A geometric approach to free energy calculations

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Abstract. We consider a particle constrained to a submanifold Σ of the configuration space $\mathbf{R}^m$. Using that the notion of holonomic constraints coincides with integrability of the corresponding vector field, we show how this property naturally determines local coordinates on Σ. We give a rigorous justification for the calculation of the mean force along a constrained coordinate, and we provide a concise geometrical interpretation of the different contributions to the mean force in terms of the unconstrained vector field and extrinsic curvature properties of Σ in $\mathbf{R}^m$. Our approach gives rise to a Hybrid Monte-Carlo based algorithm that can be used to compute the mean force acting on selected coordinates in the context of thermodynamic free energy statistics.

1. Introduction

Many simulations in molecular-dynamics (MD) applications are devoted to the calculation of free energy profiles along selected *essential coordinates* [1]. These coordinates may be slow degrees of freedom or parameterisations of certain pathes along which a reaction takes place. Here, the term "reaction" is understood in a very broad sense, and mostly refers to any conformational transition in a molecule.
Theoretically, the free energy observable could be easily computed from the invariant measure of the underlying dynamical system. However, since, e.g., conformational changes occur rather rarely, reliable sampling of these parts of the phase space measure is a relatively tedious issue [2, 3]. Thus, one approach amongst others is to constrain the system to fixed values of those coordinates one is interested in, and which correpond to rare events. Once one has succesfully identified the essential coordinates sampling the invariant measure of the remaining free coordinates should be comparably fast.
During the last few years there have been made many attempts to derive expressions for the mean force along specified coordinates computed from constrained MD simulations [4]. Most authors proposed to exploit the force of constraint, that is necessary to conserve the constraint during the course of integration. Nevertheless, there was serious disagreement and misconception (1) about the correct expression for the force acting on the reaction coordinate as well as (2) about the proper averaging procedure – which is the probability measure to be used? [5, 6, 7]. It is even frequently stated, that the constrained dynamics were not Hamiltonian [8, 9]. This is surely wrong, and we will give precise conditions insuring symplecticity for a constrained

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Hamiltonian system. If all these problems have been resolved, it is natural to ask, how the mean force can be evaluated in practical applications, or, secondly: how can the desired phase space measure be generated by the constrained dynamics. Although the results presented here are not entirely new, our mathematical elaboration of the free energy literature allows for two key issues: it (1) provides a clear and concise interpretation of the notion of mean force along a reaction coordinate, and even more important, it (2) enables us to derive a Hybrid Monte-Carlo (HMC) scheme for constrained MD simulations. With this tool at hand we are then able to compute free energy profiles along a reaction coordinate from a constrained MD trajectory. The main advantage of this novel method is that it is conceptually very simple and lucid, for it does not introduce any artificial heat bath coupling to the dynamics.
The paper proceeds as follows: In the next two sections, we will shorty explain the basic concept of holonomic constraints for an arbitrary dynamical system, and provide some concepts from differential geometry that will be needed in the subsequent. Section 4 introduces the two possible points of view on constrained Hamiltonian systems: (1) a local representation on the constraint manifold, or (2) a coordinate-free representation using a modified Poisson bracket formalism. Both points of view are fully equivalent with regard to the dynamics on the constraint surface, and we can switch arbitrarily between them. As the case arises, our choice will depend on the problem we want to solve in the course of this paper. In Section 5, an expression for the thermodynamic free energy is derived. Section 6 states how the Hybrid Monte-Carlo method can be used to compute the correct mean force from the constrained measure. Moreover, we explain how the HMC scheme works out in practical application, and we present an example. Finally, the Appendix highlights the geometric aspects of constrained motion which might be helpful in understanding some details of the proofs.

2. Introducing holonomic constraints I

Let $g : \mathbf{R}^m \to \mathbf{R}^n$ be any smooth and regular vector-valued function. Generally, a constraint is an affine subspace of the tangent space $T_q\mathbf{R}^m$ for each $q \in \mathbf{R}^m$. Starting, we define a configurational manifold of constraints as

$$\Sigma = \{q \,|\, g(q) = 0\} \,. \tag{2.1}$$

Assume, that the Jacobian $\mathbf{D}g$ has rank n everywhere. This is to say that Σ has codimension n in $\mathbf{R}^m$, i.e. the quotient space $\mathbf{R}^m/\Sigma$ is of dimension n. Differentiating each of the components of g once with respect to time yields a (hidden) condition for the elements $\dot{q}$ of the tangent space $T_q\mathbf{R}^m$

$$\langle D_q g_k(q), \dot{q}\rangle = 0 \quad \Longleftrightarrow \quad \mathbf{D}g(q)\,\dot{q} = 0\,. \tag{2.2}$$

If the above rank condition holds, the rows of $\mathbf{D}g$ define n independent Pfaffian forms $\omega^k = \partial_i g^k \mathrm{d}q^i$, such that $\omega = 0$ on $T\Sigma$. Accordingly, the hidden constraint determines a distribution D of dimension $m - n$ that is locally defined by

$$D(q) = \ker \mathbf{D}g(q) \supseteq T_q\Sigma\,. \tag{2.3}$$

Now recall the following notion [10]: a constraint is holonomic if the distribution D is involutive, i.e., for any two vectorfields X, Y defined on $T\mathbf{R}^m$

$$X, Y \in D \quad \Longrightarrow \quad [X, Y] \in D\,,$$

where the bracket $[X, Y] = \mathcal{L}_X Y$ denotes the Lie derivatives of Y along X. Geometrically, this indicates the commutativity of the flows generated by X and Y at

the point $q \in \Sigma$. Then, since $\mathbf{D}g$ merely contains the non-zero gradients of g, and the gradients are normal to the fibre $\Sigma = g^{-1}(0)$, we obtain $[X, Y] \in T_q\Sigma \subseteq D$.

2.1. Holonomic constraints and Frobenius Theorem

The Frobenius Theorem asserts that a distribution is involutive if and only if it is integrable. Integrability of a distribution $D \subset T\Sigma$ here means that for each $q \in \Sigma$ there is an integral manifold, denoted by $M \subset \Sigma$, the tangent bundle of which is exactly D restricted to M [11]. Then, in a neighbourhood of $q \in \Sigma$ we may introduce local coordinates $x^1, \ldots, x^{m-n}, y^1, \ldots, y^n$, such that the constraints (2.1) and (2.2) are expressed by

$$y^1 = \ldots = y^n = \dot{y}^1 = \ldots = \dot{y}^n = 0\,.$$

This is equivalent to state, that $\Sigma = \{(x, y) \,|\, y = 0\}$ is an integral manifold of D with dimension $m - n$ or, equivalently, Σ is an invariant manifold of the dynamics generated by D. In the following, we will discuss the consequences of this statement for the computation of free energies along constrained coordinates.

3. Coordinate embedding

Before specifying any local coordinates, we shall firstly explain in an abstract manner, how the embedding of Σ into $\mathbf{R}^m$ can be handled, and how the embedding gives rise to a Riemannian structure on Σ. In case of holonomic constraints it seems appropriate to choose normal coordinates [12, 13, 14]. Consider a tubular neighbourhood of Σ; locally, we define the normal bundle over Σ by

$$N\Sigma = \{(\sigma, n) \,|\, \sigma \in \Sigma, n \in N_\sigma\Sigma\} \subset \mathbf{R}^m \times \mathbf{R}^m\,. \tag{3.1}$$

Then, the Riemannian metric g on $TN\Sigma$ is the pullback of the Euclidean metric by the embedding, and there is a natural diffeomorphism of $N\Sigma$ into $\mathbf{R}^m$ given by

$$\iota : (\sigma, n) \mapsto \sigma + n\,.$$

Suppose, $x = x(\sigma) \in \mathbf{R}^{m-n}$ provides a local coordinate map for Σ. Conversely, the inverse $\sigma = \sigma(x)$ is a local embedding of $\mathbf{R}^{m-n}$ onto $\Sigma \subset \mathbf{R}^m$. Accordingly, once given an orthonormal frame $\{n^i\}$, the local normal coordinates are defined to be $y^i(\sigma, n) = \langle n^i(\sigma), n \rangle$. Note, that this can always be done in such a way, e.g., by using the Gram-Schmidt orthonormalisation method.
We want to decompose the tangent bundle over $N\Sigma$ into its horizontal and vertical part. We proceed by exploiting the natural bundle projection $\pi : N\Sigma \to \Sigma$, i.e., $\pi : (\sigma, n) \mapsto \sigma$. Following [15], the vertical subspace of $TN\Sigma$ is defined as the kernel of the induced tangent map $\mathrm{d}\pi : T_{(\sigma,n)}N\Sigma \to T_\sigma\Sigma$, whereas the horizontal subspace is the orthogonal complement in $TN\Sigma$ with respect to the pulled back metric g.

