An ergodic sampling scheme for constrained Hamiltonian systems with applications to molecular dynamics

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Abstract

This article addresses the problem of computing the Gibbs distribution of a Hamiltonian system that is subject to holonomic constraints. In doing so, we extend recent ideas of Cancès *et al.* (*M2AN, Vol. 41, No. 2, pp. 351-389, 2007*) who could prove a Law of Large Numbers for unconstrained molecular systems with a separable Hamiltonian employing a discrete version of Hamilton's principle. Studying ergodicity for constrained Hamiltonian systems, we specifically focus on the numerical discretization error: even if the continuous system is perfectly ergodic this property is typically not preserved by the numerical discretization. The discretization error is taken care of by means of a hybrid Monte-Carlo algorithm that allows for sampling bias-free expectation values with respect to the Gibbs measure independently of the (stable) step-size. We give a demonstration of the sampling algorithm by calculating the free energy profile of a small peptide.

1 Introduction

Consider a system assuming configurations $q \in Q$ with energy $V(q)$. A standard problem in statistical mechanics consists in computing the configuration average of an observable $f(q)$ with respect to the Gibbs distribution, i.e.,

$$\mathbf{E}f = \int f(q)\mu(dq)\,. \tag{1.1}$$

Here $\mu(dq)$ denotes the Gibbs measure at temperature $T > 0$,

$$\mu(dq) = \frac{1}{Z}\exp(-\beta V(q))\,dq\,, \quad \beta = 1/T\,, \tag{1.2}$$

and

$$Z = \int \exp(-\beta V(q))\,dq \tag{1.3}$$

is a normalization constant that normalizes the total probability to one.

Quite often the above problem is treated in the context of deterministic Hamiltonian systems assuming states (q, p): Given a set of coordinates $(q, p) = (q^1, \ldots, q^n, p_1, \ldots, p_n)$ on the phase space $T^*Q \cong Q \times \mathbf{R}^n$, we suppose that the system's energy is given by a separable Hamiltonian of the form

$$H(q, p) = \frac{1}{2} \langle p, p \rangle + V(q) \tag{1.4}$$

The energy $H = K + V$ is the sum of kinetic and potential energy, where $\langle \cdot, \cdot \rangle$ denotes usual scalar product in $\mathbf{R}^n$. (For convenience we have set the mass to unity.) For realistic, especially high-dimensional systems the integral in (1.1) is mostly not manageable by analytical or numerical means, and therefore the ensemble average is typically approximated by a time average over the solution curves of Hamilton's equations

$$\begin{aligned} \dot{q}^i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= \frac{\partial H}{\partial q^i} \,. \end{aligned} \tag{1.5}$$

Exchanging ensemble and time average assumes that the underlying dynamical process is ergodic. Ergodicity, in turn, presupposes the existence of an invariant measure of the process. As a matter of fact the canonical distribution $\rho \propto \exp(-\beta H)$ is invariant under the Hamiltonian flow. That is, if we pick initial conditions that are distributed according to the probability law ρ, then all points along the solution curves of (1.5) will follow the same law. Letting $\mathbf{E}_\rho$ denote the expectation with respect to the canonical distribution it can be readily checked that $\mathbf{E}f = \mathbf{E}_\rho f$ for any position-dependent observable f for which the integral in (1.1) exists. However the system (1.5) has infinitely many invariant probability measures (in fact every function of the Hamiltonian gives rise to an invariant probability distribution). Even worse, very few Hamiltonian systems are known to be ergodic at all, and the only candidates for ergodic invariant measures are singular with respect to the Lebesgue measure, therefore excluding the possibility of sampling the smooth canonical distribution by a single trajectory. Running many trajectories from ρ-distributed initial conditions instead is clearly not an option: if we could generate initial conditions according to the high-dimensional distribution ρ, there would not be any problem at all.

The sampling problem We shall call the task of computing the Gibbs distribution by simulating Hamilton's equations the *sampling problem*. In statistical mechanics applications it is frequently addressed by means of certain thermostatting techniques like Nosé-Hoover, Berendsen or stochastic Andersen thermostats [1, 2]. Mostly these algorithms modify the equations of motion in such a way that the dynamics samples the canonical density, provided the Hamiltonian flow is ergodic with respect to the microcanonical measure. This is a very strong assumption, and it is well-known that the ordinary Nosé-Hoover thermostat suffers from ergodicity problems for certain classes of Hamiltonians [3, 4]. This pathology can be removed by employing extensions to the single-oscillator chain or by imposing constant temperature constraints [5, 6, 7]. But even then, the sampling works well *only if* the dynamics is ergodic, and conditions to guarantee ergodicity are still lacking. Additionally all these more

sophisticated methods have in common that due to their complexity they are relatively hard to implement, and they require a careful adjustment of the parameters involved. For further details the interested reader is referred to the recent survey article [8].

Main objective In this article we are going to follow an alternative route that is in the spirit of Markov chain Monte-Carlo methods. It is based on the observation that one can systematically perturb the momentum component of the Hamiltonian trajectories $(q(t), p(t)) \subset T^*Q$ during the course of integration, such that the configuration component samples the Gibbs distribution with probability one (the momentum distribution becomes completely uncontrollable though). The approach follows the work of Schütte [9] who constructs a *stochastic* Hamiltonian system by averaging out the momenta from the associated time-disrete transfer operator. This generates a discrete diffusion-like flow $\{q_0, q_1, q_2, \ldots\}$ on configuration space that can be shown to be ergodic with respect to the Gibbs measure in the sense that the Law of Large Numbers

$$\frac{1}{N}\sum_{k=0}^{N-1} f(q_k) \to \mathbf{E}f \quad \text{as} \quad N \to \infty \tag{1.6}$$

holds true for almost all initial conditions $(q_0, p_0) = (q(0), p(0))$. Conditions on the numerical flow map that guarantee ergodicity if the Hamiltonian is of the form (1.4) are due to Schütte [9] and Cancès *et al.* [10] and will be briefly discussed in the next section. The objective of the present work is to extend their ideas to more general classes of Hamiltonians, namely, systems on manifolds and systems with holonomic constraints. In doing so, we develop an ergodic hybrid Monte-Carlo realization of the stochastic Hamiltonian system that allows for sampling the Gibbs measure on a given configuration submanifold.

2 Stochastic Hamiltonian systems

We start by considering an unconstrained natural Hamiltonian system with a Hamiltonian function of the form (1.4). To this end we let $\Phi_\tau : T^*Q \to T^*Q$ denote the flow of Hamilton's equations for a fixed integration time $\tau > 0$. Let further $\pi : (q, p) \mapsto q$ be the natural bundle projection of a phase space vector onto its position component. We introduce a stochastic Hamiltonian flow as iterates of the map

$$q_{k+1} = (\pi \circ \Phi_\tau)(q_k, p_k) \tag{2.1}$$

with p_k randomly chosen according to the Maxwell distribution

$$\varrho(p) \propto \exp\left(-\beta K(p)\right) , \quad K(p) = \frac{1}{2}\left\langle p, p\right\rangle .$$

2.1 Two approaches towards ergodicity

The iteration (2.1) defines the time-discrete Markov process on Q. If the (discrete) Hamiltonian flow Φ_τ is exactly energy-preserving with invariant probability measure $\rho \propto \exp(-\beta H)$, it is easy to show that the natural invariant

measure of the stochastic flow is the Gibbs measure $\mu \propto \exp(-\beta V)$ which is simply the marginal distribution of ρ. In the following we discuss sufficient conditions for the ergodicity of (2.1); matters of energy-preservation and numerical approximations of the flow Φ_τ will be mentioned at the end of this section.

Mixing and momentum-invertibility In [9], Schütte states a Law of Large Numbers for stochastic Hamiltonian flows that relies on what he calls *mixing* and *momentum-invertibility* conditions. Therein the following definition is given:

Definition 2.1. *The stochastic Hamiltonian flow is called mixing, iff for every pair of open subsets $B, C \subset Q$ there is a $n_0 \in \mathbf{N}$, such that*

$$\int_B T^n \chi_C(q)\mu(dq) > 0\,, \quad \forall n > n_0\,,$$

where $\chi_C(\cdot)$ is the characteristic function of $C \subset Q$ and

$$Tu(q) = \int_{\mathbf{R}^n} (u \circ \pi \circ \Phi_\tau)(q,p)\varrho(dp)$$

is the discrete transition (Koopman) operator $T : L^1 \to L^1$.

We need yet another definition.

Definition 2.2. *The Hamiltonian flow Φ_τ is momentum-invertible on sets of positive measure with respect to the Maxwell distribution, iff the following two conditions are met:*

1. *For almost every $q \in Q$ the function $F_q(p) = (\pi \circ \Phi_\tau)(q,p)$ is locally invertible, i.e., there is an open set $U \subset T_qQ$, such that $\det \mathbf{D}F_q(p) \neq 0$ for all $p \in U$.*

2. *There is a constant $c > 0$ such that*

$$\operatorname*{ess\text{-}inf}_{q \in Q} \int_U \varrho(dp) = c\,.$$

The mixing property should be distinguished from the usual definition in dynamical systems. Here mixing amounts to the accessibility of any open set of configurations with positive probability. The second property guarantees that the measure of initial conditions from which the accessible configuration space can be reached is non-zero. We have:

Proposition 2.3 (Schütte 1998). *Given $\tau > 0$, let the Hamiltonian flow Φ_τ be momentum-invertible and mixing with invariant probability measure ρ. Then, the process (2.1) is ergodic with respect to the Gibbs measure μ, i.e.,*

$$\frac{1}{N}\sum_{k=0}^{N-1} f(q_k) \to \mathbf{E}f \quad \textit{as} \quad N \to \infty \quad \textit{(almost surely)}$$

for almost all initial conditions $q_0 \in Q$, where $f \in L^1(\mu)$ is measurable.

