Topics in Computational Chemistry, CHEM*7500/CHEM 750 Fall 2021

Week 1: Introduction and Classical Mechanics

Prof. Leanne D. Chen

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Department of Chemistry

UNIVERSITY of GUELPH

Summary of Topics

- Newtonian mechanics
- Lagrangian mechanics
- Hamiltonian mechanics

Newtonian Mechanics

1. In the absence of external forces, a body will either be at rest, or execute motion along a straight line with constant velocity $\mathbf{v}$.
2. The action of an external force $\mathbf{F}$ on a body produces an acceleration $\mathbf{a}$ equal to the force divided by the mass m of the body.

$$\mathbf{a} = \frac{\mathbf{F}}{m}, \quad \mathbf{F} = m\mathbf{a} \tag{1}$$

3. If body A exerts a force on body B, then body B exerts an equal and opposite force on body A. That is, if $\mathbf{F}_{AB}$ is the force body A exerts on body B, then the force $\mathbf{F}_{BA}$ exerted by body B on body A satisfies

$$\mathbf{F}_{BA} = -\mathbf{F}_{AB}. \tag{2}$$

Newtonian Mechanics

- Newton's equations were originally intended to describe the interaction and motion of celestial bodies via gravitational forces.
- In the context of molecular modelling, this classical approach is sufficient in many cases, where the atoms are massive enough.
- There are occasions when this classical approximation breaks down, however, and quantum mechanical effects will need to be included as well.
- For now, we will focus on the classical approach to apply Newton's equations to molecular systems.

Newtonian Mechanics

The motion of an object can be described quantitatively by specifying the Cartesian position vector $\mathbf{r}(t)$ of the object in space at any time t.

$$\mathbf{r}(t) = \big(x(t), y(t), z(t)\big) \tag{3}$$

We can rewrite Newton's second law in terms of $\mathbf{r}$

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = \mathbf{F} \tag{4}$$

Using the dot notation for time derivatives

$$m\ddot{\mathbf{r}} = \mathbf{F} \tag{5}$$

As equation 5 is a second-order differential equation, it is necessary to specify two initial conditions: the initial position $\mathbf{r}(0)$ and initial velocity $\dot{\mathbf{r}}(0)$.

$$\mathbf{r}(t) = \mathbf{r}(0) + \dot{\mathbf{r}}(0)t \tag{6}$$

This is an example of a trajectory, or a specification of the object's position as a function of time and initial conditions. If no forces act on the object, then its position will be the solution of

$$\ddot{\mathbf{r}} = 0 \tag{7}$$

We will walk through the process of solving Newton's equation for the simplest case where $\mathbf{F} = 0$.

$$m\ddot{\mathbf{r}} = 0 \tag{8}$$

Here, $m \neq 0$, so really we are solving for

$$\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = 0 \tag{9}$$

$$\int_0^t \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2}\mathrm{d}t = \int_0^t 0\mathrm{d}t$$

$$\left.\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\right|_0^t = 0$$

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}(t) - \dot{\mathbf{r}}(0) = 0 \tag{10}$$

Integrating again,

$$\begin{aligned}
\frac{d\mathbf{r}}{dt}(t) &= \dot{\mathbf{r}}(0) \\
\int_0^t \frac{d\mathbf{r}}{dt}(t)dt &= \int_0^t \dot{\mathbf{r}}(0)dt \\
\mathbf{r}(t)\Big|_0^t &= \dot{\mathbf{r}}(0)t\Big|_0^t \\
\mathbf{r}(t) - \mathbf{r}(0) &= \dot{\mathbf{r}}(0)t - \dot{\mathbf{r}}(0)0 \\
\mathbf{r}(t) &= \mathbf{r}(0) + \dot{\mathbf{r}}(0)t \qquad (11)
\end{aligned}$$

Newtonian Mechanics

- Note that the straight line motion described by Equation 6 is actually the unique solution of Equation 7 for an object with initial position $\mathbf{r}(0)$ and initial velocity $\dot{\mathbf{r}}$ or $\mathbf{v}(0)$, which is constant. So Newton's second law includes the first law.
- How is this relevant to molecular simulations?
- We can break down a macroscopic system into microscopic constituents, and we can model the motions and trajectories of these particles with Newton's equations.

