{\mathrm{n}}, \hat{k}^{\mathrm{n}}\right) = \begin{cases} \tilde{\pi}\left(k^{\mathrm{n}} - \hat{k}^{\mathrm{n}}\right) & \text{if } |k^{\mathrm{n}} - \hat{k}^{\mathrm{n}}| \le \Delta k_{\max}, \\ 0, & \text{else.} \end{cases} \tag{33}$$

This implies that, for a forward shot, first, the shooting index is shifted preferably backward. After generating the new path, the new shooting index is then generated by shifting, preferably forward. This ensures that the move is reversible, and generation probabilities are symmetric (see the supplementary material). Consequently, the resulting acceptance ratio is identical to Eq. (29) and a distribution for the shooting index must be defined.

In the original spring shooting algorithm proposed by Brotzakis and Bolhuis,[16] the new shooting index k^{n} is set implicitly to $\hat{k}^{\mathrm{n}}$, the common point of the new and old path, i.e., the second shifting is omitted. While this formulation of spring shooting allows the reverse move in path space, i.e., regenerating the old path X^{o} from the new path X^{n}, it does not regenerate the old shooting index k^{o} from k^{n}. As a result, detailed balance is violated in the extended space framework. As for flexible-length aimless shooting, the ratio of shooting index distributions is not considered in the original form of the sampling scheme. For spring shooting, however, a reweighting factor for paths sampled without a defined shooting index distribution cannot be derived, due to the irreversibility of the shooting move in the extended space.

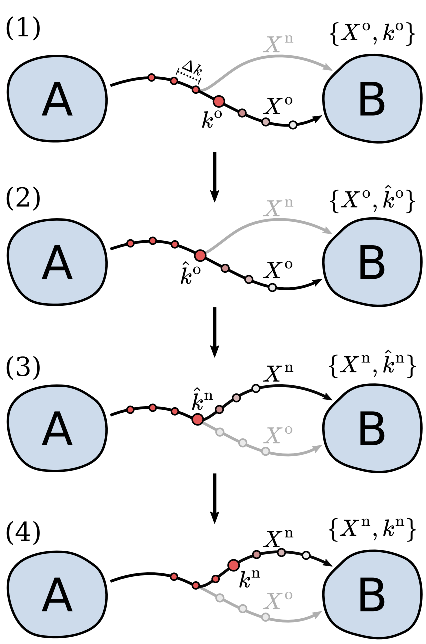

FIG. 4. Spring shooting move in the extended space of paths X and shooting indices k. (1) The move starts with the current path X^{o} and shooting index k^{o}. (2) The first index shift generating $\hat{k}^{\mathrm{o}}$ is performed by a weighted selection from neighboring points (illustrated using color gradient). (3) An extended space shooting move in the forward direction generates X^{n} and $\hat{k}^{\mathrm{n}}$. (4) A second index shift is performed, leading to k^{n}. This shift is performed with opposite weights [see Eq. (32)] and is required to ensure that the reverse move is possible (tracing bottom to top).

III. RESULTS AND DISCUSSION

As a reference for both fixed- and flexible-length path ensembles, we perform long equilibrium simulations from which we extract the transition path ensemble from spontaneous barrier crossings. All simulations are run employing overdamped Langevin dynamics in a one-dimensional, asymmetric double-well model [Fig. 5(a)] with a potential energy defined as (all simulation parameters in the supplementary material)

$$U(x) = \begin{cases} 0.2(x-1)^2\left[0.01(x-1)^2 - 1\right] & \text{if } x < 1, \\ 0.2(x-1)^2\left[0.16(x-1)^2 - 4\right], & \text{else.} \end{cases} \tag{34}$$

This barrier is about $5k_{\mathrm{B}}T$ high. We chose an asymmetric barrier rather than a symmetric one to highlight differences in the obtained shooting point distributions.