Accessibility and irreducibility In practice the above mixing and invertibility condition are difficult to check. Moreover it is not clear whether both conditions are indeed necessary. As a remedy for this problem the authors of [10] prove an ergodicity result for stochastic Hamiltonian systems with an energy of the form (1.4) that does not rely on these conditions but is based on the irreducibility of the associated time-discrete Markov process. In doing do, they employ a discrete version of Hamilton's principle to explicitly construct an integrator that satisfies an accessibility condition that is a necessary condition for irreducibility. By accessibility the following is meant:

Definition 2.4. *Let $\{q_k\}_{k\in\mathbf{N}}$ be a time-discrete Markov process on Q. For any $q, q' \in Q$ there exists an open neigbourhood $C \subset Q$ of q' such that the process has a strictly positive transition kernel, i.e., the transition probability satisfies*

$$\mathbf{P}\left[q_{k+1} \in C \,|\, q_k = q\right] > 0\,,$$

where

$$\mathbf{P}\left[q_{k+1} \in C \,|\, q_k = q\right] = \int_{\mathbf{R}^n} \chi_C\left((\pi \circ \Phi_\tau)(q_k, p)\right) \varrho(p)\, dp\,.$$

The idea of the proof is to show that we can always find a (discrete) flow map connecting q with a point in the open set B. For the Hamiltonian (1.4) the flow map is given by iterations of the Verlet algorithm and is obtained as the stationary solution of a discrete variational principle. Irreducibility of the stochastic Hamiltonian system further requires the accessibility, not only of open sets, but of arbitrary Borel sets. The Law of Large Numbers then reads:

Proposition 2.5 (Meyn & Tweedie 1993, Tierney 1994). *Let (2.1) be a Markov process with invariant probability measure μ. Assume further that the process is irreducible, i.e., its transition probabilities satisfy*

$$\mathbf{P}\left[q_{k+1} \in B \,|\, q_k = q\right] > 0 \quad \forall q \in U \subseteq Q, \forall B \subseteq \mathcal{B}(U)\,,$$

where $\mathcal{B}(U)$ is the Borel σ-algebra of $U \subseteq Q$, and $B \subseteq \mathcal{B}(U)$ has positive Lebesgue measure. Then, for any measurable function $f \in L^1(\mu)$, we have

$$\frac{1}{N}\sum_{k=0}^{N-1} f(q_k) \to \mathbf{E}f \quad \textit{as} \quad N \to \infty \quad \textit{(almost surely)}$$

for almost all initial conditions $q_0 \in Q$.

Irreducibility of the Markov process asks for a certain degree of regularity of the transition kernel, thereby imposing regularity conditions on the Hamiltonian vector field. We refer to Section 4.1.2 for the details concerning irreducibility.

So far it is not clear how irreducibility relates to mixing and momentum-invertibility conditions, and we are not going to answer this question here. Nonetheless it is the major advantage of Cancès' approach (i.e., using Hamilton's principle to construct an irreducible stochastic Hamiltonian system) that it can be easily extended to various classes of Hamiltonians.

For this reason we will take up their ideas in Section 4, where we construct an ergodic stochastic Hamiltonian flow that samples the Gibbs distribution on a given configuration submanifold.

2.2 Discretization issues and Monte-Carlo realization

Stochastic Hamiltonian systems generate a diffusion-like flow on Q. In point of fact, it has been shown [11] that for sufficiently small (i.e., stable) time step τ the Euler-Maruyama discretization of the Itô stochastic differential equation

$$dX(t) = -\nabla V(X(t))dt + \sqrt{\frac{2}{\beta}}\, dW(t)\,, \quad X(0) = q_0 \tag{2.2}$$

is an instance of the iteration (2.1), if Φ_τ is chosen to be the single-step Verlet integrator. The Euler-Maruyama scheme for (2.2) reads

$$X_{n+1} = X_n - \tau\nabla V(X_n) + \sqrt{\frac{2\tau}{\beta}}\,\xi_n\,, \quad X_0 = q_0\,,$$

where $\xi_n \sim \mathcal{N}(0, \mathbf{1})$ is a Gaussian random variable with mean zero and unit variance. (Notice that ξ_n replaces the random momentum.) Ergodicity results for discretized stochastic differential equations are rare; even worse, it has been demonstrated [12, 13] that the Euler-Maruyama disretization does not preserve ergodicity, if the vector field ∇V is not globally Lipschitz continuous.

In [9], it was demonstrated that mixing and momentum-invertibility conditions hold true, if the Hamiltonian flow Φ_τ is approximated by the Verlet integrator for a Hamiltonian of the form (1.4). A similar result regarding irreducibility of the corresponding Markov process was stated in [10]. This, however, does not guarantee that the system is ergodic as follows from the correspondence with the Euler-discretized stochastic differential equation. The reason is that the Verlet algorithm does not exactly preserve the total energy H, but rather a so-called shadow Hamiltonian $\tilde{H} = H + \mathcal{O}(\tau^2)$. Therefore a realization of the stochastic Hamiltonian system will most probably sample the marginal distribution of $\tilde{\rho} \propto \exp(-\beta\tilde{H})$ rather than the correct Gibbs density μ.

At this stage hybrid Monte-Carlo (HMC) as an algorithmic realization of the stochastic Hamiltonian system comes into play: HMC emulates the general Metropolis Monte-Carlo strategy of proposal and acceptance steps, where the proposal is generated by short runs of the numerical integrator with randomly chosen initial conditions. The acceptance procedure controls the numerical energy error, because it rejects those moves that have too large energy fluctuations. In connection with numerical short-time integration of the underlying Hamiltonian system, HMC moreover circumvents the common Monte-Carlo problem, namely, that the acceptance probability for an arbitrary random move to an energetically unfavourable state becomes incredibly small [14]. HMC is conceptually very simple (as is ordinary Metropolis Monte-Carlo) and is designed to be used with symplectic integrators such as the Verlet algorithm. In fact, it has been demonstrated in [9] and [15] that HMC for a Hamiltonian system with a separable Hamiltonian of the form (1.4) indeed preserves the correct Gibbs measure μ. In Section 4 we will generalize the available results to the numerical integration of constrained Hamiltonian systems or systems on manifolds.

We should mention yet another approach [16] that is based on what the authors call *approximate controllability*. The idea exploits an analogy with controllable (or reachable) states in control theory, where the continuous control variable is replaced by the realizations of a white noise process acting on the momenta. Although the authors state ergodicity only for the exact solution of

a sliding disc, the ansatz is promising as controllability is a well studied concept also for time-discrete control problems (see, e.g., [17]). Basic work in this direction by the same authors is [18].

3 Constrained systems

In actual simulations the Hamiltonian system is often subject to certain configuration (i.e., holonomic) constraints, and we denote by $\Sigma \subset Q$ the submanifold of admissible configurations. In this case the task of computing the expectation (1.1) with respect to the Gibbs measure changes according to

$$\mathbf{E}_\Sigma f = \int_\Sigma f(q)\mu_\Sigma(dq)\,,$$

where μ_Σ is the Gibbs measure restricted to the set Σ of admissible configurations. Instances of constrained sampling problems are manifold, e.g., in molecular dynamics: thermodynamic integration methods for rare events [19, 20], rigid-body dynamics in quaternions [21] or best-approximations of molecular systems [22] to mention just a few (see Section 5 for further details). Before we address the constrained sampling problem in detail we shall briefly review the basic properties of constrained mechanical systems.

