# Physics 127a: Class Notes

## Lecture 3: Motivation for Fundamental Postulate (Classical)

### Hamiltonian formulation of the dynamics

For $N$ particles there are $3N$ coordinates $q_1, q_2 \ldots q_{3N}$ and $3N$ conjugate momenta $p_1, p_2 \ldots p_{3N}$. Usually these would be the Cartesian coordinates $x$, $y$, $z$ of each particle and the corresponding momenta $p_x$, $p_y$, $p_z$. But sometimes other choices are convenient, e.g. for diatomic molecules we could use center of mass coordinates and separation and angular coordinates, together with the appropriate momenta (see a text book on mechanics for how you decide on the momentum conjugate to each coordinate).

The equations of motion are *first order* differential equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \tag{1a}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{1b}$$

(dot denotes the time derivative), where $H(q_1, q_2 \ldots q_{3N}, p_1, p_2 \ldots p_{3N}, t)$ is the *Hamiltonian*. For a system with time independent conditions (no explicit $t$ dependence in $H$) the Hamiltonian is just the total energy expressed in terms of coordinates and momenta. The Lagrangian-Hamiltonian formulation replacing Newton's laws of motion applies for velocity independent forces. This is usually all we need to set up a statistical mechanics problem. The one case of velocity dependent forces we commonly come across is the Lorentz force in electromagnetism: in this case the Lagrangian-Hamiltonian formulation continues to hold—we will discuss this case later on.

The $6N$ coordinates and momenta define the *phase space*: specifying the coordinate in this phase space completely specifies the system now and in the future (via integrating Eqs. (1)). This is the key advantage of using a description leading to evolution equations that are *first order* differential equations.
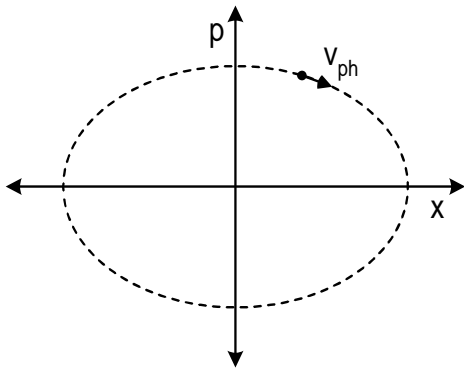


The simple harmonic oscillator illustrates these ideas. For a particle of mass $m$ tethered to a fixed point by a spring of spring constant $K$ the Hamiltonian for one dimensional displacement $x$ is

$$H = \frac{p^2}{2m} + \frac{1}{2}Kx^2. \tag{1c}$$

The Hamiltonian equations give us the *phase space velocity* $\mathbf{v}_{ph} = (\dot{x}, \dot{p}) = (p/m, -Kx)$. Check that this gives the usual simple harmonic oscillator equation $m\ddot{x} + Kx = 0$. It is easy to see that the dynamics traces out an *ellipse* in the phase space.

### Phase space distribution

A single point in phase space $(q_1, q_2 \ldots p_1, p_2 \ldots)$ — which we will also write as $(q_i, p_i)$ or schematically as $(q, p)$ — completely defines the state of the physical system i.e. defines the **microstate** of the classical particle system. For small $N$ we could explicitly follow the time evolution of $(q, p)$ in phase space tracing out a trajectory and defining a geometrical structure in phase space. This is the subject of dynamical systems theory. For $N$ large we can only hope to keep track of the dynamics statistically. Thus we define a **phase space density** $\rho(q_1, q_2 \ldots p_1, p_2 \ldots, t)$ that tells us the probability of finding a system near $(q_1, q_2 \ldots p_1, p_2 \ldots)$ at time $t$. Precisely:

$\rho(q_1, q_2 \ldots p_1, p_2 \ldots, t) \, d^{3N}q \, d^{3N}p$ is proportional to the fraction of the members of the ensemble with phase space point with coordinates between $q_1$ and $q_1 + dq_1$, $q_2$ and $q_2 + dq_2$ etc., and momenta between $p_1$ and $p_1 + dp_1$, $p_2$ and $p_2 + dp_2$ etc.

Here $d^{3N}q d^{3N}p$ is written for the $6N$ dimensional volume element of sides $dq_1, dq_2 \ldots dp_1, dp_2 \ldots$. We do not normalize $\rho$ so that it is a probability density—we will talk about the choice of proportionality constant, motivated by quantum considerations, later.