For the fixed-length path ensemble [Figs. 5(b) and 5(c)], we compare the density of points on paths $\rho(x|\mathrm{TP})$ as in Eq. (13) with the shooting point distribution as defined in Eq. (14). The density of points in the transition region between states A and B decreases for longer paths as less time is spent in the barrier region. As a result, the points at $L/2 \pm \Delta k$ are less constrained to remain at the barrier top, as the time at which the path leaves state A becomes increasingly variable [Fig. 5(c)]. For the longest paths in these simulations, there is hardly any difference between the density of points

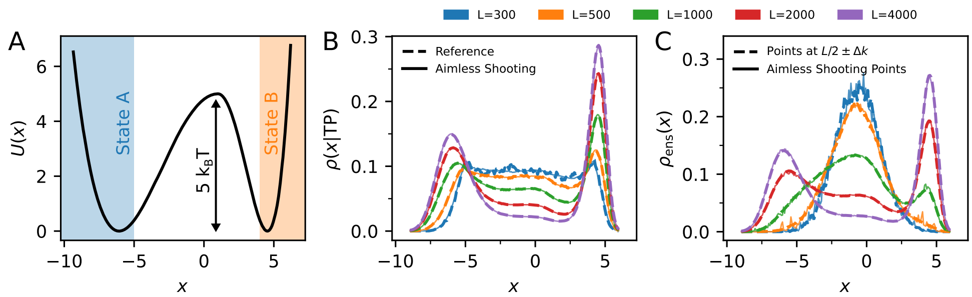

FIG. 5. Fixed-length transition path sampling using aimless shooting. (a) Potential energy function of the model system and the corresponding state definitions. (b) Density of points on transition paths for different fixed path lengths. The dashed lines correspond to the reference from a long equilibrium simulation, and the solid lines correspond to the density obtained via aimless shooting. (c) Shooting point distributions for aimless shooting (solid line) and the points at $L/2 \pm \Delta k$ on transition paths from the equilibrium simulation (dashed lines).

at $L/2 \pm \Delta k$ and $\rho(x|\mathrm{TP})$. Since aimless shooting in a fixed-length setting samples these points as shooting points, the performance of the shooting scheme will depend on the chosen path length. For long paths, both uniform, two-way, and aimless shooting initiate shooting moves effectively from the same shooting point distribution. As the shooting index is drawn independently at each trial and the shooting point distribution follows Eq. (25), the efficiency of fixed-length aimless shooting arises from shooting close to path centers, rather than from any restoring force that directs shooting points toward the barrier top. For long path lengths, the acceptance probability of the shooting move decreases, as shooting points are more frequently drawn from the stable states rather than the barrier region.

Within the flexible-length path ensemble, we observe that uniform two-way shooting converges to the reference ensemble, as indicated by overlapping $\rho(x|\mathrm{TP})$ distributions and path length distributions $p(L)$ (Fig. 6). The density of points at k denoted as $\rho_{\mathrm{ens}}(x)$ matches the reweighted density of points on paths [Eq. (17)] obtained from the reference trajectory since shooting indices are selected with a uniform $p(k|X)$ on each path. In contrast, flexible-length aimless shooting as proposed by Mullen *et al.*[14] and spring shooting as proposed by Brotzakis and Bolhuis[16] do not converge to the reference, as shown in panels (a) and (c) of Fig. 6. Panel (b) shows that the shooting points for spring shooting are much more focused around the location of the barrier. While this is a desired feature, it clearly gives rise to the wrong distribution of transition paths [panels (a) and (c)]. We note that the deviations from the reference path ensemble are less apparent at higher barriers (see the supplementary material), where the distribution of shooting points is more localized for all methods. This is also the reason why spring shooting appeared to produce seemingly converged results in Ref. 16.

Including the shooting index distribution $p(k|X)$ in the acceptance probability and, for spring shooting, performing a second shift