3.1 Introducing holonomic constraints

In treating holonomic constraints it is most convenient to start within the framework of Lagrangian mechanics. Let the function

$$L(q,\dot q) = \frac{1}{2}\,\langle \dot q, \dot q\rangle - V(q)$$

be the Lagrangian associated with our Hamiltonian system (1.4). For our purposes it suffices to define a holonomic constraint $\Sigma \subset Q$ by specifying a smooth function $\varphi : Q \to \mathbf{R}^s$, such that $\Sigma = \varphi^{-1}(0)$ is the zero level set of φ. If the Jacobian $\mathbf{D}\varphi(q)$ has maximum rank s on Σ, then Σ is a proper submanifold of codimension s in Q. Together with the natural inclusion $T\Sigma \subset TQ$ this determines the state space of the constrained system. The tangent space to $q \in \Sigma$ is then defined in the usual way considering the direction of curves in Σ which is equivalently expressed as

$$T_q\Sigma = \left\{ v \in T_qQ \,|\, \mathbf{D}\varphi(q)^T \cdot v = 0 \right\}\,.$$

Without loss of generality we may assume that Σ has codimension $s = 1$ in Q. We can now easily define a constrained Lagrangian by restricting the original one to the constrained tangent space $T\Sigma \subset TQ$. An alternative (and more common) way is to define an *augmented* Lagrangian

$$\hat L(q,\dot q,\lambda) = L(q,\dot q) - \lambda\varphi(q)\,.$$

Note that the thus defined Lagrangian is not strictly convex in the velocities, for it does not contain the velocity $d\lambda/dt$. Hence defining a constrained Hamiltonian

makes no sense at the moment. Nevertheless we can compute the stationary solution (not necessarily a minimum) of the action functional, viz.,

$$\delta \int_a^b \left(L(q(t), \dot{q}(t)) - \lambda(t)\varphi(q(t)) \right) \, dt = 0 \, .$$

where the endpoints $q(a)$ and $q(b)$ both satisfy the constraint. From this we obtain the Euler-Lagrange equations in the unknowns q and λ,

$$\begin{aligned} \frac{d}{dt}\frac{\partial \hat{L}}{\partial \dot{q}^i} &= \frac{\partial \hat{L}}{\partial q^i} \\ 0 &= \frac{\partial \hat{L}}{\partial \lambda} \, . \end{aligned} \tag{3.1}$$

Evidently, the second equation is simply the constraint $\varphi(q) = 0$. The alternative method by restricting the original Lagrangian to $T\Sigma$ amounts to endowing Σ with an appropriate set of local coordinates $(x^1, \ldots, x^d)$ with $d = n-1$, writing up the Lagrangian in these coordinates, and deriving local Euler-Lagrange equations. According to the theorem on Lagrange multipliers [23] the local Euler-Lagrange equations are equivalent to the equations (3.1). We refer to the latter as *ambient-space* formulation which is by far the most common formulation when it comes to the numerical issues [24]; further details regarding numerical discretization will be discussed in the Sections 4 and 5.

3.2 Constrained Hamiltonian systems

The transition from a Lagrangian to a Hamiltonian formulation in ambient-space representation is not straightforward as the augmented Lagrangian is not strictly convex in the velocities ($\dot{\lambda} = d\lambda/dt$ is missing). Yet we can formally define the conjugate momentum to the constrained variable q by

$$p^i = \frac{\partial \hat{L}}{\partial \dot{q}^i} \, .$$

This is the former unconstrained momentum p. If we restrict the Legendre transform $\hat{H} = \langle \dot{q}, p \rangle - \hat{L}$ to the set defined by the condition

$$0 = \frac{\partial \hat{L}}{\partial \dot{\lambda}} \, ,$$

we can derive a Hamiltonian $\hat{H}$ pretending that $\hat{L}$ is strictly convex. This yields

$$\hat{H}(q, p, \lambda) = H(q, p) + \lambda\varphi(q) \, .$$

Clearly this Hamiltonian does not give an equation for λ in the usual way. Therefore the evolution of the Lagrange multiplier is undetermined. Nevertheless, we obtain equations of motion for the variables q and p,

$$\begin{aligned} \dot{q}^i &= \frac{\partial \hat{H}}{\partial p_i} \\ \dot{p}^i &= -\frac{\partial \hat{H}}{\partial q^i} \\ 0 &= -\frac{\partial \hat{H}}{\partial \lambda} \, , \end{aligned} \tag{3.2}$$

that are equivalent to the Euler-Lagrange equations (3.1) modulo the restriction $\partial\hat{L}/\partial\dot{\lambda} = 0$. All trajectories lie on the constrained phase space

$$\mathscr{B} = \left\{(q,p) \in T^*Q \,\middle|\, q \in \Sigma \text{ and } \langle \nabla\varphi(q), D_pH(q,p)\rangle = 0\right\} ,$$

where H is the unconstrained Hamiltonian (1.4), and D_p denotes the derivative with respect to the momenta. It suffices to say that the constrained phase space is the image of the Legendre transform of $(TQ)|T\Sigma$ which will be identified with $T^*\Sigma$ in what follows. Note that the momentum constraint $\langle \nabla\varphi(q), D_pH(q,p)\rangle = 0$ equals the equality $\dot{\varphi}(q) = 0$. It is typically referred to as *hidden* constraint, as it does not appear explicitly in the equations of motion.

3.3 Ensembles of constrained systems

Let us briefly revisit the problem of relating the Gibbs measure to the canonical distribution of a Hamiltonian system. The constrained Hamiltonian system defined by (3.2) inherits all basic properties of the unconstrained one: its flow reversibly, symplectic and energy-preserving, if it is considered on the constrained phase space $\mathscr{B}$. In particular, the energy of the constrained system is the Hamiltonian H restricted to $\mathscr{B}$. Hence the constrained canonical distribution is simply the restriction of the unconstrained distribution $\rho \propto \exp(-\beta H)$, i.e.,

$$\nu_{\mathscr{B}} = \frac{1}{Z_{\mathscr{B}}} \exp(-\beta H_{\mathscr{B}})\, d\lambda_{\mathscr{B}} .$$

Here $H_{\mathscr{B}} = H|_{\mathscr{B}}$, and $d\lambda_{\mathscr{B}}$ is the Liouville measure of $\mathscr{B} \subset T^*Q$; since $\mathscr{B} \cong T^*\Sigma$ is a symplectic manifold, it is obtained in the standard way by taking exterior products of the constrained symplectic form that is obtained as the restriction of the unconstrained symplectic form [25]. It is instructive to write down the local coordinate expression of $\nu_{\mathscr{B}}$: Let $\sigma(x)$ be an embedding of Σ into Q, and let local coordinates on Σ be denoted by $x = (x^1, \ldots, x^d)$. Defining the conjugate momenta u in the usual way by $u_i = \partial L/\partial \dot{x}^i$, we obtain the local coordinate expression for the Hamiltonian

$$H_{\mathscr{B}} = \frac{1}{2} G_\Sigma^{ij}(x) u_i u_j + V(\sigma(x)) , \tag{3.3}$$

where $G_\Sigma = G_\Sigma(x)$ is the metric on Σ that is induced by the embedding $\Sigma \subset Q$. (The summation convention is in force, i.e., we sum over repeated upper and lower indices, and G_Σ^{ij} denotes the entries of the inverse of G_Σ.) In terms of the local coordinates the constrained canonical distribution now becomes

$$\nu_{\mathscr{B}}(dx, du) = \frac{1}{Z_{\mathscr{B}}} \exp(-\beta H_{\mathscr{B}}(x,u))\, dxdu .$$

with

$$Z_{\mathscr{B}} = \int_{\mathbf{R}^d \times \mathbf{R}^d} \exp(-\beta H_{\mathscr{B}}(x,u))\, dxdu .$$

Here we encounter the same problem as without constraints: the invariant measure of the system (3.2) is not unique, and the only ergodic measure, namely the microcanonical measure, is singular with respect to $d\lambda_{\mathscr{B}}$. Repeating the argument from above, we introduce a discrete stochastic constrained Hamiltonian

system. For this purpose let $\Phi_\tau : \mathscr{B} \to \mathscr{B}$ with $\tau > 0$ denote the flow generated by the constrained Hamiltonian $H_{\mathscr{B}}$. The stochastic system can be defined as

$$x_{k+1} = (\pi \circ \Phi_\tau)(x_k, u_k)\,, \quad \pi : T^*\Sigma \to \Sigma\,, \tag{3.4}$$

where u_k is chosen randomly according to the constrained Maxwell distribution

$$\varrho_x(u) \propto \exp\left(-\beta K(x,u)\right)\,, \quad K(x,u) = \frac{1}{2} G^{ij}_\Sigma(x) u_i u_j\,. \tag{3.5}$$

Following the reasoning of Section 2, we claim that the unique invariant measure of (3.4) is the one which is obtained upon integrating the constrained canonical distribution $\nu_{\mathscr{B}}$ over the momenta, i.e., the marginal distribution

$$\int_{\mathbf{R}^d} \nu_{\mathscr{B}}(\cdot, du) = \frac{1}{Z_\Sigma} \exp\left(-\beta V(\sigma(x))\right) d\sigma(x)\,,$$

where $d\sigma(x) = \sqrt{\det G_\Sigma(x)} dx$ is the surface element of $\Sigma \subset Q$, and

$$Z_\Sigma = \int_{\mathbf{R}^d} \exp\left(-\beta V(\sigma(x))\right) d\sigma(x)\,.$$

normalizes the total probability to one. Clearly the last two equations are nothing but the unconstrained Gibbs measure (1.2) restricted to Σ. In other words, the restricted Gibbs measure

$$\mu_\Sigma(dx) = \frac{1}{Z_\Sigma} \exp\left(-\beta V(\sigma(x))\right) d\sigma(x)\,, \tag{3.6}$$

is the natural invariant measure of the iteration (3.4). The next section is devoted to finding a numerical Hamiltonian flow, such that the iteration map (3.4) is ergodic with respect to the constrained Gibbs measure (3.6).

4 Constrained hybrid Monte-Carlo

Consider the symplectic and reversible discrete *numerical* flow map Ψ_τ that is generated by the constrained Hamiltonian (3.3), and consider iterates of Ψ_τ with initial momenta that are randomly chosen according to the Maxwell distribution (5.4). This generates a sequence $\{x_0, \ldots, x_{N-1}\} \subset \mathbf{R}^d$ in configuration space.