What are the forces that act on the particles in our system? Say we have a system of N particles in three dimensions. Then, each particle i where $i \in [1, N]$ experiences a force $\mathbf{F}_i$ due to all the other particles in the system and potentially the external environment. If frictional forces are present, then $\mathbf{F}_i$ could also be a function of the particle's velocity $\dot{\mathbf{r}}_i$.

$$\mathbf{F}_i\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \dot{\mathbf{r}}_i\right) = \sum_{j \neq i} \mathbf{f}_{ij}\left(\mathbf{r}_i - \mathbf{r}_j\right) + \mathbf{f}^{(\text{ext})}\left(\mathbf{r}_i, \dot{\mathbf{r}}_i\right) \tag{12}$$

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \dot{\mathbf{r}}_i\right) \tag{13}$$

Newtonian Mechanics

- The equations of motion of the system must be solved subject to a set of initial positions $\{\mathbf{r}_1(0), \ldots, \mathbf{r}_N(0)\}$ and velocities $\{\dot{\mathbf{r}}_1(0), \ldots, \dot{\mathbf{r}}_N(0)\}$.
- In a realistic system, the interparticle forces are highly nonlinear functions of the N particle positions so that equation 13 possesses enormous dynamical complexity, and it is not possible to obtain an analytic solution.
- Not enough computational resources to simulate a system with $N \sim 10^{23}$ particles.

Newtonian Mechanics

- Statistical mechanics provides the necessary connection between the microscopic laws and macroscopic observables.
- These rules, however, cannot circumvent the complexity of the system.
- How do we deal with complexity?
  - Reduce complexity so that we have closed-form expressions
  - Reduce the number of particles in the system so that the simulation becomes computationally tractable; this is feasible because many macroscopic properties are well-converged even for systems on the order of 10^2–10^9 particles $\Rightarrow$ molecular dynamics!

Phase Space

Newton's equations specify the complete set of particle positions $\{\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)\}$ and, by differentiation, the particle velocities $\{\mathbf{v}_1(t), \ldots, \mathbf{v}_N(t)\}$ at any given time t, given that the positions and velocities are known at one particular instant in time. It is often preferable to work with particle momenta $\{\mathbf{p}_1(t), \ldots, \mathbf{p}_N(t)\}$, which are related to the velocities by

$$\mathbf{p}_i = m_i \mathbf{v}_i = m_i \dot{\mathbf{r}}_i \tag{14}$$

in Cartesian coordinates.

Phase Space

Note that, in terms of momenta, Newton's second law can be written as

$$\mathbf{F}_i = m\mathbf{a}_i = m_i \frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} = \frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} \tag{15}$$

Therefore, the classical dynamics of an N-particle system can be expressed by specifying the full set of $6N$ functions, $\{\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t), \mathbf{p}_1(t), \ldots, \mathbf{p}_N(t)\}$. Equivalently, at any instant t in time, all of the information about the system is specified by $6N$ numbers (or $2dN$ in d dimensions).

Phase Space

- These $6N$ numbers constitute the *microscopic state* of the system at time t.
- That these $6N$ numbers are sufficient to characterize the system follows entirely from the fact that they are all that is needed to seed equations 13, from which the complete time evolution of the system can be determined.
- Suppose, at some instant in time, the positions and momenta of the system are $\{\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N\}$.
- These $6N$ numbers can be regarded as an ordered $6N$-tuple or a single point in a $6N$-dimensional space called *phase space*.

Phase Space

Although the geometry of this space can, under certain circumstances, be nontrivial, in its simplest form, a phase space is a Cartesian space that can be constructed from $6N$ mutually orthogonal axes. We will denote a general point in the phase space as

$$x = (\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) \tag{16}$$

This is also known as the *phase space vector*. Solving equation 13 generates a set of functions

$$x(t) = \big(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t), \mathbf{p}_1, \ldots, \mathbf{p}_N(t)\big) \equiv x_t \tag{17}$$

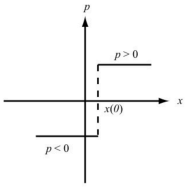
which describes a parametric path or *trajectory* in the phase space. Therefore, classical motion can be described by the motion of a point along a trajectory in phase space.

