

# Classical Equations of Motion

- Several formulations are in use
  - *Newtonian*
  - *Lagrangian*
  - *Hamiltonian*
- Advantages of non-Newtonian formulations
  - *more general, no need for “fictitious” forces*
  - *better suited for multiparticle systems*
  - *better handling of constraints*
  - *can be formulated from more basic postulates*
- Assume conservative forces

$$\vec{\mathbf{F}} = -\vec{\nabla}U \quad \textit{Gradient of a scalar potential energy}$$

# Newtonian Formulation

- Cartesian spatial coordinates  $\mathbf{r}_i = (x_i, y_i, z_i)$  are primary variables
  - for  $N$  atoms, system of  $N$  2nd-order differential equations

$$m \frac{d^2 \mathbf{r}_i}{dt^2} \equiv m \ddot{\mathbf{r}}_i = \mathbf{F}_i$$

- Sample application: 2D motion in central force field

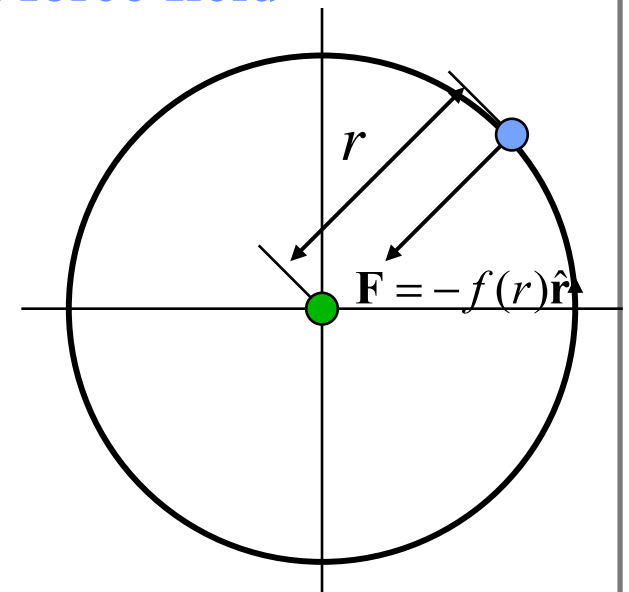
$$m\ddot{x} = \mathbf{F} \cdot \hat{\mathbf{e}}_x = -f(r) \hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_x = -xf \left( \sqrt{x^2 + y^2} \right)$$

$$m\ddot{y} = \mathbf{F} \cdot \hat{\mathbf{e}}_y = -f(r) \hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_y = -yf \left( \sqrt{x^2 + y^2} \right)$$

- Polar coordinates are more natural and convenient

$$mr^2 \dot{\theta} = \ell \quad \text{constant angular momentum}$$

$$m\ddot{r} = -f(r) + \frac{\ell^2}{mr^3} \quad \text{fictitious (centrifugal) force}$$



# Lagrangian Formulation

- Independent of coordinate system
- Define the Lagrangian
  - $L(\mathbf{q}, \dot{\mathbf{q}}) \equiv K(\mathbf{q}, \dot{\mathbf{q}}) - U(\mathbf{q})$
- Equations of motion

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0 \quad j = 1 \dots N$$

- $N$  second-order differential equations

- Central-force example

$$L = \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2) - U(r)$$

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}} \right) = \frac{\partial L}{\partial r} \Rightarrow \boxed{m\dot{r} = mr\dot{\theta}^2 - f(r)} \quad \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\theta}} \right) = \frac{\partial L}{\partial \theta} \Rightarrow \boxed{\frac{d}{dt} (mr^2\dot{\theta}) = 0}$$

$$\vec{\mathbf{F}}_r = -\vec{\nabla}_r U = -f(r)$$

# Hamiltonian Formulation 1. Motivation

- Appropriate for application to statistical mechanics and quantum mechanics
- Newtonian and Lagrangian viewpoints take the  $q_i$  as the fundamental variables
  - *$N$ -variable configuration space*
  - *$\dot{q}_i$  appears only as a convenient shorthand for  $dq/dt$*
  - *working formulas are 2nd-order differential equations*
- Hamiltonian formulation seeks to work with 1st-order differential equations
  - *$2N$  variables*
  - *treat the coordinate and its time derivative as independent variables*
  - *appropriate quantum-mechanically*