If the flow Ψ_τ were exactly energy-preserving, then the x_k would be distributed according to μ_Σ as given by (3.6). However it is impossible to find a numerical discretization scheme that is symplectic, reversible, and exactly energy-conserving at once [26]; the best we can achieve is that the energy error for a symplectic and reversible integrator remains uniformly bounded on compact time intervals and oscillates around its exact value.

The HMC method accounts for this drawback by accepting or rejecting points with a certain probability that depends on the energy error. Suppose we are at x_k and integrate up to time τ with a randomly chosen initial momentum $u_k \sim \varrho_{x_k}(\cdot)$. By this we generate a Monte-Carlo proposal $\tilde{x}_k = (\pi \circ \Psi_\tau)(x_k, u_k)$, which is accepted (i.e., $x_{k+1} = \tilde{x}_k$) with probability

$$p_\tau(x_k, u_k) = \min\left(1, \exp(-\beta \Delta H_{\mathscr{B}}(x_k, u_k; \tau))\right)\,, \tag{4.1}$$

where

$$\Delta H_{\mathscr{B}}(x_k, u_k; \tau) = (H_{\mathscr{B}} \circ \Psi_\tau)(x_k, u_k) - H_{\mathscr{B}}(x_k, u_k) \tag{4.2}$$

denotes the energy error. We reject the proposal (i.e., $x_{k+1} = x_k$) with probability $1 - p_\tau$. Proceeding in this way, HMC generates a time-discrete Markov process $\{x_1, \ldots, x_N\} \subset \mathbf{R}^d$ that induces a Markov process on the constrained configuration space $\Sigma \subset Q$ by virtue of the embedding $\sigma : \mathbf{R}^d \to \Sigma$.

4.1 Ergodicity of constrained HMC

Our approach to prove ergodicity for the just defined constrained HMC Markov process makes use of an idea of Cancès *et al.* [10] and rests upon the following strong Law of Large Numbers that is due to [27, 28].

Proposition 4.1 (Meyn & Tweedie 1993, Tierney 1994). *Let $\{x_k\}_{k\in\mathbf{N}}$ be a Markov process on $\mathbf{R}^d$ with invariant probability measure μ_Σ. If the process is irreducible, i.e., its transition probabilities satisfy*

$$\mathbf{P}\left[x_{k+1} \in B \,|\, x_k = x\right] > 0 \quad \forall x \in U \subseteq \mathbf{R}^d, \forall B \subseteq \mathcal{B}(U)\,, \tag{4.3}$$

where $\mathcal{B}(U)$ is the Borel σ-algebra of $U \subseteq \mathbf{R}^d$, and $B \subseteq \mathcal{B}(U)$ has positive Lebesgue measure, then the process obeys the strong Law of Large Numbers

$$\lim_{N\to\infty} \frac{1}{N} \sum_{i=0}^{N-1} f(\sigma(x_i)) = \int_{\mathbf{R}^d} f(\sigma(x))\mu_\Sigma(dx) \quad \textit{(almost surely)}$$

for almost all $x_0 \in \mathbf{R}^d$, where $f \circ \sigma \in L^1(\mu_\Sigma)$ is a measurable function.

It is convenient to understand f as an observable that is defined on the original n-dimensional configuration space Q, such that $f \circ \sigma$ denotes the restriction to $\Sigma \subset Q$. We shall prove ergodicity of the constrained HMC Markov process by proving that it complies with the assumptions of Theorem 4.1, namely,

1. it leaves the constrained Gibbs measure μ_Σ invariant,
2. the process is irreducible, i.e., condition (4.3) is met.

4.1.1 Invariance of the constrained Gibbs measure

Invariance of the constrained Gibbs measure can be shown following the outline of the proof in [15] for separable Hamiltonians. We cannot separate the canonical density into merely momentum and position dependent parts; we have

$$\nu_{\mathscr{B}}(dx, du) = \frac{1}{Z_{\mathscr{B}}} \underbrace{\exp(-\beta K(x,u))}_{\varrho_x(u)} \underbrace{\exp(-\beta V(\sigma(x)))}_{\eta(x)}\, dxdu\,.$$

The notation $\rho_x(u)$ indicates that the momentum density depends parametrically on the position coordinates. It is easy to see that the HMC acceptance probability (4.1)–(4.2) for a proposal step $(\tilde{x}, \tilde{u}) = \Psi_\tau(x, u)$ equals

$$p_\tau(x, u) = \min\left(1,\, \frac{\varrho_{\tilde{x}}(\tilde{u})\eta(\tilde{x})}{\varrho_x(u)\eta(x)}\right)\,, \tag{4.4}$$

which coincides with the usual Metropolis-Hastings rule [29] for a symplectic and reversible map Ψ_τ. Clearly we would have $p_\tau = 1$, if the proposal generating flow map Ψ_τ were exactly energy-conserving. The following statement is due to the author [30].

Lemma 4.2. *The constrained Gibbs measure μ_Σ is invariant under the HMC flow that is generated by a symplectic and reversible flow map Ψ_τ together with the Metropolis acceptance-rejection procedure with acceptance probability (4.4).*

Proof. It is sufficient to show that the HMC preserves expectation values with respect to μ_Σ. Let $\zeta \in \mathbf{R}^d$ be an accepted position value after a single integration and acceptance step. We assume that the initial momentum u is distributed according to $\varrho_x(u)$. Furthermore, let $\vartheta(d\zeta)$ denote the marginal distribution of the position variables after one HMC step. Hence we have to show that

$$\int_{\mathbf{R}^d} f(\sigma(x))\mu_\Sigma(dx) = \int_{\mathbf{R}^d} f(\sigma(\zeta))\vartheta(d\zeta)\,.$$

Suppose the initial positions x follow the marginal of $\nu_{\mathscr{B}}$. For each x we draw a momentum vector from $\varrho_x(u)$, and we propagate according to $(\tilde{x}, \tilde{u}) = \Psi_\tau(x, u)$. We can perform the acceptance-rejection procedure for the rightmost expectation using a change-of-variables argument. Exploiting that the constrained Liouville measure $d\lambda_{\mathscr{B}}$ is preserved under the flow Ψ_τ, we obtain

$$\begin{aligned}\int_{\mathbf{R}^d} f(\sigma(\zeta))\vartheta(d\zeta) \;&=\; \int_{\mathbf{R}^d} f(\sigma(\zeta))\, p_\tau(\Psi_{-\tau}(\zeta,\tilde{u}))\, \rho(\Psi_{-\tau}(\zeta,\tilde{u}))\, d\lambda_{\mathscr{B}} \\ &\quad + \int_{\mathbf{R}^d} f(\sigma(\zeta))\;(1 - p_\tau(\zeta,-\tilde{u}))\, \rho(\zeta,-\tilde{u})\, d\lambda_{\mathscr{B}}\,,\end{aligned}$$

where $\rho(x,u) = \varrho_x(u)\eta(x)$ denotes the density of $\nu_{\mathscr{B}}(dx,du) = \rho(x,u)dxdu$. Note that the first integral on the right hand side originates from the acceptance, the second one stems from the rejection step. Taking advantage of the identity

$$p_\tau(\Psi_{-\tau}(\zeta,\tilde{u}))\, \rho(\Psi_{-\tau}(\zeta,\tilde{u})) = p_\tau(\zeta,-\tilde{u})\, \rho(\zeta,-\tilde{u})\,,$$

using the reversibility $\Psi_{-\tau}(x,u) = \Psi_\tau(x,-u)$ of the flow and the fact that the density $\rho(x,-u) = \rho(x,u)$ is even in its second argument, the last but one equation simplifies according to

$$\begin{aligned}\int_{\mathbf{R}^d} f(\sigma(\zeta))\vartheta(d\zeta) \;&=\; \int_{\mathbf{R}^d} f(\sigma(\zeta))\, p_\tau(\Psi_{-\tau}(\zeta,\tilde{u}))\, \rho(\Psi_{-\tau}(\zeta,\tilde{u}))\, d\lambda_{\mathscr{B}} \\ &\quad + \int_{\mathbf{R}^d} f(\sigma(\zeta))\;(1 - p_\tau(\zeta,-\tilde{u}))\, \rho(\zeta,-\tilde{u})\, d\lambda_{\mathscr{B}} \\ &=\; \int_{\mathbf{R}^d} f(\sigma(\zeta))\, \rho(\zeta,\tilde{u})\, d\lambda_{\mathscr{B}} \\ &=\; \frac{1}{Z_\Sigma}\int_{\mathbf{R}^d} f(\sigma(\zeta))\eta(\zeta)\,\sqrt{\det G(\zeta)}\, d\zeta\,.\end{aligned}$$

In the last equality we have integrated over the momenta. The assertion follows, observing that the last equation is the expectation with respect to μ_Σ. □

Remark 4.3. *HMC gives a time-reversible mapping, as can be verified directly by checking detailed balance for* $(\tilde{x}, \tilde{u}) = \Psi_\tau(x, u)$*:*

$$\begin{aligned} \rho(x,u)p_\tau(x,\tilde{x}) &= \rho(x,u)\min\left(1, \frac{\rho(\tilde{x},\tilde{u})}{\rho(x,u)}\right) \\ &= \min\left(\rho(\tilde{x},\tilde{u}), \rho(x,u)\right) \\ &= \rho(\tilde{x},\tilde{u})\min\left(1, \frac{\rho(x,u)}{\rho(\tilde{x},\tilde{u})}\right) \\ &= \rho(\tilde{x},\tilde{u})p_{-\tau}(\tilde{x},x)\,. \end{aligned} \tag{4.5}$$

The third equality is due to the symmetry with respect to the initial and propagated variables in the second line. Hence HMC generates a reversible flow.