3.1. Induced metric

In order to compute the metric on $TN\Sigma$ we shall find an expression for the inner product on $TN\Sigma$. Any mechanical system involves masses for each particle. To keep a compact notation, we choose mass-scaled coordinates $q \mapsto M^{1/2}q$, where $M = \mathrm{diag}(m_i)$ denotes the diagonal mass matrix. Then, all computations can be carried out with respect to the scaled coordinates using the standard inner product

of $\mathbf{R}^m$. The tangent map $\mathrm{d}\pi$ gives rise to a projection-valued connection 1-form $\omega_{ij} = \langle n_i, \mathrm{d}n^j[\cdot]\rangle$, such that the following decomposition holds in $\mathbf{R}^m$

$$\mathbf{R}^m = T_\sigma \mathbf{R}^m = T_\sigma \Sigma \oplus N_\sigma \Sigma \,.$$

Be V_σ and $H_\sigma = \mathbf{1} - V_\sigma$ the respective orthogonal projections. Bear in mind that the tangent space is spanned by all vectors $(u, v) = (\dot{c}_\sigma(0), \dot{c}_n(0))$, where $(c_\sigma(t), c_n(t))$ is any curve with $(c_\sigma(0), c_n(0)) = (\sigma, n)$. Using that $H_\sigma + V_\sigma = \mathbf{1}$, then any tangent vector can be written as

$$(u, v) = (u, H_\sigma(v)) + (0, V_\sigma(v)) \,. \tag{3.2}$$

Considering $T_{(\sigma,n)} N\Sigma$ as a subspace of $\mathbf{R}^m \times \mathbf{R}^m$, we find for the standard Euclidean inner product of two tangent vectors at (σ, n)

$$\langle (u, v), (u', v') \rangle = \langle u + v, u' + v' \rangle \,. \tag{3.3}$$

We may now introduce local coordinates $(x, y) = (x(\sigma), y(\sigma, n)) \in \mathbf{R}^m$. Then, each vector on $N\Sigma$ has the form $(\sigma(x), y_i\, n^i(\sigma))$. Moreover, let the local frame on $TN\Sigma$ be denoted by $\partial/\partial x^1, \ldots, \partial/\partial x^{m-n}, \partial/\partial y^1 \ldots, \partial/\partial y^n$. Thus, in accordance with (3.2), we find for the components of a tangent vector

$$\begin{aligned} X_k &:= H_\sigma(u, v)_k = (\partial\sigma/\partial x^k, y_i \mathrm{d}n^i[\partial_k \sigma]) \in \mathbf{R}^m \,, \\ Y_l &:= V_\sigma(u, v)_l = (0, n^l) \in \mathbf{R}^m \,, \end{aligned}$$

where $k = 1, \ldots, m-n$ and $l = 1, \ldots, n$. Here, $\mathrm{d}n^i[\partial_k \sigma] \in \mathbf{R}^m$ is the k-th component of the vector $\mathrm{d}n^i = \partial n^i/\partial\sigma^j \partial\sigma^j/\partial x^k$. We further see that, the first component of a tangent vector does not lie in $\mathrm{span}\{\partial/\partial y^l\}$. We can now evaluate the metric elements of the tangent bundle using the relation (3.3) for the inner product:

$$g = \begin{pmatrix} \langle X_i, X_j \rangle & \langle X_i, Y_j \rangle \\ \langle Y_i, X_j \rangle & \mathbf{1} \end{pmatrix} .$$

The elements of the off-diagonal $(m-n) \times n$ block matrices are $Z_{ij} = \langle y_l \mathrm{d}n^l[\partial_i \sigma], n^j \rangle$. We may split up the horizontal terms in the upper left, having the size $(m-n)\times(m-n)$ according to $\langle X_i, X_j \rangle = G_{ij}(x) + A_{ij}(x, y)$ with

$$\begin{aligned} G_{ij} &= \langle \partial_i \sigma, \partial_j \sigma \rangle \\ A_{ij} &= y_l \left\langle \mathrm{d}n^l[\partial_j \sigma], \partial_i \sigma \right\rangle + y_l \left\langle \partial_j \sigma, \mathrm{d}n^l[\partial_i \sigma] \right\rangle \\ &\quad + y_k y_l \left\langle \mathrm{d}n^k[\partial_i \sigma], \mathrm{d}n^l[\partial_j \sigma] \right\rangle \,, \end{aligned}$$

where clearly G is the metric of Σ. Furthermore the connection 1-form is related to Z as $\omega_{ij} = \langle n_i, \mathrm{d}n^j[\cdot] \rangle$. Physically spoken, it indicates whether or not the constraints are ideal and Lagrange-d'Alembert's principle holds [12, 16]. After all, we find

$$g = \begin{pmatrix} G + A & Z \\ Z^T & \mathbf{1} \end{pmatrix} = \begin{pmatrix} \mathbf{1} & Z \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \cdot \begin{pmatrix} G + A & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{1} & Z \\ \mathbf{0} & \mathbf{1} \end{pmatrix}^T \,. \tag{3.4}$$

Thus, in accordance with (3.2) we can directly read off the projectors

$$V_\sigma = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ Z^T & \mathbf{1} \end{pmatrix} \,, \quad H_\sigma = \mathbf{1} - V_\sigma = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ -Z^T & \mathbf{0} \end{pmatrix} .$$

Obviously, a clever choice of the normal frame is essential, and we shall see in the next Section, that in case of Σ being a regular hypersurface in $\mathbf{R}^m$ one can always find local coordinates such that the connection 1-form vanishes.

4. Introducing holonomic constraints II

Throughout the paper we will use the subscript Σ to denote functions that are defined merely on the constraint manifold $T\Sigma$ or $T^*\Sigma$, respectively. Let $\mathcal{L}$ be a regular Lagrange function $\mathcal{L} : T\mathbf{R}^m \to \mathbf{R}$ with a potential function U. As we have mentioned, a holonomic constraint Σ gives rise to an integrable subbundle of $T\mathbf{R}^m$ or distribution, respectively. Since naturally the inclusion $T\Sigma \subset T\mathbf{R}^m$ holds, we can construct a constrained Lagrangian $\mathcal{L}_\Sigma$ from the restriction of $\mathcal{L}$ to $T\Sigma$. Then, the corresponding Euler-Lagrange equations are given in their local form by

$$\ddot{x}^i + \Gamma^i_{jk}\dot{x}^j\dot{x}^k + G^{ij}\partial_j U = 0\,, \tag{4.1}$$

where G^{ij} are the metric elements of the inverse metric tensor G^{-1} and the Γ^i_{jk} are the Christoffel symbols associated with the Levi-Civita derivative on $T\Sigma$. Alternatively, we can proceed from the variational principle for a constrained Lagrangian in full space. Be $c : [a, b] \to \mathbf{R}^m$ any smooth curve with fixed endpoints $q_a, q_b \in \Sigma$, and consider the Routh construction $\mathcal{L}' = \mathcal{L} - \lambda^k g_k$ for the Lagrangian $\mathcal{L}$ with an action functional $\mathcal{S}'$ for a certain vector $\lambda = \lambda(q, \dot{q})$. The prime indicates that $\mathcal{L}'$ is defined on the full space but takes only values on $T\Sigma$. This leads to the equations of motion for $\mathcal{L}'$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}^i} - \frac{\partial \mathcal{L}}{\partial q^i} + \lambda^k \frac{\partial g_k}{\partial q^i} = 0\,, \quad g(q) = 0\,. \tag{4.2}$$

Now, the Hamiltonian variational principle states, that for an ideally constrained particle a curve $c \subseteq \Sigma$ is a critical point of the constrained action functional $\mathcal{S}_\Sigma$ associated with $\mathcal{L}_\Sigma$ if and only if (λ, c) is a critical point of $\mathcal{S}'$. This is expressed in the following Proposition, a proof of which can be found in several textbooks, e.g. [17]:

Proposition 1 *The equations of motion (4.2) for $\mathcal{L}' : T\mathbf{R}^{m+n} \to \mathbf{R}$ in the variables (q, λ) with the constraint $g(q) = 0$ are equivalent to the Euler-Lagrange equations on $T\Sigma$ corresponding to $\mathcal{L}_\Sigma : T\Sigma \to \mathbf{R}$, and which are given by (4.1).*

Nicely, the equations of motion (4.1) offer a clear geometrical interpretation of the different contributions to the constrained vector field, although we will mostly refer to (4.2). Apparently, there are two contributions: (1) the restriction of the potential part to the constraint manifold, and (2) the velocity dependent geodesic spray of G. The first point can be made explicit by means of the linear map $G^\sharp : T^*\Sigma \to T\Sigma$ associated with G^{-1} sending an element of the cotangent space to the tangent space:

$$\operatorname{grad} U(x) = G^\sharp(\mathrm{d}U(x))\,.$$

Whereas this constribution should be clear, the latter one demands for further explanation: let the second order vector field S describe the geodesic spray in $\mathbf{R}^m$, i.e., its trajectories are straight lines in the Euclidean sense. Then, if we denote the orthogonal projection onto the horizontal bundle by $TH_\sigma : T^2N\Sigma \to T^2\Sigma$, the spray S_Σ according to the embedding of Σ is given by $S_\Sigma = TH_\sigma \circ S$, which is exactly the spray of the metric tensor G.
The distinction between (1) and (2) will become crucial in what follows, since our Hybrid Monte-Carlo algorithm requires that we carefully distiguish between the different contributions to the free energy – velocity or merely coordinate dependent.

4.1. Hamiltonian formulation

The motivation to formulate the constrained system in the form (4.1) is twofold: (1) we have a geometrical intuition concerning the constrained motion, and (2) the

Lagrangian $\mathcal{L}'$ is not regular as a function of (q, λ), since it contains no velocities in λ, and thus the evolution of λ is undetermined by the Hamiltonian equations of motion, whereas the Lagrangian $\mathcal{L}_\Sigma$ associated with (4.1) is regular. From $\mathcal{L}_\Sigma$, the reduced Hamiltonian is easily obtained by Legendre transform

$$\begin{aligned}\mathcal{H}_\Sigma(x,u) &= \langle u, \dot{x}\rangle - \mathcal{L}_\Sigma(x,\dot{x}) \\ &= \frac{1}{2}\langle u, u\rangle_{G^{-1}} + U_\Sigma(x)\,,\end{aligned}$$

where u denotes the conjugated momentum to x. For an ideally constrained system, it is solely obtained by applying the linear map $G^\flat : T\Sigma \to T^*\Sigma$

$$u = G^\flat(\dot{x}) = D_{\dot{x}}\mathcal{L} \in T^*_\sigma\Sigma\,.$$

It is frequently stated that the flow corresponding to a constrained system were not Hamiltonian, for the Lagrangian multipliers in (4.2) depend on velocities. However, it should be clear from the Proposition above that this is not true. As we will see below, we can even define a Hamiltonian function of the form $\mathcal{H}' = \mathcal{H} + \lambda^k g_k$ analogously to the Lagrange function $\mathcal{L}' = \mathcal{L} - \lambda^k g_k$, and we shall give precise conditions, so that the dynamics generated by $\mathcal{H}'$ on the constraint manifold is equivalent to that of $\mathcal{H}_\Sigma$.

