

S4 Phase Space and Observables

4.1 Symplecticity

In 1.3(...), we determined the Hamiltonian Equations

$$\frac{d}{dt} \begin{pmatrix} \underline{q} \\ \underline{p} \end{pmatrix} = \underline{\underline{J}} \nabla H(\underline{q}, \underline{p})$$

or with the phase space coordinate $\underline{x} = (\underline{q}, \underline{p})$

$$\dot{\underline{x}} = \underline{\underline{J}} \nabla H(\underline{x}) \quad (*)$$

The solution map (phase flow) was defined as

$$\Phi_t: (\underline{x}_0) \mapsto \underline{x}(t) \quad \forall t$$

Such a phase flow of a Hamiltonian system is also known as Hamiltonian flow.

A property of Hamiltonian flows is symplecticity.

From (*) it follows that

$$\frac{d}{dt} \Phi_t(\underline{x}) = \underline{\underline{J}} \nabla_{\underline{x}} H(\Phi_t(\underline{x})).$$

Taking now the derivative with respect to \underline{x}

$$\frac{d}{dt} \underbrace{\nabla_{\underline{x}} \Phi_t(\underline{x})}_{W_t(\underline{x})} = \underline{\underline{J}} \nabla_{\underline{x}}^2 H(\Phi_t(\underline{x})) \nabla_{\underline{x}} \Phi_t(\underline{x})$$

W_t(\underline{x}) Jacobian of the flow.

\mathcal{F} flow (differentiable map) $\phi_t : \mathbb{R}^{6N} \rightarrow \mathbb{R}^{6N}$ is called symplectic

$$w_t^T(x) \stackrel{def}{=} w_t(x) = \frac{1}{\|x\|}$$

This is the case for Hamiltonian systems.

4.1.1. What does symplecticity mean in geometric terms?

Consider a bilinear form

$$\mathcal{L}(\underline{x}_2, \underline{x}_1) := -\underline{x}_2 \nabla \underline{x}_1$$

and in particular for the sake of argument a

1D case:

$$\underline{x}_1 = \begin{pmatrix} q_1 \\ p_1 \end{pmatrix} \quad \underline{x}_2 = \begin{pmatrix} q_2 \\ p_2 \end{pmatrix}.$$

With this the bilinear form

$$S_2(x_2, x_1) = q_2 p_1 - p_2 q_1.$$

Upon (close?) inspection, this should be familiar, as it is the signed area of a parallelogram spanned by \underline{x}_1 and \underline{x}_2 in \mathbb{R}^2 .

In general, $S_L(\underline{x}_2, \underline{x}_1)$ is the sum of signed areas of projections on the (q_i, p_i) planes of the parallelogram spanned by \underline{x}_2 and \underline{x}_1 .

4.1.2 How is $\sigma_2(x_2, x_1)$ related to the flow?

Imagine a tiny parallelogram with infinitesimal sides $d\underline{x}_1$ and $d\underline{x}_2$ and evaluate:

$$\mathcal{L}(d\underline{x}_1, d\underline{x}_2) = -d\underline{x}_1^T \underline{\underline{J}} d\underline{x}_2$$

Now, the flow maps this parallelogram to another one at a different time t : $\Phi_t(d\underline{x}_1, d\underline{x}_2)$ with sides $W_t d\underline{x}_1$, $W_t d\underline{x}_2$ and the bilinear form yields:

$$\begin{aligned} \mathcal{L}(W_t d\underline{x}_1, W_t d\underline{x}_2) &= -d\underline{x}_1^T W_t^T \underline{\underline{J}} W_t d\underline{x}_2 \\ &= \underline{\underline{J}} \quad \text{simply} \\ &= -d\underline{x}_1^T \underline{\underline{J}} d\underline{x}_2 = \mathcal{L}(d\underline{x}_1, d\underline{x}_2) \end{aligned}$$

This shows that simplicity implies invariance of the bilinear form under flow.

4.1.3 Phase space volume conservation

Let A denote a volume of phase space. Then $A_t = \Phi_t(A)$ and $V(t) = \text{vol}(A_t)$, then

$$\boxed{\frac{dV(t)}{dt} = 0}$$

Liouville's Theorem

i.e., the phase space volume is conserved.

To show, consider

$$\frac{dV}{dt} = \frac{d}{dt} \int_{A_t} d\underline{x} = \int_{\partial A_t} \dot{\underline{x}} \cdot \underline{n} dS$$

Leibnitz

$$= \int_{A_t} \nabla_{\underline{x}} \cdot \dot{\underline{x}} d\underline{x} \quad \text{divergence Theorem}$$

Let's take a closer look at the integrand:

$$\begin{aligned} \nabla_{\underline{x}} \cdot \dot{\underline{x}} &= \nabla_{\underline{x}} \left(\frac{1}{2} \nabla_{\underline{x}} H(\underline{x}) \right) \\ &= (\nabla_{\underline{q}} \nabla_{\underline{p}} - \nabla_{\underline{p}} \nabla_{\underline{q}}) H(\underline{q}, \underline{p}) = 0 \end{aligned}$$

4.2 Observables

How can we use phase space information – including the symplecticity property – to obtain information about a "real" physical system?

An observable is a phase space function $f(\underline{q}, \underline{p}, t)$.

