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Hamiltonian Molecular Dynamics for Computational Mechanicians and Numerical Analysts

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Abstract

Molecular dynamics (MD) is a computer simulation technique where the time evolution of a set of interacting atoms is approximated by integrating their equations of motion. Our goal is to explain the mathematical background of MD for practitioners and researchers in numerical analysis and computational mechanics. The vast majority of these practitioners and researchers work with continuum mechanics. In contrast, an atomistic method such as MD is both culturally and intellectually distinct. The recent interest in multiscale analysis, in particular, Atomistic-to-Continuum coupling necessitates a sophisticated understanding of MD, its goals, limitations and computational aspects.

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Contents

Appendix

Figures

1 Introduction

Molecular dynamics (MD) is a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion. Our goal is to motivate the methods of MD for practitioners and researchers in numerical analysis and computational mechanics. The vast majority of these practitioners and researchers work with continuum mechanics. In contrast, an atomistic method such as MD is both culturally and intellectually distinct. The recent interest in multiscale analysis, in particular, Atomistic-to-Continuum coupling necessitates a sophisticated understanding of MD, its goals, methods, and limitations.

In contrast to continuum methods where accurate trajectories are of interest, MD is rarely concerned with accurate trajectories. In point of fact, computing accurate trajectories is, in general, not possible. Instead, quantities of interest are statistical averages computed during the sampling of phase space. Primarily, our manuscript indicates why MD works from a mathematical perspective. We point out that our manuscript does not focus on geometric time integration issues, rather what are the relevant features of a time integrator that results in an acceptable sampling of phase space. Much of our discussion revolves around explaining in a mathematical fashion, both formally and informally, what the MD community of users and researchers has learned via dint of hard work and careful physical reasoning.

Key concepts. We identified in the literature a number of concepts that play key roles in assessing the numerical integration of a Hamiltonian system in order to ascertain whether phase space is sampled accordingly.

1. **Measure preservation:** This concept relates a map (transformation) $T : \mathscr{X} \to \mathscr{X}$ to a probability-measure μ on the space $\mathscr{X}$: T is said to preserve the measure μ if for all measurable sets $A \subset \mathscr{X}$, the preimage[1] of A has the same measure as A, that is: $\mu(T^{-1}(A)) = \mu(A)$. If T is differentiable, and if μ is available in analytic form, then measure-preservation of μ by T is mathematically verifiable (see Section 4).

2. **Ergodicity:** A measure-preserving map $T : \mathscr{X} \to \mathscr{X}$ is said to be ergodic if $\mathscr{X}$ cannot be divided into two non-trivial pieces that are T-invariant[2]. In this context, a set is non-trivial if its measure is neither 0 nor 1. In the statistical physics literature ergodicity is typically defined to be the property that for any statistical quantity Ψ, if we view the map T as a transition from one moment to the next, the "time"-averages of T converge to the average of T over the space $\mathscr{X}$, that is:
$$\lim_{n\to\infty} \frac{1}{n} \sum_{i=0}^{n-1} \Psi(T^i x) = \int_{\mathscr{X}} \Psi(y) d\mu(y) \tag{1.1}$$
for almost all $x \in \mathscr{X}$. As usual, $T^i(x)$ means $\overbrace{T(T(\ldots(T}^{i \text{ times}}(x)\ldots)$, with $T^0(x) = x$. The equality (1.1) is useful for computations because it allows approximating the spatial average on its right-hand side – the desired quantity – by means of the time-averages on the left-hand side, which are available through computations. The mathematical community regards (1.1)

[1] The preimage of A (through T) is the collection of points $x \in \mathscr{X}$ such that $T(x) \in A$.

[2] The set A is T-invariant if $T^{-1}(A) = A$, which means that x belongs to A if and only if $T(x)$ belongs to A.

rather as a consequence of ergodicity than ergodicity itself. We emphasize that assessing the ergodicity of a map in practical situations is usually a difficult task for high-dimensional systems.

3. **Sensitive dependence on initial conditions (SDIC):** A map $T : \mathscr{X} \to \mathscr{X}$ is said to have SDIC if to each point $x \in \mathscr{X}$ there are arbitrarily close points x', such that the positive orbit[3] starting at x' eventually diverges from the one starting at x. As a consequence, trajectories for a map having SDIC cannot be computed numerically for long periods of time in a classical sense (that is, point-to-point matching between exact value and computed value), because even the unavoidable round-off error will naturally be magnified, thus potentially rendering computed values that are far from the actual values.

4. **Symplecticity:** A differential map $T : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ is symplectic if at each point $x \in \mathbb{R}^{2d}$ its Jacobian $T'(x)$ satisfies the algebraic equation (2.8). If an analytic expression is given for T, then the symplecticity of T is normally analytically verifiable. As will be shown in Sections 2 and 5, the concept of symplecticity is intimately related to the definition of Hamiltonian systems of differential equations.

There are various links between these concepts in the context of Hamiltonian systems. First, the flow map of a Hamiltonian system is symplectic. Second, a symplectic map from $\mathbb{R}^{2d}$ to itself preserves the Lebesgue measure, though symplecticity is much stronger than just this. Third, it has been observed empirically that the flows of many systems arising in molecular dynamics simulations have SDIC and are ergodic. The former property implies that we cannot expect to compute accurate trajectories of the Hamiltonian flow map. SDIC and ergodicity are two phenomenon playing complementary roles in computing long-term trajectories of flow-maps: while SDIC prevents the computation of accurate trajectories, ergodicity allows the extraction of statistical information from the same computations. In terms of numerical computations, the current state of affairs is that, if a discretization of the flow map $T \approx \Phi_{\Delta t}$ is symplectic, then averages of a statistic Ψ computed along orbits of T will converge to the desired spatial average as the time step Δt converges to 0. Justifying this situation mathematically is a challenging open problem. Another open question is whether symplecticity is necessary for accurately capturing accurate statistics, or if weaker conditions suffice. Our conjecture is that if T approximately conserves energy and preserves the projection onto S of the Lebesgue measure, then accurate statistical information is extracted from T.

The paper is organized as follows: In Section 2 we review the basic properties of Hamiltonian systems. In Section 3 we present three classes of examples of Hamiltonian systems which we will use to demonstrate points later in the paper. We provide more mathematical background and language for the discussion above in Section 4. Section 5 is devoted to the question of what are necessary and sufficient conditions for numerical integrators to compute correct statistics, in light of the discussion from Section 4. We formulate some concluding remarks in the final section.

[3]The positive orbit of T starting at x is the set $\{T^n(x) \ : \ n \geq 0\}$.

2 Background information

This section quickly provides some background information on Hamiltonian dynamics. The reader is referred to [15] and the sources cited for an excellent introduction to Hamiltonian dynamics.

2.1 Mathematical model

The object of our discussion is the classical n-body problem for the regime of MD-simulations. As usual, if we denote the positions of n particles at time t particles by $\mathbf{q}(t) \in \mathbb{R}^{3n}$, then Newton's second law is

$$\mathbf{M}\ddot{\mathbf{q}} = \mathbf{F}(\mathbf{q}), \quad \mathbf{q}(0) = \mathbf{q}_0,\ \mathbf{p}(0) = \mathbf{p}_0 \tag{2.1}$$

where $\mathbf{M}$ is a diagonal matrix consisting of the particle masses. We assume that the force field is conservative, that is, there exists a *potential* $V : \mathbb{R}^{3n} \to \mathbb{R}$, such that

$$\mathbf{F}(\mathbf{q}) = -\nabla_{\mathbf{q}} V(\mathbf{q}) \ .$$

An additional level of abstraction is achieved by introducing the *Hamiltonian* or *energy* functional

$$H(\mathbf{q},\mathbf{p}) = \frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p} + V(\mathbf{q}), \tag{2.2}$$

where the vector of particle-momenta is denoted by $\mathbf{p} = \mathbf{M}\dot{\mathbf{q}}$. This notation implies that the system (2.1) is equivalent to

$$\left\{ \begin{array}{rcl} \dot{\mathbf{q}} & = & \nabla_{\mathbf{p}} H(\mathbf{q},\mathbf{p}) \\ \dot{\mathbf{p}} & = & -\nabla_{\mathbf{q}} H(\mathbf{q},\mathbf{p}) \end{array} \right. . \tag{2.3}$$

We define the matrix $\mathbf{J} = \left[\begin{array}{cc} 0 & \mathbf{I}_d \\ -\mathbf{I}_d & 0 \end{array} \right] \in \mathbb{R}^{2d\times 2d}$, and vector $\mathbf{z} = \left[\begin{array}{c} \mathbf{q} \\ \mathbf{p} \end{array} \right] \in \mathbb{R}^{2d}$, respectively, where $d = 3n$. Therefore, (2.3) can be rewritten as

$$\dot{\mathbf{z}} = \mathbf{J}\nabla_{\mathbf{z}} H(\mathbf{z}). \tag{2.4}$$

Under suitable assumptions [4] on (2.4), there is a unique solution for every initial condition, and we define the *flow map*

$$(\mathbf{z}_0, t) \mapsto \mathbf{z}(t) \stackrel{\text{def}}{=} \Phi_t(\mathbf{z}_0) \ .$$

The flow map $t \mapsto \Phi_t(\mathbf{z})$ satisfies (2.4) with initial condition $\Phi_0(\mathbf{z}) = \mathbf{z}$, i.e.,

$$\frac{d}{dt}\Phi_t(\mathbf{z}) = \mathbf{J}\nabla_{\mathbf{z}} H(\Phi_t(\mathbf{z})) \ . \tag{2.5}$$

At this point we need to introduce some terminology. The space given by the vectors $\mathbf{z}$ defined by (2.4) is called *phase space*. If we consider the trajectory of a single point in phase space under the action of the Hamiltonian flow we get a curve parametrized by time t.

A basic property satisfied by a solution of (2.4) is energy conservation. A simple calculation yields

$$\frac{d}{dt}H(\mathbf{z}) = (\nabla_{\mathbf{q}} H)^T\dot{\mathbf{q}} + (\nabla_{\mathbf{p}} H)^T\dot{\mathbf{p}} = (\nabla_{\mathbf{q}} H)^T\nabla_{\mathbf{p}} H + (\nabla_{\mathbf{p}} H)^T(-\nabla_{\mathbf{q}} H) = 0 \ ,$$

[4] For example, that $\nabla_{\mathbf{z}} H$ is globally Lipschitz continuous.

therefore $H(\mathbf{z})$ is constant of motion. A functional that is constant on solutions of (2.4) is called a *first integral*, therefore the Hamiltonian function is a first integral.

2.2 Symplecticity

Hamiltonian flows have another strong property: symplecticity. By differentiating (2.5) with respect to $\mathbf{z}$ we conclude that the derivative with respect to the initial condition, or Jacobian

$$\mathbf{F}_t(\mathbf{z}) = \frac{\partial}{\partial \mathbf{z}} \Phi_t(\mathbf{z}) \tag{2.6}$$

satisfies the linear differential equation

$$\frac{d}{dt}\mathbf{F}_t(\mathbf{z}) = \mathbf{J}\partial^2_{\mathbf{zz}} H(\Phi_t(\mathbf{z}))\mathbf{F}_t(\mathbf{z}) \,, \tag{2.7}$$

with $\mathbf{F}_0(\mathbf{z}) = \mathbf{I}_{2d}$. A differentiable map $\mathbf{T} : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ is called symplectic if the Jacobian $\mathbf{A} \equiv \partial \mathbf{T}/\partial \mathbf{z}$ satisfies the matrix relation

$$\mathbf{A}^T \mathbf{J} \mathbf{A} = \mathbf{J} \tag{2.8}$$

for all points $\mathbf{z}$.

Theorem 2.1. *For all t, the Jacobian of the flow map (given by* (2.6)*) satisfies (2.8), i.e.*

$$(\mathbf{F}_t(\mathbf{z}))^T \mathbf{J} \mathbf{F}_t(\mathbf{z}) = \mathbf{J}, \tag{2.9}$$

for all $t \in \mathbb{R}$ and $\mathbf{z} \in \mathbb{R}^{2d}$ and so the flow Φ_t is symplectic.

