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

$$\vec{\mathbf{F}} = -\vec{\nabla} U$$

Gradient of a scalar potential energy

Newtonian Formulation

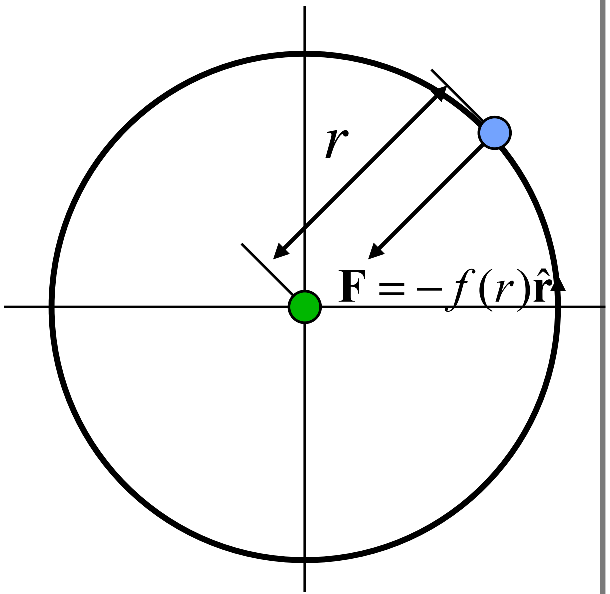
- Cartesian spatial coordinates $\mathbf{r}_i = (x_i, y_i, z_i)$ are primary variables
  - *for N atoms, system of N 2nd-order differential equations*

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

- 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*

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

$$m\ddot{r} = -f(r) + \frac{\ell^2}{mr^3}$$ *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

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

  - *N second-order differential equations*
- Central-force example

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

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

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

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

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* $p_j = \dfrac{\partial L}{\partial \dot{q}_j}$
  - *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* $\dfrac{dp_j}{dt} = \dfrac{\partial L}{\partial q_j}$
- 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. Defintion

- …a Legendre transform!
- Define the *Hamiltonian, H*

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

- 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

$$dL = \frac{\partial L}{\partial q} dq + \frac{\partial L}{\partial \dot{q}} d\dot{q}$$

$$= \dot{p}\, dq + p\, d\dot{q}$$

Legendre transform

$$H = -(L - p\dot{q})$$

$$dH = -(\dot{p}\, dq - \dot{q}\, dp)$$

$$dH = -\dot{p}\, dq + \dot{q}\, dp$$

$$\frac{dp}{dt} = \dot{p} = \frac{\partial L}{\partial q}$$ Lagrange's equation of motion

$$p = \frac{\partial L}{\partial \dot{q}}$$ Definition of momentum

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

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

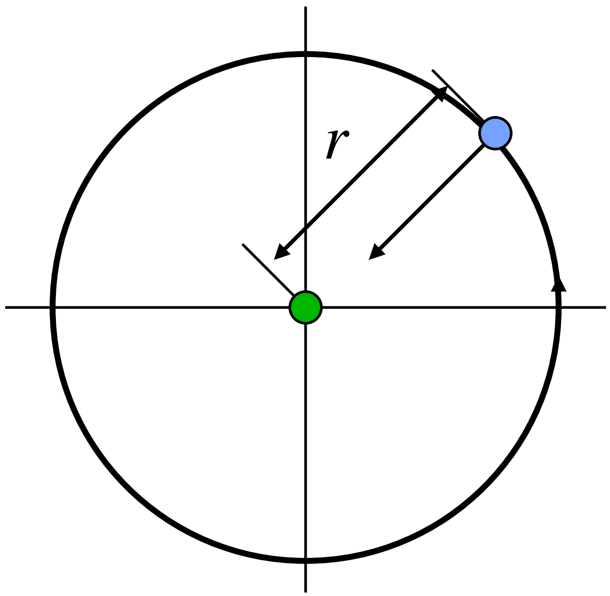
Hamilton's equations of motion

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

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

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

Lagrange's equations

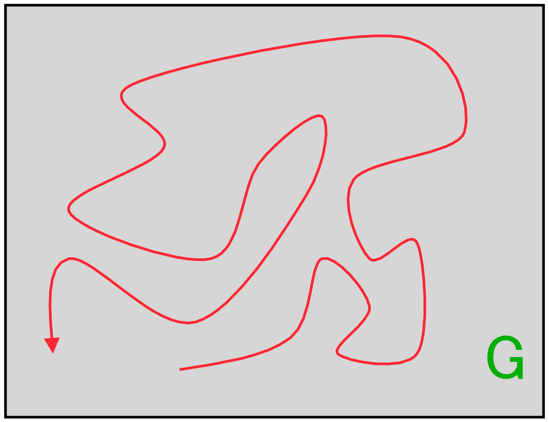
$$m\ddot{r} = mr\dot{\theta}^2 - f(r)$$

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

- 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*
    - → G = (p^N, 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

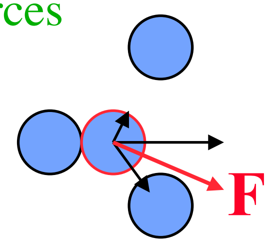
Equations of motion in cartesian coordinates

$$\frac{d\mathbf{r}_j}{dt} = \frac{\mathbf{p}_j}{m}$$

$$\frac{d\mathbf{p}_j}{dt} = \mathbf{F}_j$$

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

$$\mathbf{F}_j = \sum_{\substack{i=1\\ i\neq j}}^{N} \mathbf{F}_{ij}$$ 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)*

(the last two) More on these later

Verlet Algorithm
1. Equations

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

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

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

- Add these together

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

- Rearrange

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

  - *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*

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

Verlet Algorithm 5. Performance Issues

- Time reversible
  - *forward time step*

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

  - *replace dt with −dt*

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

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

  - *same algorithm, with same positions and forces, moves system backward in time*
- Numerical imprecision of adding large/small numbers

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

$O(dt^1)$ — $\mathbf{r}(t+\delta t) - \mathbf{r}(t)$

$O(dt^1)$ — $\mathbf{r}(t) - \mathbf{r}(t-\delta t)$

$O(dt^0)$ — $\mathbf{r}(t)$

$O(dt^0)$ — $\mathbf{r}(t-\delta t)$

$O(dt^2)$ — $\tfrac{1}{m}\mathbf{F}(t)\delta t^2$

Leapfrog Algorithm

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

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

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

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- Mathematically equivalent to Verlet algorithm

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

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r(t) as evaluated from previous time step

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

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

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

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

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

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

Leapfrog Algorithm. 3. Loose Ends

Initialization

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

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

Obtaining the velocities

- *interpolate*

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