# Handout 4. Classical Mechanics

January 19, 2011

## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Lagrangian and Hamiltonian</td>
<td>3</td>
</tr>
<tr>
<td>1.1 Notation</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Lagrangian formulation</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Legendre transform</td>
<td>5</td>
</tr>
<tr>
<td>1.4 Hamiltonian formulation</td>
<td>7</td>
</tr>
<tr>
<td>2 Phase space</td>
<td>10</td>
</tr>
<tr>
<td>3 Liouville’s theorem</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Flow of incompressible fluid in 3D</td>
<td>13</td>
</tr>
<tr>
<td>3.2 Flow in phase space</td>
<td>14</td>
</tr>
<tr>
<td>4 Ensemble</td>
<td>17</td>
</tr>
<tr>
<td>5 Summary</td>
<td>20</td>
</tr>
</tbody>
</table>
In this lecture, we will discuss

1. Hamilton’s equation of motion
   ↓

2. System’s trajectory as flow in phase space
   ↓

3. Ensemble of points flow in phase space as an incompressible fluid
   ↓

4. Evolution equation for density function in phase space (Liouville’s Theorem)

The path from Hamilton’s equation of motion to density evolution in phase space is analogous to the path we took from the random walk model to diffusion equation.

Reading Assignment

• Landau and Lifshitz, Mechanics, Chapters 1, 2 and 7

Reading Assignment:
1 Lagrangian and Hamiltonian

In statistical mechanics, we usually consider a system of a large collection of particles (e.g. gas molecules) as the model for a macroscopic system (e.g. a gas tank).

The equation of motion of these particles are accurately described by classical mechanics, which is, basically,

$$\mathbf{F} = m \mathbf{a}$$

(1)

In principle, we can use classical mechanics to follow the exact trajectories of these particles, (just as we can follow the trajectories fo planets and stars) which becomes the method of Molecular Dynamics, if you use a computer to solve the equation of motion numerically.

In this section, we review the fundamental “machinery” (math) of classical mechanics. We will discuss

- Hamiltonian and Lagrangian formulations of equation of motion.
- Legendre transform that links Lagrangian $\leftrightarrow$ Hamiltonian. We will use Legendre transformation again in both thermodynamics and statistical mechanics, as well as in classical mechanics.
- The conserved quantities and other symmetries in the classical equation of motion. They form the basis of the statistical assumption.

1.1 Notation

Consider a system of $N$ particles whose positions are $(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = (q_1, q_2, \cdots, q_{3N})$, where $\mathbf{r}_1 = (q_1, q_2, q_3), \mathbf{r}_2 = (q_4, q_5, q_6), \cdots$.

The dynamics of the system is completely specified by trajectories, $q_i(t), i = 1, 2, \cdots, 3N$.

The velocities are: $v_i = \dot{q}_i \equiv \frac{dq_i}{dt}$.

The accelerations are: $a_i = \ddot{q}_i \equiv \frac{d^2q_i}{dt^2}$.

For simplicity, assume all particles have the same mass $m$. The interaction between particles is described by a potential function $U(q_1, \cdots, q_{3N})$ (such as the gravitation potential between planets and stars).

The equation of motion for the system was given by Newton:

$$F_i = ma_i$$

(2)

where $F_i = -\partial U / \partial q_i$ and $a_i = \ddot{q}_i$, which leads to

$$\ddot{q}_i = -\frac{1}{m} \frac{\partial U}{\partial q_i} \quad i = 1, \cdots, 3N$$

(3)
The trajectory can be solved from the above ordinary differential equation (ODE) given the initial condition \( q_i(t = 0), \dot{q}_i(t = 0), i = 1, \cdots, 3N \).

All these should look familiar and straightforward. But we can also write into more “odd-looking” ways in terms of Hamiltonian and Lagrangian. But why? Why create more work for ourselves?