Let's inspect its total time derivative:

$$\frac{df(\underline{q}, \underline{p}, t)}{dt} = \frac{\partial f}{\partial t} + \sum_{i=1}^N \left[(\partial_{\underline{q}_i} f) \dot{q}_i + (\partial_{\underline{p}_i} f) \dot{p}_i \right]$$

or again with the phase space notation $\underline{x} = (\underline{q}, \underline{p})$

and $\dot{\underline{x}} = \underline{v} = (\dot{q}, \dot{p})$

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \underline{v} \cdot \text{grad } f$$

We can also use the Hamiltonian eq. $\dot{q}_i = \partial_{p_i} H$

and $\dot{p}_i = -\partial_{q_i} H$:

$$\begin{aligned} \frac{df}{dt} &= \frac{\partial f}{\partial t} + \sum_{i=1}^N \left[(\partial_{q_i} f) (\partial_{p_i} H) - (\partial_{p_i} f) (\partial_{q_i} H) \right] \\ &= \frac{\partial f}{\partial t} + \boxed{\{f, H\}} \quad \text{Poisson brackets} \end{aligned}$$

In particular, if we consider the Hamiltonian function $f(q, p, t) = H(q, p) \neq \text{Func}(t)$, we immediately see that

$$\frac{dH(q, p)}{dt} = 0 \Rightarrow H(q, p) = E = \text{const.}$$

Hamiltonian system \Leftrightarrow energy conservation

With regards to observables, in physical system, we are interested in measurables. A measure is an average of a phase space function, e.g.,

$$\langle f(x, t) \rangle := \int f(x) S(x, t) d^{6N}x$$

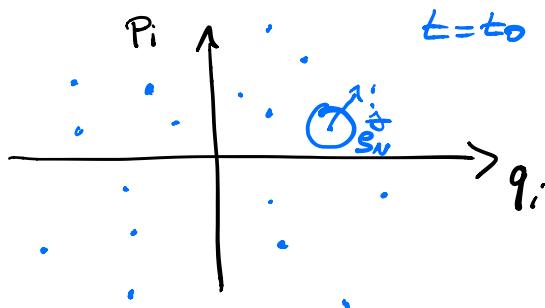
To evaluate this integral, we require information about how likely it is that a certain phase space configuration $\underline{x}(t)$ is realized. This information is available via the probability density $s(\underline{x}, t)$. This density is normalized according to:

$$\int s(\underline{x}, t) d^6x = \int s(\underline{x}, t) d\Gamma = 1.$$

4.3 Liouville Equation

How do we determine the probability density $s(\underline{x}, t)$? So far we have explicitly seen that the energy E of a Hamiltonian system is constant. Implicitly, also the physical volume V and the number of particles N is constant.

Let's now look at a 2D representation of phase space.



The dynamical variables q and p change with time, which means that $\underline{x}(t)$ flows in phase space according to the application of the Hamilton flow ϕ_t . We can describe this by current density $j = s_N \dot{\underline{x}}$ and since the probability is normalized and conserved, its explicit

time derivative follows a continuity equation:

$$\frac{\partial S(x,t)}{\partial t} = -\operatorname{div} \underline{f}(x,t)$$

Important realization but not practical. Let's continue by inspecting the total derivative of the probability density:

$$\frac{dS}{dt} = \frac{\partial S}{\partial t} + \sum_{i=1}^N \partial_{x_i} S \dot{x}_i = \frac{\partial S}{\partial t} + \dot{\underline{x}} \cdot \operatorname{grad} S$$

$$= -\operatorname{div} \underline{f}(x,t) + \dot{\underline{x}} \cdot \operatorname{grad} S$$

cont. eq.

$$= -\dot{\underline{x}} \cdot \operatorname{grad} S - S \operatorname{div} \dot{\underline{x}} + \dot{\underline{x}} \cdot \operatorname{grad} S$$

Or, in summary:

$$\frac{dS(x,t)}{dt} + S \cdot \operatorname{div} \dot{\underline{x}} = 0$$

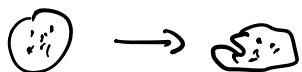
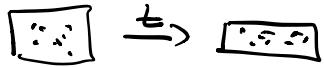
We have already seen that $\operatorname{div} \dot{\underline{x}} = 0$. In other words, the phase space flow is free of sources and sinks, as a consequence we find

$$\frac{dS(x,t)}{dt} = 0$$

Probability density flows in phase space like an incompressible fluid.

While the phase space volume is conserved, the shape of

a finite volume is not!



Making use of $\operatorname{div} \dot{x} = 0$ in the continuity equation leads to:

$$\begin{aligned}\frac{\partial s(x,t)}{\partial t} &= -\dot{x} \cdot \operatorname{grad} s(x,t) \\ &= -\sum_{i=1}^n [(\partial_{p_i} H)(\partial_{q_i} s) - (\partial_{q_i} H)(\partial_{p_i} s)]\end{aligned}$$

and with the Poisson bracket notation:

$$\boxed{\frac{\partial s(x,t)}{\partial t} = -\{s, H\}}$$

Liouville
Equation

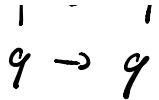
Remarks

① Probability densities $s(x) \neq \text{Func}(t)$ are solutions to the stationary Liouville Equation:

$$0 = -\{s, H\} = -\dot{x} \cdot \operatorname{grad} s(x)$$

② Every probability density $s = s(H)$ is a solution to the stationary Liouville eq.

③ The stationary L-Eq. is the basis of a classical theory of equilibrium processes and is invariant to time reversal (\sim simplicity): $t \rightarrow -t$
 $\theta \rightarrow -\theta$



- ④ How the equilibrium is reached is not covered by the stationary Liouville equation, as it is a non-equilibrium process.

The above realization have immediate implications for performing and analyzing molecular simulations.

\Rightarrow next week