Remark on the invariant measure I: Let $\{\cdot,\cdot\}_\Sigma : T^*\Sigma \to \mathbf{R}$ denote the Poisson bracket on $T^*\Sigma$. We introduce the Liouville equation $\dot{\mu}_\Sigma = \{\mu_\Sigma, \mathcal{H}_\Sigma\}$ for a function $\mu_\Sigma \in L^1(\mathrm{d}\omega)$, the solution of which provides an invariant measure for the Hamiltonian dynamics. It is easy to check, that a solution is given by the canonical density

$$\mu_\Sigma = Z_\Sigma^{-1}\exp\left(-\beta\mathcal{H}_\Sigma\right), \quad \text{with } Z_\Sigma = \int \exp\left(-\beta\mathcal{H}_\Sigma\right)\mathrm{d}\omega \tag{4.3}$$

using the common notation $\beta = 1/T$. Here, the differential 2-form $\mathrm{d}\omega = \mathrm{d}x \wedge \mathrm{d}u$ is the symplectic form on $T^*\Sigma$. Given a concrete expression for the inverse metric tensor, we are able to write down μ_Σ explicitely. However, the notion of free energy relies on the definition of a conditional measure $\mu(q, p \,|\, q \in \Sigma)$ rather than on a constrained measure μ_Σ above. The difference is that the latter is generated by the constrained dynamics obeying the velocity/momentum constraint (2.2), whereas for the conditional measure the momenta are left free. Clearly, neither does the conditional measure correspond to any Hamiltonian system nor will there be any dynamical system with a *holonomic* constraint generating this measure. Such a system would be excluded by Frobenius' Theorem. Anyhow, it is possible to construct the conditional measure from approriately reweighting μ_Σ, a procedure known as *blue moon ensemble method*. Later on, we will shortly address this topic.

4.2. Poisson structures

The above formulation suffers from the severe disadvantage, that numerical computations are commonly performed in Euclidean coordinates using any suitable discretisation scheme of (4.2), but we have presented the constrained Liouville equation only in its local form on $T^*\Sigma$. Yet, we can define an evolution equation for the density in full space analogously to (4.2). This is achieved by a convenient modification of the Poisson bracket or Dirac bracket, respectively [18, 19].
Provided that the unconstrained Lagrange function $\mathcal{L}$ is regular, $\mathcal{L}' = \mathcal{L} - \lambda g$ denotes the constrained Lagrangian on $T\mathbf{R}^{m+1}$. Then, formally, the corresponding Hamiltonian on $T^*\mathbf{R}^{m+1}$ is defined by [17]

$$\mathcal{H}'(q,p,\lambda,\pi) = \mathcal{H}(q,p) + \lambda(q,p)g(q)\,,$$

where π is the conjugated momentum to λ. As noted before, $\mathcal{L}'$ is not regular in λ, and therefore $\mathcal{H}'$ does not provide evolution equations for λ. Particularly, $\mathcal{H}'$ is not simply obtained by a Legendre transform of $\mathcal{L}'$. Now, let $\Lambda \subset T^*\mathbf{R}^{m+1}$ be the set defined by $\pi = 0$ (*primary constraint set*). Then, on Λ, the Hamiltonian function $\mathcal{H}'$ is the image of the Legendre transform of $\mathcal{L}'$, and we can pull back the symplectic form to Λ, yielding the standard equations of motion for q and p under the dynamics of $\mathcal{H}'$. The pulled back symplectic form is then $\mathrm{d}q \wedge \mathrm{d}p$ restricted to $T^*\Sigma$.
Furthermore, this construction guarantees, that $g, \dot{g}$ are weak invariants of the dynamics in the sense of Dirac, if the condition $\{g, \dot{g}\} \neq 0$ is met [20]; the meaning of the last condition will soon become clear. To see, how the constraint has an impact on the Poisson bracket, we write down the equations of motion for any scalar function F

$$\begin{aligned}\dot{F}_\Sigma = \{F, \mathcal{H}'\} &= \{F, \mathcal{H}\} + \{F, g\}\lambda \\ &= \{F, \mathcal{H}\} + \{F, g\}\{g, \dot{g}\}^{-1}\{\dot{g}, \mathcal{H}\}\,.\end{aligned}$$

Here, we only used the definition $\lambda = \{g, \dot{g}\}^{-1}\{\dot{g}, \mathcal{H}\}$ for the Lagrange multiplier. It is easily obtained from differentiating the constraint twice with respect to time, and then setting $\ddot{g} = 0$ (see the Appendix). We shall denote the bracket defined on the left-hand side again by a prime, in order to indicate the relationship with $\mathcal{H}'$, i.e., $\{\cdot, \mathcal{H}\}' := \{\cdot, \mathcal{H}'\}$. Thus note, that although the symplectic structure on Σ is simply obtained by restricting it to the constraint surface, the same does not hold true for the Poisson bracket. It is straighforward to show, that $(\Sigma, \{\cdot, \cdot\})$ is not a Poisson manifold, since it does not satisfy the Jacobi identity. However the evolution equation for F under $\mathcal{H}'$ above suggests that $(\Sigma, \{\cdot, \cdot\}')$ is Poisson-like with

$$\{F, G\}' = \{F, G\} + \{F, g\}\{g, \dot{g}\}^{-1}\{\dot{g}, G\}\,, \tag{4.4}$$

where F, G are defined on the ambient space $T^*\mathbf{R}^m$ to the constraint manifold. Hence, $\{\cdot, \cdot\}'$ is defined for functions in full $T^*\mathbf{R}^m$ but takes only values on $T^*\Sigma$. It can be further shown [17], that up to sign, the last term in (4.4) is the Euclidean expression for the vertical projector $V_\sigma^* = gV_\sigma g^{-1}$ acting on cotangent vectors, and defined in accordance with Section 3. In particular, $\{q, \mathcal{H}\}'$ defines a vector field on Σ that has no component normal to $T^*\Sigma$, while in general $\{q, \mathcal{H}\}$ surely has. A very important property of (4.4) is that the notation is coordinate independent.
The condition that $\{g, \dot{g}\}$ be invertible is called the *cosymplecticity condition* on Σ, which is sufficient for the constrained dynamics being Hamiltonian. It guarantees that the symplectic form on Σ is non-degenerate and closed, which obviously cannot hold without the hidden constraint $\dot{g} = 0$. At the same time, it is a necessary condition to ensure that the bracket $\{\cdot, \cdot\}'$ is well-defined.

Remark on the invariant measure II: We may now use the relation (4.4) to compute the constrained invariant measure from the ordinary canonical density $\mu = Z^{-1}\exp(-\beta\mathcal{H})$ on $T^*\mathbf{R}^m$. The Liouville equation reads in full space

$$\dot{\mu} = \{\mu, \mathcal{H}\}\,, \quad \mu = Z^{-1}\exp\left(-\beta\mathcal{H}\right) \;\Rightarrow\; \dot{\mu} = 0\,,$$

where Z denotes the normalisation constant. This density is clearly not unique, since any smooth function $f(\mathcal{H})$ of the Hamiltonian satisfies $\dot{f} = 0$. Therefore, it seems hopeless to compute *the* constrained invariant measure by means of (4.4). Yet, we can figure out what the constraint does to the canonical density μ

$$\begin{aligned}\dot{\mu}_\Sigma = \{\mu, \mathcal{H}\}' &= \dot{\mu} + \{\mu, g\}\{g, \dot{g}\}^{-1}\{\dot{g}, \mathcal{H}\} \\ &= \dot{\mu} \quad \text{on} \quad T^*\Sigma\,.\end{aligned}$$

This identity is owed to the fact, that $\{\mu, g\}$ is proportional to $\langle p, D_q g\rangle$, which is zero on condition the constraint is satisfied. Note, that since we are using mass-scaled coordinates, we can identify $T^*\Sigma$ with $T\Sigma$ and therefore $D_q g$ is perpendicular to $T^*\Sigma$, too. This is a nice result, because it shows that the unconstrained canonical density μ evaluated on $T^*\Sigma$ is indeed the constrained invariant density μ_Σ from (4.3) given in Euclidean coordinates. Finally, our aim will be to compute averages with respect to the conditional measure which is related to the constrained measure μ_Σ only through a reweighting procedure. For a discretisation of the constrained euations of motion it seems more appealing to refer to (4.2), because we can stick to the Euclidean setting. So far however, it is by no means obvious how a discretisation of (4.2) should put forth a *canonical* measure rather than the *microcanonical* one. This problem will be tackled by means of a Hybrid Monte-Carlo method as we will explain in Section 6.

5. Conditional free energy

For the sake of simplicity, we may restrict our attention to the codimension $n = 1$ case, and we introduce a *reaction coordinate* ξ' by means of the holonomic constraint $g(q) = \xi(q) - \xi'$. We wish to express the free energy as a function of ξ'. To this end, we slightly change our notion: let $Z(\xi')$ denote the conditional probability density associated with the unconstrained Hamiltonian

$$Z(\xi') = \int \exp\left(-\beta\mathcal{H}(q,p)\right)\delta(\xi(q) - \xi')\,\mathrm{d}p \wedge \mathrm{d}q\,.$$

The relation to the normalisation constant Z_Σ from the definition (4.3) of the constrained invariant measure μ_Σ above will soon become clear. Following the relevant literature [21], we define the free energy with respect to the reaction coordinate:

Definition 1 *Be $\Sigma \subset \mathbf{R}^m$ a smoothly embedded submanifold of $\mathbf{R}^m$ with codimension n=1, that is globally defined by $\xi(q) - \xi' = 0$. Then, the free energy with respect to the parameter ξ' (reaction coordinate) is given by*

$$F(\xi') = -\beta^{-1}\ln Z(\xi')\,. \tag{5.1}$$

Taking the derivatives with respect to ξ' on either sides, we obtain the average force onto the reaction coordinate. Writing $\mathrm{d}\Omega = \mathrm{d}q\wedge\mathrm{d}p = \mathrm{d}x\wedge\mathrm{d}u + \mathrm{d}y\wedge\mathrm{d}v$ for the standard symplectic form, the right hand side then contains the term

$$\begin{aligned}\partial_{\xi'} Z =& \int \exp\left(-\beta\mathcal{H}(q,p)\right)\partial_{\xi'}\delta(\xi(q) - \xi')\,\mathrm{d}\Omega \\ =& -\int \exp\left(-\beta\mathcal{H}(q,p)\right)\partial_{\xi}\delta(\xi(q) - \xi')\,\mathrm{d}\Omega\,.\end{aligned}$$