Reasons for Hamiltonian/Lagrangian of classical Mechanics:

1. Give you something to brag about after you have learned it. (Though I have to admit that the formulation is beautiful and personally appealing.)
2. Hamiltonian formulation connects well with Quantum Mechanics.
3. Lagrangian formulation connects well with Optics.
4. Provides the language to discuss conserved quantities and symmetries in phase space. i.e. the symplectic form (and symplectic integrators in molecular simulations).
5. Allows derivation of equation of motion when \( q_i \)'s are not cartesian coordinates.

1.2 Lagrangian formulation

At the most fundamental level of classical mechanics is the Lagrangian Formulation.

Lagrangian is a function of \( q_i \) (position) and \( \dot{q}_i \) (velocity), and is kinetic energy \( K \) minus potential energy \( U \).

\[
L(\{q_i\}, \{\dot{q}_i\}) = K - U \tag{4}
\]

when \( q_i \)'s are cartesian coordinates of particles,

\[
L(\{q_i\}, \{\dot{q}_i\}) = \sum_{i=1}^{3N} \frac{1}{2} m \dot{q}_i^2 - U(\{q_i\}) \tag{5}
\]

Lagrange’s equation of motion

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \left( \frac{\partial L}{\partial q_i} \right) = 0 \quad \text{for every } i = 1, \cdots, 3N \tag{6}
\]

Equivalence between Lagrange’s equation of motion and Newton’s can be shown by

\[
\frac{\partial L}{\partial \dot{q}_i} = m \dot{q}_i \equiv p_i \tag{7}
\]

\[
\frac{\partial L}{\partial q_i} = -\frac{\partial U}{\partial q_i} \tag{8}
\]

\[
\frac{d}{dt} (m \dot{q}_i) - \left( -\frac{\partial U}{\partial q_i} \right) = 0 \tag{9}
\]

\[
\Rightarrow \dot{q}_i = -\frac{1}{m} \frac{\partial U}{\partial q_i} \tag{10}
\]
Note that $L$ is a function of $q_i$ and $\dot{q}_i$. This means that

$$dL = \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

How does $L$ change with time?

$$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial L}{\partial \dot{q}_i} \frac{d\dot{q}_i}{dt} = \sum_i \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) \dot{q}_i + \frac{\partial L}{\partial \dot{q}_i} \frac{d\dot{q}_i}{dt}$$

$$= \frac{d}{dt} \sum_i \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i$$ (11)

Hence $L$ is not a conserved quantity, but

$$\frac{d}{dt} \left( \sum_i \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L \right) = 0$$ (12)

In other words,

$$H = \sum_i \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L$$ (13)

is a conserved quantity, i.e.

$$\frac{dH}{dt} = 0$$ (14)

### 1.3 Legendre transform

The above expression can be rewritten (simplified) using the definition of momentum

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$$ (15)

Using the Lagrange’s equation of motion

$$\frac{\partial L}{\partial \dot{q}_i} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) = \frac{d}{dt} p_i = \dot{p}_i$$ (16)

we have

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}$$ (17)

$$\dot{p}_i \equiv \frac{\partial L}{\partial q_i}$$ (18)
Using the new variable \( p_i \), the change of Lagrangian \( L \) can be expressed as,

\[
dL = \sum_i \partial L / \partial q_i \ dq_i + \partial L / \partial \dot{q}_i \ d\dot{q}_i \]

(19)

\[
dL / dt = \sum_i \dot{p}_i \ dq_i + p_i \ d\dot{q}_i = \sum_i \dot{p}_i \ dq_i + p_i \ d\dot{q}_i
\]

(20)

\[
\frac{d}{dt} \left( \sum_i p_i \dot{q}_i - L \right) = 0
\]

(21)

Hence \( H = \sum_i p_i \dot{q}_i - L \) is a conserved quantity.

The transformation from \( L \) to \( H \) is a Legendre transform.