4.1.2 Irreducibility

To verify the irreducibility condition (4.3) we basically have to show that there is a discrete flow map that connects any two points $x(0) \in U \subseteq \mathbf{R}^d$ and $x(\tau) \in B$, where $B \in \mathcal{B}(U)$. To this end we exploit an argument in the work of Cancès *et al.* [10], where the irreducibility condition in case of an unconstrained, separable system has been proved. Therein the authors use a discrete version of Hamilton's principle assuming that the system is bounded, i.e., either $U \cong \mathbf{T}^d$ (compact) or $V \circ \sigma$ is uniformly bounded from above. The boundedness assumption is needed in order to guarantee existence of a discrete minimizer of the action integral. Herein we do not assume that the (smooth) potential is bounded; instead we replace this condition by the requirement that $\|x(0) - x(\tau)\|$ and $\tau > 0$ are sufficiently small, which guarantees that a stationary (not necessary minimal) solution to the discrete action principle exist [31]. The latter condition basically requires that we cannot make arbitrary large deterministic moves in space. However this does not affect the irreducibility property as we can always reach distant points in space by multiple iterates of the HMC chain.

The proof of the irreducibility condition proceeds two steps: In a first step we follow the approach in [10] and construct ambient-space sample paths that satisfy the irreducibility condition in $\Sigma \subset Q$. In doing so, it turns out that the problem boils down to a standard symplectic discretization of constrained systems. In a second step we demonstrate that the ambient-space discretization has an equivalent formulation in local coordinates which is consistent with the formulation of the invariant measure in the preceding paragraph.

For the ambient-space formulation we endeavour a discrete variant of Hamilton's action principle. Following [31], we introduce a discrete Langrangian as a map $L_h : Q \times Q \to \mathbf{R}$. The discrete counterpart of the continuous action integral is a mapping $S_h : Q^{N+1} \to \mathbf{R}$, that is defined as the sum

$$S_h = \sum_{k=0}^{N-1} L_h(q_k, q_{k+1}) \tag{4.6}$$

where $q_k \in Q$ and k labels the discrete time. Given fixed endpoints $q_0, q_N \in Q$ the discrete variational principle states that the discretized equations of motion minimize the action sum. The discretized equations are obtained by variation over the $q_1, \ldots, q_{N-1}$ which yields the *discrete Euler-Lagrange* equations

$$\mathbf{D}_2 L_h(q_{k-1}, q_k) + \mathbf{D}_1 L_h(q_k, q_{k+1}) = 0\,, \quad \forall k \in \{1, \ldots, N-1\}\,, \tag{4.7}$$

where $\mathbf{D}_1, \mathbf{D}_2$ denote the derivatives with respect to the first and second slot. If $\mathbf{D}_2 L_h$ (the generalized discrete momentum) is invertible, then (4.7) implicitly defines a discrete flow by means of the map $(q_{k+1}, q_k) = \Phi_h(q_k, q_{k-1})$. The particular discretization scheme that leads to (4.6) is open to choice and should depend on the problem; for the details we refer to the seminal work of Marsden and West [31].

Lemma 4.4. *Suppose the potential $V : Q \to \mathbf{R}$ is sufficiently smooth and uniformly bounded from below. Given $q_0, q_\tau \in \Sigma$, there is a symplectic mapping $(q(\tau), p(\tau)) = \Phi_\tau(q(0), p(0))$ and an open neighbourhood $B \subset \Sigma$ of q_τ, such that*

$$\mathbf{P}\left[q(\tau) \in B \,|\, q(0) = q_0\right] > 0\,.$$

Proof. We set $\Sigma = \varphi^{-1}(0)$ for a regular value 0 of the smooth function $\varphi : Q \to \mathbf{R}$, and we let the function $L : TQ \to \mathbf{R}$ denote the continous Lagrangian

$$L(q, \dot{q}) = \frac{1}{2}\,\langle \dot{q}, \dot{q} \rangle - V(q)\,.$$

The discrete Lagrangian $L_h : Q \times Q \to \mathbf{R}$ for a time step $h > 0$ is chosen to be

$$L_h(q_k, q_{k+1}) = \frac{1}{2}\left(L\left(q_{k+1}, \frac{q_{k+1} - q_k}{h}\right) + L\left(q_k, \frac{q_{k+1} - q_k}{h}\right)\right)$$

giving rise to the augmented Lagrangian $\hat{L}_h = L_h - \lambda\varphi$. Fixing endpoints $q_0, q_N \in \Sigma$ and setting $q_N = q_\tau$ a stationary solution

$$\delta \sum_{k=0}^{N-1} \left(L_h(q_{k+1}, q_k) - \lambda_k \varphi(q_k)\right) = 0\,,$$

of the unconstrained action sum exists for $\|q_0 - q_N\|$ and τ being sufficiently small. Taking the variation yields the discrete Euler-Lagrange equations [32]

$$\begin{aligned} 0 &= \mathbf{D}_2 L_h(q_{k-1}, q_k) + \mathbf{D}_1 L_h(q_k, q_{k+1}) + \lambda_k \nabla\varphi(q_k) \\ 0 &= \varphi(q_k) \end{aligned} \tag{4.8}$$

for all $k \in \{1, \ldots, N-1\}$. Given $q_{k-1}, q_k \in \Sigma$, i.e., $\varphi(q_k) = \varphi(q_{k-1}) = 0$, we can evaluate the derivatives of the discrete Lagrangian L_h and solve the last equation for q_{k+1} subject to the condition that $q_{k+1} \in \Sigma$. We find

$$\begin{aligned} q_{k+1} - 2q_k + q_{k-1} &= -h^2(\nabla V(q_k) + \lambda_k \nabla\varphi(q_k)) \\ 0 &= \varphi(q_{k+1})\,, \end{aligned} \tag{4.9}$$

which is known as the SHAKE algorithm [33]. The Lagrange multiplier λ_k is chosen such as to enforce the constraint at time $k+1$. The conjugate momentum is defined by the discrete Legendre transform of $\hat{L}_h = L_h - \lambda\varphi$, viz.,

$$p_k = -\mathbf{D}_1 L_h(q_k, q_{k+1}) + \lambda_k \nabla\varphi(q_k)\,. \tag{4.10}$$

Hence we can rewrite the SHAKE algorithm as a symplectic mapping $\Psi_h : (q_k, p_k) \mapsto (q_{k+1}, p_{k+1})$. By choosing initial conditions $q(0) = q_0$ and $p(0) = -\mathbf{D}_1 \hat{L}_h(q_0, q_1, \lambda_0)$ the discrete flow generates a discrete trajectory that connects q_0 and q_τ. Finally, it follows by continuity of the numerical flow Ψ_τ on the initial conditions that the endpoints of trajectories with perturbed initial momenta $p_\epsilon(0) = p(0) + \epsilon$ remain in $B \subset \Sigma$ whenever ϵ is sufficiently small. □

A frequently used variant of the SHAKE algorithm is called RATTLE and goes back to [34]. It can be considered as a constrained version of the ordinary velocity Verlet scheme. SHAKE and RATTLE are equivalent by dint of (4.10). Moreover they are variational with the discrete Lagrangian L_h defined above, and therefore both SHAKE and RATTLE are symplectic (see also [35, 36]).

Lemma 4.4 guarantees accessibility from any point $q \in \Sigma$ to any open set. However condition (4.3) requires accessibility of any Borel set of positive Hausdorff measure (irreducibility), which excludes certain pathologies that otherwise might occur in the HMC transition probabilities. This is expressed in:

Lemma 4.5. *Let $\Psi_\tau : T^*\Sigma \to T^*\Sigma$ denote the symplectic numerical flow as defined by the algorithm (4.9)–(4.10). The HMC transition probabilities obey*

$$\mathbf{P}\left[q(\tau) \in B \,|\, q(0) = q_0\right] > 0 \quad \forall q \in \Sigma \subset Q$$

for all $B \in \mathcal{B}(\Sigma)$ with positive Hausdorff measure $\mathcal{H}^d$ on Σ.

Proof. Given an initial point $q \in \Sigma$, we have to show that any Borel set B of positive measure can be reached from a set of momenta with positive measure.