Any property of the system is given by a function of the phase space coordinate $f(q_1, q_2 \ldots p_1, p_2 \ldots)$. For example for noninteracting particles the energy is given by the function

$$E = \frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m} + \frac{p_{2x}^2}{2m} + \cdots . \tag{2}$$

The *ensemble average* of such a quantity at time $t$ is

$$\langle f(t) \rangle = \frac{\int \ldots \int f(q, p) \rho(q, p, t) d^{3N}q \, d^{3N}p}{\int \ldots \int \rho(q, p, t) d^{3N}q \, d^{3N}p} \tag{3}$$

where the denominator is needed because we did not normalize the distribution to unit probability.

An ensemble is said to be *stationary* if for all time and *at each (fixed) q and p* the phase space density is time independent, i.e.

$$\frac{\partial \rho}{\partial t} = 0 \tag{4}$$

with the partial implying fixed $q, p$. Since the ensemble average $\langle f \rangle$ of any quantity $f$ is time independent with such a distribution, we suppose that an equilibrium system is represented by such a distribution.

## Liouville's Theorem

Liouville's theorem will tell us a second property of the phase space density, namely that if we move with a phase space point as it evolves under the Hamiltonian, the phase space density of the surrounding neighborhood is constant.

First notice that Hamiltonian dynamics preserves "volumes in phase space".
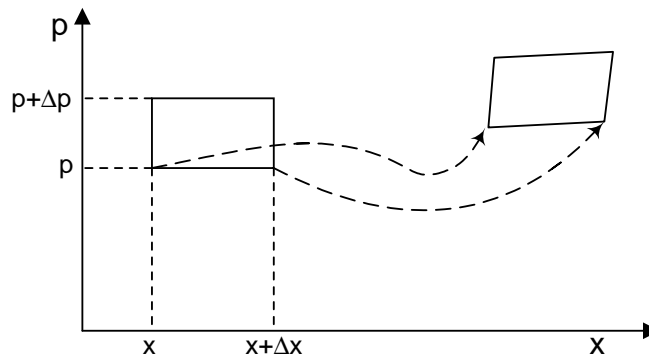


Consider a small area with corners $(x, p)$, $(x + \Delta x, p)$, $(x, p + \Delta p)$, $(x + \Delta x, p + \Delta p)$. (These would correspond to 4 *different* systems of 1 particle moving in 1 dimension.) Under a small time interval $\delta t$ the four points evolve under the Hamiltonian dynamics, and they now defining a new area. The length of the side of length $\Delta x$ changes because the endpoints have different $x$-velocities, and becomes

$$\Delta x + \frac{\partial}{\partial x}(\dot{x}) \Delta x \delta t + O(\delta t^2). \tag{5}$$

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(The different values of $\dot{p}$ will slightly rotate the side from horizontal, but only changes the length at order $\delta t^2$.) Similarly the length of the side of original length $\Delta p$ becomes

$$\Delta p + \frac{\partial}{\partial p}(\dot{p}) \Delta p \delta t + O(\delta t^2). \tag{6}$$

Thus the volume element in phase space (area in this example) $\Delta V(t) = \Delta x \Delta p$) evolves to

$$\Delta V(t + \delta t) = \Delta V(t) \left[ 1 + \left( \frac{\partial}{\partial x}(\dot{x}) + \frac{\partial}{\partial p}(\dot{p}) \right) \delta t + O(\delta t^2) \right], \tag{7}$$

so that

$$\frac{d\Delta V}{dt} = \Delta V \, \nabla_{ph} \cdot \mathbf{v}_{ph} \tag{8}$$

where the "divergence of the phase space velocity" is

$$\nabla_{ph} \cdot \mathbf{v}_{ph} = \frac{\partial}{\partial x}(\dot{x}) + \frac{\partial}{\partial p}(\dot{p}). \tag{9}$$

This is zero for Hamiltonian dynamics.

The argument easily generalizes to the $6N$ dimensional volume element for the $6N$ dimensional phase space of $N$ particles: Eq. (8) still applies with now $\mathbf{v}_{ph} = (\dot{q}_1, \dot{q}_2 \ldots \dot{p}_1, \dot{p}_2 \ldots)$ and

$$\nabla_{ph} \cdot \mathbf{v}_{ph} = \sum_{i=1}^{3N} \left( \frac{\partial}{\partial q_i} \dot{q}_i + \frac{\partial}{\partial p_i} \dot{p}_i \right) \tag{10}$$

which is again zero for Hamiltonian dynamics.