Notice what happened when going from \( L \) to \( H \):

1. \( L(q_i, \dot{q}_i) \Rightarrow L \) is a function of \( q_i \) and \( \dot{q}_i \).
2. \( p_i \equiv \partial L / \partial \dot{q}_i \)
3. \( H \equiv \sum_i p_i \dot{q}_i - L \)

We notice that \( dH = \sum_i -\dot{p}_i dq_i + \dot{q}_i dp_i \), which means \( H \) is a function of \( q_i \) and \( p_i \), no longer a function of \( q_i \) and \( \dot{q}_i \). This is an important property of the Legendre transform.

Example 1.

To help illustrate the point, we can perform Legendre transform on a one-dimensional function \( f(x) \). Notice that

\[
df = \frac{\partial f}{\partial x} \ dx
\]

(22)

Define \( p \equiv \partial f / \partial x \), then \( df = p \ dx \). The Legendre transform of \( f(x) \) is \( g(p) = px - f \). Notice that,

\[
dg = p \ dx + x \ dp - p \ dx = x \ dp
\]

(23)

This means that \( g \) is a function of \( p \) and \( x \equiv \partial g / \partial p \).

Find the Legendre transform of \( f(x) = x^3 \).
1.4 Hamiltonian formulation

Because $H$ is a function of $q_i$ and $p_i$, (i.e., we will treat $q_i$ and $p_i$ as independent variables when discussing $H$).

We expect

$$dH = \sum_i \frac{\partial H}{\partial q_i} dq_i + \frac{\partial H}{\partial \dot{q}_i} d\dot{q}_i$$  \hspace{1cm} (24)$$

Comparing with the previous equation ($dH = \sum_i -\dot{p}_i dq_i + \dot{q}_i dp_i$), we get the

**Hamilton’s equation of motion**

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$ \hspace{1cm} (25)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$ \hspace{1cm} (26)$$

* In principle, classical mechanics can also be formulated, starting from a Hamiltonian $H(\{q_i\}, \{p_i\})$ and the Lagrangian $L$ can be obtained from Legendre transform. But it is conceptually easier to start with $L(q_i, \dot{q}_i) = K - U$. It is easy to make mistakes when trying to identify the correct $(q_i, p_i)$ pair when $q_i$ is not a Cartesian coordinate.

**Example 2.**

When $q_i$ is the Cartesian coordinate of particles,

$$L(\{q_i\}, \{\dot{q}_i\}) = \sum_i \frac{1}{2} m \dot{q}_i^2 - U(\{q_i\})$$  \hspace{1cm} (27)$$

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = m \dot{q}_i$$ \hspace{1cm} (28)$$

$$H = \sum_i p_i \dot{q}_i - L = \sum_i m \dot{q}_i^2 - \frac{1}{2} m \dot{q}_i^2 + U(\{q_i\})$$

$$= \sum_i \frac{1}{2} m \dot{q}_i^2 + U(\{q_i\})$$

$$= \sum_i \frac{p_i^2}{2m} + U(\{q_i\})$$ \hspace{1cm} (29)$$

$$H = K + U$$ \hspace{1cm} (30)$$

where $K, U$ correspond to kinetic energy and potential energy, respectively.

$dH/dt = 0$ means conservation of energy.
Example 3. Pendulum (motion in 2D)

Consider a mass $m$ attached to rigid rode of length $R$.

The coordinate $(x, y)$ must satisfy the constraint $\sqrt{x^2 + y^2} = R$. If we write the equation in terms of $x, y$ then, we need to worry about the constraint. Alternatively, we can deal with a single variable $\theta$ and forget about the constraint. Then what is the equation of motion in terms of $\theta$? This is when the Lagrangian formulation becomes handy.

Here are the 4 steps to derive the equation of motion for a generalized (i.e. non-cartesian) coordinate. (The direction of $y$-axis is opposite to that of Landau and Lifshitz “Mechanics”, p.11.)