Phase Space

Although phase space trajectories can only be visualized for a one-particle system in one spatial dimension, it is, nevertheless, instructive to study several such examples. Consider, first, a free particle with coordinate x and momentum p, described by the one-dimensional analogue of equation 6,

$$x(t) = x(0) + \frac{p}{m}t \tag{18}$$

where p is the particle's momentum which is a constant.



Phase Space

Another important example of a phase space trajectory is that of a simple harmonic oscillator, for which the force law is given by Hooke's law

$$F(x) = -kx \tag{19}$$

where k is a constant known as the *force constant*, is always positive, and is related to the stiffness of the oscillation. For this system, Newton's second law takes the form

$$m\ddot{x} = -kx \tag{20}$$

Phase Space

To solve the second-order differential equation, we have

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + kx = 0 \tag{21}$$

What this means is that we need a function x for which the second derivative is a multiple of itself. Functions that fit this criteria include exponential functions and certain trigonometric functions. We will use an exponential function here

$$x = e^{\lambda t} \quad \frac{\mathrm{d}^2x}{\mathrm{d}t^2} = \lambda^2 e^{\lambda t} \tag{22}$$

Phase Space

Substituting exponential functions into Equation 21

$$m\lambda^2 e^{\lambda t} + ke^{\lambda t} = 0 \tag{23}$$

Since $e^{\lambda t}$ is never 0, we divide through by this term

$$m\lambda^2 + k = 0 \tag{24}$$

Solve for λ

$$\lambda = \pm\sqrt{\frac{k}{m}}i \tag{25}$$

We then have

$$x(t) = C_1 \cos\left(\sqrt{\frac{k}{m}}t\right) + C_2 \sin\left(\sqrt{\frac{k}{m}}t\right) \tag{26}$$

For a given initial condition x_0 and p_0, the solution becomes

$$x(t) = x_0 \cos(\omega t) + \frac{p_0}{m\omega} \sin(\omega t) \tag{27}$$

where

$$\omega = \sqrt{\frac{k}{m}} \tag{28}$$

Phase Space

To obtain an expression for the momentum, we differentiate once with respect to t and multiply by m

$$p(t) = p_0 \cos(\omega t) - m\omega x_0 \sin(\omega t) \tag{29}$$

Note that $p(t)$ and $x(t)$ are related by

$$\frac{\left[p(t)\right]^2}{2m} + \frac{1}{2}m\omega^2\left[x(t)\right]^2 = C \tag{30}$$

where C is a constant determined by initial conditions according to

$$C = \frac{p_0^2}{2m} + \frac{1}{2}m\omega^2 x_0^2 \tag{31}$$

Phase Space

Different initial conditions give rise to different values of C, which changes the size of the ellipse. Changing the mass and frequency changes the shape of the ellipse. Phase space plots determine the values of position and momentum the system will visit along a trajectory for a given set of initial conditions.

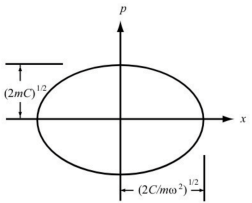


Figure 1: Phase space of the one-dimensional harmonic oscillator.

Lagrangian Mechanics

- Statistical mechanics is concerned with characterizing the number of microscopic states available to a system and, therefore, requires a formulation of classical mechanics that is more closely connected to the phase space description than the Newtonian formulation.
- Since phase space provides a geometric description of a system in terms of positions and momenta, or equivalently in terms of positions and velocities, it is natural to look for an algebraic description of a system in terms of these variables.
- In particular, we seek a “generator” of the classical equations of motion that takes the positions and velocities or positions and momenta as its inputs and produces, through some formal procedure the classical equations of motion.