We can now integrate by parts, assuming that the canonical density gives no boundary contributions, i.e., we use the formal rule for taking derivatives in the distributional sense $\delta'[\mu] = -\delta[\mu']$. Therefore, we end up with the well-known expression

$$\begin{aligned}\partial_{\xi'} Z =& \int \partial_\xi \exp\left(-\beta\mathcal{H}\right)\delta(\xi - \xi')\,\mathrm{d}\Omega \\ =& -\beta\int \partial_\xi\mathcal{H}\exp\left(-\beta\mathcal{H}\right)\delta(\xi - \xi')\,\mathrm{d}\Omega\,.\end{aligned}$$

For the moment, let us forget about the problem how expectation values with respect to the conditional measure can be accessed from a constrained simulation generating a

constrained measure, and let $\mathbf{E}[\,\cdot\,|\xi=\xi']$ stand for the conditional average associated with the probability density $Z(\xi')$. It is defined as follows

$$\mathbf{E}\left[\,\mathcal{B}\,\Big|\,\xi=\xi'\right] = Z(\xi')^{-1}\int \mathcal{B}\,\exp\left(-\beta\mathcal{H}\right)\delta(\xi-\xi')\,\mathrm{d}\Omega\,, \tag{5.2}$$

where $\mathcal{B}=\mathcal{B}(q,p)$ is an arbitrary observable, for which the integral exists. Concluding, we use the relation $\beta F'=-Z'/Z$ and write the conditional free energy as

$$F(\xi') = -\int (\beta Z)^{-1} Z'(s)\,\mathrm{d}s = \int \mathbf{E}\left[\,\partial_\xi\mathcal{H}\Big|\xi=s\right]\,\mathrm{d}s\,. \tag{5.3}$$

At the end of this paper, we will comment on the matter, whether or not the hidden constraint $\dot\xi=0$ has some impact on this average; it will turn out that we can understand the *position dependent part* of $\mathbf{E}[\,\cdot\,|\xi=\xi']$ as a weighted average over the constrained position ensemble, where the weight is given by the so-called blue moon factor [22]. Strictly speaking, the weigthing is not due to *dynamical* effects arising from the hidden constraint. As we have emphasized before, the hidden constraint $\dot\xi=0$ is not artificially imposed to the dynamics but rather results in a natural manner from fixing ξ. Thus, the weight solely reflects the formal definition of the *conditional* probability measure with no restriction on the momenta.
One point is noteworthy: since $\mathcal{H}$ above acts on full $T^*\mathbf{R}^m$ but only in a small tubular neighbourhood of $T^*\Sigma$, we may switch to normal coordinates $(q,p)\mapsto(x,y,u,v)$, where y is the normal coordinate on $\mathrm{span}\{n\}=N_\sigma\Sigma$, and v denotes the conjugate momentum. As a matter of fact, this transformation is symplectic, and we can expand the constraint to first order by $\xi-\xi'\approx\langle D_q\xi,n\rangle\,y=\|D_q\xi\|\,y$ with the gradient evaluated on Σ. Note, that any scalar constraint can be written in this linear form. The essential point now is, that we can carry out all computation involving the reaction coordinate as well in terms of the normal coordinate y. This decision does not affect our result, but clarifies the relation to the Frobenius Theorem, and it considerably simplifies our proof below. We find an expression for the mean force, which should be compared to the results in [6, 5, 23, 4]:

Lemma 1 *Be $\xi'\in\mathbf{R}$ a reaction coordinate defined by the holonomic constraint $\Sigma=\{q|\xi(q)-\xi'=0\}$, and be λ the Lagrange undetermined multiplier added to the unconstrained Lagrangian. If we let $\mathbf{E}[\,\cdot\,|\xi=\xi']$ denote the conditional expectation value in the canonical ensemble, the average force on ξ' is given by*

$$F'(\xi') = -\mathbf{E}\left[\,\lambda(q,\dot q)-\Pi(\dot q,\dot q)\,\Big|\xi=\xi'\right]\,, \tag{5.4}$$

where $\Pi(\dot q,\dot q)$ with $\dot q\in T_q\Sigma$ is the second fundamental form of the embedding.

Proof: To evaluate the partial derivative of the unconstrained Hamiltonian with respect to the reaction coordinate, we again make use of the expression (4.4) for the restricted Poisson bracket. First of all, consider a symplectic change of coordinates according to $(q,p)\mapsto(x,y,u,v)$. Then, the constrained Dirac Hamiltonian reads

$$\mathcal{H}'(x,0,u,0) = \mathcal{H}(x,y,u,v)+\lambda\|D_q\xi\|y\,.$$

As noted above, $\mathcal{H}'$ provides the standard Hamiltonian equations for a set of canonical coordinates on the primary constraint set. Hence, it follows from (4.4) that

$$\begin{aligned}\dot v = \{v,\mathcal{H}\}' &= \{v,\mathcal{H}\}+\lambda\{v,\xi\}\\ &= -\partial_y\mathcal{H}-\lambda\|D_q\xi\|\end{aligned}$$

where we inserted the definition of the Lagrangian multiplier $\lambda = \{\xi, \dot{\xi}\}^{-1}\{\dot{\xi}, \mathcal{H}\}$. As we found in Section 3, the metric tensor on $TN\Sigma$ has the following block structure:

$$g(x,y) = \begin{pmatrix} G(x) + A(x,y) & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

with $G = G(x)$ denoting the metric of the constraint surface Σ. Bear in mind, that for an ideally constraint system the horizontal momentum had no contributions from the vertical bundle. Physically, this is expressed by the Lagrange-d'Alembert principle; geometrically, it follows from a vanishing connection 1-form $\omega = \langle n, \mathrm{d}n[\cdot]\rangle$ on $TN\Sigma$. Therefore vice versa, the vertical momentum has no contribution from the horizontal motion. This is to say

$$\omega = 0 \quad \Rightarrow \quad v = (V_\sigma^* \circ g^\flat)(\dot{x}, \dot{y}) = \mathbf{0}\dot{x} + \mathbf{1}\dot{y} = \dot{y}\,,$$

where $V_\sigma^* = gV_\sigma g^{-1}$ denotes the projector onto the vertical subbundle of $T^*N\Sigma$. Now note the following difference: though we have $\ddot{y} = 0$ above, reflecting the fact that the normal acceleration is zero, the normal force depends on the horizontal motion. This is due to the fact that the acceleration $\ddot{y}$ is not a tangent vector, whereas

$$\dot{v} = \nabla_t \dot{y} = \ddot{y} + \Gamma^m_{jk}\dot{x}^j\dot{x}^k = \Gamma^m_{jk}\dot{x}^j\dot{x}^k\,, \tag{5.5}$$

is a tangent vector to the vertical subspace of $T^*N\Sigma$. Here, ∇_t denotes the covariant time derivative (Levi-Civita connection) and Γ^m_{lk} is the associated Christoffel symbol. Then, applying chain rule $\partial_y = \|D_q\xi\|\partial_\xi$ for the partial derivative in (5.3) and the equation of motion for $\dot{v}$ the above expression turns out to be

$$F'(\xi') = -\mathbf{E}\left[\,\lambda(q,\dot{q}) - \Pi(\dot{q},\dot{q})\,\middle|\,\xi = \xi'\right]\,.$$

Here, we used the second Corollar from Appendix B, namely that the normal force $\dot{v}$ above divided by $\|D_q g\|$ reduces to the second fundamental form of the embedding. From this we obtain the desired result (5.4). ∎

Apparently, the force acting on the reaction coordinate is the constraint force λ plus some curvature constribution, which comes into play due to the embedding of the constraint surface into $\mathbf{R}^m$. The mean force on ξ' is then obtained from an appropriate average over the constraint force, and the decisive question is, in what sense "appropriate average" has to be understood. In the end, we shall remark, that the result is independent of a specific choice of coordinates, insofar as the Lagrange undetermined multipliers do not depend on the paramerisation of the constraint surface [6]. However the result depends on the chosen extension of the manifold Σ to the embedding space $\mathbf{R}^m$; this is clearly wanted, for the quantity of interest is in fact the force along a *specific* coordinate ξ', stipulating this choice.

6. Hybrid Monte-Carlo

In order to calculate averages as it is needed for free energy calculations by means of (5.3) and (5.4), respectively, we want to develop an algorithmic concept, that (1) allows for computing canonical averages, and that (2) does not involve any artificially added heat bath dynamics; it seems adequate to adopt the HMC approach [24].

We start with a local representation according to Section 4; the invariant measure of the constrained dynamics is given by (4.3). On $T^*\Sigma$ we cannot distinguish between merely momentum and position dependent parts, and so we write $\mu_\Sigma = Q(x)P_x(u)$, indicating that the kinetic energy depends on the position coordinates. In order to see

how the constrained HMC scheme works with μ_Σ, we let the one-parameter semigroup Φ^τ denote a symmetric and symplectic flow map that is consistent with the constrained equations of motion (4.2). Then, for a single integration step $(x', u') = \Phi^\tau(x, u)$ the HMC acceptance function is defined by

$$\begin{aligned} A(x, x') &= \min\left(1, \frac{\mu_\Sigma(x', -u')}{\mu_\Sigma(x, u)} \frac{\mathrm{d}(-u') \wedge \mathrm{d}x'}{\mathrm{d}u \wedge \mathrm{d}x}\right) \\ &= \min\left(1, \frac{Q(x')P_{x'}(-u')}{Q(x)P_x(u)} \frac{\mathrm{d}(-u') \wedge \mathrm{d}x'}{\mathrm{d}u \wedge \mathrm{d}x}\right) \\ &= \min\left(1, \frac{Q(x')P_{x'}(u')}{Q(x)P_x(u)}\right) . \end{aligned}$$

In the transformations we used (1) the symmetry of $P_x(u)$ with respect to momentum inversion $u \mapsto -u$ and (2) the invariance of $\mathrm{d}\omega = \mathrm{d}u \wedge \mathrm{d}x$ under Φ^τ, where $\mathrm{d}\omega$ is the restricted symplectic form on $T^*\Sigma$. We now have to show that propagating according to the HMC transition function – which indeed is the acceptance function $A(x, x')$ for a deterministic flow – leaves the canonical density μ_Σ invariant. This is by no means trivial, since the invariant measure of the dynamical system (4.1) is not unique. We will proof that the following statement holds