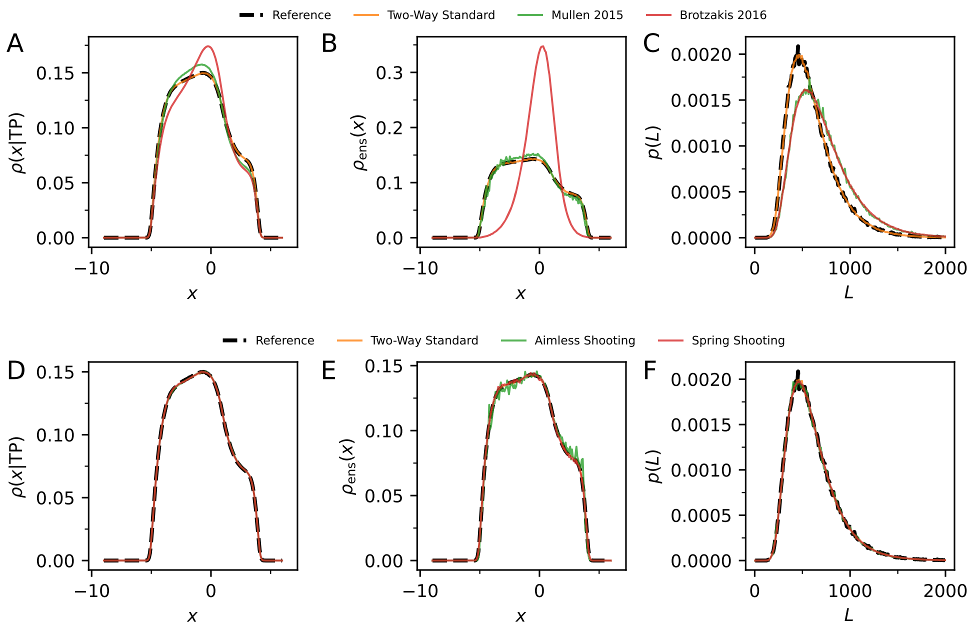

FIG. 6. Flexible-length transition path sampling using aimless shooting as proposed by Mullen *et al.*[14] and spring shooting as proposed by Brotzakis and Bolhuis[16] (top row) and with the proposed corrections (bottom row). (a) and (d) Comparison of the density of points on paths between the equilibrium reference (dashed line) and path sampling algorithms. (b) and (e) Distribution of points after integrating out k in the (X, k) extended ensemble for the different path sampling algorithms. The reference distribution was obtained via reweighting the reference density in panel A with a factor proportional to $1/L(X)$. (c) and (f) Distribution of path lengths obtained using the different path sampling schemes.

of the shooting index recovers the convergence to the reference path ensemble [panels (d)–(f) of Fig. 6). However, even though the methods differ in the way a new shooting index is drawn in each trial, shooting moves are now initiated from the same points as in standard uniform two-way shooting since we impose the same shooting index distribution. In addition, the small displacements of the shooting index in aimless and spring shooting introduce correlations between shooting points that are absent in uniform one- or two-way shooting. These correlations result in slow exploration of shooting points away from the barrier top (see the supplementary material). For flexible length aimless shooting and spring shooting, the shooting points were also generated disproportionately near the barrier regions. To maintain this desired focus, small displacements of the shooting points were performed in successive trials. This behavior is partially retained in the revised algorithms in the early stages of sampling, as the initial shooting index is often selected near the barrier top. However, with the imposed uniform shooting index distribution, the shooting index occasionally drifts away from the barrier to ensure full sampling of the entire index distribution. This leads to low acceptance probabilities and extended sequences of rejected pathways, until the index returns to the barrier top by multiple small displacements in the right direction. The resulting persistent correlations considerably lower the efficiency of the algorithm. In standard TPS, on the other hand, the shooting index is redrawn independently at each trial, allowing it to move away from and return to the barrier instantaneously without such correlations.

IV. CONCLUSION

We have proposed a theoretical framework to describe transition path sampling in an extended ensemble that includes paths and respective shooting indices. Revisiting algorithms that evolve the shooting point from trial to trial, we derived detailed balance equations for the extended ensemble, which led to corrections for aimless and spring shooting in flexible-length settings. While the deviation of path ensembles sampled via aimless shooting or spring shooting from the correct path ensemble is system-dependent, our experiments demonstrate a significant overlap in the distributions, suggesting that previous studies may be critically assessed and qualitative conclusions may remain largely valid. With recent advances in interface-based sampling schemes, such as stone skipping[23] and wire fencing,[24] for transition interface sampling and virtual interface exchange[25] for transition path sampling, we anticipate further development of shooting schemes for TPS that require minimal information about the system of interest.

SUPPLEMENTARY MATERIAL

See the supplementary material for simulation details, additional derivations for various algorithms, an analysis of convergence rates, and pseudo-codes for the TPS algorithms discussed in the main text.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Sebastian Falkner: Conceptualization (equal); Data curation (lead); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (lead); Validation (lead); Visualization (lead); Writing – original draft (equal); Writing – review & editing (equal). **Alessandro Coretti**: Conceptualization (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Baron Peters**: Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Peter G. Bolhuis**: Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Christoph Dellago**: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (lead); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

All data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.14753554, Ref. 26.

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