Lagrangian Mechanics

The formal structure we seek is embodied in the *Lagrangian* and *Hamiltonian* formulations of classical mechanics. The introduction of such a formal structure places some restrictions on the form of the force laws. Specifically, the forces are required to be *conservative*. Conservative forces are defined to be vector quantities that are derivable from a scalar function, via

$$\mathbf{F}_i\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) = -\nabla_i U\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) \tag{32}$$

where $\nabla_i = \partial/\partial \mathbf{r}_i$. Consider the work done by the force $\mathbf{F}_i$ in moving particle i from points A to B along a particular path. This work is

$$W_{\mathrm{AB}} = \int_{\mathrm{A}}^{\mathrm{B}} \mathbf{F}_i \cdot \mathrm{d}\mathbf{l} \tag{33}$$

Since $\mathbf{F}_i = -\nabla_i U$ is conserved, the line integral simply becomes the difference in potential energy between path endpoints A and B, $W_{AB} = U_A - U_B$, independent of the path taken. It follows that along a closed path

$$\oint \mathbf{F}_i \cdot d\mathbf{l} = 0 \tag{34}$$

Given the N particle velocities, $\dot{\mathbf{r}}_1, \ldots, \dot{\mathbf{r}}_N$, the kinetic energy of the system is given by

$$K\left(\dot{\mathbf{r}}_1, \ldots, \dot{\mathbf{r}}_N\right) = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2 \tag{35}$$

Lagrangian Mechanics

The Lagrangian $\mathcal{L}$ of a system is defined as the difference between the kinetic and potential energies expressed as a function of positions and velocities

$$\mathcal{L}\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \ldots, \dot{\mathbf{r}}_N\right) = K\left(\dot{\mathbf{r}}_1, \ldots, \dot{\mathbf{r}}_N\right) - U\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) \tag{36}$$

The Lagrangian serves as the generator of the equations of motion via the Euler-Lagrange equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i}\right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0 \tag{37}$$

It can be easily verified that substitution of equation 36 into equation 37 gives equation 13

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} &= m_i \dot{\mathbf{r}}_i \\
\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i}\right) &= m_i \ddot{\mathbf{r}}_i \\
\frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} &= -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i \\
\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i}\right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} &= m_i \ddot{\mathbf{r}}_i - \mathbf{F}_i = 0
\end{aligned} \tag{38}$$

and we have recovered Newton's second law of motion.

Lagrangian Mechanics

We will now apply the Euler-Lagrange equation to the previous example of the one-dimensional harmonic oscillator. Hooke's law $F(x) = -kx$ can be derived from a potential function

$$U(x) = \frac{1}{2}kx^2 \tag{39}$$

so that the Lagrangian takes the form

$$\mathcal{L}\left(x, \dot{x}\right) = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2 \tag{40}$$

Thus, the equation of motion is derived as follows

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial \dot{x}} &= m\dot{x} \\ \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) &= m\ddot{x} \\ \frac{\partial \mathcal{L}}{\partial x} &= -kx \\ \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) - \frac{\partial \mathcal{L}}{\partial x} &= m\ddot{x} + kx = 0 \end{aligned} \tag{41}$$

which is the same as equation 20.

It is important to note that when the forces in a particular system are conservative, then the equations of motion satisfy an important conservation law, namely the conservation of energy. The total energy is given by the sum of kinetic and potential energies:

$$E = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{42}$$

In order to verify that E is a constant, we need only show that $\mathrm{d}E/\mathrm{d}t = 0$. Differentiating equation 42 with respect to time yields

$$\begin{aligned}
\frac{\mathrm{d}E}{\mathrm{d}t} &= \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i + \sum_{i=1}^{N} \frac{\partial U}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i \\
&= \sum_{i=1}^{N} \dot{\mathbf{r}}_i \cdot \left[m_i \ddot{\mathbf{r}}_i + \frac{\partial U}{\partial \mathbf{r}_i} \right] \\
&= \sum_{i=1}^{N} \dot{\mathbf{r}}_i \cdot \left[m_i \ddot{\mathbf{r}}_i - \mathbf{F}_i \right] \\
&= 0 \qquad (43)
\end{aligned}$$

Example: Motion in a central potential Consider a single particle in three dimensions subject to a potential $U(\mathbf{r})$ that depends only on the particle's distance from the origin. This means

$$U(\mathbf{r}) = U(|\mathbf{r}|) = U(r) \tag{44}$$

where

$$r = \sqrt{x^2 + y^2 + z^2} \tag{45}$$

and is known as a *central potential*.