Proof. For example, see [15, p 54]. □

To understand what symplecticity is in geometric terms we need to define a particular bilinear form (see also [15, pp 56–61]):

$$\Omega(\mathbf{z}_2, \mathbf{z}_1) \stackrel{\text{def}}{=} -\mathbf{z}_2^T \mathbf{J} \mathbf{z}_1, \quad \text{for } \mathbf{z}_1, \mathbf{z}_2 \in \mathbb{R}^{2d} \,. \tag{2.10}$$

If $d = 1$, then

$$\Omega(\mathbf{z}_2, \mathbf{z}_1) = x_2 y_1 - y_2 x_1, \quad \mathbf{z}_1 \equiv \begin{bmatrix} x_1 \\ y_1 \end{bmatrix}, \quad \mathbf{z}_2 \equiv \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}, \quad x_i, y_i \in \mathbb{R}. \tag{2.11}$$

The right-hand-side of (2.11) is the signed area of the parallelogram spanned by the vectors $\mathbf{z}_1$ and $\mathbf{z}_2$ in $\mathbb{R}^2$. In general, where

$$\mathbf{z}_1 \equiv \begin{bmatrix} \mathbf{x}_1 \\ \mathbf{y}_1 \end{bmatrix}, \quad \mathbf{z}_2 \equiv \begin{bmatrix} \mathbf{x}_2 \\ \mathbf{y}_2 \end{bmatrix}, \quad \mathbf{x}_i, \mathbf{y}_i \in \mathbb{R}^d,$$

we have that

$$\Omega(\mathbf{z}_2, \mathbf{z}_1) = \mathbf{x}_2^T \mathbf{y}_1 - \mathbf{y}_2^T \mathbf{x}_1 = \sum_{i=1}^{d} \mathbf{x}_{2,i} \mathbf{y}_{1,i} - \mathbf{y}_{2,i} \mathbf{x}_{1,i}. \tag{2.12}$$

In words, $\Omega(\mathbf{y}, \mathbf{x})$ is obtained by summing up the signed areas of the projections on the (q_i, p_i)-planes of the parallelogram spanned by $\mathbf{z}_2$ and $\mathbf{z}_1$.

To see the relation between this two-form and the flow, let us imagine a tiny parallelogram at point $\mathbf{z}$ in phase space with infinitesimal sides $\mathbf{dz}_1, \mathbf{dz}_2$. If we apply the two-form Ω to this parallelogram we get $\Omega(\mathbf{dz}_1, \mathbf{dz}_2)$. Now under the flow map this rectangle is mapped to a parallelogram at $\Phi_t(\mathbf{z}_1, \mathbf{z}_2)$ with sides $\mathbf{F}_t(\mathbf{z})\mathbf{dz}_1$, $\mathbf{F}_t(\mathbf{z})\mathbf{dz}_2$. Looking at the two form applied to the sides of this parallelogram we obtain (dropping the dependence on $\mathbf{z}$)

$$\Omega(\mathbf{F}_t\mathbf{dz}_1, \mathbf{F}_t\mathbf{dz}_2) = -\mathbf{dz}_1^T\mathbf{F}_t^T\mathbf{J}\mathbf{F}_t\mathbf{dz}_2 = -\mathbf{dz}_1^T\mathbf{J}\mathbf{dz}_2 = \Omega(\mathbf{dz}_1, \mathbf{dz}_2),$$

where we have used (2.9). So symplecticity is equivalent to the invariance of the bilinear form Ω under the flow.

An equivalent way to express symplecticity is through the Helmholtz circulation theorem [14, p.180]. Imagine a two-dimensional surface Ω in $(\mathbf{q}, \mathbf{p})$ phase space, with a closed simply connected boundary curve $\partial\Omega$. When we map the surface and loop forward with the flow map, we again obtain a surface $\Phi_t(\Omega)$ with a boundary curve given by the closed, simply connected loop $\Phi_t(\partial\Omega)$, since the flow is one-to-one and continuous. We define the circulation $\partial\Omega$ to be the following integral around the loop

$$\int_{\partial\Omega} \mathbf{p}\cdot\mathbf{dq} = \sum_{i=1}^{d} \int_{\partial\Omega} p_i dq_i.$$

By the Stokes Theorem

$$\int_{\partial\Omega} p_i dq_i = \int_{\Omega} dp_i dq_i,$$

which is just the area of the surface Ω projected onto the (q_i, p_i) plane. If the flow map is symplectic then the sum of all these areas is preserved and hence so is the circulation of $\partial\Omega$. This is Helmholtz's circulation theorem: the circulation of a closed curve in $(\mathbf{q}, \mathbf{p})$ space is preserved by the flow of a Hamiltonian system:

$$\int_{\partial\Omega} \mathbf{p}\cdot\mathbf{dq} = \int_{\Phi_t(\partial\Omega)} \mathbf{p}\cdot\mathbf{dq}\ .$$

We have seen that the flow Φ_t generated by the Hamiltonian differential equations (2.4) is symplectic for all t. However, it is not true that any family of symplectic maps Φ_t continuously parametrized by $t \geq 0$ with $\Phi_0 = I$ is the flow of a system of equations of the form (2.4). However, the statement is true if we replace the autonomous Hamiltonian systems of (2.4) with time-varying Hamiltonian systems. That is, Φ_t is a symplectic flow if and only if there is a function $H(\mathbf{z}, t)$ such that Φ_t is the time-t flow map of the equations

$$\dot{\mathbf{z}} = \mathbf{J}\nabla_{\mathbf{z}} H(\mathbf{z}, t). \tag{2.13}$$

This result will be important later when we consider symplectic integration of Hamiltonian systems. Note that solutions to (2.13) do not conserve an energy, though it is true that along solution trajectories $\mathbf{z}(t)$

$$\frac{dH}{dt}(\mathbf{z}, t) = \frac{\partial H}{\partial t}(\mathbf{z}, t),$$

where the total derivative dH/dt is given by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{\mathbf{z}}\nabla_{\mathbf{z}}. \tag{2.14}$$

Later, we will use this total derivative again where we will refer to it as the material derivative.

2.3 Phase space volume conservation

The Hamiltonian set of equations (2.3) gives rise to an important conservation law that has an analogy in continuum mechanics.

Theorem 2.2 (Liouville[5])**.** *Let the Hamiltonian set of equations (2.3) be given. If Ω denotes a region, or volume, of phase space, denote $\Omega_t = \Phi_t(\Omega)$, and by $V(t) = \mathrm{vol}(\Omega_t)$. Then*

$$\frac{dV(t)}{dt} = 0. \tag{2.15}$$

Proof. We have

$$\frac{dV}{dt} = \frac{d}{dt}\int_{\Omega_t} d\mathbf{z} = \int_{\partial\Omega_t} \dot{\mathbf{z}}\cdot\mathbf{n}dS = \int_{\Omega_t} \nabla_{\mathbf{z}}\cdot\dot{\mathbf{z}}\, d\mathbf{z}.$$

Liouville's theorem is established because

$$\nabla_{\mathbf{z}}\cdot\dot{\mathbf{z}} = \nabla_{\mathbf{z}}\cdot\mathbf{J}\nabla_{\mathbf{z}}H(\mathbf{z}) = (\nabla_{\mathbf{q}}\cdot\nabla_{\mathbf{p}} - \nabla_{\mathbf{p}}\cdot\nabla_{\mathbf{q}})H(\mathbf{q},\mathbf{p}) = 0, \tag{2.16}$$

where we used the Hamiltonian set of equations (2.4). □

The identity $\nabla_{\mathbf{z}}\cdot\dot{\mathbf{z}} = 0$ also arises as a constraint when describing an incompressible fluid. So the flow of points in phase space is like an incompressible fluid. We often say that the flow of a Hamiltonian system preserves phase space volume.

Phase space volume preservation can also be viewed as a direct consequence of symplecticity and also holds true for time-varying Hamiltonian flows such as (2.13). To see this, take the determinant of both sides of (2.9). Since the determinant of $\mathbf{J}$ is one, it follows that $|\det\mathbf{F}_t| = 1$, which shows that sets do not change their volume under the action of the flow map. This implies that a symplectic map preserves the Lebesgue measure, a result which will be important for us later.

2.4 Ensembles

Often in molecular dynamics we do not consider trajectories started from a single initial condition, but what happens to an infinite collection of points in phase space distributed according to some probability density. These densities are often called *ensembles* in the MD literature. Continuing our analogy with the fluid flow, if phase space volume corresponds to an incompressible fluid, we can think of an ensemble as the local density of a passive trace in that fluid.

Let $\rho(\mathbf{z},t)$ be the density of a tracer at time t and point $\mathbf{z}$ in a fluid with velocity field $\dot{\mathbf{z}}$. For now we will not assume that the fluid is incompressible. To understand how ρ evolves in time consider a fixed volume of phase space V and let $A(t)$ be the amount of tracer in it at time t. Since $A(t)$ is the integral of $\rho(\mathbf{z},t)$ over V we have

$$\dot{A}(t) = \int_V \frac{\partial}{\partial t}\rho(t,\mathbf{z})d\mathbf{z}.$$

The rate of change of $A(t)$ is determined by the rate of flow of ρ into the volume:

$$\dot{A}(t) = \int_{\partial V} \rho(t,\mathbf{z})\dot{\mathbf{z}}\cdot d\mathbf{S}(\mathbf{z}) = \int_V \nabla_{\mathbf{z}}\cdot(\rho(\mathbf{z})\dot{\mathbf{z}})d\mathbf{z},$$

[5] Joseph Liouville, French mathematician (1809 - 1882).

where we have used the divergence theorem, ∂V is the boundary surface of V and $d\mathbf{S}$ is a volume element of the surface. Equating these two expressions for $\dot{A}(t)$ and noting that they hold for all volumes V we obtain

$$\frac{\partial}{\partial t}\rho + \nabla_{\mathbf{z}} \cdot (\dot{\mathbf{z}}\rho) = 0.$$

This is the equation for the density of a passive tracer in a general fluid with velocity field $\dot{\mathbf{z}}$.

When we make the assumption that the fluid is incompressible, which phase fluid is, we use $\nabla_{\mathbf{z}} \cdot \dot{\mathbf{z}} = 0$ to obtain

$$\frac{\partial \rho}{\partial t} + \dot{\mathbf{z}} \cdot \nabla_{\mathbf{z}} \rho = 0. \tag{2.17}$$

This is the Eulerian view of the evolution of a density of states. To get the Lagrangian view we use the material derivative introduced in (2.14) to get

$$\frac{d}{dt}\rho = 0.$$

In words, the local density of states in an ensemble remains constant as we follow the motion of one point in phase space along a trajectory.

The ensembles that are of particular interest in molecular dynamics are invariant ensembles, ones ρ for which $\partial\rho/\partial t = 0$ for all z. These are also called invariant distributions or densities. They must satisfy

$$\dot{\mathbf{z}} \cdot \nabla_{\mathbf{z}} \rho = 0.$$

A simple sufficient condition for an ensemble to be invariant is if $\rho(\mathbf{z}) = f(H(\mathbf{z}))$ for some function f. To see this, note that

$$\begin{aligned} \dot{\mathbf{z}} \cdot \nabla_{\mathbf{z}} f(H(\mathbf{z})) &= (\mathbf{J}\nabla_{\mathbf{z}} H(\mathbf{z}))^T f'(H(\mathbf{z}))\nabla_{\mathbf{z}} H(\mathbf{z}) \\ &= f'(H(\mathbf{z}))(\nabla_{\mathbf{z}} H(\mathbf{z})^T \mathbf{J}\nabla_{\mathbf{z}} H(\mathbf{z})). \end{aligned}$$

Since $\mathbf{J}^T = -\mathbf{J}$ it can be checked that $\mathbf{z}^T\mathbf{J}\mathbf{z} = 0$ for all vectors $\mathbf{z}$. This shows that ρ is invariant under the flow. Two important families of invariant ensembles in molecular dynamics are the *canonical ensemble* given by

$$\rho(\mathbf{z}) \propto e^{\beta H(\mathbf{z})}$$

for a parameter β, and the *micro-canonical ensemble* given by

$$\rho(\mathbf{z}) \propto \delta(H(\mathbf{z}) - E)$$

for parameter E where δ is the Dirac delta function. Be warned that the latter expression is easy to misinterpret. We shall discuss it in detail in Section 4.

3 Examples of Hamiltonian systems

Here we present three examples of families of Hamiltonian systems. We will refer back to these later in the article.