To this end consider the subset $M_B(q) \subset T^*_q\Sigma$ that is determined by all initial momenta p for which $(\pi \circ \Psi_\tau)(q,p) \in B$. Omitting the positive acceptance probability (4.4), the transition probabilities $p(q,B,\tau) = \mathbf{P}\left[q(\tau) \in B \,|\, q(0) = q\right]$ can be written as

$$p(q,B,\tau) = \int_{M_B(q)} \varrho_q(q)\, dp\,.$$

Since the constrained Maxwell density $\varrho_q(p)$ is strictly positive, it is enough to show that $M_B(q)$ has positive measure. Since we can naturally identify all cotangent spaces $T^*_q\Sigma$ with the d-dimensional subspaces of $\mathbf{R}^n$ that are determined by the hidden constraint $\nabla\varphi(q) \cdot D_pH(q,p) = 0$, we have to show that $M_B(q)$ has positive d-dimensional Hausdorff measure $\mathcal{H}^d$. Now suppose the contrary, i.e., assume $\mathcal{H}^d(M_B(q)) = 0$, and consider the map $F_q : M_B(q) \to B$, $p \mapsto (\pi \circ \Psi_\tau)(q,p)$. By definition, F_q is onto and thus [37]

$$\mathcal{H}^d(B) = \mathcal{H}^d(F_q(M_B(q))) \leq L\mathcal{H}^d(M_B(q)) = 0$$

where $0 < L < \infty$ is the Lipschitz constant of F_q (since Ψ_τ is volume-preserving, such a constant obviously exists). If $\mathcal{H}^d(B) > 0$, the last equation yields a contradiction, and the assertion follows. □

We have carried out the proof of invariance of μ_Σ in local coordinates (Lemma 4.2). Hence it remains to show that the flow $(q_k, p_k) \to (q_{k+1}, p_{k+1})$ has an equivalent counterpart $(x_k, u_k) \mapsto (x_{k+1}, u_{k+1})$ in local coordinates. As we know from the continuous world, the local coordinate version of the Euler-Lagrange equations can be derived from the restricted Lagrangian $L_\Sigma = L|_{T\Sigma}$. Accordingly we define the constrained discrete Lagrangian as $L_{\Sigma,h} = (L|_{T\Sigma})_h$. Given an embedding $\sigma : \mathbf{R}^d \to \Sigma \subset Q$ we can define the constrained discrete Lagrangian $L_{\Sigma,h} : \Sigma \times \Sigma \to \mathbf{R}$ as the map

$$L_{\Sigma,h}(x_k, x_{k+1}) = L_h\left(\sigma(x_k), \sigma(x_{k+1})\right)\,,$$

which gives rise to the following discrete Euler-Lagrange equations

$$0 = \mathbf{D}_2 L_{\Sigma,h}(x_{k-1}, x_k) + \mathbf{D}_1 L_{\Sigma,h}(x_k, x_{k+1})\,. \tag{4.11}$$

Solving the equation for x_{k+1} given x_k, x_{k-1} defines a map $\Theta_h : \mathbf{R}^d \to \mathbf{R}^d$. By computing the conjugate momenta $u_k = -\mathbf{D}_1 L_{\Sigma,h}(x_k, x_k + 1)$ we can lift the iteration Θ_h to a symplectic map $\Psi_h : T^*\mathbf{R}^d \to T^*\mathbf{R}^d$. We have:

Lemma 4.6 (Wendlandt & Marsden 1997). *Equation (4.8) has a solution $(q_{k+1}, q_k) = \Phi_h(q_k, q_{k-1})$, iff $(x_{k+1}, x_k) = \Theta_h(x_k, x_{k-1})$ is a solution of (4.11). Furthermore Φ_h and Θ_h are equivalent in the sense that $\Phi_h = \sigma \circ \Theta_h$.*

This completes the proof that the HMC Markov chain with the RATTLE iteration (4.9)–(4.10) is irreducible. Together with Lemma 4.2 stating the invariance of the constrained Gibbs measure μ_Σ we therefore conclude:

Proposition 4.7. *Let $\{q_k\}_{k=0,\tau,2\tau,\dots}$ be the Markov process that is defined by the RATTLE iteration (4.9)–(4.10) with random initial momenta following the constrained Maxwell distribution and an HMC acceptance-rejection procedure due to (4.4). Then for sufficiently small $\tau > 0$ the strong Law of Large Numbers,*

$$\frac{1}{N} \sum_{i=0}^{N-1} f(q_i) \to \mathbf{E}_\Sigma f \quad \text{as} \quad N \to \infty \quad \text{(almost surely)},$$

holds true for almost all initial values $q_0 \in \Sigma$.

Note that the algorithm converges for any stable step-size without introducing a bias. However the last assertion does not tell us anything about the speed of convergence, which remains an open problem; see [10, 39] for some numerical studies. In particular the speed of convergence depends upon the choice of the HMC integration time $\tau = Nh$, where h is the integration step-size. Exploring state space becomes certainly faster if τ is increased. However increasing τ while keeping the step-size h constant decreases the acceptance probability as energy fluctuations become an issue.

Remark 4.8. *As already mentioned the HMC algorithm with lag time $\tau = h$ but without the acceptance-rejection procedure is equivalent to an Euler discretization of the Smoluchowski equation (which does not preserve ergodicity). Letting the acceptance step account for the discretization error, HMC can be regarded as an exact discretization of the Smoluchowski equation at step-size $\tau = h$. In this sense HMC generates an ergodic diffusion-like flow [11]. In point of fact, related results for constrained diffusion processes have recently become available in the work of Lelièvre* et al. *[40]. Therein, however, the authors prove ergodicity only for the time-continuous process, while disregarding discretization issues.*

5 Algorithmic issues and examples

We briefly explain how the constrained hybrid Monte-Carlo algorithm can be used in molecular applications. To this end, it is convenient to represent the equations of motion and the invariant measure in terms of the ambient-space variable (q, p). We shall also drop the assumption that the system has unit mass; if we let $M \in \mathbf{R}^{n\times n}$ denote the symmetric and positive-definite molecular mass matrix, the unconstrained Lagrangian becomes

$$L(q, v) = \frac{1}{2} \langle Mv, v \rangle - V(q)\,.$$

The respective unconstrained Hamiltonian thus reads

$$H(q,p) = \frac{1}{2}\left\langle M^{-1}p, p\right\rangle + V(q)\,.$$

Introducing the reaction coordinate constraint $\varphi(q) = \xi$, the constrained equations of motion (3.1) are then generated by the augmented Lagrangian $\hat{L} = L - \lambda^i(\varphi_i(q) - \xi_i)$. The SHAKE discretization of the equations of motion for a time step $h > 0$ and multiple constraints $\varphi_1, \ldots, \varphi_s$ is

$$\begin{aligned} q_{n+1} - 2q_n + q_{n-1} &= -h^2 M^{-1}\left(\nabla V(q_n) + \mathbf{D}\varphi(q_n)^T\lambda_n\right) \\ \xi &= \varphi(q_{n+1})\,. \end{aligned} \tag{5.1}$$

In the original formulation by Ryckaert *et al.* [33], the momentum is approximated as

$$p_n = M\left(\frac{q_{n+1} - q_{n-1}}{h}\right)\,. \tag{5.2}$$

This approximation has two major drawbacks: Firstly, the mapping $(q_n, p_n) \mapsto (q_{n+1}, p_{n+1})$ defined by (5.1)–(5.2) is not symplectic.[1] Secondly, the three-term recursion in (5.1) may lead to an accumulation of round-off errors. Therefore the scheme may become unstable, as has been pointed out in [24]. A remedy for both problems is to make the iteration (5.1)–(5.2) a variational integrator, replacing (5.2) by the correct discrete conjugate momentum (4.10). This amounts to formulating SHAKE as the one-step RATTLE algorithm [34]

$$\begin{aligned} p_{n+1/2} &= p_n - \frac{h}{2}\left(\nabla V(q_n) + \mathbf{D}\varphi(q_n)^T\lambda_n\right) \\ q_{n+1} &= q_n + hM^{-1}p_{n+1} \\ \xi &= \varphi(q_{n+1}) \\ p_{n+1} &= p_{n+1/2} - \frac{h}{2}(\nabla V(q_{n+1}) + \mathbf{D}\varphi(q_{n+1})^T\mu_n) \\ 0 &= \mathbf{D}\varphi(q_{n+1})M^{-1}p_{n+1}\,, \end{aligned} \tag{5.3}$$

The Lagrange multipliers λ_n, μ_n are chosen, such that the two constraints are satisfied. The RATTLE integrator (or SHAKE considered as a mapping $T^*\Sigma \to T^*\Sigma$, respectively) is symplectic as following from its variational nature; cf. the related works [35, 36].

Implicit solvers and stability Approximating expectation values by sufficiently long trajectories poses the question of long-term stability of the integrator. For nonlinear constraints both SHAKE and RATTLE are semi-implicit schemes, and their stability properties will depend upon the choice of the nonlinear solver that is used. A convenient numerical scheme for solving the implicit part $\Phi(q_{n+1}) = \xi$ is provided by original SHAKE iteration [33] which can be considered a nonlinear one-step Gauss-Seidel-Newton iteration for the linearized constraints. As has been demonstrated in [41], the Gauss-Seidel-Newton iteration is almost unconditionally stable for moderate step-sizes — even if the

[1] The mapping preserves the Liouville volume though. However the thus defined flow is not a map $T^*\Sigma \to T^*\Sigma$, since the momenta do not satisfy the hidden constraint $\mathbf{D}\varphi M^{-1}p = 0$.

algebraic constraints are highly nonlinear. Moreover the iteration is remarkably fast (as compared to ordinary Newton techniques) and can be combined with overrelaxation strategies. In contrast to that, naïve Newton techniques may suffer from condition problems as has been pointed out on various occasions, e.g., [42, 43]. An alternative method in this respect is the discrete null-space method [43, 44] that proceeds by eliminating the Lagrange multiplier and which is in the spirit of index reduction techniques. Since the method is variational as following from the work of Maddocks *et al.* [45, 46], the ergodicity results of Section 4 should easily generalize to the null-space method. A final remark is in order. For energy-conserving systems penalty methods provide a useful alternative to the method of Lagrange multipliers as has been argued in [47]. But what is useful in a microcanonical (i.e., non-Gibbsian) setting is forbidden here: the Gibbs distribution of a constrained system is different from the one of a penalized system in the limit of infinite penalization, and therefore the two methods are no longer equivalent; we refer to [48, 22] for detailed considerations of penalization limits of thermalized systems.