1. Write down $L(\theta, \dot{\theta}) = K - U$.

$$K = \frac{1}{2} m (x^2 + y^2)$$
$$= \frac{1}{2} m (R^2 \cos^2 \theta + R^2 \sin^2 \theta) \dot{\theta}^2$$
$$= \frac{1}{2} m R^2 \dot{\theta}^2$$

$$U = mgy = -mgR \cos \theta$$

$$\Rightarrow L(\theta, \dot{\theta}) = \frac{1}{2} m R^2 \dot{\theta}^2 + mgR \cos \theta$$

2. Write down Lagrangian equation of motion

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\theta}} \right) - \frac{\partial L}{\partial \theta} = 0$$

$$\frac{\partial L}{\partial \dot{\theta}} = mR^2 \dot{\theta}, \quad \frac{\partial L}{\partial \theta} = -mgR \sin \theta$$

$$\frac{d}{dt} (mR^2 \dot{\theta}) + mgR \sin \theta = 0$$

$$\Rightarrow \ddot{\theta} = -\frac{g}{R} \sin \theta$$
3. Find Hamiltonian by Legendre transformation, starting with the momentum

\[ p_\theta \equiv \frac{\partial L}{\partial \dot{\theta}} = mR^2\dot{\theta} \quad (38) \]

Notice that \( p_\theta \neq mR\dot{\theta} \), as might have been guessed naively. This is why it’s always a good idea to start from the Lagrangian.

The Hamiltonian is

\[
H = p_\theta \dot{\theta} - L \\
= mR^2\dot{\theta}^2 - \frac{1}{2}mR^2\dot{\phi}^2 - mgR\cos \theta \\
= \frac{1}{2}mR^2\dot{\theta}^2 - mgR\cos \theta \\
H(\theta, p_\theta) = \frac{p_\theta^2}{2mR^2} - mgR\cos \theta \quad (39)
\]

4. Double check by writing down Hamiltonian’s equation of motion

\[
\dot{p}_\theta = -\frac{\partial H}{\partial \theta} \quad \dot{\theta} = \frac{\partial H}{\partial p_\theta} \quad (41)
\]

---

**Example 4.** Pendulum with moving support (from Landau & Lifshitz, p.11)

Write down the Lagrangian for the following system. A simple pendulum of mass \( m_2 \), with a mass \( m_1 \) at the point of support which can move on a horizontal line lying in the plane in which \( m_2 \) moves.
2 Phase space

The instantaneous state of a system of $N$ particles is completely specified by a $6N$-dimensional vector,

$$\mu = (q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N})$$

Given $\mu(0)$ (initial condition), the entire trajectory $\mu(t)$ is completely specified by Hamiltonian’s equation of motion.

$$\begin{bmatrix}
\dot{q}_i = \frac{\partial H}{\partial p_i} \\
\dot{p}_i = -\frac{\partial H}{\partial q_i}
\end{bmatrix} \iff
\dot{\mu} = \begin{bmatrix}
0 & I_{3N \times 3N} \\
-I_{3N \times 3N} & 0
\end{bmatrix} \frac{\partial H}{\partial \mu} \text{ (in matrix form)} \quad (42)
$$

Equation of motion in phase space can be written as

$$\dot{\mu} = \omega \frac{\partial H}{\partial \mu} \quad (43)$$

where

$$\omega \equiv \begin{bmatrix}
0 & I_{3N \times 3N} \\
-I_{3N \times 3N} & 0
\end{bmatrix} \quad (44)$$

This seems deceivingly simple.

The trajectories of all $N$-particles are equivalent to the motion of a point ($\mu(t)$) in $6N$-dimensional space, which is called the phase space ($\Gamma$).

* The $3N$-dimensional space of all the positions $q_i$ is called the configurational space.

A system of $N$ particles

$$\{q_i, p_i, i = 1, 2, \cdots, 3N\} \iff \mu$$

An ensemble of systems,

each containing $N$ particles.

How do we imagine “an ensemble of systems, each consisting a large number $N$ of particles”?

Let’s say each system is a gas tank containing $N = 10^9$ particles. Now imagine $10^6$ gas tanks → that’s $10^{15}$ particles.
1. That’s a lot of molecules to think about!