3.1 Linear oscillators

One important basic example of a Hamiltonian system is the simple harmonic oscillator with Hamiltonian

$$H(q,p) = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}kq^2$$

where k and m are positive constants. Given initial conditions, the exact solution is available for all times t. A natural generalization is the case of d oscillators on the line with Hamiltonian

$$H(\mathbf{q},\mathbf{p}) = \frac{1}{2}\mathbf{p}^T\mathbf{M}^{-1}\mathbf{p} + \frac{1}{2}\mathbf{q}^T\mathbf{K}\mathbf{q} \tag{3.1}$$

where $\mathbf{M}$ is a $d \times d$ diagonal matrix with positive entries and $\mathbf{K}$ is symmetric positive definite. This Hamiltonian leads to the system of differential equations

$$\dot{\mathbf{q}} = \mathbf{M}^{-1}\mathbf{p}, \quad \dot{\mathbf{p}} = -\mathbf{K}\mathbf{q},$$

which can be written as

$$\mathbf{M}\ddot{\mathbf{q}} = -\mathbf{K}\mathbf{q}.$$

This system can be decomposed into a system of d independent oscillators using a theorem from matrix analysis [11, Theorem 4.5.15]: if $\mathbf{M}$ and $\mathbf{K}$ are symmetric and $\mathbf{M}^{-1}\mathbf{K}$ is diagonalizable, then there is a non-singular matrix $\mathbf{S}$ such that both $\widetilde{\mathbf{M}} = \mathbf{S}\mathbf{M}\mathbf{S}^T$ and $\widetilde{\mathbf{K}} = \mathbf{S}\mathbf{K}\mathbf{S}^T$ are diagonal. (The matrix $\mathbf{M}^{-1}\mathbf{K}$ is diagonalizable because it is similar to the symmetric matrix $\mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2}$.) Letting $\mathbf{S}\widetilde{\mathbf{q}} = \mathbf{q}$ gives

$$\widetilde{\mathbf{M}}\ddot{\widetilde{\mathbf{q}}} = -\widetilde{\mathbf{K}}\widetilde{\mathbf{q}}.$$

If we let $\mathbf{S}\widetilde{\mathbf{p}} = \mathbf{p}$ then we obtain

$$\dot{\widetilde{\mathbf{q}}} = \widetilde{\mathbf{M}}^{-1}\widetilde{\mathbf{p}}, \quad \dot{\widetilde{\mathbf{p}}} = -\widetilde{\mathbf{K}}\widetilde{\mathbf{q}}.$$

But this is equivalent to d uncoupled one-degree-of-freedom systems

$$\dot{\widetilde{q}}_i = m_i^{-1}\widetilde{p}_i, \quad \dot{\widetilde{p}}_i = -k_i\widetilde{q}_i.$$

So our system has d first integrals: the quantities $\widetilde{p}_i^2/2m_i + k_i\widetilde{q}/2$ for $i = 1,\ldots,d$. This shows that the system with Hamiltonian function (3.1) is an example of an **integrable** Hamiltonian system. An integrable Hamiltonian system has d independent first integrals.

Though the Hamiltonian systems that arise in molecular dynamics are almost never integrable, this example provides an important extreme example of the kind of behavior a Hamiltonian system can exhibit.

3.2 Sinai scatterers

Consider a two-dimensional periodic domain with two particles in motion on it. The particles consist of perfect circles of a fixed radius r. When the centers of the particles are further than $2r$ apart they undergo free motion. However, when they meet they undergo a perfectly elastic instantaneous collision. This means that energy (and momentum) are conserved and they do not overlap at all. The particles can be thought of as idealized billiard balls that move around a periodic pool table without friction or dissipation of any kind. Formally, we can describe this system as a Hamiltonian system with Hamiltonian

$$H(\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2) = V(\|\mathbf{q}_1 - \mathbf{q}_2\|) + \frac{1}{2}\|\mathbf{p}_1\|^2 + \frac{1}{2}\|\mathbf{p}_2\|^2 \tag{3.2}$$

where V is defined for $x \geq 0$ by

$$V(x) = \begin{cases} \infty, & \text{if } x < 2r, \\ 0, & \text{otherwise.} \end{cases}$$

An interesting symmetry of this system is that increasing the velocity of both particles by a constant scalar factor is equivalent to running the system twice as fast:

$$\Phi_t(\mathbf{q}, \alpha\mathbf{p}) = \Phi_{\alpha t}(\mathbf{q}, \alpha\mathbf{p}).$$

Besides, the Hamiltonian H the system has a few other first integrals. Since the particles only experience forces due to mutual collisions, total momentum $\mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2$ is conserved. Since $\dot{\mathbf{q}} = \mathbf{p}$, if we start with the initial conditions such that $\mathbf{p}(0) = \mathbf{0}$, then $\mathbf{q}(t) = \mathbf{q}(0)$ for all time. So a system in 8-dimensional phase space has 5 conserved quantities and therefore moves on a submanifold of dimension 3.

One way to simplify this system conceptually is to eliminate the motion of the center of mass. Let $\bar{\mathbf{q}} = (\mathbf{q}_1 + \mathbf{q}_2)/\sqrt{2}$, $\bar{\mathbf{p}} = (\mathbf{p}_1 + \mathbf{p}_2)/\sqrt{2}$, and $\bar{\mathbf{q}} = (\mathbf{q}_1 + \mathbf{q}_2)/\sqrt{2}$, $\bar{\mathbf{p}} = (\mathbf{p}_1 + \mathbf{p}_2)/\sqrt{2}$. This is a canonical change of variables, so the equations remain Hamiltonian with function

$$\tilde{H}(\widetilde{\mathbf{q}}, \widetilde{\mathbf{p}}, \bar{\mathbf{q}}, \bar{\mathbf{p}}) = V(\sqrt{2}\|\widetilde{\mathbf{q}}\|) + \frac{1}{2}\|\widetilde{\mathbf{p}}\|^2 + \frac{1}{2}\|\bar{\mathbf{p}}\|^2.$$

Ignoring the dynamics of $\bar{\mathbf{q}}$ and $\bar{\mathbf{p}}$, we can reinterpret this system physically. Since $\widetilde{q}_1$ and $\widetilde{q}_2$ live in the two-dimensional torus $\mathbb{T}^2$ so does $\widetilde{q}$. So we can imagine our system to be a point particle in motion on $\mathbb{T}^2$. The particle moves freely except for collisions with a circular scatterer of radius $\sqrt{2}r$. Sinai [23] proved that this system is ergodic on the surface of constant energy for any non-zero energy.

One important way the Sinai scatterer has been modified is to have a soft scatterer rather than a hard one. Instead of the hard potential given in (3.2) a smooth potential is used, but still maintaining $V(x) = 0$ for $x \geq 2r$. This had been investigated extensively by Donnay and Liverani. For some choices of V the system is ergodic and for others it is not.

3.3 Lennard–Jones liquid

Here finally we consider a realistic system from the point of view of molecular dynamics simulations. This class of systems contains all the problems and features of more realistic systems. This is a model for a three-dimensional system of particles interacting on a periodic domain.

Consider a three-dimensional periodic domain of size $L \times L \times L$ units. We imagine a system of n point particles interacting through a potential. We let $\mathbf{q} \in \mathbb{T}^{3n}$ and $\mathbf{p} \in \mathbb{R}^{3n}$ denote the positions and velocities of the particles, with $q_i \in \mathbb{T}^3, p_i \in \mathbb{R}^3$ denoting the position and velocity of particle i. The motion of the system is described with Hamiltonian

$$H(\mathbf{q},\mathbf{p}) = \frac{1}{2}\sum_i \|p_i\|^2 + \sum_{i<j} V_{LJ}(\|q_i - q_j\|).$$

Here V_{LJ} denotes the famous Lennard-Jones potential. In order to make the range of interaction of particles finite normally a truncated version of the potential is being used:

$$V_{LJ}(r) = \begin{cases} 4\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right), & \text{if } r \le r_{\text{cutoff}}, \\ 0, & \text{otherwise.} \end{cases}$$

Like the Sinai system of two balls on a periodic domain, this system also has first integrals besides H. In particular, total linear momentum is conserved. And if this quantity is initialized to 0 then then the sum of all the positions is conserved. Normally, this reduction is not performed analytically. Typically, when simulating the system the total linear momentum is initialized to 0.

4 Computing statistics, ergodicity, and chaotic behavior

The flow map associated with a Hamiltonian is a family of *measure-preserving* transformations in phase-space. When numerically simulated, the high-dimensional Hamiltonian systems that arise in molecular dynamics appear to be *chaotic* and *ergodic*. While the dynamics being chaotic prevents the possibility of numerically following trajectories for a long time, the dynamics being ergodic gives that almost all trajectories sample the phase-space correctly, thus allowing to compute global statistical information. *Generically*, measure-preserving maps are both chaotic and ergodic. However, Hamiltonian flow-maps are not generic within the set of measure-preserving transformations. In this section we introduce the mathematical framework in which the ideas above reside. In the end we summarize the ideas in light of the discussed concepts.

4.1 Measure preservation and the microcanonical measure

We have shown in Theorem 2.2 that the Hamiltonian flow preserves volume in the phase-space $\mathbb{R}^{2d}$. At the same time, the flow preserves energy as well, meaning that the actual dynamics occurs on a subsurface of $\mathbb{R}^{2d}$, namely the surface of constant energy

$$\mathscr{S}_E = \{z \in \mathbb{R}^{2d} \ : \ H(z) = E\} \ .$$

Therefore global volume conservation, as expressed in (2.15), is less relevant for the dynamics than would be a statement about measure-preservation **on the surface** $\mathscr{S}_E$.

Abstract measure preservation. As mentioned in Section 1, given a probability space $(\mathscr{X}, \Sigma, \mu)$[6], a map $T : \mathscr{X} \to \mathscr{X}$ is said to preserve the measure μ if

$$\mu(T^{-1}(A)) = \mu(A), \ \forall A \subset \mathscr{X}, \ A \text{ measurable} \ , \tag{4.1}$$

where $T^{-1}(A)$ is the pre-image of A, that is, $T^{-1}(A) = \{x \in \mathscr{X} \ : \ T(x) \in A\}$. If T is one-to-one, onto, and T^{-1} is measurable, then (4.1) is equivalent to

$$\mu(T(A)) = \mu(A), \ \forall A \subset \mathscr{X}, \ A \text{ measurable} \ , \tag{4.2}$$

where $T(A)$ is the image of A. Since the flows of Hamiltonian systems are always one-to-one, we will restrict our discussion to this case and often use the definition of measure-preservation in (4.2).

If $\mathscr{X}$ is equipped with a differentiable structure as well, and if the probability measure is given by a density m with respect to a volume-form dS, i.e $\mu = m\,dS$, then the change-of-variable formula (see [25]) implies that

$$\int_A m(x)\,dS(x) = \mu(A) \ = \ \mu(T(A)) = \int_{T(A)} m(y)\,dS(y) \overset{y=T(x)}{=} \int_A |\det T'(x)| m(T(x))\,dS(x) \ ,$$

where $T'(x)$ is the Jacobian matrix of T at x. Since the above holds for every measurable set A, we conclude that T preserves the measure μ if and only if the integrands above are equal almost

[6] Σ is a σ-algebra of subsets of $\mathscr{X}$, and $\mu : \Sigma \to [0,\infty)$ is a probability measure.

everywhere (a.e.) with respect to the measure dS, that is,

$$|\det T'(x)| = \frac{m(x)}{m(T(x))},\ a.e.\ [dS]\ . \tag{4.3}$$

For example, if $\mathscr{X} = \mathbb{R}^N$ and $m \equiv 1$, then μ is the Lebesgue measure, and T preserves μ if and only if $|\det T'(x)| = 1$ a.e.

Microcanonical measure. The fact that the Hamiltonian flow Φ_t preserves energy may be restated as $\Phi_t(\mathscr{S}_E) \subseteq \mathscr{S}_E$. Since the dynamics is restricted to the surface $\mathscr{S}_E$, the question is to identify a nontrivial measure supported on $\mathscr{S}_E$ that is preserved by Φ_t. For all Hamiltonian systems there is at least one invariant measure supported on $\mathscr{S}_E$ called the microcanonical measure. There are two equivalent ways of describing it.

Firstly, it can be described via an integral of a generalized function over all of $\mathbb{R}^{2d}$. This is how it is usually described in the statistical mechanics and MD literatures (see, for example, [13, 21, 27]):

$$\mu_E(A) = \int_A \delta(H(\mathbf{z}) - E)d\mathbf{z}\ ,\ \text{for } A \subseteq \mathbb{R}^{2d}, \tag{4.4}$$

with δ the Dirac delta-function. Note that the measure μ_E is defined for all subsets of $\mathbb{R}^{2d}$, but is singular, since it is supported on $\mathscr{S}_E$. The formula (4.4) often gives the false impression that the all points on $\mathscr{S}_E$ are weighted equally, which is not the case. One way to interpret this formula is to consider a sequence of functions $\delta_n \colon \mathbb{R} \to \mathbb{R}$ that converge to δ weakly[7] as $n \to \infty$. This means that

$$\int \delta_n(x)f(x)dx \to \int \delta(x)f(x)dx = f(0)$$

as $n \to \infty$ for all smooth $f \colon \mathbb{R} \to \mathbb{R}$. Then we define $\mu_E(A)$ as the limit as $n \to \infty$ of

$$\mu_{E,n}(A) = \int_A \delta_n(H(\mathbf{z}) - E)d\mathbf{z}. \tag{4.5}$$

This limit exists and does not depend on the specific choice of functions δ_n, as we show in Appendix A.