In this case, the most natural coordinates are not the Cartesian coordinates (x, y, z), but rather spherical polar coordinates (r, θ, ϕ) given by

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \tan^{-1}\left(\frac{\sqrt{x^2 + y^2}}{z}\right), \quad \phi = \tan^{-1}\left(\frac{y}{x}\right) \tag{46}$$

which can be inverted to give

$$x = r\sin(\theta)\cos(\phi), \quad y = r\sin(\theta)\sin(\phi), \quad z = r\cos(\theta) \tag{47}$$

The expression for the Lagrangian for this system is

$$\mathcal{L} = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2(\theta)\dot{\phi}^2\right) - U(r) \tag{48}$$

In order to obtain the equations of motion from the Euler-Lagrange equation, derivatives of $\mathcal{L}$ with respect to each of the variables and their time derivatives are required. These are given by

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial \dot{r}} &= m\dot{r}, & \frac{\partial \mathcal{L}}{\partial r} &= mr\dot{\theta}^2 + mr\sin^2\theta\dot{\phi}^2 - \frac{\mathrm{d}U}{\mathrm{d}r} \\
\frac{\partial \mathcal{L}}{\partial \dot{\theta}} &= mr^2\dot{\theta}, & \frac{\partial \mathcal{L}}{\partial \theta} &= mr^2\sin\theta\cos\theta\dot{\phi}^2 \\
\frac{\partial \mathcal{L}}{\partial \dot{\phi}} &= mr^2\sin^2\theta\dot{\phi}, & \frac{\partial \mathcal{L}}{\partial \phi} &= 0
\end{aligned} \tag{49}$$

Lagrangian Mechanics

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_j}\right) = \frac{\partial \mathcal{L}}{\partial q_j} \tag{50}$$

Lagrange's equations are more useful than Newton's equations in many problems because it is usually much easier to write down an expression for the potential energy in some appropriate coordinate system than it is to recognize all the various forces. (The Lagrangian formalism is based on the potential energy of the system, whereas the Newtonian approach is based on the forces acting on the system.)

Legendre Transforms

Our next goal is to derive the Hamiltonian formulation of classical mechanics. Before we are able to do so, we need to introduce the concept of a *Legendre transform*. Consider a simple function $f(x)$ of a single variable x. Suppose we wish to express $f(x)$ in terms of a new variable m, where m and x are related by

$$m = f'(x) \equiv g(x) \tag{51}$$

with $f'(x) = \mathrm{d}f/\mathrm{d}x$. Can we determine $f(x)$ at a point x_0 given only $m_0 = f'(x_0) = g(x_0)$? We cannot do this, because any function $f(x) + c$ where c is a constant will satisfy these conditions. We need to specify both the slope $m_0 = f'(x_0)$ as well as the y-intercept, $b(x_0)$ of the tangent line to the function at x_0 in order to uniquely determin $f(x_0)$.

Legendre Transforms

In fact, $f(x_0)$ will be given by the equation of the tangent line of the function at x_0:

$$f(x_0) = f'(x_0)x_0 + b(x_0) \tag{52}$$

Equation 52 shows how we may transform from a description of $f(x)$ in terms of x to a new description in terms of m. First, since equation 52 is valid for all x_0, it can be written generally in terms of x as

$$f(x) = f'(x)x + b(x) \tag{53}$$

Legendre Transforms

Then, recognizing that $f'(x) = g(x) = m$ and $x = g^{-1}(m)$, and assuming that $m = g(x)$ exists and is a one-to-one mapping, it is clear that the function $b\left(g^{-1}(m)\right)$, given by

$$b\left(g^{-1}(m)\right) = f\left(g^{-1}(m)\right) - mg^{-1}(m) \tag{54}$$

contains the same information as the original $f(x)$ but expressed as a function of m instead of x. We call the function $\tilde{f}(m) = b\left(g^{-1}(m)\right)$ the *Legendre transform* of $f(x)$. The function $\tilde{f}(m)$ can be written compactly as

$$\tilde{f}(m) = f\left(x(m)\right) - mx(m) \tag{55}$$

where $x(m)$ serves to remind us that x is a function of m through the variable transformation $x = g^{-1}(m)$.