Fortunately, the 1,000,000 gas tanks only exist in our imagination (which has $\infty$ capacity). We do not need to really create 1,000,000 gas tanks and do experiments on them to test the predictions of statistical mechanics.

2. Ok, so the other 999,999 gas tanks are not real. That’s great, because I only have one gas tank in my lab. But why do I need to even imagine those “ghost” gas tanks?

– They form the concept of “microcanonical” ensemble from which all laws of thermodynamics can be derived. The price we pay is to imagine many-many gas tanks — I’d say it’s a good deal!
<table>
<thead>
<tr>
<th>From Random Walk to Diffusion Equation</th>
<th>From Classical Mechanics to Thermodynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step 1</strong></td>
<td></td>
</tr>
<tr>
<td>one particle jump on a lattice</td>
<td>one point move in 6N-dimensional phase space (deterministic)</td>
</tr>
<tr>
<td>(random)</td>
<td></td>
</tr>
<tr>
<td><strong>Step 2</strong></td>
<td></td>
</tr>
<tr>
<td>many independent particles (random walkers) on a lattice</td>
<td>many copies of the system (gas tanks) corresponding to many points in the 6N-dimensional phase space</td>
</tr>
<tr>
<td>– an ensemble of random walkers</td>
<td>– an ensemble of gas tanks</td>
</tr>
<tr>
<td>– so many that a density function</td>
<td>– so many that a density function</td>
</tr>
<tr>
<td>$C(x)$ makes sense</td>
<td>$\rho(q_i,p_i)$ in $\Gamma$ make sense</td>
</tr>
<tr>
<td><strong>Step 3</strong></td>
<td></td>
</tr>
<tr>
<td>$X(t) = X(0) + \sum_i l_i$</td>
<td>$\dot{\mu} = \omega \frac{\partial H}{\partial \mu}$</td>
</tr>
<tr>
<td>going to the continuum limit $\rightarrow$</td>
<td>going to the continuum limit $\rightarrow$</td>
</tr>
<tr>
<td>Diffusion equation</td>
<td>Liouville’s theorem</td>
</tr>
<tr>
<td>$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$</td>
<td>$\frac{d\rho}{dt} \equiv D \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i} \dot{q_i} + \sum_i \frac{\partial \rho}{\partial p_i} \dot{p_i} = 0$</td>
</tr>
<tr>
<td>PDE for $C(x,t)$</td>
<td>PDE for $\rho(q_i,p_i,t)$ (incompressible flow in $\Gamma$)</td>
</tr>
</tbody>
</table>
3 Liouville’s theorem

Liouville’s theorem states that the phase space density $\rho(\mu, t)$ behaves like an incompressible fluid.

So, after going to the continuum limit, instead of the diffusion equation, we get an equation in fluid mechanics.

How can we prove it?

3.1 Flow of incompressible fluid in 3D

Let’s first familiarize ourselves with the equations in fluid mechanics. Imagine a fluid consisting of a large number of particles with density $\rho(x, t) \equiv \rho(x, y, z, t)$. Imagine that the particles follow a deterministic (no diffusion) flow field $v(x)$, i.e. $v_x(x, y, z)$, $v_y(x, y, z)$, $v_z(x, y, z)$ (velocity of the particle only depends on their current location). This tells us how to follow the trajectory of one particle.

How do we obtain the equation for $\rho(x, t)$ from the flow field $v(x)$?

1. mass conservation (equation of continuity)

$$\frac{\partial \rho(x, t)}{\partial t} = -\nabla \cdot J = -\left(\frac{\partial}{\partial x} J_x + \frac{\partial}{\partial y} J_y + \frac{\partial}{\partial z} J_z\right). \tag{45}$$