Secondly, we can define the microcanonical measure via a surface integral on $\mathscr{S}_E$. The dynamical systems literature [4] provides the following explicit formula for the microcanonical measure μ_E in terms of the volume-form dS_{2d-1} of $\mathscr{S}_E$. Namely, for measurable $A \subset \mathbb{R}^{2d}$

$$\mu_E(A) = \int_{A \cap \mathscr{S}_E} \frac{dS_{2d-1}(\mathbf{z})}{\|\nabla H(\mathbf{z})\|}\ , \tag{4.6}$$

where $\|\nabla H\|$ is the Euclidean norm of the gradient of the Hamiltonian. The two formulae (4.4) and (4.6) can be shown to be equivalent using the identity:

$$\int_{\mathbb{R}^{2d}} f(\mathbf{z})\delta(g(\mathbf{z}))d\mathbf{z} = \int_{g(\mathbf{z})=0} \frac{f(\mathbf{z})}{\|\nabla g(\mathbf{z})\|} dS(\mathbf{z})$$

where dS is the volume element on the surface $\{g(\mathbf{z}) = 0\}$. We prove this identity in Appendix A.

[7] A sequence of measures ν_n is said to converge *weakly* to another measure ν if $\int f d\nu_n \to \int f d\nu$ for all integrable functions f.

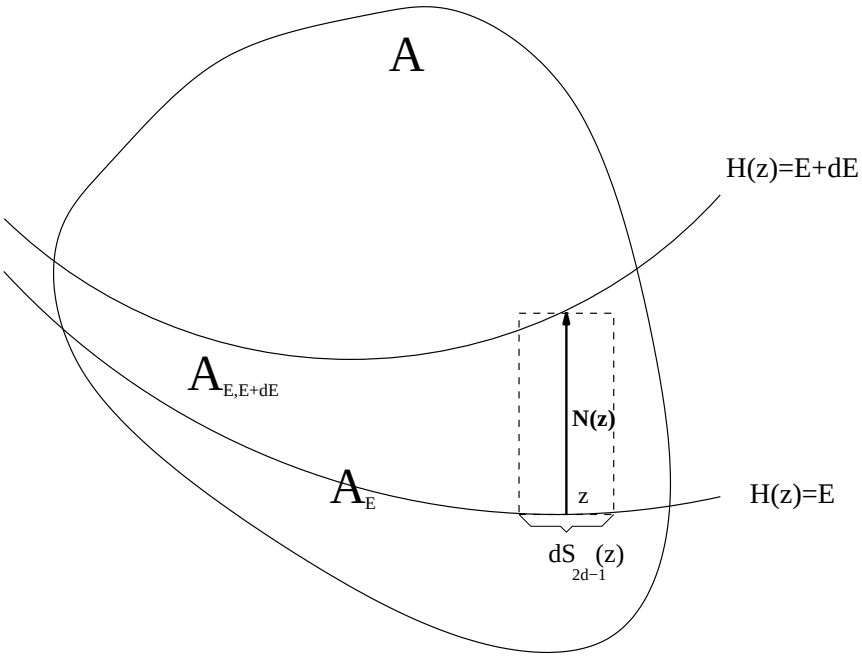

Figure 1.

To give a more intuitive way of seeing that the two formulae are equivalent, for $dE > 0$ a small number, we make a specific choice of δ_{dE} and see what the limit gives. Let $\delta_{dE}(x) = \frac{1}{dE}\mathbf{1}_{\{x\in[E,E+dE]\}}$[8]. We define a family of measures $\mu_{E,E+dE}$ on $\mathbb{R}^{2d}$ for $dE \geq 0$:

$$\mu_{E,E+dE}(A) = \int_A \delta_{dE}(H(\mathbf{z}) - E)d\mathbf{z}\ .$$

Since $\delta_{dE} \to \delta$ weakly as $dE \downarrow 0$, we see that $\mu_{E,E+dE}(A) \to \mu_E(A)$ as $dE \to 0$. If we denote by $A_{E,E+dE}$ the set $A \cap \{E \leq H(\mathbf{z}) \leq E + dE\}$, and by A_E the set $A \cap \mathscr{S}_E$ on the surface $\mathscr{S}_E$ we have

$$\mu_{E,E+dE}(A) = (dE)^{-1}\mathrm{vol}(A_{E,E+dE}).$$

With the help of Figure 1 we can express this volume as follows. We have

$$\mathrm{vol}(A_{E,E+dE}) = \int_{A_E} \|\vec{N}(\mathbf{z})\| dS_{2d-1}(\mathbf{z})\ , \tag{4.7}$$

where, for $\mathbf{z} \in A_E$, the vector $\vec{N}(\mathbf{z})$ is orthogonal to A_E at $\mathbf{z}$ and "ends" on the surface A_{E+dE} (see Figure 1). So $H(\mathbf{z} + \vec{N}(\mathbf{z})) = E + dE$. Since $\vec{N}(\mathbf{z})$ is orthogonal to A_E, $\vec{N}(\mathbf{z}) = t\nabla H(\mathbf{z})$ for some scalar t depending on $\mathbf{z}$. Using Taylor's theorem and neglecting terms of order dE^2

$$dE = H(\mathbf{z} + t\nabla H(\mathbf{z})) - H(\mathbf{z}) \approx t\|\nabla H(\mathbf{z})\|^2.$$

Hence we obtain the value

$$t \approx \frac{dE}{\|\nabla H(\mathbf{z})\|^2}\ .$$

[8]The *indicator function* of the set A is denoted by $\mathbf{1}_A$, and takes the value 1 for $x \in A$ and 0 for $x \notin A$.

So $\vec{N}(\mathbf{z}) = dE \cdot \nabla H(\mathbf{z})/\|\nabla H(\mathbf{z})\|$ and $\|\vec{N}(\mathbf{z})\| = dE/\|\nabla H(\mathbf{z})\|$. Putting it all together gives

$$\begin{aligned}\int_A \delta(H(\mathbf{z})-E)d\mathbf{z} &= \lim_{dE\downarrow 0} dE^{-1}\mathrm{vol}(A_{E,E+dE}) \\ &= \lim_{dE\downarrow 0} dE^{-1}\left(\int_{A_E}\frac{dE}{\|\nabla H(\mathbf{z})\|}dS_{2d-1}(\mathbf{z})+\mathscr{O}(dE^2)\right) = \int_{A_E}\frac{dS_{2d-1}(\mathbf{z})}{\|\nabla H(\mathbf{z})\|}\,.\end{aligned}$$

as required.

To show that the microcanonical measure is invariant under the system's flow we need to show that

$$\mu_E(A) = \mu_E(\Phi_t A) \tag{4.8}$$

for all measurable A and t. First we show that a measure ν given by a smooth density $\rho(\mathbf{z})$ is invariant when ρ is a stationary solution of Liouville's equation. For each set A

$$\nu(\Phi_t A) = \int_{\Phi_t A}\rho(\mathbf{y})d\mathbf{y} \overset{\mathbf{y}=\Phi_t(\mathbf{z})}{=} \int_A \rho(\Phi_t z)\underbrace{|\det(\Phi_t')(\mathbf{z})|}_{1}dz = \int_A \rho(\Phi_t z)dz\,.$$

Taking derivatives gives

$$\frac{d}{dt}\nu(\Phi_t A) = \int_A \frac{d}{dt}\rho(\Phi_t z)dz = \int_A \nabla_{\mathbf{z}}\rho\cdot\dot{\mathbf{z}}d\mathbf{z}$$

which is zero if ρ is an invariant density, thus establishing (4.8).

Recall that any density ρ of the form $\rho(\mathbf{z}) = f(H(\mathbf{z}))$ where f is a smooth function is invariant under Liouville's equation. So choosing δ_n to be smooth functions weakly converging to δ, the measures $\mu_{E,n}$ as defined in (4.5) are invariant:

$$\mu_{E,n}(A) = \mu_{E,n}(\Phi_t A)$$

for all A, n, and t. Taking the limit as $n\to\infty$ shows that μ_E is invariant as well. Thus the microcanonical measure of a Hamiltonian system is invariant under the flow of the Hamiltonian system. Another proof of this fact is given in Appendix B. Note that $\mu_E(A)$ is **not** proportional to the $(2d-1)$-dimensional area of $A\cap\mathscr{S}_E$, since there is a factor of $\|\nabla H\|^{-1}$ in the computation of $\mu_E(A)$, which normally varies with the point $\mathbf{z}$.

Throughout the reminder of this report, whenever it is assumed that $\mu_E(\mathscr{S}_E)<\infty$ we rescale μ_E in order to produce an invariant probability measure, that is, $\mu_E(\mathscr{S}_E)=1$.

Additional first integrals. Though the microcanonical measure is invariant for all E for any Hamiltonian system, if there are conserved quantities besides H, then the flow cannot be ergodic with respect to the microcanonical measure. For instance, suppose there is a first integral $K\colon \mathbb{R}^{2d}\to\mathbb{R}$ such that $K(\mathbf{z}) = K(\Phi_t\mathbf{z})$ for all $t,\mathbf{z}$. Then K may be "slicing" $\mathscr{S}_E$ into nontrivial flow-invariant sets. For example, if $k_1<k_2$ then the set $A=\{\mathbf{z}\in\mathscr{S}_E\ :\ k_1<K(\mathbf{z})<k_2\}$ is invariant, and it may have nontrivial measure, that is, $0<\mu_E(A)<1$, thus yielding a non-ergodic flow. In fact, the flow occurs on the intersection of levels sets of H with level sets of K:

$$\mathscr{S}_{E,L} = \{H(\mathbf{z})=E\}\cap\{K(\mathbf{z})=L\}\,.$$

If the level sets intersect transversely (the normal vectors of the two surfaces are not collinear at any point on the intersection), then the intersection is a surface (differentiable manifold) of dimension $(2d-2)$, and there is an invariant measure $\mu_{E,L}$ on $\mathscr{S}_{E,L}$ that plays the role of the microcanonical measure (see Appendix B for more details). This is generalized to any finite number of first integrals.

4.2 Sensitive dependence on initial conditions

Given a set $\mathscr{X} \subset \mathbb{R}^{2d}$, a map $T : \mathscr{X} \to \mathscr{X}$ is defined to be chaotic in the sense of Devaney [5, §1.8] if it has the following three properties:

1. It has **sensitive dependence on initial conditions (SDIC)**: There exists $\delta > 0$ such that, for any $x \in \mathscr{X}$ and any neighborhood V of x there exists $y \in V$ and an $n \geq 0$ such that $|T^n(x) - T^n(y)| > \delta$.

2. It is **topologically transitive**: For any two open sets $U, V \subset \mathscr{X}$ there is an $n \geq 0$ such that $T^n(U) \cap V \neq \emptyset$.

3. It has a dense set of periodic points: Any open set $U \subset \mathscr{X}$ contains at least one point x such that $T^n(x) = x$ for some $n \geq 0$.

To relate this definition to molecular dynamics, we consider the Hamiltonian flow map Φ_t for some fixed t restricted to $\mathscr{S}_E$ and ask whether it is chaotic. First we consider the empirical evidence from numerical experiments for this question, then we consider what theory has to say.

Empirical evidence. There is strong indirect evidence from molecular dynamics calculations that suggests flow maps have SDIC and are transitive. There is no numerical evidence either way to show that these maps have a dense set of periodic points, though this is unimportant. We review this evidence here.

We note that all the evidence available comes from studying numerical approximations to the flows of Hamiltonian systems and not the Hamiltonian systems themselves. Many properties of flows are not certainly not preserved exactly by numerical maps (for instance, energy conservation). It is conceivable that numerical discretization introduces spurious chaotic behavior in molecular dynamics systems, though no one believes it.

It appears that SDIC holds very strongly in almost all molecular dynamics simulations. A simple way to test this is to start with any $\mathbf{z} \in \mathscr{S}_E$ and simulate numerically with $\mathbf{z}$ as an initial condition. Make a small perturbation to the initial condition to get $\mathbf{z} + \delta\mathbf{z}$ and simulate starting from here for the same duration. Typically the two trajectories will rapidly diverge from one another. This behavior does not appear to depend on $\mathbf{z}$ or on the perturbation $\delta\mathbf{z}$. Moreover, the rate at which they diverge appears to be exponential for short time intervals.

Choose an initial condition and simulate it for a while. Make a perturbation to the initial condition on the order of machine precision and run the simulation again. The two trajectories will eventually diverge. This does not appear to depend on the system, the starting initial condition, or the direction or size of the perturbation.

The second property that is observed in many systems in molecular dynamics is that of topological transitivity. It should be remarked that transitivity is never observed directly, since the systems of MD are typically very high dimensional. What is observed is ergodicity, which we discuss in the next section.