Proposition 2 *Be $(x', u') = (A \circ \Phi^\tau)(x, u)$ with an initial momentum u distributed according to $\mu_\Sigma(x, \cdot) = Q(x)P_x(\cdot)$. Furthermore, let $\eta(x', u')$ denote the distribution of the primed position coordinates, i.e., after one HMC step. Then, for any position dependent observable $\mathcal{B} \in L^1(\mu_\Sigma)$ the identity $\mathbf{E}_\eta[\mathcal{B}] = \mathbf{E}_Q[m(x)\mathcal{B}]$ holds, where $m(x)$ depends only on the Riemannian structure of the constraint surface Σ.*

Proof: For notational convenience, we drop the subscript Σ. Suppose, the initial position x follows the canonical distribution $\mu(\cdot, u)$. Then, for a given x we draw a momentum vector from $P_x(u)$, and propagate a single time-step according to Φ^τ. Following [24], this yields for the expectation value

$$\begin{aligned} \mathbf{E}_\eta[\mathcal{B}] = \int \mathcal{B} \Bigg\{ & \mu(\Phi^{-\tau}(x', u')) \min\left(1, \frac{\mu(x', u')}{\mu(\Phi^{-\tau}(x', u'))}\right) \det(\mathbf{D}\Phi^{-\tau}) \\ & + \mu(x', u') \left(1 - \min\left(1, \frac{\mu(\Phi^{-\tau}(x', u'))}{\mu(x', u')}\right)\right) \Bigg\} \, \mathrm{d}\omega' , \end{aligned}$$

where the first term of the right-hand side of the equation comes from the acceptance, the second one stems from the rejection step. Furthermore, we made use of the symmetry of Φ^τ in the second term. On condition that Φ^τ is symplectic, $\det(\mathbf{D}\Phi^{-\tau})$ equals one. From integrating out the momenta we easily find that

$$\begin{aligned} \mathbf{E}_\eta[\mathcal{B}] = & \int \big\{ \mathcal{B}\mu(x', u') + \mathcal{B} \min\big(\mu(\Phi^{-\tau}(x', u')), \mu(x', u')\big) \\ & - \mathcal{B} \min\big(\mu(x', u'), \mu(\Phi^{-\tau}(x', u'))\big) \big\} \, \mathrm{d}\omega' \\ = & \int \mathcal{B}\, \mu(x', u') \, \mathrm{d}\omega' \\ = & \int \mathcal{B} \sqrt{\det G(x')} Q(x') \mathrm{d}x' . \end{aligned}$$

The square root in the very last expression originates from the inverse metric tensor G^{-1} on the horizontal subbundle $T^*\Sigma$. We therefore have $m = \sqrt{\det G}$ which yields the correct marginal distribution in the position variables. ∎

So, why does HMC give a symplectic and time-reversible mapping, too? Certainly, the HMC inherits symplecticity from the discrete flow. Time-reversibility can be verified by checking the – clearly more restrictive – detailed balance condition:

$$\begin{aligned}\mu(x,u)A(x,x') &= \mu(x,u)\min\left(1,\,\frac{\mu(x',u')}{\mu(x,u)}\right)\\ &= \min\left(\mu(x',u'),\mu(x,u)\right)\end{aligned}$$

The last equation is symmetric in regard to the primed and unprimed variables, hence $\mu(x,u)A(x,x') = \mu(x',u')A(x',x)$, and the detailed balance condition is satisfied.

6.1. Average constraint force

The task of computing free energies using HMC poses the following problem: The constraint force or the Lagrange undetermined multipliers as well as the second fundamental form depend on the velocities or momenta, respectively. Therefore, we have to get rid of the velocity dependent part of the constraint force in advance, because HMC can only manage distributions in the position variables. As we will show in the Appendix the velocity contribution of the constraint force is also provided by the second fundamental form of the embedding, $\mathrm{II}(\dot q,\dot q) = \langle S(q)\dot q,\dot q\rangle$ with S denoting the symmetric matrix of the Weingarten map (see Appendix A). Obviously, the Proposition above still holds if we use a velocity dependent observable, if we can explicitely compute its marginal distribution.
We want to switch again to Euclidean coordinates. Let the quadratic form for the kinetic energy T be defined by $2T = \langle\dot q,\dot q\rangle$. The corresponding invariant measure has the Maxwellian density $P(\dot q) = \exp\left(-\beta T(\dot q)\right)$. Recall, that there is no velocity constraint for the conditional expectation. Thus, if we want to integrate out the velocity part of the observable in (5.3) we have to solve the following integral:

$$\int \mathrm{II}(\dot q,\dot q)\,P(\dot q)\,\mathrm{d}\dot q = \int \langle S(q)\dot q,\dot q\rangle\,\exp\left(-\beta T(\dot q)\right)\mathrm{d}\dot q\,.$$

So, the work to be done is to compute the covariance matrix for the Maxwellian velocity distribution. But since T is diagonal, and S is a function of q only, all cross-terms involving $\dot q^i\dot q^j$ must vanish. Then, the variances of the remaining terms are simply given by one over β. From inserting the definition (A.4) of the second fundamental form with the matrix S depending on q only we obtain an expression which has a concise and intuitive geometrical meaning:

$$\int \mathrm{II}(\dot q,\dot q)\,P(\dot q)\,\mathrm{d}\dot q = \beta^{-1}\mathrm{tr}(S) = (\beta\|D_q\xi\|)^{-1}\mathrm{tr}(D_q^2\xi)\,. \tag{6.1}$$

Bear in mind, that up to the dimensional factor from the arithmetic mean the trace of the Weingarten map, is the mean curvature of Σ in $\mathbf{R}^m$. For that reason S is often called the shape operator. Consequently, (6.1) describes the mean curvature of the constraint manifold gauged versus the mass-scaled Euclidean basis. We emphasize, that for simple length constraints of the form $\|q\|^2 = c$, making up most of the MD applications, the mean curvature term is constant. See below for a non-trivial example with a torsion angle constraint for a Butane molecule.

6.2. Blue moon ensemble method

As aforementioned, the measure generated by the constrained dynamics is not the conditional measure we want to use for computing expectation values. Unfortunately,

the blue moon method applies for positional observables only, whereas the constraint force is velocity dependent. However, we may investigate how the curvature contribution of the Lagrange undetermined multiplier reveals under the impact of the constrained measure. Intriguingly, it turns out that the average of the second fundamental form with respect to the constraint measure generates an additional curvature term (*geodesic curvature*) which is not contained in the conditional average. An explanation for this surprising effect is, that the *averaged* geodesic curvature is zero, and therefore did not occur in the average above.
Let us have a look at this phenomenon: to this end, we compute the expectation of the curvature contribution for the Maxwellian distribution under the velocity constraint. We will show in the Appendix, that up to normalisation the density restricted to the constraint surface $T\Sigma$ is given by

$$P_\Sigma(q,\dot{q}) = \exp\left(-\frac{\beta}{2}\left\langle H_\sigma^T\,\mathbf{1}H_\sigma\,\dot{q},\dot{q}\right\rangle\right) \tag{6.2}$$

where $H_\sigma = \mathbf{1} - V_\sigma$ is symmetric and of rank $m-1$, and denotes the projector onto the constraint surface. The challenge is thus to compute the covariance matrix for P_Σ. We can use the following transformation property of Gaussian distributions: Be $X \sim N(0,K)$ any Gaussian random variable with covariance matrix K. Then, the random variable $Y = AX$ is distributed according to $Y \sim N(0, A^TKA)$. Hence,

$$\begin{aligned}\int \Pi(q,\dot{q})\,P_\Sigma(q,\dot{q})\,\mathrm{d}\dot{q} &= \beta^{-1}\mathrm{tr}(H_\sigma^T S H_\sigma)\\ &= \beta^{-1}\left(\mathrm{tr}(S) - \langle n, Sn\rangle\right)\,.\end{aligned}$$

Here again, n denotes the unit normal vector to $T\Sigma$. The negative sign comes into play, because after resolving $H_\sigma = \mathbf{1} - n\,\langle n,\cdot\rangle$ we can rotate the operators under the trace and exploit the idempotency of the projector, and the linearity of the trace. Apparently, the geodesic curvature contribution arises artificially from the constrained average, and therefore has to be corrected when computing averages from a constrained trajectory. Concluding, we can insert the expression (A.4) for the Lagrange undetermined multiplier into (5.3) correcting the bias from the geodesic curvature. This leads to the known result for the mean force along a reaction coordinate [6, 7, 23]:

$$f(\xi') = \mathbf{E}\Big[\,\langle n, D_qU\rangle - 2\kappa_m + 2\kappa^\perp\,\Big|\,\xi = \xi'\Big]\,, \tag{6.3}$$

where the expectation is carried out in the conditional ensemble, and $\kappa_m, \kappa^\perp$ stand for mean and geodesic curvature contributions, respectively, originating from the velocity average of the second fundamental form. However, this is only half of the story, since we have to account for the fact that though the restriction of the symplectic form according to $\mathrm{d}\Omega \mapsto \mathrm{d}\Omega|_\Lambda$ does not change the Liouville measure, restricting the position and leaving the velocities untouched does. The first point stated is expressed by the cosymplecticity condition: the restricted 2-form $\mathrm{d}\Omega \mapsto \mathrm{d}\Omega|_\Lambda$ is the standard symplectic form $\mathrm{d}\omega = \mathrm{d}x\wedge\mathrm{d}u$ on $T^*\Sigma$. The second point has been discussed extensively [22, 6, 8], and therefore we will not pick up this topic in too much detail. Intuitively, if we set $\xi = \xi'$, i.e., $\mathrm{d}\xi = 0$ keeping the full momentum space including p_ξ, we obtain a volume deformation according to $\mathrm{d}p_\xi = \|D_q\xi\|^{-1}\mathrm{d}v$. Likewise, the problem can be understood in a more geometrical manner: Constrained motion is motion on a manifold. Therefore, computing expectation values means integrating over forms on manifolds, which includes functional determinants due to the embedding. By definition, canonical transformations leave the (symplectic) volume form invariant.

But as we have seen in Section 5, the canonical choice to $\xi = \xi'$ would be $p_\xi = 0$. Consequently, the measure corresponding to the conditional density with arbitrary p_ξ is not the Liouville measure, and creates a non-trivial functional determinant which has to be corrected. We shall show in the Appendix, how this metric correction can be explicitely accessed.