2. flux for deterministic flow $J(x) = \rho(x) v(x)$

$$\frac{\partial \rho(x, t)}{\partial t} = -\nabla \cdot (\rho(x) v(x))$$

$$= -\left[\frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z)\right]$$

$$= -\left[\left(\frac{\partial}{\partial x} \rho\right)v_x + \left(\frac{\partial}{\partial y} \rho\right)v_y + \left(\frac{\partial}{\partial z} \rho\right)v_z\right] +$$

$$\left[\rho \left(\frac{\partial}{\partial x} v_x\right) + \rho \left(\frac{\partial}{\partial y} v_y\right) + \rho \left(\frac{\partial}{\partial z} v_z\right)\right] \tag{46}$$

$$\frac{\partial \rho}{\partial t} = -(\nabla \rho) \cdot v - \rho(\nabla \cdot v) \tag{47}$$
\[ \frac{\partial \rho(x, y, z, t)}{\partial t} \] describes the change of \( \rho \) with \( t \) at a fixed point \((x, y, z)\).

We may also ask about how much the density changes as we move together with a particle, i.e., or how crowded a moving particle “feels” about its neighborhood. This is measured by the total derivative,

\[
\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + (\nabla \rho) \cdot \mathbf{v} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} v_x + \frac{\partial \rho}{\partial y} v_y + \frac{\partial \rho}{\partial z} v_z
\]  

(48)

Hence the density evolution equation can also be expressed as

\[
\frac{d\rho}{dt} = -\rho (\nabla \cdot \mathbf{v})
\]  

(49)

For incompressible flow,

\[
\frac{d\rho}{dt} = 0, \quad \nabla \cdot \mathbf{v} = 0
\]  

(50)

a particle always feels the same level of “crowdedness”.

### 3.2 Flow in phase space

Why do we say the collective trajectories of an ensemble of points following Hamiltonian dynamics can be described by incompressible flow in phase space?
All points considered together follows incompressible flow. A point always find the same numbers of neighbors per unit volume as it moves ahead with time.

<table>
<thead>
<tr>
<th>real flow in 3D</th>
<th>flow in 6N-D phase space</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x, y, z$</td>
<td>$q_1, q_2, \cdots, q_{3N}, p_1, p_2, \cdots, p_{3N}$</td>
</tr>
<tr>
<td>$\nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$</td>
<td>$\nabla = \left( \frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \cdots, \frac{\partial}{\partial q_{3N}}, \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \cdots, \frac{\partial}{\partial p_{3N}} \right)$</td>
</tr>
<tr>
<td>$v = (\dot{x}, \dot{y}, \dot{z})$</td>
<td>$v = (\dot{q}_1, \dot{q}<em>2, \cdots, \dot{q}</em>{3N}, \dot{p}_1, \dot{p}<em>2, \cdots, \dot{p}</em>{3N})$</td>
</tr>
<tr>
<td>$\frac{\partial \rho}{\partial t} = -\nabla(\rho v)$</td>
<td>$\frac{\partial \rho}{\partial t} = -\left[ \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right]$</td>
</tr>
<tr>
<td>$\frac{\partial \rho}{\partial t} = -\nabla(\rho v) = -\nabla (\rho \nabla \cdot v)$</td>
<td>$\frac{\partial \rho}{\partial t} = -\left[ \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}<em>i \right] - \left[ \sum</em>{i=1}^{3N} \rho \frac{\partial \dot{q}_i}{\partial q_i} + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right]$</td>
</tr>
<tr>
<td>flow is incompressible if $\nabla \cdot v = 0$</td>
<td>flow is incompressible if $\sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$ (is this true?)</td>
</tr>
</tbody>
</table>
Proof of Liouville’s theorem \((d\rho/dt = 0)\)

Start from Hamilton’s equation of motion

\[
\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \rightarrow \quad \frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} \tag{51}
\]

\[
\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \rightarrow \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i} \tag{52}
\]

\[
\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0 \tag{53}
\]

Therefore, we obtain

\[
\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0 \tag{54}
\]

which is Liouville’s theorem.