SDIC and measure-preserving maps. The reason we discuss chaotic behavior lies in the fact that measure-preserving maps are generically chaotic, as described in Section 4.4. Both transitivity and SDIC are properties that impact the numerical simulation of Hamiltonian systems. As seen above, a map T has SDIC if small perturbations in the initial state are magnified by propagation through T. For example, a linear map T has SDIC if it has an expanding direction, i.e., an eigenvector v associated with an eigenvalue λ with $|\lambda| > 1$[9]. For a nonlinear map, a strong indication of SDIC is when its linearization $T'(x)$ has an expanding direction at each point x. If T is measure-preserving in $\mathbb{R}^{2d}$ then $|\det(T'(x))| = 1$, therefore

$$\prod_{\lambda \in \sigma(T'(x))} |\lambda| = 1 \, .$$

Therefore, unless all eigenvalues in $\sigma(T'(x))$ have absolute value 1, we will find at least one $\lambda \in \sigma(T'(x))$ with $|\lambda| > 1$. Loosely speaking, the linearization of a measure-preserving map is expected to have an expanding direction around each point. Hence, measure-preserving maps are expected to have SDIC. This heuristic argument is supported by rigorous mathematics, as explained in Section 4.4 (see also Theorem C.2(ii)); however, it should suffice to convince the reader that numerically following individual orbits of a measure-preserving map such as Φ_t for a long time period is an impossible task.

4.3 Phase-space sampling and ergodic theory

As stated in Section 4.2, generic measure-preserving maps are expected to have dense orbits. Assume that Φ_t has a dense orbit $O(\mathbf{z}_0) = \{\Phi_t(\mathbf{z}_0) \ : \ t > 0\}$, that is, an orbit that visits every neighborhood of every point on the surface $\mathscr{S}_E$. The idea of ergodicity is to use dense orbits such as $O(\mathbf{z}_0)$ for retrieving statistical information about the $\mathscr{S}_E$. So what does it mean to retrieve statistical information? The basic assumption is that the probability measure μ_E defined in (4.6) measures the fraction of time the dense orbit $O(\mathbf{z}_0)$ spends in a set A:

$$\mu_E(A) = \lim_{t\to\infty} \frac{\lambda(\{s \in [0,t] \ : \ \Phi_s(\mathbf{z}_0) \in A\})}{t} \, , \tag{4.9}$$

where λ is the Lebesgue measure on the real line. Given a statistic Ψ, that is, an integrable function on $\mathscr{S}_E$, we expect the long-term averaged value of Ψ on the orbit to be equal to the spatial average value of Ψ with respect to μ_E:

$$\lim_{t\to\infty} \frac{1}{t} \int_0^t \Psi(\Phi_s(\mathbf{z}_0)) ds = \int_{\mathscr{S}_E} \Psi(\mathbf{z}) d\mu(\mathbf{z}) \, . \tag{4.10}$$

We should point out that (4.9) is a particular case of (4.10) with $\Psi = 1_A$. The question arises whether different orbits gives rise to a different probability measures in (4.9), that is, if they sample phase-space differently. The answer in general is positive as can be seen by looking at periodic points

[9] For any x_0 and ε we have $\|T^n(x_0) - T^n(x_0 + \varepsilon v)\| = \|\varepsilon T^n(v)\| = \varepsilon|\lambda|^n \|v\| \to_{n\to\infty} \infty$.

(expected to be dense) or at the case when $\mathbf{z}_0$ is a fixed point, case in which the Dirac measure at $\mathbf{z}_0$ plays the role of the measure μ for this particular orbit. Hence (4.9) and (4.10) are expected to hold only for certain orbits. Molecular dynamics simulations operate under the assumption that the *ergodic hypothesis* holds, namely that (4.9) and (4.10) hold for **almost all** points $\mathbf{z}_0 \in \mathscr{S}_E$ and all integrable functions Ψ. From a strict mathematical standpoint, it has been proved that the averages on the left-hand side of (4.10) – or rather their discrete counter-part – converge for almost all starting points $\mathbf{z}_0$; however, in general the limit depends on the starting point as is shown in the following classical result of ergodic theory [10]:

Theorem 4.1 (Birkhoff's strong ergodic theorem)**.** *Let T be a measure-preserving transformation of the probability space $(\mathscr{X}, \Sigma, \mu)$, and let $\Psi : \mathscr{X} \to \mathbb{R}$ be integrable. Then there exists a integrable function Ψ^* such that for almost every $x \in \mathscr{X}$*

$$\lim_{n\to\infty} \frac{1}{n} \sum_{j=0}^{n-1} \Psi(T^j(x)) = \Psi^*(x) \ . \tag{4.11}$$

Moreover, Ψ^* is T-invariant, in the sense that

$$\Psi^*(Tx) = \Psi^*(x) \ \text{ almost everywhere} \ , \tag{4.12}$$

and $\int_X \Psi d\mu = \int_X \Psi^* d\mu$.

If we let $T = \Phi_{\Delta t}$ ($\Delta t > 0$), then Theorem 4.1 shows that the time-averages

$$\frac{1}{n} \sum_{j=0}^{n-1} \Psi(\Phi_{n\Delta t}(\mathbf{z}))$$

converge to a limit function $\Psi^*(\mathbf{z})$ that is $\Phi_{\Delta t}$-invariant. If, in addition, we knew that $\Phi_{\Delta t}$ had no invariant functions other than constants it would follow that

$$\Psi^*(\mathbf{z}) = \int_{\mathscr{S}_E} \Psi d\mu_E \quad \text{almost everywhere,} \tag{4.13}$$

thus showing the ergodic hypothesis to hold.

A measure-preserving map T is said to be *ergodic* if the only functions that are T-invariant are the constants. It can be proved that T is ergodic if and only if all T-invariant sets are trivial, in the sense that they have either measure 0 or 1. Proving that an individual map T is ergodic in this strict mathematical sense is in general a very difficult task. Standard, simple examples of ergodic maps can be found in any textbook on ergodic theory (e.g, see [10]; see also Examples 4.1 and 4.2 below). However, there is an important positive result: Ulam and Oxtoby [18] have shown that, under certain conditions, **measure-preserving maps are generically ergodic**, which essentially means that the set of ergodic maps is large in a topological sense. We will return to this statement in Section 4.4.

Example 4.1 (Dyadic permutations of unit interval). We divide the unit interval in N equal intervals $I = [0,1] = \cup_{i=1}^{N} I_k$, with $I_k = [(k-1)/N, k/N]$. For a permutation $\sigma \in \mathscr{S}_N$ we define T_σ to map I_k onto $I_{\sigma(k)}$ by translation. Then T_σ is measure-preserving. If σ is cyclic, then T_σ is also ergodic.

Example 4.2. Consider the flow-map of the differential equation

$$\dot{\varphi}_1 = \alpha_1 \quad \dot{\varphi}_2 = \alpha_2,$$

defined by $\Phi_t(\mathbf{z}) = \mathbf{z} + t\alpha$ on the two-dimensional torus $\mathbb{T}^2$, where $\alpha = (\alpha_1, \alpha_2)$. The system is trivially Hamiltonian with

$$H(\mathbf{z}) = \alpha_1 p - \alpha_2 q, \;\; \mathbf{z} = (q, p).$$

It is shown in [21, pp. 219–220] (see also [3, p. 73]) that, if α_1/α_2 is irrational, then Φ_t is ergodic.

Ergodicity for flow-maps of Hamiltonian systems has been established mostly for billiards. We refer the reader to the survey article [26] for specific results. We prefer to summarize the state of the art knowledge on ergodicity of Hamiltonian systems by citing from [28]: 'To the best of our knowledge, the only examples of physically realizable Hamiltonian systems of ODEs that are ergodic on some energy level are given in [6] and [12] and are both quite specific in their construction. Ergodicity has not been proved for any system that has been seriously investigated with molecular dynamics simulations.' This should not be surprising, since Markus and Meyer [17] have shown that Hamiltonian systems are generically **not** ergodic, in the sense that for the (topological) majority of smooth Hamiltonians, the set of energy levels for which the flow is non-ergodic is non-negligible. These statements suggest that ergodicity is a property that is not robust with respect to perturbations. Even if a specific Hamiltonian system $\mathscr{H}$ of interest is shown to be ergodic for a set of energy levels that present interest, we can find Hamiltonians arbitrarily close to $\mathscr{H}$ that are not ergodic for a non-trivial (in a measure-theoretical sense) set of energy levels. At the same time we can find arbitrarily close measure-preserving transformations that **are** ergodic. These statements do not exclude the possibility of finding, say, a one-parameter family of ergodic Hamiltonians that includes $\mathscr{H}$.

The above facts suggest that ergodicity, in this strict mathematical sense, may not be the right context for discussing the ability of numerical integrators to sample phase-space. After all, numerical orbits do not follow exactly orbits of some Hamiltonian system, and statistics obtained from averages along numerical orbits are expected to compute only approximately the spatial average $\int_{\mathscr{S}_E} \Psi d\mu_E$. Consequently, for the purpose of numerical analysis it may be sufficient to discuss weaker notions of ergodicity. Tupper [28] introduced the notion of δ-*ergodicity* with respect to a function: a measure-preserving transformation T on a measure space $(\mathscr{X}, \Sigma, \mu)$ is called δ-ergodic with respect to a function Ψ if

$$E\left(\lim_{n\to\infty} \frac{1}{n} \sum_{j=0}^{n-1} \Psi(T^j(\mathbf{z})) - E(\Psi) \right) \leq \delta \,,$$

where $E(f) = \int_X f d\mu$ denotes the expected value of a function f. This is essentially a relaxation of condition (4.13), in the sense that the 'almost everywhere' in (4.13) has been replaced by an approximate equality that holds only on the average, and only for a specified function Ψ. Formally, it follows that a map T is ergodic if and only if it is 0-ergodic with respect to every integrable function Ψ on X. It is also shown that a measure-preserving flow is δ-ergodic with respect to an *almost constant* function Ψ, that is, a function that is close to its average in the sense of expected value:

$$E|\Psi(\mathbf{z}) - \overline{\Psi}| \leq \delta \,,$$

where $\overline{\Psi} = E(\Psi)$. The concept is important, since oftentimes functions of interest share this property (see Section 2 of [28]).

The main attractiveness of δ-ergodicity lies in the fact that it is robust to small perturbations: given a Hamiltonian flow that is δ-ergodic with respect to Ψ and and $\varepsilon > 0$ it is shown in [28] that a sufficiently small perturbation of the flow is $\delta + \varepsilon$ ergodic with respect to Ψ. This notion is useful in connection to the study of the capability of symplectic numerical integrators to sample the phase-space, and we will return to this in Section 5.3.

4.4 Topological genericity

We used the term *generically* when we referred to a property held by a "topological majority". Technically, a property (P) is called *generic* if the set of all elements satisfying (P) contains a countable intersection of dense open sets. While the technical definition may not be very illuminating in the absence of a detailed presentation of the corresponding mathematical theory, we try to convince the reader that genericity is correlated with "majority" by stating three main facts: 1. if a property (P) is generic, then (P) is satisfied by a dense[10] (hence non-empty) set of elements; 2. if (P) is generic, then the opposite property (non-P) is not generic; 3. if properties (P_1) and (P_2) are generic then so is the property (P_1 and P_2). For example, if $(P1)$ reads '*a map is ergodic*' and $(P2)$ reads '*a map is chaotic*', and both $(P1)$ and $(P2)$ are generic in a certain context, then a generic map is expected to be **both** chaotic and ergodic.

The more familiar concept of measure-theoretic majority serves as a good analogy to topological genericity: from a measure-theoretic standpoint a property is satisfied by a majority of points if it is satisfied by almost all points. We should point out that the three facts above are valid also for the measure-theoretic majority, however, the two concepts of majority are different. A simple example of a generic property is that of a number in $[0,1]$ to be irrational. The complementary property, i.e., that of a number to be rational is not generic, even though it is also satisfied by a dense set of numbers; hence 'generic' is more restrictive than '(P) is satisfied by a dense set of elements'. In this example (topological) genericity coincides with measure-theoretic majority, since almost all numbers in $[0,1]$ are irrational. However, there are examples of topologically generic sets that are negligible from a measure-theoretic standpoint (see Example C.1). We provide exact definitions and basic results that justify the use of topological genericity in Appendix C. Another example is that of continuous functions that are nowhere differentiable. While most continuous functions we use in practice are differentiable at most points (e.g., spline functions), continuous functions are generically nowhere differentiable (see [19]). Oftentimes this fact is used as a argument to show the existence of such functions. Instead of constructing an example of a nowhere differentiable function, one can show that they form a topological majority, therefore there exists at least one.

The definition of generic as a countable intersection of dense open sets means that the notion of genericity depends on the topological space we consider. For example, if we consider the space C of continuous functions on a compact interval, the natural topology is that induced by the supremum norm. This means that a sequence of functions x_n converges to x if and only if

$$\sup_{t\in[0,T]} |x_n(t) - x(t)| \to 0$$

as $n \to \infty$. In this topological space the set of nowhere differentiable functions is generic [19]. However, if we consider the space C_1 of continuous functions with continuous derivatives on a compact interval, a different topology is the natural one. We say that x_n converges to x if and only if

$$\sup_{t\in[0,T]} \left\{ |x_n(t) - x(t)| + |x_n'(t) - x'(t)| \right\} \to 0$$

as $n \to \infty$. Obviously, in this topology being differentiable is generic. The moral is that one must choose the topological space carefully in order to extract meaning from statements of genericity.