6.3. HMC algorithm

We will now shortly describe, how the constrained HMC algorithm works. All numerical integrations are carried out using the `RATTLE` symplectic integrator. In order to sufficiently guarantee long-time stability, the constraint has to be satisfied more or less exactly, which is done by means of a Newton iteration in order to solve the nonlinear equations [25].
The HMC scheme consists of proposal and acceptance step, with the numerical integration in between. The proposal velocity is generated as follows: First, for each value of q randomly choose a velocity vector $\dot{q} \in \mathbf{R}^m$, that is distributed according to $N(0, M)$ for the respective inverse temperature β. Applying the projection according to $\dot{q} \mapsto H_\sigma \dot{q}$, then produces velocities that (1) satisfy the constraints, and (2) are distributed due to $N(0, H_\sigma^T M H_\sigma)$, which is the correctly constrained density. The rest of the algorithm is straighforward: compute the total energy $\mathcal{H}_0 = T_0 + U_0$ right after the projection, propagate using the discrete flow from the constraint algorithm, evaluate the total energy $\mathcal{H}_1 = T_1 + U_1$ again and perform the ordinary HMC acceptance step with the probability $\exp(-\beta(\mathcal{H}_1 - \mathcal{H}_0))$.
Then, the conditional expectation of an arbitrary position dependent observable $\mathcal{B}(q)$ is obtained from the definition (5.2) in connection with the blue moon weight $Z = \|D_q \xi\|^2$ correcting the factor $m = \sqrt{\det G}$ originating from the metric tensor of the constrained invariant measure. The explicit form of the metric tensor and its determinant in Euclidean coordinates will be derived in the Appendix. Then, we replace the conditional average by a properly weighted constrained average, and we are led to the famous blue moon relation [22]

$$\mathbf{E}\left[\, \mathcal{B}(q) \,\middle|\, \xi = \xi' \right] = \frac{\mathbf{E}\Big[Z(q)^{-1/2}\, \mathcal{B}(q) \,\Big|\, \xi = \xi', \dot{\xi} = 0 \Big]}{\mathbf{E}\Big[Z(q)^{-1/2} \,\Big|\, \xi = \xi', \dot{\xi} = 0 \Big]} \,,$$

where $\mathbf{E}[\cdot | \xi = \xi', \dot{\xi} = 0]$ on the right hand side denotes the average over the constrained invariant measure μ_Σ. Note, that we clearly have to rescale back to the original coordinates according to $q \mapsto M^{-1/2} q$, and so $\|\cdot\|$ denotes a norm which is weighted with M^{-1}. This whole procedure is then repeated for all fixed values of the reaction coordinate ξ'. The resulting force is integrated over ξ', in order to obtain the free energy along the reaction coordinate. After removing the mass-scaling, the explicit expression for the observable to be averaged over is

$$\begin{aligned} \mathcal{B}(q) = \; &+ \left\langle n, D_q U \right\rangle_{M^{-1}} - 2(\beta Z)^{-1} \mathrm{tr}(D_q^2 \xi \, M^{-1}) \\ &+ 2(\beta Z)^{-1} \left\langle n, D_q^2 \xi \, M^{-1} n \right\rangle_{M^{-1}} \,, \end{aligned}$$

where Z is defined as above, and also the normal vector n is normalised with respect to the weighted norm. This turns out, if we substitute the mean and geodesic curvatures terms in 6.3 by their explicit counterparts. As an example in order to illustrate the constrained HMC algorithm, the figure below shows the free energy or potential of mean force, respectively, for a Butane molecule. We used the united-atoms (UA) force

field by Ryckaert and Bellmanns [26]. Since the UA force field contains no Lennard-Jones interaction for Butane, the free energy ought to be identical to the torsion potential for all temperatures. All data were calculated from a $50ps$ HMC trajectory at $1fs$ step size and the acceptance-rejection step every $50fs$ with the provided simulation scheme and the `RATTLE` symplectic integrator at $T = 1/\beta = 600K$.
Let us concludingly comment on two outstanding numerical aspects: (1) for very high temperatures above $T = 1000K$, the Jacobian in the Newton iteration solving for the constraint will be badly scaled and will have a poor condition number. (2) for torsion angle constraints we recommend to carefully deal with the mean curvature term; though it is very small, it is not identically zero, and cannot be neglected. However, computing the trace of the the shape operator is numerically unstable due to extinction effects. Then, dividing the mean curvature term by Z which is a very small number again, amplifies the absolute error dramatically as the figure illustrates.

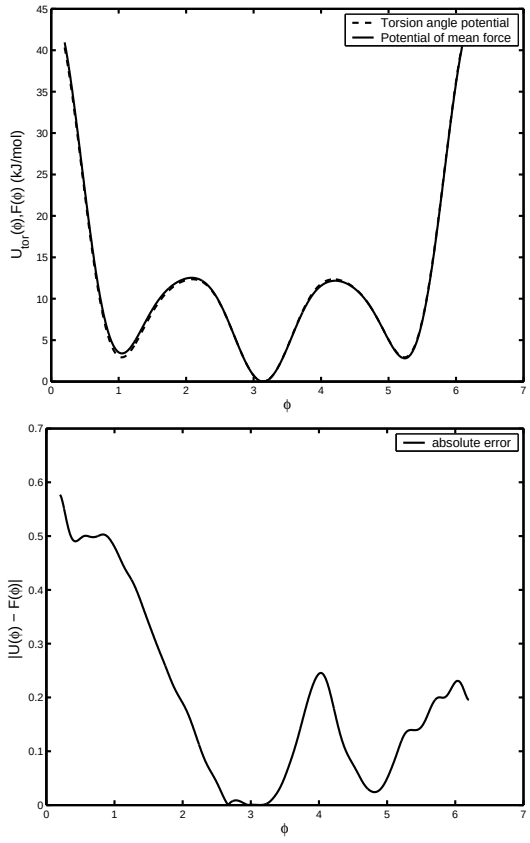

Figure 1. Torsion angle potential $U(\phi)$ and potential of mean force $F(\phi)$ for Butane in UA representation. The data were calculated from a 50ps HMC trajectory with the provided simulation scheme at 600K. The second graphics shows the absolute error which essentially arises from the mean curvature contribution κ_m.

Appendix A. Geometry of the constrained motion

Since, we want to compute averages over a positional (blue moon) ensemble, it is necessary to separate out the velocity dependent part of the constraint force. Though we have stated yet, that for the Lagrange undetermined multiplier the relation $\lambda = \{g, \dot{g}\}^{-1}\{\dot{g}, \mathcal{H}\} = \{\xi, \dot{\xi}\}^{-1}\{\dot{\xi}, \mathcal{H}\}$ holds with a scalar-valued function $g(q) = \xi(q) - \xi'$, we will derive an explicit expression for the constraint force, here. To this end, consider the Euler-Lagrange equation (4.2) in its mass-scaled version

$$\ddot{q} = -D_q U - \lambda\, D_q g\,, \quad g = 0\,. \tag{A.1}$$

It is well-known that (A.1) represents a DAE of index three. Differentiating the constraint again two times with respect to time yields two hidden constraints

$$\dot{g} = \langle D_q g, \dot{q}\rangle\,, \tag{A.2}$$

$$\ddot{g} = \langle D_q g, \ddot{q}\rangle + \left\langle D_q^2 g\, \dot{q}, \dot{q}\right\rangle\,. \tag{A.3}$$

We may stress, that by no means the mass-scaling affects our considerations, since the Lagrange-d'Alembert principle, which is equivalent to Frobenius' integrability condition still holds true for the scaled equations of motion. It is thus reasonable to demand $\dot{g} = \ddot{g} = 0$, and we can insert the equation of motion (A.1) into the last equation (A.2), solving for the Lagrange undetermined multiplier

$$\lambda = \|D_q g\|^{-2}\left(\left\langle D_q^2 g\, \dot{q}, \dot{q}\right\rangle - \langle D_q g, D_q U\rangle\right)\,, \tag{A.4}$$

which after reinserting this expression into the equation of motion brings

$$\ddot{q} = -D_q U + n\left(\langle n, D_q U\rangle - \|D_q g\|^{-1}\left\langle D_q^2 g\, \dot{q}, \dot{q}\right\rangle\right)\,.$$

Here, $n = D_q g \|D_q g\|^{-1}$ denotes the unit normal vector to $\Sigma = g^{-1}(0)$, normalised in the Euclidean vector norm. Since n spans the normal bundle to Σ, we can understand

$$V_\sigma^* : T^*\mathbf{R}^m \to N\Sigma \quad \text{with} \quad V_\sigma^* = n\,\langle n, \cdot\rangle$$

as the vertical projector of cotangent vectors onto the vertical tangent bundle, and accordingly, $H_\sigma^* = \mathbf{1} - V_\sigma^*$ as the projector onto the horizontal subbundle of the tangent bundle, respectively. Note, that we may identify $T\mathbf{R}^m$ with $T^*\mathbf{R}^m$, for we have eliminated the masses. Thus, we can rewrite the last equation into

$$\begin{aligned}\ddot{q} =& -(\mathbf{1} - V_\sigma^*)D_q V - n\left\langle D_q^2 g\, \|D_q g\|^{-1}\, \dot{q}, \dot{q}\right\rangle \\ =& -H_\sigma^* D_q V + n\,\langle S\,\dot{q}, \dot{q}\rangle \quad \text{with} \quad S = -D_q^2 g\, \|D_q g\|^{-1}\,,\end{aligned}$$

called the underlying ODE to (A.1). Obviously, the term $n\,\langle S\,\dot{q}, \dot{q}\rangle$ is orthogonal to Σ, and it represents the velocity dependent part of the constraint force. We will provide a geometric interpretation for this contribution now.