Hamiltonian Mechanics

- For a first application of the Legendre transformation, we will derive a new formulation of classical mechanics in terms of positions and momenta rather than positions and velocities.
- Recall that the Cartesian momentum of a particle $\mathbf{p}_i$ is just $\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$.
- Because the only dependence of the Lagrangian on velocities is in the kinetic energy term, we can write

$$\mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = \frac{\partial}{\partial \dot{\mathbf{r}}_i} \left[\sum_{j=1}^{N} \frac{1}{2} m_j \dot{\mathbf{r}}_j^2 - U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right] = m_i \dot{\mathbf{r}}_i \tag{56}$$

Hamiltonian Mechanics

We seek to derive a new function of positions and momenta as a Legendre transform of the Lagrangian with respect to the velocities. Note that, by way of equation 56, the velocities can be easily expressed as functions of momenta, $\dot{\mathbf{r}}_i = \dot{\mathbf{r}}_i(\mathbf{p}_i) = \mathbf{p}_i/m_i$. The new Lagrangian, denoted $\tilde{\mathcal{L}}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$, is given by

$$\begin{aligned}
\tilde{\mathcal{L}}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) &= \mathcal{L}\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \dot{\mathbf{r}}_1(\mathbf{p}_1), \ldots, \dot{\mathbf{r}}_N(\mathbf{p}_N)\right) - \sum_{i=1}^{N} \mathbf{p}_i \cdot \dot{\mathbf{r}}_i(\mathbf{p}_i) \\
&= \frac{1}{2}\sum_{i=1}^{N} m_i \left[\frac{\mathbf{p}_i}{m_i}\right]^2 - U(\mathbf{r}_1, \ldots, \mathbf{r}_N) - \sum_{i=1}^{N} \mathbf{p}_i \cdot \frac{\mathbf{p}_i}{m_i} \\
&= -\frac{1}{2}\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \qquad (57)
\end{aligned}$$

The function $\tilde{\mathcal{L}}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$ is known as the *Hamiltonian* $\mathcal{H}$:

$$\mathcal{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) = \frac{1}{2} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{58}$$

In other words, the Hamiltonian is the total energy of the system expressed as a function of positions and momenta. It is related to the Lagrangian by

$$\mathcal{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) = \sum_{i=1}^{N} \mathbf{p}_i \cdot \dot{\mathbf{r}}_i(\mathbf{p}_i) - \mathcal{L}\left(\mathbf{r}_1, \ldots, \mathbf{r}_N, \dot{\mathbf{r}}_1(\mathbf{p}_1), \ldots, \dot{\mathbf{r}}_N(\mathbf{p}_N)\right) \tag{59}$$

Hamiltonian Mechanics

- To recap briefly, we obtained the Hamiltonian by Legendre transforming the Lagrangian. We can now obtain the equations of motion for a system from the Hamiltonian using

$$\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}, \quad \frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \tag{60}$$

- Equations 60 are known as *Hamilton's equations of motion*.
- Whereas the Euler-Lagrange equations constitute a set of $3N$ second-order differential equations, Hamilton's equations constitute an equivalent set of $6N$ first-order differential equations.
- When subject to the same initial conditions, the Euler-Lagrange and Hamiltonian equations of motion must yield the same trajectory.

Hamiltonian Mechanics

To recover Newton's second law of motion from equations 60,

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i(\mathbf{r})\end{aligned} \tag{61}$$

Taking the time derivative of both sides of the first part and substituting the result into the second part of equation 61 yields

$$\begin{aligned}\ddot{\mathbf{r}}_i &= \frac{\dot{\mathbf{p}}_i}{m_i} \\ \dot{\mathbf{p}}_i &= m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i(\mathbf{r}_1, \ldots, \mathbf{r}_N)\end{aligned} \tag{62}$$

Thank you!

Please feel free to unmute yourself or raise your hand to ask a question.