[10] A set Q is called dense in a metric space $\mathscr{X}$ if for every element in $\mathscr{X}$ we can find arbitrarily close elements that belong to Q.

The topological context of interest for the present discussion is the metric space $\mathscr{M}(\mathscr{S}_E, \mu_E)$ of measure-preserving maps from $(\mathscr{S}_E, \mu_E)$ onto itself. We define the *uniform metric* on $\mathscr{M}(\mathscr{S}_E, \mu_E)$:

$$\delta(T_1, T_2) \stackrel{\text{def}}{=} \text{ess sup}_{x \in \mathscr{S}_E} d(T_1(x), T_2(x)) \ . \tag{4.14}$$

Recall that (4.14) implies that

$$d(T_1(x), T_2(x)) \leq \delta(T_1, T_2) \quad a.e.[\mu_E].$$

Two properties of interest to us are generic in this metric space: **ergodicity**, and the property of being **chaotic** (see [2] and Theorem C.2), which implies that **we expect a generic measure-preserving map to be both ergodic and chaotic**. However, Hamiltonian flow maps are a small subset of all measure-preserving maps, therefore results about generic properties do not automatically apply to them. In fact, the aforementioned result of Markus and Meyer [17] states quite the opposite: they have shown that, in the space of smooth Hamiltonians, equipped with the C^∞ topology, generically a Hamiltonian flow is non-ergodic for a set of energy values that has positive measure. In other words a generic Hamiltonian will have a nontrivial (from a measure-theoretic standpoint) set of energy levels at which the flow is non-ergodic. Buried underneath this statement are earlier results from KAM theory, showing that Hamiltonians are expected to have invariant sets of positive measure composed of a union of invariant tori with dimension half of that of the phase-space. This does not rule out the possibility of the phase-space having a large invariant component on which the flow is ergodic, which, if quantified properly, would probably suffice for assessing the capability of the flow map of sample the phase-space.

Summary. The flow map of a Hamiltonian systems preserves the microcanonical measure on the surface $\mathscr{S}_E$. Measure-preserving maps are generically chaotic and ergodic in certain, naturally occurring settings. Orbits of chaotic flows cannot be followed numerically for long periods of time. Orbits of ergodic maps sample the underlying space correctly, and offer hope that numerically orbits can do the same. Hamiltonian flow-maps are not expected to be ergodic in a strict mathematical sense, however, they may be ergodic in a weaker sense that may be sufficient for retrieving certain statistical quantities. In the next section we address the question of what are necessary and sufficient properties that a numerical integrator of a Hamiltonian ODE has to possess so that it samples phase-space correctly.

5 Which numerical integrators capture statistics?

We have argued in Section 4 that for long-term simulations of Hamiltonian systems individual orbits cannot be followed by numerical orbits, because of sensitive dependence on initial conditions. However, these orbits carry statistical information because they are expected to sample the phase-space correctly. The question thus arises as to what are necessary and sufficient conditions that a *numerical integrator* (NI) has to satisfy, in order for the statistical information extracted from a numerically computed orbit to approximate well that obtained from a continuous orbit. The problem of finding such conditions is still an active area of research, and no ultimate theoretical answers have yet been obtained [30]. A common belief, based both on practice and a series of theoretical results, is that a sufficient condition is that the integrator be symplectic, while approximative energy and volume conservation are necessary conditions. In this section we will make an attempt to review the main arguments that lie at the basis of these beliefs, as follows from the literature.

Limitations of current methods are well-known to the molecular dynamics community. Rapid oscillations characteristic to molecular systems force using step sizes on the order of femtoseconds (10^{-15} seconds) in connection with methods that are generally accepted to produce good results (see [15], Chapter 11), while the desired duration of a simulation corresponds to a physical time ranging from milliseconds to seconds. This means that current algorithms would require to run for 10^{12}–10^{15} time steps in order to capture the information of interest. It is not envisioned that even the most optimistic predictions in computing-speed increase over the next years will close the gap between what we can compute today and the long-term goals of molecular dynamics. Thus it becomes critical to design algorithms that sample the phase space much more effectively than the current methods, and for that it is essential to understand what are the conditions under which correct sampling is achieved.

For traditional applications of n-body problems, where tracking individual orbits forms the central problem (e.g., control of satellite orbits, robotics) numerical methods are designed so that relevant geometric properties of the continuous orbit are preserved by the numerical orbit. In order for the simulated behavior to be relevant for the "true" physical system it is very important to conserve energy and/or angular momentum if the continuous system does so. It is well known [15] that generic of-the-shelf NIs such as forward and backward Euler, or Runge-Kutta methods produce solutions that exhibit energy drift over long periods of time. For example, computing the time evolution of a single harmonic oscillator using the backward Euler method brings the oscillator to a standstill over a period of time the length of which depending on the step size (see [15], Ch.2). However, even if energy is the only conserved quantity for the continuous system, numerical schemes designed to exactly conserve energy (projection-type methods) often do not yield satisfying qualitative results [29]. As seen in Section 2, two additional key properties of the continuous system are phase-space volume conservation and the more restrictive property called symplecticity. As it turns out, symplecticity is the property that appears sufficient.

5.1 What statistics do we compute?

The types of information that are extracted from molecular dynamics simulations usually fall into one of the following classes. These examples all describe averages with respect to an invariant probability measure. All can be generalized to non-invariant measures.

Phase space averages. Let $\Psi : \mathbb{R}^{2d} \to \mathbb{R}$ be a function on the phase space of the system. Often researchers wish to know what the average of the function over phase space is with respect to some invariant measure. Usually the physically relevant invariant measure is the canonical ensemble at a particular temperature. For many high-dimensional systems of interest and for many choices of function Ψ the average of Ψ with respect to the microcanonical ensemble at a particular energy is believed to be an excellent approximation to that of the canonical ensemble at a given temperature. This allows us to approximate the average via an MD simulation. This is usually written

$$\langle \Psi \rangle_{NVE} = \int_{\mathbf{R}^{2d}} \Psi(\mathbf{z}) d\mu_E(\mathbf{z}).$$

For example, a quantity of interest in chemistry is the pair density function $g(r)$, defined to be the probability of a finding a pair of atoms at a distance r (see [1]). This is computed by

$$g(r) = \int_{\mathbf{R}^{2d}} \sum_{1 \le i < j \le n} \delta_\varepsilon(|q_i - q_j| - r) d\mu_E(\mathbf{z}) \ ,$$

where $q_i = q_i(\mathbf{z})$ is the position of the i^{th} particle, and δ_ε is an approximation of the Dirac δ-function.

Correlation functions. Let $\Psi, \Theta : \mathbb{R}^{2d} \to \mathbb{R}$ be two functions on the phase space of the system. For any $\tau \in \mathbb{R}$ we can ask what is

$$\langle \Psi(t)\Theta(t+\tau) \rangle = \int_{\mathbf{R}^{2d}} \Psi(\mathbf{z})\Theta(\Phi_\tau \mathbf{z}) d\mu_E(\mathbf{z})$$

A simple to state example of this is what $\Psi = \Theta =$ the velocity of a single particle. This is referred to as $C(\tau)$, and C is called the velocity autocorrelation function. This is interesting because it gives the rate of diffusion of one particle through its neighbors. Of course, more complicated correlation functions of the form $\langle \Psi(t)\Theta(t+\tau_1)\Xi(t+\tau_2) \rangle$ are also possible, but these are seldom computed. Another type of measurement that can be put into the framework of correlation functions is transition rates. Suppose we divide $\mathbb{R}^{2d}$ into two disjoint sets A and B. Imagine observing the system moving through phase space but only keeping track of whether it is in set A or B.

Requiring that correlation functions are computed correctly is a much more restrictive requirement than that phase space averages are correct. For example, suppose we simulate a system perfectly except that it evolves twice as slowly than it should. All phase space averages will be computed correctly. However, all non-trivial correlation functions will be computed incorrectly. A more realistic example is provided by Monte Carlo methods. These methods use a random sequence of jumps to move through phase space. (They are most natural for sampling from the canonical ensemble.) These methods are competitive with MD for computing phase space averages, but there is no time variable to compute correlation functions with respect to.

5.2 Symplectic numerical integrators and phase-space sampling

We start with the questions regarding the relation between symplecticity and the capability of NIs to correctly sample the phase space.

What does it mean for a NI to be symplectic? In general a NI can be described as a method for computing an approximation to $\Phi_h(\mathbf{z})$ given a state $\mathbf{z}$ in the phase-space $\mathbb{R}^{2d}$, where $h>0$ is a given time-lapse; basically a NI is family of maps $\widetilde{\Phi}_h : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ indexed by $h \in (0, h_{\max}]$. According to the definition of a symplectic map, a NI is symplectic if the map $\widetilde{\Phi}_h$ is differentiable and its Jacobian satisfies equation (2.8). We should note that for simple NIs such as the Störmer-Verlet method, where the scheme is described analytically, symplecticity is easy to verify. Moreover, significant efforts have been devoted to devising methods for designing symplectic NIs, and the literature on the subject is vast (see [24, 15, 9] and the references therein).

Error analysis and ergodic averages. The classical purpose of error analysis for a NI is to show that a numerical orbit approximates a continuous orbit for a given amount of time, and that the approximation converges at a certain rate when the step size goes to zero. More precisely, given a fixed time-interval $[0, T = nh]$, the goal is to show an estimate of the form

$$|(\widetilde{\Phi}_h)^n(z) - \Phi_T(z)| \leq C(T)h^p \ , \tag{5.1}$$

for the global truncation error, with $p>0$ being the order of the method. It is easy to see that if the estimate (5.1) is valid on $[0,T]$, numerical ergodic averages of a statistic Ψ are close to the continuous ergodic averages:

$$\left| \frac{1}{n}\sum_{k=0}^{n-1} \Psi\left((\widetilde{\Phi}_h)^k(z)\right) - \frac{1}{n}\sum_{k=0}^{n-1} \Psi\left(\Phi_{kh}(z)\right) \right| \leq C_1(T)h^p \ . \tag{5.2}$$

The critical aspect is the evolution of the constant $C(T)$. Forward error analysis predicts an exponential growth of $C(T)$, which renders (5.1) useful only for very short time-intervals. While for certain systems this is overly pessimistic, $C(T)$ being quite tame in fact, for systems exhibiting SDIC, such as Hamiltonian systems, in reality $(\widetilde{\Phi}_h)^n(z)$ and $\Phi_{nh}(z)$ do not remain close even for modest values of n (see [30] for a simple example).

Backward error analysis, symplecticity, and Hamiltonian systems. The connection between symplectic NIs and Hamiltonian systems becomes more evident in the context of *backward error analysis* (BEA). The idea of BEA is that the numerical solution operator $\widetilde{\Phi}_h$ of a general differential equation

$$\dot{\mathbf{z}} = F(\mathbf{z}) \tag{5.3}$$

satisfies a modified equation with a higher accuracy than the original equation. More precisely, if the NI has a local truncation error of order $O(h^{p+1})$, there exists a modified vector field

$$\widetilde{F}(\mathbf{z},h) = F(\mathbf{z}) + O(h^p) \ ,$$

so that $\widetilde{\Phi}_h$ integrates the modified differential equation

$$\dot{\mathbf{z}} = \widetilde{F}(\mathbf{z},h) \tag{5.4}$$

with higher accuracy than the original equation:

$$\|\widetilde{\Phi}_h(\mathbf{z}) - \Phi_{h,\widetilde{F}}(\mathbf{z})\| = O(h^r) \ , \text{ with } r > p+1 \ , \tag{5.5}$$

where $\Phi_{t,\widetilde{F}}$ is the continuous flow associated with (5.4). The modified vector field $\widetilde{F}$ can be constructed in such a way that it inherits certain geometrical features from F. In particular, it is shown (see [15, 9] and the references therein) that if the original equation (5.3) is Hamiltonian, i.e., $F(\mathbf{z}) = \mathbf{J}\nabla_{\mathbf{z}}H(\mathbf{z})$, and if the NI is symplectic, then the modified equation can be chosen to be Hamiltonian as well, that is, $\widetilde{F}(\mathbf{z}) = \mathbf{J}\nabla_{\mathbf{z}}\widetilde{H}(\mathbf{z},h)$ with

$$\widetilde{H}(\mathbf{z},h) = H(\mathbf{z}) + O(h^p) \ . \tag{5.6}$$

We should stress that the modified vector field depends on the original Hamiltonian H, the numerical method used, and the step size h. While the higher truncation error is not infinitely small, that is, the discrete flow is not **identical** to the continuous flow of a modified equation, it is shown (e.g., see [8, 20]) that the modified Hamiltonian $\widetilde{H}$ can be chosen so that the local truncation error is exponentially small in the step size h:

$$\|\widetilde{\Phi}_h(\mathbf{z}) - \Phi_{h,\widetilde{F}}(\mathbf{z})\| = O(he^{-\frac{\gamma}{h}}) \ , \tag{5.7}$$

with γ independent of h. The estimate (5.7) has two major implications. First, a simple calculation ([15], pp. 121) shows that for symplectic NIs the **energy drift stays exponentially small** for an exponentially long time. Second, it shows that the numerical and the continuous orbits of the modified system stay exponentially close together for a time interval $[0,T]$ with $T \ll O(\gamma/h)$. As a consequence, numerical ergodic averages will be close to continuous ergodic averages of the modified Hamiltonian. If the flow of the modified Hamiltonian is ergodic, then

$$\frac{1}{n}\sum_{k=0}^{n-1}\Psi((\widetilde{\Phi}_h)^k(\mathbf{z})) \approx \frac{1}{n}\sum_{k=0}^{n-1}\Psi(\Phi_{kh,\widetilde{F}}(\mathbf{z})) \approx \int_{\mathbf{R}^{2d}}\Psi d\widetilde{\mu}_E \ , \tag{5.8}$$

where E is the $\widetilde{H}$-energy level of the initial state, and $\widetilde{\mu}_E$ is the microcanonical measure on the surface $\{\widetilde{H}(\mathbf{z},h) = E\}$ as defined in (4.6). In conjunction with (5.6) this would imply

$$\frac{1}{n}\sum_{k=0}^{n-1}\Psi((\widetilde{\Phi}_h)^k(\mathbf{z})) = \int_{\mathbf{R}^{2d}}\Psi d\mu_E + O(h^p) \ , \tag{5.9}$$

provided that n is large enough. The problem with this reasoning lies the fact that the approximation (5.7) is valid only for $nh = T \ll O(\gamma/h)$, which is still too short for molecular dynamics. Therefore this approach does not yet explain why ergodic averages computed with symplectic NIs approximate well the continuous ergodic averages [30].