Appendix A.1. Second fundamental form

In case that the codimension of the constraint manifold Σ in $\mathbf{R}^m$ is one, we may define the second fundamental form of the embedding by

$$\Pi(X, Y) = \langle \mathrm{d}Y[X], n\rangle = \langle \mathrm{d}X[Y], n\rangle$$

with X, Y being tangent vectors from $T\Sigma$, and again $\mathrm{d}X[Y]$ denoting the directional derivative of X along the curves of Y. By construction, for any tangent vector X, the relation $\langle X, n\rangle = 0$ holds with n as defined previously. This gives after differentiation $\langle \mathrm{d}X[Y], n\rangle + \langle X, \mathrm{d}n[Y]\rangle = 0$, and from this we find

$$\Pi(X, Y) = -\,\langle X, \mathrm{d}n[Y]\rangle\,.$$

We should compare this expression to the matrix in the last scalar product in the underlying ODE above, the i-th row of which reads

$$\mathcal{S}^i_j = -\|D_q g\|^{-1}(\partial_i D_q g)^T \quad j = 1, \ldots, m\,.$$

On the other hand, we can take the derivative of the unit normal vector and obtain

$$\begin{aligned}\partial_i n &= \|D_q g\|^{-2}\left(\|D_q g\|\partial_i D_q g - \left\langle D_q g \|D_q g\|^{-1}, \partial_i D_q g\right\rangle D_q g\right)\\ &= \|D_q g\|^{-1}\left(\partial_i D_q g - n\,\langle n, \partial_i D_q g\rangle\right)\\ &= \|D_q g\|^{-1}(\mathbf{1} - V^*_\sigma)\,\partial_i D_q g\\ &= -\left(S^j_i - V^*_\sigma S^j_i\right),\end{aligned}$$

where S^j_i denotes the column vector drawn from the matrix S with fixed column index i, and j running freely from $1, \ldots, m$. Now, let q be a solution of the constrained system (A.1). Then, we know that $\dot q$ lies in the horizontal subbundle of $T\mathbf{R}^m$, since it has to satisfy the constraints, i.e., $\dot q \in T_q\Sigma$. Therefore, we have $\left\langle V^*_\sigma S^i_j, \dot q\right\rangle = 0$ and so

$$\left\langle S^i_j, \dot q\right\rangle = \left\langle H^*_\sigma S^i_j, \dot q\right\rangle = -\left\langle \partial_i n, \dot q\right\rangle\,.$$

If we compare this to the scalar product in the underlying ODE we are led to the conclusion that $\Pi(\dot q, \dot q) = \langle S(q)\,\dot q, \dot q\rangle$, where S appears to be the matrix of the Weingarten map associated with the second fundamental form. Now, the result follows:

$$\ddot q = -H^*_\sigma D_q U + n\,\Pi(\dot q, \dot q)\,. \tag{A.5}$$

For our reaction coordinate problem the constraint force is equal to the Lagrange undetermined multiplier. Recall, that the eigenvalues of the Weingarten map (*shape operator*) are the principal curvatures of the embedded manifold Σ. Hence, there are two constributions to the constraint force: (1) the coordinate dependent part given by the projection $-V^*_\sigma$ of the total force $D_q U$, and (2) the velocity dependent part, induced by the curvature properties of the constraint along the mass-scaled basis.

Appendix B. Fixing local coordinates: Codimension $n = 1$

Let us now address the problem how to evaluate the metric in practical issues. A hypersurface Σ defined by the scalar equation $g(q) = 0$ is called non-singular, if $D_q g \neq 0$ on the surface [27, 28]. Then, the following Lemma holds:

Lemma 2 *Be $q^* \in \Sigma$ any non-singular point of the hypersurface, and let $U_\epsilon(q^*)$ denote a sufficiently small tubular neighbourhood including that point. Then, there is a parameterisation of Σ in $U_\epsilon(q^*)$ given by $\{q^1, \ldots, q^{m-1}, f\}$, where $f : \mathbf{R}^{m-1} \to \mathbf{R}$ is the local inverse of g defined by $q^m = f(q^1, \ldots, q^{m-1})$.*

Proof: Suppose, q^* is a non-singular point of Σ, and say $\partial_m g \neq 0$ at $q^* \in \Sigma$. In this case, the *Implicit Function Theorem* guarantees that we can locally solve the equation $g(q) = 0$ for q^m, obtaining a smooth function of the remaining coordinates. Let this function be denoted by $q^m = f(q^1, \ldots, q^{m-1})$, such that $g(q^1, \ldots, q^{m-1}, f) = 0$. Consequently, the set $\{\sigma^i\} = \{q^1, \ldots, q^{m-1}, f(q^1, \ldots, q^{m-1})\}$ yields a valid parameterisation in $\Sigma \cap U_\epsilon(q^*)$. ∎

Note, that the assumption $\partial_m g \neq 0$ does not affect our considerations, for we can always choose a different parameterisation $\tilde\sigma$, say with $q^1 = \tilde f(q^2, \ldots, q^m)$. Then, if g is of class C^∞, the transition functions $\psi = \sigma \circ \tilde\sigma^{-1}$ are C^∞, too. Thus Σ will be

globally smooth. Furthermore, if we bear in mind the identity $q^m = f$, we obtain from implicit differentiation of $g(q^1, \ldots, q^{m-1}, f) = 0$

$$\partial_i f = -\partial_i g \left(\partial_m g\right)^{-1}, \quad q \in U_\epsilon(q^*)\,. \tag{B.1}$$

Now, defining local coordinates is pretty much straightforward: Let an embedding be given by $\sigma = \sigma(q)$ as indicated above. Take local coordinates $\{x^1, \ldots, x^{m-1}, y\}$ with $x^i = q^i$ for $i = 1, \ldots, m-1$. Then, $\{x^1, \ldots, x^{m-1}\}$ provide local mass-scaled coordinates on Σ. Moreover, we regard $y \in \mathbf{R}$ as normal cordinate, such that the submanifold $\Sigma \subset \mathbf{R}^m$ is fixed by the condition $y = 0$. Carrying out all partial derivatives, we see immediately that $Z = \mathbf{0}$, which is a known and hardly amazing result, that follows from the fact that $\langle \mathrm{d}n[\partial_i \sigma], n\rangle = 0$, since the variation of the unit normal vector to Σ along curves in Σ is perpendicular to the vector itself. Physically speaking, the constraints are imposed such that $\|n(\sigma)\|^2$ is conserved, and therefore the normal flow commutes with the motion on $T\Sigma$. Thus, the horizontal metric has the elements

$$\begin{aligned} G_{ij} &= \delta^i_j + \partial_i f\, \partial_j f = \delta^i_j + \partial_i g\, \partial_j g \left(\partial_m g\right)^{-2}\,, \\ A_{ij} &= 2y \left\langle \mathrm{d}n[\partial_i \sigma], \partial_j \sigma \right\rangle + y^2 \left\langle \mathrm{d}n[\partial_i \sigma], \mathrm{d}n[\partial_j \sigma] \right\rangle\,. \end{aligned}$$

Note, that the masses are hidden due to the scaling $q \mapsto M^{1/2} q$. Let us shortly remark, that the horizontal submatrix has a clear geometrical meaning in terms of the second fundamental form of the embedding. It can be shown [15], that $G + A = G(\mathbf{1} - S)^2$, where S is the matrix of the Weingarten map written in the basis of the $\{\partial_k \sigma\}$. One immediately sees, that the matrix A vanishes on the constraint manifold, where $y = 0$. For the general case of codimension $n > 1$ the reader is referred to a forthcoming paper.

Appendix B.1. Some useful expressions

Recall, that the square root in the very last expression from the HMC section originates from the inverse metric tensor G^{-1}, i.e., $m(x) = \sqrt{\det G(x)}$:

Lemma 3 *Be $\Sigma = \{q \,|\, g(q) = 0\}$ a smoothly embedded hypersurface in $\mathbf{R}^m$ with a Riemannian metric G. Locally, Σ be parameterised by $\sigma = \{x^1, \ldots, x^{m-1}, f\}$. Then, the square root of the determinant of G is equal to*

$$m(x) = \sqrt{\det G(x)} = \|D_x g\| |\partial_m g|^{-1}$$

Proof: The result follows from purely geometrical considerations. Concretely, the term $m = \sqrt{\det G}$ describes the deformation of the unit volume form evaluated on Σ. On the other hand, this deformation factor is basically given by the Jacobian of the embedding, and therefore on Σ the deformed volume element can be written as

$$\begin{aligned} \mathrm{d}\sigma &= \|D_x f\|\, \mathrm{d}x^1 \wedge \ldots \wedge \mathrm{d}x^{m-1} \\ &= \|D_x g\| |\partial_m g|^{-1}\, \mathrm{d}x^1 \wedge \ldots \wedge \mathrm{d}x^{m-1}\,, \end{aligned}$$

where we applied the partial derivatives identity (B.1) from above to obtain the desired result. So far this is the result in mass-weighted local coordinates $x \in R^{m-1}$, where the gradient is understood as the gradient in $\mathbf{R}^m$. ∎

Corollary 1 *Let $G(q) \in \mathbf{R}^{m \times m}$ with $q \in \Sigma$ denote the constrained metric tensor extendend to $\mathbf{R}^m$. Then, the blue moon factor is equal to* $\det G = \|D_q g\|^2$.

Without loss of generality, we may rotate our coordinate system, such that the m-axis is perpendicular to $T\Sigma$, and realise the missing coordinate by $y = q^m$. Note, that then $n = D_q g$ is no longer perpendicular to $T\Sigma$. Nevertheless, after Taylor expanding g around Σ in $\mathrm{span}\{\partial/\partial q^m\}$, we can blow up G to become a constrained metric tensor in $\mathbf{R}^{m\times m}$. We then find that for the full constrained metric tensor the identity $\det G = \|D_q g\|^2$ holds, where in order to avoid confusion with the constraint function, $G = G(q^1, \ldots, q^{m-1}, q^m = 0)$ denotes the constrained metric tensor extended to full space. Finally after rescaling back to Euclidean coordinates according to $q \mapsto M^{-1/2}q$, we end up with the correct blue moon weight.
Recall, that in the proof in Section 5, we had to evaluate the term $\Gamma^m_{jk}\dot{x}^j\dot{x}^k$. We can now exploit the block structure of the metric tensor in order to compute an expression for the corresponding Christoffel symbols of the Levi-Civita connection, and then explicitely compute the expression for the force acting on the normal coordinate:

Lemma 4 *Be $\Sigma = \{q \,|\, g(q) = 0\}$ a smoothly embedded hypersurface in $\mathbf{R}^m$ with a Riemannian metric tensor $G = G(x, y = 0) \in \mathbf{R}^{m\times m}$. Locally, Σ be parameterised by $\sigma = \{x^1, \ldots, x^{m-1}, f\}$. We let ∇ denote the torsion-free affine connection compatible with G. Then, the Christoffel symbol Γ^m_{jk} associated with ∇ is given by*

$$\Gamma^m_{jk}(x) = -(\partial_m g)^{-1}\ (\partial_j\partial_k g - \partial_k g\,\Theta(g', g''))\ , \tag{B.2}$$

where the function $\Theta = \Theta(g', g'')$ is an abbrevation for the sum of first and second order partial derivatives with respect to x^j, x^m, which does not depend on $\partial_k g$.