Since the volume associated with a collection of phase space points remains constant under the dynamics, the phase space density is constant as we follow a phase space point, i.e. $\rho(q(t), p(t)) = \rho(q(t = 0), p(t = 0)) = \rho_0$, where $q(t), p(t)$ evolve according to the phase space dynamics. We write this as

$$\frac{d\rho}{dt} = 0 \tag{11}$$

where $d/dt$ is the *total derivative* following a phase space point. This is **Liouville's theorem**.

**Equal Probabilities**

Together, Eqs. (4) and (11) show that for an equilibrium Hamiltonian system the phase space density is the same at every point visited by a trajectory in the phase space. In a complicated, many particle system we might expect the phase space trajectory to visit every region of phase space that is not forbidden by the known macroscopic conservation laws (i.e. conserved energy, particle number, and maybe other quantities such as momentum, spin etc., depending on the details of the system)—this is the notion of *ergodicity*. In this case

$$\rho(q, p) = \rho_0 \text{ over all accessible phase space.} \tag{12}$$

This is the fundamental postulate. The ensemble described by the distribution Eq. (12) is known as the **microcanonical ensemble**.

**Formal Derivation**

The conservation of probability is

$$\frac{\partial}{\partial t} \int_V dV \, \rho = -\int_S \mathbf{dS} \cdot \rho \mathbf{v}_{ph} \tag{13}$$

with $S$ the volume bounding some volume $V$ in phase space (the number of members of the ensemble within $V$ changes only because of the flux of phase-space points through the bounding surface). The divergence theorem (Gauss's theorem) reduces this to

$$\int_V dV \left[ \frac{\partial \rho}{\partial t} + \nabla_{ph} \cdot (\rho \mathbf{v}_{ph}) \right] = 0. \tag{14}$$

Since this applies for any volume $V$ this implies

$$\frac{\partial \rho}{\partial t} + \nabla_{ph} \cdot (\rho \mathbf{v}_{ph}) = 0. \tag{15}$$

For Hamiltonian dynamics $\nabla_{ph} \cdot \mathbf{v}_{ph} = 0$, and so we have

$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \mathbf{v}_{ph} \cdot \nabla_{ph} \rho = 0. \tag{16}$$

This is Liouville's theorem.

For equilibrium $\partial \rho / \partial t = 0$ and then

$$\mathbf{v}_{ph} \cdot \nabla_{ph} \rho = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right) \equiv \{\rho, H\} = 0, \tag{17}$$

using $\mathbf{v}_{ph} = (\partial H / \partial p, -\partial H / \partial q)$. The summed quantity is known as the *Poisson bracket* $\{\rho, H\}$.

We have *derived* the result Eq. (17). Now we have to "guess" what $\rho$ is consistent with this.

A sufficient condition on $\rho$ is

$$\rho(q, p) = \rho(H(q, p), C_1(q, p), C_2(q, p) \ldots), \tag{18}$$

where $H$ and $C_m$ are the conserved quantities (constant of the motion). For then

$$\{\rho, H\} = \sum_m \frac{\partial \rho}{\partial C_m} \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial C_m}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial C_m}{\partial p_i} \right) \tag{19}$$

(the sum $m$ runs over the conserved quantities with $C_0 \equiv H$). But the time dependence of $C_m$ (zero for a conserved quantity) is given by

$$0 = \dot{C}_m = \sum_{i=1}^{3N} \left( \frac{\partial C_m}{\partial q_i} \dot{q}_i + \frac{\partial C_m}{\partial p_i} \dot{p}_i \right) = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial C_m}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial C_m}{\partial p_i} \right), \tag{20}$$

hence showing such a $\rho$ satisfies Eq. (17).

The assumption of ergodicity is that the phase space trajectories visit every region of the phase space consistent with the conserved quantities, e.g. there are no other "hidden" variables that constrain $\rho$. Equation (18) is the general result (and applies to other "ensembles" we will introduce a little later). For an isolated system the quantities $C_m$ are rigorously constant, independent of $q, p$. Hence, with the assumption of ergodicity, the fundamental postulate results. Since the conditions for ergodicity in a precisely defined physical system are not understood rigorously, the fundamental postulate provides a more secure foundation for building the theory, and is usually the preferred starting point. The final justification is the excellent agreement of the predictions based on this theory with observations.