Shadowing and convergence of averages. The best known result on the problem of why symplectic NIs produce correct ergodic averages was obtained by Reich [20]. The result is based on BEA and the shadowing lemma [22]. Unlike BEA, where the numerical orbit is shown to be close to an exact orbit of a modified system starting at the same point as the numerical orbit, *shadowing* refers to the existence of a nearby orbit of the continuous, unmodified system (the shadowing orbit), but starting at a different point. In essence Reich has shown that, under the assumptions that the Hamiltonian system is uniformly hyperbolic and analytic, a numerical orbit $\widetilde{\mathbf{z}}_n = (\widetilde{\Phi}_h)^n(\mathbf{z})$ is shadowed by some exact orbit $\mathbf{z}'_n = \Phi_{hn}(\mathbf{z}')$, in the sense that

$$\widetilde{\mathbf{z}}_n = \mathbf{z}'_n + O(h^p) \ , \text{ for } n \leq \alpha e^{\beta/h} \ ,$$

provided that the numerical integrator $\widetilde{\Phi}_h$ is analytic and symplectic. As a consequence, the average of a statistic Ψ on the numerical orbit converges to the average of Ψ one the shadowing orbit with the correct order, that is:

$$\frac{1}{n}\sum_{i=0}^{n-1}\Psi(\widetilde{\mathbf{z}}_i) = \frac{1}{n}\sum_{i=0}^{n-1}\Psi(\mathbf{z}'_i) + O(h^p)\ , \tag{5.10}$$

for an exponentially long time. Uniform hyperbolicity also allows the application of a *large deviation theorem* [31] to show that the average on the right-hand side of (5.10) converges to the desired spatial average $\int_{\mathscr{S}_E}\Psi d\mu$ with a probability approaching 1 exponentially with the time-step $h\to 0$. In other words, for sufficiently small h it is very likely that the computed numerical average on the left-hand side of (5.10) converges to $\int_{\mathscr{S}_E}\Psi d\mu$. The weak side of this result lies in the fact that uniform hyperbolicity has never been established for realistic systems [30], and the work in [12, 16] suggests that it is unlikely to hold for them.

Heuristics and speculations. Backward error analysis has shown that symplectic NIs preserve the energy of a nearby Hamiltonian $\widetilde{H}$ exponentially well for an exponentially long time; neither can it be shown that the energy of a nearby Hamiltonian $\widetilde{H}$ is preserved **exactly**, or that the energy drift (the variation of $\widetilde{H}$ over time) is exponentially small for an **infinite** time interval. However, we briefly explore, as an useful exercise, what conclusions could be drawn if a symplectic NI preserved the modified Hamiltonian exactly (for all time).

First, the arguments used for showing flow-invariance of the microcanonical measure lead to

Theorem 5.1. *Let $T:\mathbb{R}^{2d}\to\mathbb{R}^{2d}$ be a measure-preserving transformation, and let $H:\mathbb{R}^{2d}\to\mathbb{R}$ be so that $\nabla H(\mathbf{z})\neq 0, \forall \mathbf{z}\in\mathbb{R}^{2d}$. If H is T-invariant, that is, $H(T(\mathbf{z}))=H(\mathbf{z})$, $\forall\mathbf{z}\in\mathbb{R}^{2d}$, then for all energy levels $E\in\mathbb{R}$ the measure μ_E on $\mathscr{S}_E$ defined in* (4.6) *is T-invariant.*

Proof. Let $E\in\mathbb{R}$ and $\delta_n:\mathbb{R}\to\mathbb{R}$ be smooth functions as in Theorem A.1, so that $\delta_n\to\delta$ weakly. We define the measures ν_n on $\mathbb{R}^{2d}$ by

$$\nu_n(A) = \int_A \delta_n(H(\mathbf{u})-E)d\mathbf{u}\ .$$

Then

$$\begin{aligned}\nu_n(T(A)) &= \int_{T(A)}\delta_n(H(\mathbf{u})-E)d\mathbf{u} \overset{\mathbf{u}=T(\mathbf{v})}{=} \int_A \delta_n\left(H(T(\mathbf{v}))-E\right)\cdot|\det(T')(\mathbf{v})|d\mathbf{v}\\ &= \int_A \delta_n(H(\mathbf{v})-E)d\mathbf{v} \;=\; \nu_n(A)\ .\end{aligned}$$

Since, by Theorem A.1 $\nu_n\to\mu_E$ weakly we get

$$\mu_E(A) = \mu_E(T(A))\ .$$

□

Now consider a sympletic NI denoted by $\widetilde{\Phi}_h$ and a fixed $h\ll 1$. We know that $\widetilde{\Phi}_h$ almost preserves a nearby Hamiltonian $\widetilde{H}(\cdot,h)$ (see (5.6)). If $\widetilde{\Phi}_h$ preserved $\widetilde{H}(\cdot,h)$ exactly, then by Theorem 5.1,

$\widetilde{\Phi}_h$ would preserve the microcanonical ensemble $\widetilde{\mu}_E$ of the modified Hamiltonian $\widetilde{H}$. Hence, **generically**, $\widetilde{\Phi}_h$ would be ergodic on $\widetilde{\mathscr{S}_E} = \{\mathbf{z} : \widetilde{H}(\mathbf{z},h) = E\}$, therefore it samples $\widetilde{\mathscr{S}_E}$ correctly. Given the scarcity of rigorous proofs of ergodicity for realistic systems, a result stating that sympletic NI are generically expected to sample phase-space correctly (within $O(h^p)$) rather than guaranteed to do so might be satisfactory to the MD community.

While the above scenario is certainly not expected to hold since, at the very least, no NI will be perfectly symplectic due to round-off error, it allows us to speculate on how it could lead to more rigorous mathematical arguments to show that sympletic NIs capture statistical information. First, given $\widetilde{\Phi}_h$ one may ask whether there exists a $\widetilde{\Phi}_h$-invariant probability measure μ_E^h which is weakly $O(h^p)$-close to μ_E, that is,

$$\int_{\mathbf{R}^{2d}} \Psi d\mu_E^h = \int_{\mathbf{R}^{2d}} \Psi d\mu_E + O(h^p), \forall\, \Psi \text{ integrable} .$$

One would expect μ_E^h to be close to the singular measure $\widetilde{\mu}_E$, since $\widetilde{\mu}_E$ is almost $\widetilde{\Phi}_h$-invariant. Then $\widetilde{\Phi}_h$ is generically expected to be ergodic with respect to μ_E^h, and the desired conclusion (5.9) would follow. Second, one could consider working with almost measure preserving maps and use ergodic theorems for such. Third, one could consider a slightly different notion of ergodicity, a path that is developed in [28] and explained below.

5.3 Towards finding necessary and sufficient conditions for phase-space sampling

Both the work in [20] and computational practice of many specialists have accredited the idea that statistical information is computed accurately by means of symplectic NIs, therefore symplecticity appears to be sufficient condition. As for necessary conditions, one is very natural, namely energy conservation: since continuous orbits sample only a certain subset of phase-space, namely the constant energy surface $\mathscr{S}_E$, one should require the discrete orbits to stay close to $\mathscr{S}_E$ as well. Carefully conducted case-studies [29] comparing the Störmer Verlet-method with three step-and-project methods suggest that energy conservation is not sufficient. Since capturing statistics is associated with ergodicity, which assumes measure preservation, an additional necessary condition would be volume-preservation. As seen in Section 5.2, symplecticity implies both approximative energy conservation and exact volume conservation. More recent work [28] addresses the question whether these two conditions are sufficient. While there is no explicit hypothesis regarding symplecticity, and BEA is also not used explicitly, estimates similar to the ones obtained for symplectic NIs via BEA are being assumed. Under the additional hypothesis that the continuous flow is δ-ergodic with respect to a function Ψ, it is shown that for any $\varepsilon > 0$ the numerical averages are $(\delta+\varepsilon)$-ergodic with respect to Ψ for sufficiently small time-steps; this is exactly the desired result provided that $\delta+\varepsilon = O(h^p)$, with p being the convergence order of the numerical method. However, the author remarks that this accuracy is only guaranteed when the trajectories are accurately computed over long periods of time, which is not the regime in which most MD calculations are performed. In order for the theorem to apply, for a general case it would require a step size of order $\Delta t \approx e^{-C\varepsilon^{-2}/p}$. The situation is more optimistic for functions Ψ that are nearly constant, case in which the theory allows the maximum time-step to be the same as the one required for keeping the energy from drifting drifting away.

6 Conclusions

We have investigated the question of what are necessary and sufficient conditions for NIs to sample the phase space of Hamiltonian systems. This problem has received a significant amount of attention over the last decade, however, to the best of our understanding, a satisfactory solution has not been obtained yet. This may be due to the fact that the problem escapes the traditional, deterministic framework of numerical analysis, where the problem is to show that continuous solutions are approximated well by discrete solutions. Even if the norms for computing the approximation usually depend on the type of equation, in spirit, a point-to-point matching is attempted. In the computational regime of molecular dynamics continuous orbits are simply not expected to be followed accurately for the length of time desired. And yet, most theoretical results were obtained by showing a point-to-point matching between the computed discrete orbit and some continuous orbit. The best-known results contain either additional hypotheses or very small time-steps in order to enable point-to-point matching.

Still, various parts of the puzzle have been assembled, and it seems that a sufficient condition for NIs to sample phase-space correctly is symplecticity, while some form of approximative energy and volume preservation are necessary conditions. From a theoretical standpoint, the question is probabilistic in nature, therefore we may expect the answer to be the same. In other words, the answer may not take the forms of **guarantees** under which correct sampling is achieved, but rather conditions under which sampling **is generically expected** to hold. We consider that a quantitative, mathematically precise statement to support the above would be an essential milestone for achieving further progress on the practical matter of designing significantly faster methods for sampling the phase-space in molecular dynamics.

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A An identity for the δ-function.

Theorem A.1. *Let $\delta_n\colon \mathbb{R} \to \mathbb{R}$, $n = 1, 2\ldots$ be a sequence of integrable functions converging to δ weakly, and such that for any neighborhood U of 0, δ_n is supported on U for large enough n. Let $f, g\colon \mathbb{R}^k \to \mathbb{R}$. Let $\mathscr{S} = \{\mathbf{z} \in \mathbb{R}^k | g(\mathbf{z}) = 0\}$ and suppose $\nabla g(\mathbf{z})$ is never zero on $\mathscr{S}$. Then*

$$\lim_{n\to\infty} \int_{\mathbb{R}^k} f(\mathbf{z})\delta_n(g(\mathbf{z}))d\mathbf{z} = \int_{\mathscr{S}} \frac{f(\mathbf{y})}{\|\nabla g(\mathbf{y})\|} dS(\mathbf{y}),$$

where dS is the surface element on $\mathscr{S}$.