Using Liouville’s theorem, the equation of evolution for the density function \(\rho(q_i, p_i, t)\) can be written as

\[
\frac{\partial \rho}{\partial t} = -\sum_i \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = -\sum_i \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \tag{55}
\]

This can be written concisely using Poisson’s bracket,

\[
\frac{\partial \rho}{\partial t} = -\{\rho, H\} \tag{56}
\]

Poisson’s bracket

\[
\{ A, B \} \equiv \sum_{i=1}^{3N} \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right) \tag{57}
\]

Obviously, \(\{ A, B \} = -\{ B, A \}\) and \(\{ A, A \} = 0\).

Not so obviously, \(\{ A, A^2 \} = 0\), and \(\{ A, B \} = 0\) if \(B\) is a function of \(A\), i.e. \(B = f(A)\).
4 Ensemble

An ensemble is a large number of points in the phase space that can be described by a density function $\rho(\{q_i\}, \{p_i\})$.

$\rho(\{q_i\}, \{p_i\})$ is like a probability density function (PDF) — the probability of picking any particular point out of the entire ensemble.

Now, consider an arbitrary function $A(\{q_i\}, \{p_i\})$ which takes different value at different points in phase space, such as the kinetic energy

$$E_{\text{kin}} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

What is the average value for $A$ among all these points?

The ensemble average can be written as

$$\langle A \rangle \equiv \int \prod_{i=1}^{3N} dq_i \; dp_i \; A(\{q_i\}, \{p_i\}) \rho(\{q_i\}, \{p_i\}) \quad (58)$$

This is same as expectation value if we interpret $\rho(\{q_i\}, \{p_i\})$ as PDF.

Notice that $A(\{q_i\}, \{p_i\})$ is not an explicit function of time. It is a function defined on the phase space. But the ensemble average will depend on time $t$ if $\rho$ evolves with time.

$$\langle A \rangle(t) \equiv \int \prod_{i=1}^{3N} dq_i \; dp_i \; A(\{q_i\}, \{p_i\}) \rho(\{q_i\}, \{p_i\}, t) \quad (59)$$

How does the ensemble average evolve with time?

$$\frac{d\langle A \rangle}{dt} = \int \prod_{i=1}^{3N} dq_i \; dp_i \; \left( \frac{\partial}{\partial t} \rho(\{q_i\}, \{p_i\}) \right) A(\{q_i\}, \{p_i\}) \rho(\{q_i\}, \{p_i\}, t)$$

$$= \int \prod_{i=1}^{3N} dq_i \; dp_i \; \left( \sum_{j=1}^{3N} \left( \frac{\partial \rho}{\partial p_j} \frac{\partial H}{\partial q_j} - \frac{\partial \rho}{\partial q_j} \frac{\partial H}{\partial p_j} \right) \right) \cdot \rho(\{q_i\}, \{p_i\}, t)$$

$$= -\int \prod_{i=1}^{3N} dq_i \; dp_i \; \left( \frac{\partial A}{\partial p_j} \frac{\partial H}{\partial q_j} - \frac{\partial A}{\partial q_j} \frac{\partial H}{\partial p_j} \right) \cdot \rho(\{q_i\}, \{p_i\}, t)$$

$$= \int \prod_{i=1}^{3N} dq_i \; dp_i \; \{A, H\} \cdot \rho(\{q_i\}, \{p_i\}, t) \quad (60)$$

$$\frac{d\langle A \rangle}{dt} = \langle \{A, H\} \rangle \quad (61)$$
(Very similar equation appears in quantum mechanics!)

For example, average total energy among all points in the ensemble

\[ E_{\text{tot}} \equiv \langle H \rangle \]  
\[
\frac{dE_{\text{tot}}}{dt} = \frac{d\langle H \rangle}{dt} = \langle \{ H, H \} \rangle = 0
\]  

This is an obvious result, because the total energy of each point is conserved as they move through the phase space. As a result, the average total energy also stays constant.

**Example 5.** Pendulum with Hamiltonian

\[ H(\theta, p_{\theta}) = \frac{p_{\theta}^2}{2mR^2} + mgR\cos\theta \]

Phase space is only 2-dimensional \((\theta, p_{\theta})\).