# Hamiltonian Formulation 2. Preparation

## ○ Mathematically, Lagrangian treats $q$ and $\dot{q}$ as distinct

- $L(q_j, \dot{q}_j, t)$

- *identify the generalized momentum as*

$$p_j = \frac{\partial L}{\partial \dot{q}_j}$$

- *e.g. if  $L = K - U = \frac{1}{2}m\dot{q}^2 - U(q)$ ;  $p = \partial L / \partial \dot{q} = m\dot{q}$*

- *Lagrangian equations of motion  $\frac{dp_j}{dt} = \frac{\partial L}{\partial q_j}$*

## ○ We would like a formulation in which $p$ is an independent variable

- *$p_i$  is the derivative of the Lagrangian with respect to  $\dot{q}_i$ , and we're looking to replace  $\dot{q}_i$  with  $p_i$*

- *we need ...?*

## Hamiltonian Formulation 3. Definition

- ...a Legendre transform!
- Define the *Hamiltonian*,  $H$

$$\begin{aligned} H(\mathbf{q}, \mathbf{p}) &= -\left[ L(\mathbf{q}, \dot{\mathbf{q}}) - \sum p_j \dot{q}_j \right] \\ &= -K(\mathbf{q}, \dot{\mathbf{q}}) + U(\mathbf{q}) + \sum \frac{\partial K}{\partial \dot{q}_j} \dot{q}_j \\ &= -\sum a_j \dot{q}_j^2 + U(\mathbf{q}) + \sum (2a_j \dot{q}_j) \dot{q}_j \\ &= +\sum a_j \dot{q}_j^2 + U(\mathbf{q}) \\ &= K + U \end{aligned}$$

- $H$  equals the total energy (kinetic plus potential)

# Hamiltonian Formulation 4. Dynamics

## ○ Hamilton's equations of motion

- *From Lagrangian equations, written in terms of momentum*

Differential change in L

$$\begin{aligned} dL &= \frac{\partial L}{\partial q} dq + \frac{\partial L}{\partial \dot{q}} d\dot{q} \\ &= \dot{p} dq + p d\dot{q} \end{aligned}$$

Legendre transform

$$\begin{aligned} H &= -(L - p\dot{q}) \\ dH &= -(\dot{p}dq - \dot{q}dp) \\ dH &= -\dot{p}dq + \dot{q}dp \end{aligned}$$

$$\left. \begin{aligned} \dot{q} &= +\frac{\partial H}{\partial p} \\ \dot{p} &= -\frac{\partial H}{\partial q} \end{aligned} \right\}$$

$$\frac{dp}{dt} = \dot{p} = \frac{\partial L}{\partial q}$$

Lagrange's equation  
of motion

$$p = \frac{\partial L}{\partial \dot{q}}$$

Definition of momentum

Hamilton's equations of motion

Conservation of energy

$$\frac{dH}{dt} = -\dot{p} \frac{dq}{dt} + \dot{q} \frac{dp}{dt} = -\dot{p}\dot{q} + \dot{q}\dot{p} = 0$$

# Hamiltonian Formulation 5. Example

## ○ Particle motion in central force field

$$H = K + U$$

$$= \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + U(r)$$

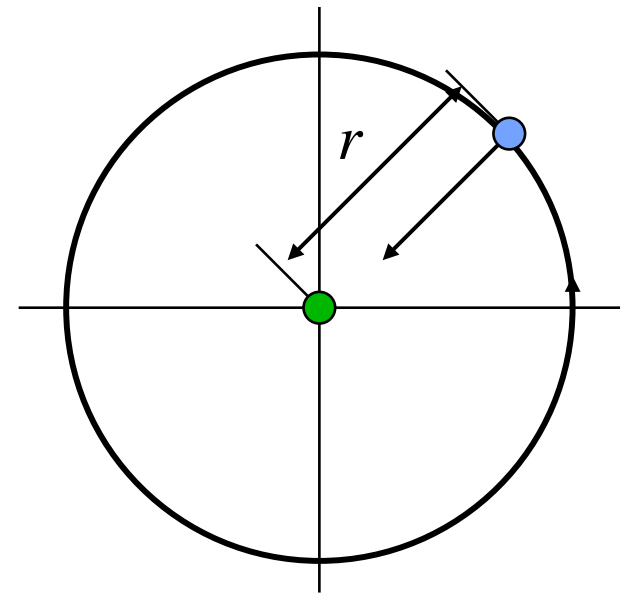
$$\dot{q} = + \frac{\partial H}{\partial p}$$