Constrained Maxwell density in ambient-space coordinates At each Monte-Carlo step HMC requires that we draw an initial momentum from the constrained Maxwell distribution which depends parametrically on the constrained position variables. This can be understood as follows: consider the unconstrained kinetic energy in terms of the velocity variables,

$$T(v) = \frac{1}{2}\,\langle Mv, v\rangle := \frac{1}{2}\,\langle v, v\rangle_M\ ,$$

where $\langle\cdot,\cdot\rangle_M$ denotes the metric with respect to the positive-definite and symmetric mass matrix M. As we have shown in Section 3.3 the constrained canonical probability distribution is simply the restriction of the unconstrained distribution. In order to restrict the Maxwell density to the constrained tangent space $T_q\Sigma$, $q \in \Sigma$, we define the M-orthogonal projection $P_{M,T} : T_q\mathbf{R}^n \to T_q\Sigma$

$$P_{M,T} = \mathbf{1} - M^{-1}J_\varphi^T(J_\varphi M^{-1}J_\varphi^T)^{-1}J_\varphi\,, \quad J_\varphi = \mathbf{D}\varphi(q)$$

that is defined point-wise for each $q \in \Sigma$. Strictly speaking, $P_{M,T}$ sends vectors $v \in \mathbf{R}^n$ to vectors in $\tilde{v} \in \mathbf{R}^n$, such that $\tilde{v}$ satisfies the hidden constraint $\mathbf{D}\varphi\cdot\tilde{v} = 0$. It can be readily checked that (i) the matrix $P_{M,T}$ meets the idempotency property $P_{M,T}^2 = P_{M,T}$, and that (ii) it is symmetric with respect to the mass-weighted scalar product $\langle\cdot,\cdot\rangle_M$. That is,

$$\langle P_{M,T}\,u, v\rangle_M = \langle u, P_{M,T}\,v\rangle_M$$

for any two vectors $u, v \in \mathbf{R}^n$. Hence $P_{M,T}$ is an orthogonal projection with respect to the metric $\langle\cdot,\cdot\rangle_M$. Consequently, we shall refer to $P_{M,T}$ as M-orthogonal projection. Since $P_{M,T}$ maps to the constrained velocity space, we obtain the restricted Maxwell density $\exp(-\beta T_\Sigma)$ by restricting the kinetic energy,

$$T_\Sigma(q,v) := T(P_{M,T}\,v) = \frac{1}{2}\,\langle P_{M,T}v, v\rangle_M\ .$$

Defining $K(p) = T(M^{-1}p)$, the phase space analogue of T_Σ is found to be

$$K_\Sigma(q,p) := \frac{1}{2}\,\langle P_{M,T}^* p, p\rangle_{M^{-1}}\ , \quad P_{M,T}^* = MP_{M,T}M^{-1}\,.$$

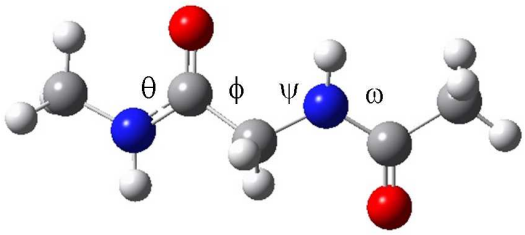

Figure 1: Glycine dipeptide in its extended C5 conformation.

It is easy to see that $P^*_{M,T}$ is idempotent and symmetric with respect to inner product $\langle \cdot, \cdot \rangle_{M^{-1}}$. Hence $P^*_{M,T}$ is the M^{-1}-orthogonal projection onto the constrained momentum space $T^*_q\Sigma$. In other words, $P^*_{M,T}$ sends $p \in \mathbf{R}^n$ to $\tilde{p} \in \mathbf{R}^n$, such that $\tilde{p}$ satisfies the hidden constraint $\mathbf{D}\varphi M^{-1}\tilde{p} = 0$. Omitting normalization, the constrained Maxwell distribution reads

$$\varrho_\Sigma(q,p) \propto \exp(-\beta K_\Sigma(q,p))\,, \quad K_\Sigma = \frac{1}{2}\left\langle P^*_{M,T}p, p\right\rangle_{M^{-1}} \tag{5.4}$$

which is exactly the ambient-space analogue of the constrained density (3.5).

The easiest way to draw momenta from the constrained distribution (5.4) is to generate a random vector p from the unconstrained Maxwell distribution $\exp(-\beta K(p))$, and then apply the projection $P^*_{M,T}$. This then yields a vector $\tilde{p} = P^*_{M,T}\,p$ that is distributed according to (5.4). In this way the projection maintains the full dimensionality for the HMC algorithm, and we can completely work in the ambient-space coordinates q and p.

The HMC algorithm We summarize the considerations from Section 4 and the last few paragraphs. Given an initial position q_0 that satisfy the constraint $\varphi(q_0) = \xi$, the constrained hybrid Monte-Carlo algorithm proceeds as follows.

1. Draw a random vector due to the unconstrained momentum distribution
$$p \sim \exp(-\beta K(p))\,, \quad K(p) = \frac{1}{2}\left\langle M^{-1}p, p\right\rangle\,.$$
2. Compute $p_0 = P^*_{M,T}\,p$, such that p_0 satisfies the hidden constraint, where
$$P^*_{M,T} = \mathbf{1} - J_\varphi^T(J_\varphi M^{-1} J_\varphi^T)^{-1} J_\varphi M^{-1}\,, \quad J_\varphi = \mathbf{D}\varphi(q_0)\,.$$
3. Propagate $(\tilde{q}_1, \tilde{p}_1) = \Psi_\tau(q_0, p_0)$, where Ψ_τ is the numerical flow up to time $\tau > 0$, that is defined by the RATTLE discretization (5.3).
4. Accept $q_1 = \tilde{q}_1$ with probability
$$r = \min\left(1, \frac{\exp(-\beta H(\tilde{q}_1, \tilde{p}_1))}{\exp(-\beta H(q_0, p_0))}\right)\,,$$
or reject, i.e., set $q_1 = q_0$. (Here $H = K + V$ is the unconstrained Hamiltonian.)
5. Repeat.

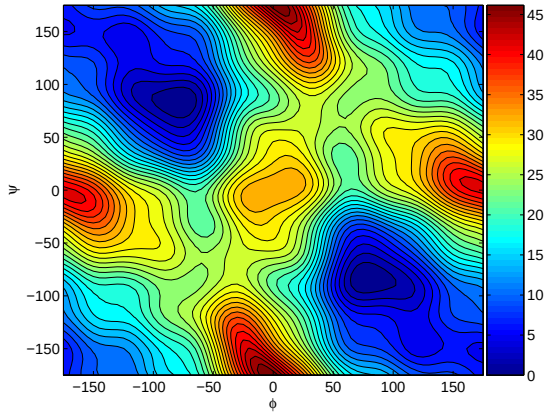

Figure 2: Helmholtz free energy $F(\phi, \psi)$ at $T = 300\text{K}$.

5.1 Numerical test: free energy calculation

We shall demonstrate the performance of the HMC scheme by a numerical example that is nontrivial and still allows for some comparison with known results. One such instance is the calculation of two-dimensional free energy profiles of a glycine dipeptide analogue in vacuum along its central torsion angles (see Figure 1). This model system is particularly suited for our purposes as it is not too small in dimension and exhibits a certain point symmetry we wish to recover in the free energy (i.e., in the sampled probability distribution). The symmetry-preservation may then serve as a consistency test.

If we label the two central torsion angles of glycine by $\varphi = (\varphi_1, \varphi_2)$, $\varphi : Q \to \mathbf{T}^2 \subset \mathbf{R}^2$, the Helmholtz free energy is defined as

$$F(\phi, \psi) = -\beta^{-1} \ln \int_{\Sigma} \exp\left(-\beta V\right) \left(\operatorname{vol} J_{\varphi}\right)^{-1} d\sigma \,, \tag{5.5}$$

where

$$\operatorname{vol} J_{\varphi}(q) = \sqrt{\det \mathbf{D}\varphi(q) \mathbf{D}\varphi(q)^T}$$

is the generalized matrix volume of the rectangular matrix $J_{\varphi} = \mathbf{D}\varphi \in \mathbf{R}^{2 \times n}$, and $\Sigma = \Sigma_{\phi,\psi} \subset Q$ denotes the family of codimension-two submanifolds

$$\Sigma_{\phi,\psi} = \{q \in Q \,|\, \varphi_1(q) = \phi,\, \varphi_2(q) = \psi\} \,.$$

Obviously, $F(\phi, \psi)$ is the marginal Gibbs density of the two torsion angles (ϕ, ψ). However sampling the marginal distribution is a tedious issue, since the dynamics in this direction has to overpass large energetic barriers and thus convergence is extremely slow.