Proof: Since we are free to choose any extension of Γ^m_{jk} to the ambient space, we may assume, that now $G = G(x, y = 0)$ has block structure according to (3.4). Consider the definition of the symmetric Christoffel symbols:

$$\begin{aligned}\Gamma^m_{jk} &= \frac{1}{2}G^{ml}\,(\partial_j G_{lk} + \partial_k G_{lj} - \partial_l G_{kj})\\ &= G^{ml}\partial_l f\,\partial_j\partial_k f = \partial_j\partial_k f\,.\end{aligned}$$

In the first transformation, we used the symmetry of the second partial derivatives. The second identity is owed to the fact that G^{-1} inherits the block structure of G, which means that $G^{ml} = \delta^{ml}$. By means of (B.1) and chain rule the result follows. ∎

Corollary 2 *Be the Christoffel symbol Γ^m_{jk} corresponding to the normal direction be defined as above, and be $v \in \mathrm{span}\{\mathrm{d}y\}$ the vertical momentum. Then, the normal force $\dot{v}$ evaluated on the constraint surface reduces to*

$$\dot{v} = -\left\langle D^2_q g\,\dot{q}, \dot{q}\right\rangle\ , \quad \dot{q} \in T_q\Sigma \tag{B.3}$$

By construction, $T\Sigma = \mathrm{span}\{\partial/\partial x^k\}$ and $n \perp T\Sigma$. Therefore, we can rearrange the order of summation, such that all terms in $\Gamma^m_{jk}\dot{x}^j\dot{x}^k$ including $\partial_k g\,\dot{x}^k$ vanish. Since anyway $\Theta(g, g'') = 0$ for Γ^m_{jm} if $q \in \Sigma$, we can be incautious with the extension of $\dot{x}$ to $\mathbf{R}^m$ and thus simply replace $\dot{x}$ by $\dot{q}$. Finally, regarding q^m as an independent variable removes the residuum $(\partial_m g)^{-1}$ from the restriction to Σ. Then, the consideration from Appendix A made clear that the above expression is related to the second fundamental form by $\mathrm{II}(\dot{q}, \dot{q}) = \left\langle D^2_q g\,\|D_q g\|^{-1}\dot{q}, \dot{q}\right\rangle$. This identity was used in the first Lemma.

Appendix C. Restriction of the invariant measure

In order to implement the HMC algorithm, we have to randomly draw a velocity or momentum vector, respectively, from the constrained canonical density μ_Σ. As we

have shown by means of the Poisson bracket identity (4.4), the constrained density is simply obtained from a restriction of the Euclidean canonical density to $T^*\Sigma$, and we shall shortly explain, how the restriction can be managed in practice:
For obvious reasons, we may restrict our attention to the velocity contribution of the invariant density, and for the sake of clearness, we will drop the mass-scaling. The kinetic energy can be expressed generally by the quadratic form $T = \langle MX, X\rangle$, describing a hypersphere in a mass-weighted Euclidean norm. Here, the mass-matrix M takes over the role of the covariance matrix of the Maxwellian velocity distribution. Let us get an idea of the geometry of the distribution in velocity space. Suppose, we set $T = 1$, which means to define a unit hypersphere S^{m-1}, or – in probabilistic terms, an isodensite – in velocity space, respectively. Furthermore, we know that

$$H_\sigma = \mathbf{1} - V_\sigma \quad \text{with} \quad V_\sigma = n\,\langle n, \cdot\rangle$$

is the orthogonal projector onto the constraint manifold, since a constraint g is called ideal, if it satisfies the Lagrange-d'Alembert principle. That is, we demand, that the constraint force $\lambda D_q g$ is orthogonal to $T_q\Sigma$ with respect to the standard scalar product. Now, normalisation of the vector n is understood in regard to the standard norm. Geometrically, the restricted density is the intersection of the tangent plane $T_\sigma\Sigma$ at the point $\sigma \in \Sigma$ with the isodensite $I = \{X \in T_\sigma\mathbf{R}^m \,|\, T(X) = 1\}$. Thus, we have $H_\sigma \circ S^{m-1} = S^{m-2}$, where we have to identify the norm, in which S^{m-2} is again a unit hypersphere – of lower dimension however. Obviously, for any point X on $T_\sigma\Sigma$, the identity $H_\sigma X = X$ holds, and so does it on $T_\sigma\Sigma \cap I$. Hence, for $Y \in T_\sigma\Sigma \cap I$ the following relation holds:

$$1 = \langle H_\sigma Y, MH_\sigma Y\rangle = \left\langle Y, H_\sigma^T M H_\sigma Y\right\rangle \,,$$

describing a degenerate unit hyperellipse in the metric, given by the projected mass-matrix $H_\sigma^T M H_\sigma$. It is degenerate, because the projector $H_\sigma = H_\sigma^T$ has reduced rank $m-1$, but $Y \in \mathbf{R}^m$. Consequently, we found the equation for the isodensite $T = 1$ of the restricted density in Euclidean coordinates, maintaining the full dimensionality of the problem. This kind of degeneracy desired for the HMC algorithm.

References

[1] C. Chipot and D.A. Pearlman. Free energy calculations. The long and winding gilded road. *Mol. Sim.*, 28(1-2):1–12, 2002.

[2] B. Roux. The calculation of the potential of mean force using computer simulations. *Comp. Phys. Comm.*, 91:275–282, 1995.

[3] J. VandeVondele and U. Rothlisberger. Efficient multidimensional free energy calculations for ab initio molecular dynamics using classical bias potentials. *J. Chem. Phys.*, 113(12):4863–4868, 2000.

[4] E. Darve, M.A. Wilson, and A. Pohorille. Calculating free energies using a scaled-force molecular dynamics algorithm. *Mol. Sim.*, 28(1-2):113–144, 2002.

[5] T. Mülders, P. Krüger, W. Swegat, and L. Schlitter. Free energy as the potential of mean force. *J. Chem. Phys.*, 104(12):4869–4870, 1996.

[6] M. Sprik and G. Ciccotti. Free energy from constrained molecular dynamics. *J. Chem. Phys.*, 109(18):7737–7744, 1998.

[7] W.K. den Otter and W.J. Briels. The calculation of free-energy differences by constrained molecular-dynamics simulations. *J. Chem. Phys.*, 109(11):4139–4146, 1998.

[8] M.E. Tuckerman, Y. Liu, G. Ciccotti, and G.J. Martyna. Non-Hamiltonian molecular dynamics: Generalizing Hamiltonian phase space principles to non-Hamiltonian dynamics. *J. Chem. Phys.*, 115(4):1678–1702, 2001.

[9] S. Melchionna. Constrained systems and statistical distribution. *Phys Rev. E*, 61(6):6165–6170, 2000.

[10] A.J. van der Schaft and B.M. Maschke. On the Hamiltonian formulation of nonholonomic mechanical systems. *Rep. Math. Phys.*, 34(2):225–233, 1994.

[11] R. Abraham, J.E. Marsden, and T. Ratiu. *Manifolds, Tensor Analysis, and Applications.* Springer, New York, 1988.

[12] G. Gallavotti. *The Elements of Mechanics.* Springer, New York, 1983.

[13] V.I. Arnold. *Mathematical Methods of Classical Mechanics.* Springer, New York, 1978.

[14] H. Rubin and P. Ungar. Motion under a strong constraining force. *Comm. Pure Appl. Math.*, 10:65–87, 1957.

[15] R. Herbst and I. Froese. Realizing holonomic constraints in classical and quantum mechanics. *Commun. Math. Phys.*, 220:489–535, 2001.

[16] A.D. Lewis. Simple mechanical control systems with constraints. *IEEE Transactions on Automatic Control*, 45(8):117–125, 2000.

[17] J.E. Marsden and T.S. Ratiu. *Introduction to Mechanics und Symmetry.* Springer, New York, 1999.

[18] V. Guillemin and S. Sternberg. *Symplectic Techniques in Physics.* Cambridge University Press, 1984.

[19] R. I. McLachlan and C. Scovel. Equivariant constrained symplectic integration. *J. Nonlinear Sci.*, 5:233–256, 1995.

[20] B. Leimkuhler and S. Reich. Symplectic integration in constrained Hamiltonian systems. *Math. Comp.*, 63:589–605, 1994.

[21] D. Frenkel and B Smit. *Understanding Molecular Dynamics: From Algorithms to Applications.* Academic Press, London, 2002.

[22] E.A. Carter, G. Ciccotti, J.T. Hynes, and R. Kapral. Constrained reaction coordinate dynamics for the simulation of rare events. *Chem. Phys. Lett.*, 156(5):472–477, 1989.

[23] W.K. den Otter. Thermodynamic integration of the free energy along a reaction coordinate in Cartesian coordinates. *J. Chem. Phys.*, 112(17):7283–7286, 2000.

[24] J.S. Liu. *Monte Carlo Strategies in Scientific Computing.* Springer, New York, 2001.

[25] E. Hairer, C. Lubich, and G. Wanner. *Geometric Numerical Integration.* Springer, Berlin, 2002.

[26] J.-P. Ryckart and A. Bellmanns. Molecular dynamics of liquid n-Butane near its boiling point. *Chem. Phys. Lett.*, 30(1):123–125, 1975.

[27] M.P. do Carmo. *Riemannian Geometry.* Birkhäuser, Boston, 1992.

[28] B.A. Dubrovin, A.T. Fomenko, and S.P. Novikov. *Modern Geometry – Methods and Applications: Part I. The Geometry of Surfaces, Transformation Groups, and Fields.* Springer, Berlin, 1984.