$$\dot{p} = - \frac{\partial H}{\partial q}$$

$$(1) \frac{dr}{dt} = \frac{p_r}{m} \quad (2) \frac{d\theta}{dt} = \frac{p_\theta}{mr^2}$$

$$(3) \frac{dp_r}{dt} = \frac{p_\theta^2}{mr^3} - f(r) \quad (4) \frac{dp_\theta}{dt} = 0$$

$$\vec{F}_r = -\vec{\nabla}_r U = -f(r)$$



Lagrange's equations

$$m\ddot{r} = mr\dot{\theta}^2 - f(r)$$

$$\frac{d}{dt}(mr^2\dot{\theta}) = 0$$

## ○ Equations no simpler, but theoretical basis is better



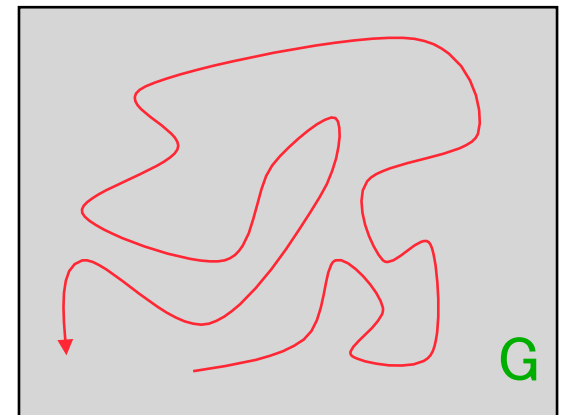
# Phase Space (again)

## ○ Return to the complete picture of phase space

- *full specification of microstate of the system is given by the values of all positions and all momenta of all atoms*
  - $\mathbf{G} = (\mathbf{p}^N, \mathbf{r}^N)$
- *view positions and momenta as completely independent coordinates*
  - connection between them comes only through equation of motion

## ○ Motion through phase space

- *helpful to think of dynamics as “simple” movement through the high-dimensional phase space*
  - facilitate connection to quantum mechanics
  - basis for theoretical treatments of dynamics
  - understanding of integrators



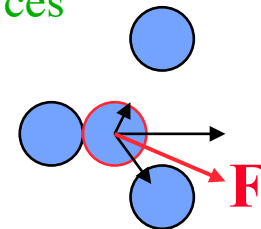
# Integration Algorithms

## ○ Equations of motion in cartesian coordinates

$$\begin{aligned} \frac{d\mathbf{r}_j}{dt} &= \frac{\mathbf{p}_j}{m} \\ \frac{d\mathbf{p}_j}{dt} &= \mathbf{F}_j \end{aligned}$$

$$\left. \begin{aligned} \mathbf{r} &= (r_x, r_y) \\ \mathbf{p} &= (p_x, p_y) \end{aligned} \right\} \text{2-dimensional space (for example)}$$

$$\mathbf{F}_j = \sum_{\substack{i=1 \\ i \neq j}}^N \mathbf{F}_{ij} \quad \text{pairwise additive forces}$$



## ○ Desirable features of an integrator

- *minimal need to compute forces (a very expensive calculation)*
- *good stability for large time steps*
- *good accuracy*
- *conserves energy and momentum*
- *time-reversible*
- *area-preserving (symplectic)*

More on these later

# Verlet Algorithm

## 1. Equations

- Very simple, very good, very popular algorithm
- Consider expansion of coordinate forward and backward in time

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \frac{1}{m} \mathbf{p}(t) \delta t + \frac{1}{2m} \mathbf{F}(t) \delta t^2 + \frac{1}{3!} \ddot{\mathbf{r}}(t) \delta t^3 + O(\delta t^4)$$

$$\mathbf{r}(t - \delta t) = \mathbf{r}(t) - \frac{1}{m} \mathbf{p}(t) \delta t + \frac{1}{2m} \mathbf{F}(t) \delta t^2 - \frac{1}{3!} \ddot{\mathbf{r}}(t) \delta t^3 + O(\delta t^4)$$