Proof. Since $\nabla g(\mathbf{z})$ is never zero on $\mathscr{S}$, the latter is a manifold of co-dimension 1. Let U_i be a countable collection of open sets such that $\mathscr{S} \subset \cup_i U_i$ and for each i there is a coordinate map $\psi_i : V_i \to U_i$, with $V_i \subset \mathbb{R}^{n-1} \times \mathbb{R}$, such that

$$g(\psi(u, e)) = e, \tag{A.1}$$

for $(u, e) \in V_i$. (That such coordinate maps exist is a consequence of the Local Submersion Theorem [7, p. 20].)

Let $f = f^* + \sum_i f_i$ where the f_i are smooth and have support on U_i, and f^* is zero in a neighbourhood of $\mathscr{S}$. For large enough n

$$\int_{\mathbf{R}^k} f(\mathbf{z})\delta_n(g(\mathbf{z}))d\mathbf{z} = \sum_i \int_{U_i} f_i(\mathbf{z})\delta_n(g(\mathbf{z}))d\mathbf{z}.$$

Our result will hinge on doing a change of variables from $\mathbf{z}$ coordinates to (u, e) coordinates. To this end, we will need to work with the determinant of the Jacobian $J(u, e)$ of ψ_i:

$$J(u, e) = \frac{\partial \psi_i(u, e)}{\partial(u, e)} = \begin{bmatrix} \bar{J}(u, e) & \psi_e(u, e) \end{bmatrix}$$

where $\bar{J}(u, e) = \partial\psi_i/\partial u$ is the first $k-1$ columns of J and $\psi_e(u, e) = \partial\psi/\partial e$. Let's differentiate (A.1) to get

$$\nabla g \cdot \psi_e = 1, \qquad \nabla g \cdot \psi_{u_i} = 0, \quad i = 1, \ldots, k-1.$$

Let $\psi_{e\perp}$ be the component of ψ_e perpendicular to the ϕ_{u_i}, and thus necessarily parallel to ∇g. Now since $\psi_{e\perp}$ can be obtained from ψ_e by subtracting multiples of the columns of $\bar{J}$

$$\det(J) = \det\left(\begin{bmatrix} \bar{J} & \psi_{e,\perp} \end{bmatrix}\right).$$

Since $\psi_{e,\perp}$ is perpendicular to the columns of $\bar{J}$ we get

$$|\det(J)| = \sqrt{\det(J^T J)} = \sqrt{\det\left(\begin{bmatrix} \bar{J}^T\bar{J} & 0 \\ 0 & \|\psi_{e,\perp}\|^2 \end{bmatrix}\right)} = \sqrt{\det(\bar{J}^T\bar{J})}\|\psi_{e,\perp}\|.$$

To find $\|\psi_{e,\perp}\|$ we write $\psi_e = c\nabla g$ and then take the dot product with ∇g. We get $c = \|\nabla g\|^{-2}$ and so $\psi_{e,\perp} = \nabla g/\|\nabla g\|^2$ and so $\|\psi_{e,\perp}\| = \|\nabla g\|^{-1}$. At the end of the day we get

$$|\det J| = \|\nabla g\|^{-1}\sqrt{\det \bar{J}^T\bar{J}}$$

Now for each i, using the formula for a surface integral above

$$\begin{aligned}
\lim_{n\to\infty}\int_{U_i} f_i(\mathbf{z})\delta_n(g(\mathbf{z}))d\mathbf{z} &= \lim_{n\to\infty}\int_{\mathbf{R}^{k-1}}\int_{\mathbf{R}} f_i(\psi_i(u,e))\delta_n(g(\psi_i(u,e)))|J(u,e)|de\,du \\
&= \lim_{n\to\infty}\int_{\mathbf{R}^{k-1}}\int_{\mathbf{R}} f_i(\psi_i(u,e))\delta_n(e)|J(u,e)|de\,du \\
&= \int_{\mathbf{R}^{k-1}} f_i(\psi_i(u,0))|J(u,0)|du \\
&= \int_{\mathbf{R}^{k-1}} \frac{f_i(\psi_i(u,0))}{\|\nabla g(\psi_i(u,0)\|}\sqrt{\bar{J}(u,0)^T\bar{J}(u,0)}du \\
&= \int_{\mathscr{S}} \frac{f_i(\mathbf{y})}{\|\nabla g(\mathbf{y})\|}dS(\mathbf{y}),
\end{aligned}$$

since $\partial\psi_i(u,0)/\partial u = \bar{J}(u,0)$. Summing with respect to i gives the desired result.

□

B An invariant measure on the constant-energy surface

Lemma B.1 (invariant measure on the surface)**.** *The measure μ defined in* (4.6) *is preserved by the flow restricted to $\mathscr{S}_E$.*

Proof. Let $z_0 \in \mathscr{S}_E$. Since $\mathscr{S}_E$ is flow-invariant, the jacobian $\partial_z \Phi_t(z_0)$ maps the tangent plane $\mathscr{T}_{z_0}\mathscr{S}_E$ at z_0 to the surface $\mathscr{S}_E$ onto the tangent plane $\mathscr{T}_{\Phi_t(z_0)}\mathscr{S}_E$ at $\Phi_t(z_0)$. If we choose an orthonormal basis in each of the two planes, the relevant quantity for volume preservation on the surface $\mathscr{S}_E$ is

$$\det\left(\partial_z \Phi_t(z_0)|_{\mathscr{T}_{z_0}\mathscr{S}_E}\right) .$$

Let $N(t) = \nabla_z H(\Phi_t(z_0))$, be the unnormalized vector orthogonal to $\mathscr{S}_E$ at the point $\Phi_t(z_0)$, and $n(t) = \nabla_z H(\Phi_t(z_0))/\left\|\nabla_z H(\Phi_t(z_0))\right\|$ be the unit normal vector. We have

$$\begin{aligned}
&\partial_t \left(\partial_z \Phi_t(z_0)\cdot n(0), N(t)\right) \\
&\quad = \quad \left(\partial_t(\partial_z \Phi_t(z_0))\cdot n(0), N(t)\right) + \left(\partial_z \Phi_t(z_0)\cdot n(0), \partial_t N(t)\right) \\
&\quad \overset{(2.5),\,(2.7)}{=} \quad \left(\mathbf{J}\cdot \partial^2_{zz} H(\Phi_t(z_0))\cdot \partial_z \Phi_t(z_0)\cdot n(0), \nabla_z H(\Phi_t(z_0))\right) + \\
&\qquad\qquad \left(\partial_z \Phi_t(z_0)\cdot n(0), \partial^2_{zz} H(\Phi_t(z_0)\cdot \mathbf{J}\cdot \nabla_z H(\Phi_t(z_0))\right) \\
&\quad \overset{\mathbf{J}^T=-\mathbf{J}}{=} \quad 0 .
\end{aligned}$$

Since $N(t) = \|N(t)\|\cdot n(t)$ and $\partial_z \Phi_t(z_0)|_{t=0} = I$ we obtain

$$\|N(0)\| = \left(\partial_z \Phi_t(z_0)\cdot n(0), n(t)\right)\cdot \|N(t)\| . \tag{B.1}$$

Symplecticity implies that

$$\det(\partial_z \Phi_t(z_0)) = \det\left(\partial_z \Phi_t(z_0)|_{\mathscr{T}_{z_0}\mathscr{S}_E}\right)\cdot \left(\partial_z \Phi_t(z_0)\cdot n(0), n(t)\right) = 1 . \tag{B.2}$$

This together with (B.1) implies

$$\frac{\det\left(\partial_z \Phi_t(z_0)|_{\mathscr{T}_{z_0}\mathscr{S}_E}\right)}{\|\nabla_z H(\Phi_t(z_0))\|} = \frac{1}{\|\nabla_z H(z_0)\|} , \tag{B.3}$$

which, by (4.3), completes the proof. □

It should also be mentioned that an invariant measure similar to μ can be given explicitly when more than one first integral is known.

Lemma B.2. *Assume $H_1 = H, H_2, \ldots, H_k$ are constants of the motion that are linearly independent, and denote by $\mathscr{S}_{E_1,\ldots,E_k} = \cap_{i=1}^k \{z \in \mathbb{R}^{2d} \ : \ H_i(z) = E_i\}$ the submanifold on which the flow is restricted. We define the measure*

$$\nu(A) = \int_A \frac{d\sigma_{2d-k}}{\mathrm{vol}_k(\nabla_z H_1, \ldots, \nabla_z H_k)} , \quad \text{for } A \subset \mathscr{S}_{E_1,\ldots,E_k} . \tag{B.4}$$

where $\mathrm{vol}_k(\nabla_z H_1, \ldots, \nabla_z H_k)$ is the k-dimensional volume of the parallelepiped formed by the vectors $\nabla_z H_1, \ldots, \nabla_z H_k$. Then Φ_t preserves ν.

C Topological genericity

In this section we state the precise results behind various statements regarding topological genericity in Section 4. The fact behind this concept is the following fundamental result by Baire[11] [19].

Theorem C.1 (Baire)**.** *Let $\mathscr{X}$ be a complete metric space[12], and G_n a sequence of dense open sets[13] in $\mathscr{X}$. Then the intersection $\bigcap_{i=1}^{\infty} G_n$ is dense in $\mathscr{X}$.*

Countable intersections of dense open sets are called G_δ sets. It is natural to consider a dense open set to be "overwhelmingly" large for three reasons: first, trivially, it is non-empty; second, its complement is not dense (nor is it open); third, the intersection of two dense open sets is dense and open. If we drop the word "open" the last two properties may not hold: for example the set of rational numbers $\mathbb{Q}$ and the set $\mathbb{Q}+\sqrt{2}$ are both dense but their intersection is empty. Baire's theorem adds a crucial perk: countable intersections of dense, open sets are also dense (but not open). Hence a set that contains is a dense G_δ set is still overwhelmingly large, and the three properties above still hold. Therefore dense G_δ sets form a larger class which can be thought of as overwhelmingly large.

Definition C.1 (generic property)**.** A property (P) referring to points in a complete metric space $\mathscr{X}$ is called *generic*, if the set of all points satisfying (P) contains a dense G_δ set.

The metric space of interest in this study is the space of measure-preserving maps $\mathscr{M}(\mathscr{X},\mu)$ from a measure-space $(\mathscr{X},\Sigma,\mu)$ to itself, which is equipped with the uniform metric defined in (4.14).

Theorem C.2 (genericity)**.** *Let $\mathscr{X}=[0,1]^N$ be the unit cube equipped with the Lebesgue measure and the usual Euclidian metric. Then*

(i) the set of ergodic maps is generic in $\mathscr{M}(\mathscr{X},\mu)$;

(ii) the set of chaotic maps is generic in $\mathscr{M}(\mathscr{X},\mu)$.

Part (i) of Theorem C.2 is due to Oxtoby and Ulam [18] and is the main result of their theory. A proof of the statements in Theorem C.2, nearby results, and further discussions of the subject can be found in [2]. We should point out that from the fact that generically measure-preserving maps are chaotic and ergodic, we cannot automatically come to the same conclusion if additional information is known about the map. In particular *no conclusion can be drawn about an individual map with respect to its ergodicity other than that there exists a nearby map that is both ergodic and chaotic*. An extreme example is the identity map: is preserves any measure, but it is neither chaotic nor ergodic.

The following example shows that the measure-theoretical (resp. probabilistic) notion of majority "almost everywhere" (resp. "with probability 1") can sometimes collide with topological majority represented by genericity.

[11] René-Louis Baire - French mathematician (1874 - 1932)

[12] A metric space is complete if every Cauchy sequence is convergent.

[13] A set G is open if $\forall g \in G$ there exists an open ball centered at g that is entirely contained in G; the set G is called dense if for every point $x \in \mathscr{X}$ there exists a sequence $(g_n)_{n\in\mathbf{N}}$ of elements in G so that g_n converges to x.

Example C.1 (A generic set of zero measure). Arrange the rationals in $[0,1]$ in a sequence $r_1, r_2, \ldots$, and define the sets

$$\mathbb{Q}_\varepsilon = \left(\cup_{k=1}^{\infty} (r_k - \frac{\varepsilon}{2^{k+1}}, r_k + \frac{\varepsilon}{2^{k+1}}) \right) \cap [0,1] \; .$$

Then $\mathbb{Q}_\varepsilon$ is a dense open set in $[0,1]$, with Lebesgue measure

$$\lambda(\mathbb{Q}_\varepsilon) \leq \varepsilon \sum_{k=1}^{\infty} \frac{1}{2^k} = \varepsilon \; .$$

The set

$$\mathbb{Q}_0 = \cap_{n=1}^{\infty} \mathbb{Q}_{\frac{1}{n}}$$

is generic (a dense set of type G_δ). Since $\mathbb{Q}_{\frac{1}{n+1}} \subseteq \mathbb{Q}_{\frac{1}{n}}$, $\lambda(\mathbb{Q}_0) = \lim_{n\to\infty} \lambda(\mathbb{Q}_{\frac{1}{n}}) = 0$, therefore $\mathbb{Q}_0$ is negligible from a measure-theoretical perspective.

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