Equilibrium motion of one point in phase space is

\[ \dot{\theta} = \frac{\partial H}{\partial p_{\theta}} \quad \dot{p}_{\theta} = -\frac{\partial H}{\partial \theta} \]  

Now consider a large number of points in the \((\theta, p_{\theta})\) space. \(p(\theta, p_{\theta}, t)\) describes their density distribution at time \(t\).

What is the evolution equation for \(\rho\)?

\[
\frac{\partial p(\theta, p_{\theta}, t)}{\partial t} = -\frac{\partial \rho}{\partial \theta} \dot{\theta} - \frac{\partial \rho}{\partial p_{\theta}} \dot{p}_{\theta} = -\frac{\partial \rho}{\partial \theta} \frac{\partial H}{\partial p_{\theta}} + \frac{\partial \rho}{\partial p_{\theta}} \frac{\partial H}{\partial \theta} \equiv -\{\rho, H\}
\]
From $\frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{mR^2}$, $\frac{\partial H}{\partial \theta} = -mgR \sin \theta$

$$\Rightarrow \frac{\partial \rho}{\partial t} = -\frac{\partial \rho}{\partial \theta} \frac{p_\theta}{mR^2} - \frac{\partial \rho}{\partial p_\theta} mgR \sin \theta \quad (66)$$

Suppose $A = \theta^2$, the ensemble average of $A$ is

$$\langle A \rangle = \int d\theta dp_\theta \theta^2 \rho(\theta, p_\theta, t) \quad (67)$$

How does $\langle A \rangle$ changes with time?

$$\frac{d\langle A \rangle}{dt} = \langle \{ A, H \} \rangle \quad (68)$$

$$\{ A, H \} = \frac{\partial \theta^2}{\partial \theta} \frac{\partial H}{\partial p_\theta} - \frac{\partial \theta^2}{\partial p_\theta} \frac{\partial H}{\partial \theta} = 2\theta(-mgR \sin \theta) \quad (69)$$

$$\Rightarrow \frac{d\langle A \rangle}{dt} = \frac{d\langle \theta^2 \rangle}{dt} = -2mgR \langle \theta \sin \theta \rangle \quad (70)$$

Example 6. Consider an ensemble of pendulums described in Example 5. At $t = 0$, the density distribution in the ensemble is,

$$\rho(\theta, p_\theta, t = 0) = \frac{1}{2\pi} \frac{1}{\sqrt{2\pi\sigma}} \exp \left[ -\frac{p_\theta^2}{2\sigma^2} \right] \quad (71)$$

where $-\pi \leq \theta < \pi$, $-\infty < p_\theta < \infty$.

(a) Verify that $\rho(\theta, p_\theta, t = 0)$ is properly normalized.

(b) What is $\frac{\partial \rho}{\partial t}|_{t=0}$? Mark regions in phase space where $\frac{\partial \rho}{\partial t}|_{t=0} > 0$ and regions where $\frac{\partial \rho}{\partial t}|_{t=0} < 0$.

(c) How can we change $\rho(\theta, p_\theta, t = 0)$ to make $\frac{\partial \rho}{\partial t} = 0$?
5 Summary

By the end of this lecture, you should:

- be able to derive the equations of motion of a mechanical system by constructing a Lagrangian, and obtain the Hamiltonian through Legendre transform. (This is important for Molecular Simulations.)

- agree with me that the flow of an ensemble of points in phase space, each following the Hamilton’s equation of motion, is the flow of an incompressible fluid.

- be able to write down the relation between partial derivative and total derivative of \( \rho(q_i, p_i, t) \).

- be able to write down the equation of Liouville’s theorem (close book, of course).

- be able to express the ensemble average of any quantity as an integral over phase space, and to write down the time evolution of the ensemble average (be ware of the minus sign!)

The material in this lecture forms (part of) the foundation of statistical mechanics.

As an introductory course, we will spend more time on how to use statistical mechanics.

A full appreciation of the foundation itself will only come gradually with experience.

Nonetheless, I think an exposure to the theoretical foundation from the very beginning is a good idea.

References