In praxi sampling free energy profiles is therefore often carried out by constraining the variables (φ_1, φ_2) and sampling the respective partial derivatives. Eventually the free energy can be recovered by numerical integration along

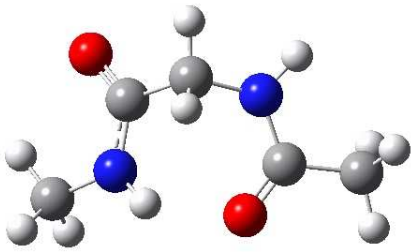

Figure 3: Glycine dipeptide in its C7 conformation.

(ϕ, ψ) from which the profile can be eventually recovered by numerical integration. This technique is known by the name of Thermodynamic Integration and goes back to Kirkwood [49]. Indeed, one can show [50] that

$$F(\phi, \psi) = G(\phi, \psi) + \beta^{-1} \ln \mathbf{E}_\Sigma (\mathrm{vol}\, J_\varphi)^{-1} \,, \tag{5.6}$$

where $\mathbf{E}_\Sigma$ denotes the expectation with respect to the constrained Gibbs measure μ_Σ. Here G is the potential of mean constraint force, i.e.,

$$\nabla G(\phi, \psi) = \mathbf{E}_\Sigma \bar{\lambda}$$

with $\bar{\lambda} = (\bar{\lambda}_1, \bar{\lambda}_2)$ as the momentum-averaged Lagrange multiplier [22]

$$\bar{\lambda} = (J_\varphi M^{-1} J_\varphi^T)^{-1} \left(J_\varphi M^{-1} \nabla V - \beta^{-1} \mathrm{tr} \left(P^*_{M,T} \nabla^2 \varphi M^{-1} \right) \right) \,,$$

where $P^*_{M,T} = \mathbf{1} - J_\varphi^T (J_\varphi M^{-1} J_\varphi^T)^{-1} J_\varphi M^{-1}$ is the point-wise projection onto $T_q^* \Sigma$, and the rightmost term is understood component-wise for $\varphi = (\varphi_1, \varphi_2)$.

In principle, one could even use the numerical Lagrange multiplier of the RATTLE scheme. But the distribution of the numerical multiplier λ_n along the HMC trajectory is determined by the distribution of (q_n, p_n), and we cannot be sure whether the momenta p_n are correctly sampled by the scheme. (We expect them to be close by though). Accordingly we use the explicit expression for $\bar{\lambda}$ instead of the RATTLE multiplier.

In order to compute the free energy, we perform Thermodynamic Integration in the Ramachandran plane (i.,e., in the two angles (ϕ, ψ)) using the GROMOS96 force field of GROMACS [51, 52] together with the native Java interface METAMACS [53]. Intriguingly, such calculations are rare (e.g., [54]), although easy-to-use Thermodynamic Integration formulae in more than one dimension have been put forward during the last few years (see also [55] where a simplified force expression was used). We cover the Ramachandran plane with a two-dimensional, uniform 36×36 grid, and run constrained hybrid Monte-Carlo simulations at $T = 300$K on each grid point (ϕ_i, ψ_j). The step-size was chosen to be $h = 1$fs with 100 integration steps between between the Monte-Carlo

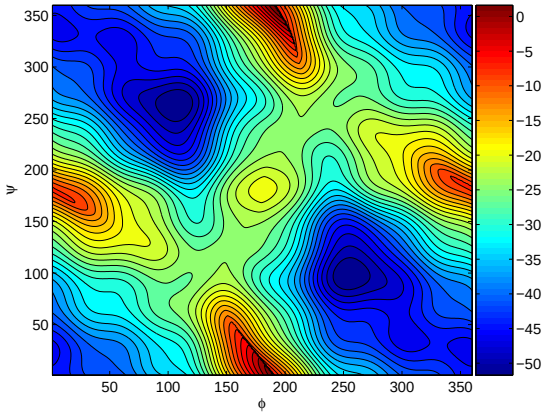

Figure 4: Minimized potential energy landscape of the backbone angles.

points. Starting from an energy-minimized configuration, each simulation involves $N = 10\,000$ sample points, hence equivalently 1ns of total integration time for each ϕ, ψ combination. Taking advantage of the reaction coordinate's periodicity, we reconstruct the smooth free energy surfaces by first expanding G into a truncated, two-dimensional Fourier series [56] and then adding the correction according to (5.6). The respective Fourier coefficients are determined from the averaged $\bar{\lambda}$ in a least-squares sense.

The result is shown in Figure 2. The plot clearly reveals the so-called C7 conformation depicted in Figure 3 at about $(\phi, \psi) = (\pm 80°, \mp 80°)$. Moreover, but less clearly, we can see the extended C5 conformation around $(\phi, \psi) = (\pm 180°, \pm 150°)$ which is about $5 - 10$kJ/mol higher than the C7 conformation which agrees with the results obtained in [57] (for a different force field though). For the sake of comparison the minimized potential energy function projected onto the Ramachandran plane is shown in Figure 4 below. The most noticeable difference is that the energy barriers of the strongly repulsive O-O ring-like state at $\phi = 0°$ and the H-H ring-like state at $\psi = 0°$ are far more pronounced than in the free energy landscapes. Furthermore we recognize that the sampled free energy landscape is exactly point symmetric around the origin as could be expected from the molecules symmetry under parity transformations $(\phi, \psi) \mapsto (-\phi, -\psi)$. Latter property may be considered as numerical evidence for the symmetry of the underlying constrained Gibbs distribution.

5.2 Related problems

The calculation of free energy profiles is just one possible application for sampling of the constrained Gibbs measure. Yet another example is a rigid body at constant temperature that is parametrized in terms of quaternions [21]. Other examples of molecular dynamics applications involve best-approximations [58, 22] or averaging techniques [59] for systems with slow and fast degrees of

freedom that typically assume the form

$$\begin{aligned} \dot{\phi}_\epsilon(t) &= f(\phi_\epsilon(t), z_\epsilon(t)) \\ \epsilon \dot{z}_\epsilon(t) &= g(\phi_\epsilon(t), z_\epsilon(t)) \,, \quad 0 < \epsilon \ll 1 \,. \end{aligned} \tag{5.7}$$

The scalar $\epsilon > 0$ is a small parameter that indicates the time scale separation between the slow and fast variables ϕ and z. Given that certain technical conditions are met, the slow subsystem can be described by a closed equation,

$$\dot{\xi}(t) \quad = \quad \bar{f}(\xi(t)) \,, \quad \bar{f}(\xi) = \int f(\xi, z) \mu_\xi(dz) \,,$$

that approximates the slow dynamics in the limit $\epsilon \to 0$. Here $\mu_\xi(dz)$ denotes the invariant measure that is sampled by the fast process

$$\dot{z}_\xi(t) \quad = \quad g(\xi, z_\xi(t))$$

and which depends parametrically on the value ξ of the slow variable ϕ. For example, if the system describes diffusion in a potential energy landscape (gradient flow), then $\mu_\xi(dz) \propto \exp(-\beta V(\xi, z)) d\sigma(z)$ will typically be the Gibbs measure conditioned by the slow variable. In this case we can sample the averaged vector field $\bar{f} = \mathbf{E}_\Sigma f$ by running the HMC algorithm with the constraint $\phi = \xi$.

Very similar in spirit are so-called equation-free approaches [60, 61]. The idea of equation-free calculations allows for computing the effective drift of certain coarse (macroscopic) variables without explicitly splitting the equations of motion as in (5.7). The effective drift is estimated by averaging over short runs of an ensemble of microstates conditional on the coarse variable. Other than in the constrained sampling procedure the coarse variables are not constrained, but it is assumed that they do not move on a time scale that is below the correlation time of the microscopic variables. This assumption is certainly met if, e.g., the microscopic variables are much faster than the coarse variables. Moreover it often suffices to collect only local information from a short propagation of the micro-ensemble rather than sampling the exact conditional expectation with a very long constrained trajectory which renders the equation-free method very efficient. However, the computed average will heavily depend on how the conditional ensemble of microstates is initialized, and a clever choice will certainly involve knowledge about the invariant probability measure of the micro-dynamics. For example, if the original system is Hamiltonian one can use short realizations of the constrained HMC Markov process to generate a particular ensemble, namely, the Gibbs ensemble.

Remark 5.1. *Both best-approximations (e.g., averaging) and equation-free approaches yield effective models for the dynamics of the coarse variables. However it is important to note that, in general, the effective dynamics is not governed by the coarse variable's free energy, althought the free energy is frequently called* the potential of mean force. *In fact the Helmholtz free energy F reflects an asymptotic equilibrium property of the coarse variables in the sense that their probability distribution will eventually approach $\rho \propto \exp(-\beta F)$. Nonetheless the free energy F does not give rise to a force in any physically meaningful way, since its derivative ∇F does not transform as a 1-form under changes of the coarse variables which can be easily inferred from the formulae (5.5) or (5.6); we refer to [50, 22] for a detailed discussion.*

Further notice that the free energy is clearly a meaningful equilibrium quantity, no matter if the coarse variables are slow variables or not (as compared to the remaining ones); the proposed sampling method does not presuppose any kind of time scale separation as the coarse variables are artificially fixed by the constraint, while the remaining variables are allowed to sample their Gibbs distribution. Hence the constrained sampling method seems always appropriate when it comes to an accurate estimation of observables in thermodynamic equilibrium at constant temperature, whereas on-the-fly methods such as the equation-free approach seem better suited to consider nonequilibrium processes.

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