- Add these together

$$\mathbf{r}(t + \delta t) + \mathbf{r}(t - \delta t) = 2\mathbf{r}(t) + \frac{1}{m} \mathbf{F}(t) \delta t^2 + O(\delta t^4)$$

- Rearrange

$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{1}{m} \mathbf{F}(t) \delta t^2 + O(\delta t^4)$$

- *update without ever consulting velocities!*

# Verlet Algorithm. 4. Loose Ends

## ○ Initialization

- *how to get position at “previous time step” when starting out?*
- *simple approximation*

$$\mathbf{r}(t_0 - \delta t) = \mathbf{r}(t_0) - \mathbf{v}(t_0)\delta t$$

## ○ Obtaining the velocities

- *not evaluated during normal course of algorithm*
- *needed to compute some properties, e.g.*

→ temperature

→ diffusion constant

- *finite difference*

$$\mathbf{v}(t) = \frac{1}{2\delta t} [\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)] + O(\delta t^2)$$

# Verlet Algorithm 5. Performance Issues

## ○ Time reversible

- *forward time step*

$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{1}{m}\mathbf{F}(t)\delta t^2$$

- *replace  $dt$  with  $-dt$*

$$\mathbf{r}(t + (-\delta t)) = 2\mathbf{r}(t) - \mathbf{r}(t - (-\delta t)) + \frac{1}{m}\mathbf{F}(t)(-\delta t)^2$$

$$\mathbf{r}(t - \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t + \delta t) + \frac{1}{m}\mathbf{F}(t)\delta t^2$$

- *same algorithm, with same positions and forces, moves system backward in time*

## ○ Numerical imprecision of adding large/small numbers

$$\mathbf{r}(t + \delta t) - \mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{1}{m}\mathbf{F}(t)\delta t^2$$

Diagram illustrating numerical imprecision in the Verlet algorithm. The equation is shown with boxes around terms and labels indicating their order of magnitude:

- $\mathbf{r}(t + \delta t) - \mathbf{r}(t)$  is labeled  $O(dt^1)$ .
- $\mathbf{r}(t)$  is labeled  $O(dt^0)$ .
- $\mathbf{r}(t - \delta t)$  is labeled  $O(dt^0)$ .
- $\frac{1}{m}\mathbf{F}(t)\delta t^2$  is labeled  $O(dt^2)$ .

# Leapfrog Algorithm

- Eliminates addition of small numbers  $O(dt^2)$  to differences in large ones  $O(dt^0)$
- Algorithm

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t + \frac{1}{2}\delta t)\delta t$$

$$\mathbf{v}(t + \frac{1}{2}\delta t) = \mathbf{v}(t - \frac{1}{2}\delta t) + \frac{1}{m}\mathbf{F}(t)\delta t$$

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- Mathematically equivalent to Verlet algorithm

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \left[ \mathbf{v}(t - \frac{1}{2}\delta t) + \frac{1}{m}\mathbf{F}(t)\delta t \right] \delta t$$

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$\mathbf{r}(t)$  as evaluated from  
previous time step

$$\mathbf{r}(t) = \mathbf{r}(t - \delta t) + \mathbf{v}(t - \frac{1}{2}\delta t)\delta t$$



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# Leapfrog Algorithm

- Eliminates addition of small numbers  $O(\delta t^2)$  to differences in large ones  $O(\delta t^0)$
- Algorithm

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t + \frac{1}{2} \delta t) \delta t$$

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$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{1}{m} \mathbf{F}(t) \delta t^2 \quad \text{original algorithm}$$

# Leapfrog Algorithm. 3. Loose Ends

## ○ Initialization

- *how to get velocity at “previous time step” when starting out?*
- *simple approximation*

$$\mathbf{v}(t_0 - \delta t) = \mathbf{v}(t_0) - \frac{1}{m} \mathbf{F}(t_0) \frac{1}{2} \delta t$$

## ○ Obtaining the velocities

- *interpolate*

$$\mathbf{v}(t) = \frac{1}{2} \left[ \mathbf{v}(t + \frac{1}{2} \delta t) + \mathbf{v}(t - \frac{1}{2} \delta t) \right]$$