Equations of motion:

(1a) $\dot{\vec{r}}_i = \dfrac{\vec{p}_i}{m_i}$

(1b) $\dot{\vec{p}}_i = \vec{F}_i$ for each particle i

Take time derivative of (1a)

$$\ddot{\vec{r}}_i = \frac{\dot{\vec{p}}_i}{m_i} = \frac{\vec{F}_i}{m}$$

Numerically solve dN 2nd order differential equations or 2dN 1st order differential equations

Energy Conservation

$$E = K + V \qquad \underbrace{K = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}_{\text{function of } p_i\text{'s}} \qquad \underbrace{V = \sum_{i>j} V(r_{ij})}_{\text{function of } \vec{r}_i\text{'s}}$$

$$\frac{dE}{dt} = \sum_i \frac{\partial K}{\partial \vec{p}_i} \cdot \frac{\partial \vec{p}_i}{\partial t} + \sum_i \frac{\partial V}{\partial \vec{r}_i} \cdot \frac{\partial \vec{r}_i}{\partial t} + \cancel{\text{explicit time dependence}}^{\,0}$$

$$\frac{dE}{dt} = \sum_i \frac{\vec{p}_i}{m} \cdot \frac{\partial \vec{p}_i}{\partial t} + \sum_i -\vec{F}_i \cdot \frac{\vec{p}_i}{m}$$

$$\frac{dE}{dt} = \sum_i \frac{\vec{p}_i}{m}\left(\frac{\partial \vec{p}_i}{\partial t} - \vec{F}_i\right) = 0$$

Lack of energy conservation arises from Approximate numerical solution of (1a) (1b)

variance $\delta E^2 = \langle E^2 \rangle - \langle E \rangle^2$ $\qquad \delta E$ vs. Δt

standard deviation $\sigma_E = \sqrt{\delta E^2}$

Two sources of Error

- Round-off (finite precision)
- Finite time step

Total Energy does not fluctuate, but temperature does.

Based on equipartition Theorem $2T = \langle \vec{v}_i^{\,2} \rangle$, define instantaneous temperature

$$T_k(t) = \frac{1}{N_f} \sum_{i=1}^{N} m_i \vec{v}_i^{\,2} \simeq \frac{2K}{N_f}$$

— # of Kinetic degrees of freedom

$$= \frac{2K(t)}{dN}$$

Temperature is T_k averaged over time

$$T = \langle T_k(t) \rangle = \frac{2}{dN} \langle K(t) \rangle$$

In 2D, T is average K.E. per particle

T_K fluctuates, Calculate fluctuations

$$\Delta = \frac{\sigma^2_{T_K}}{\langle T_K\rangle^2} = \frac{\langle T_k^2\rangle - \langle T_K\rangle^2}{\langle T_K\rangle^2}$$

In 2d $\quad T_K = \frac{1}{2N}(\vec{v}_1^{\,2} + \vec{v}_2^{\,2} + \dots) \qquad \langle T_K\rangle = \frac{1}{2N}\cdot N\langle \vec{v}^{\,2}\rangle$

$$T_k^2 = \frac{1}{4N^2}(\vec{v}_1^{\,4} + \vec{v}_2^{\,4} + \dots + 2\vec{v}_1^{\,2}\vec{v}_2^{\,2} + 2\vec{v}_1^{\,2}\vec{v}_3^{\,2} + \dots)$$

$$\langle T_k^2\rangle = \frac{1}{4N^2}\left[N\langle \vec{v}^{\,4}\rangle + N(N-1)\langle \vec{v}^{\,2}\rangle^2\right]$$

$$\Delta = \frac{1}{4N^2}\left[\frac{N\langle \vec{v}^{\,4}\rangle + N(N-1)\langle \vec{v}^{\,2}\rangle^2 - N^2\langle \vec{v}^{\,2}\rangle^2}{1/4\,\langle \vec{v}^{\,2}\rangle^2}\right]$$

$$\Delta = \frac{1}{N}\,\frac{\langle \vec{v}^{\,4}\rangle - \langle \vec{v}^{\,2}\rangle^2}{\langle \vec{v}^{\,2}\rangle^2}$$

$$\vec{v}^{\,4} = (v_x^2 + v_y^2)^2 = v_x^4 + 2v_x^2 v_y^2 + v_y^4$$

$$\langle v_x^4\rangle = 3T^2 \qquad \langle v_x^2 v_y^2\rangle = T^2$$

$$\langle \vec{v}^{\,4}\rangle = 8T^2$$

$$\langle \vec{v}^{\,2}\rangle = 2T$$

$$\Delta = \frac{1}{N}\left(\frac{8T^2 - 4T^2}{4T^2}\right) = \frac{1}{N}$$

Fluctuations nonzero, but decrease w/ system-size

Equations of motion have the following properties. Integration schemes should possess these properties.

1. energy conservation
2. time-reversibility

$$t' = -t \qquad \dot{\vec{r}}_i' = \vec{p}_i'/m_i$$

$$\vec{p}' = -\vec{p} \qquad \underline{\dot{\vec{p}}_i}' = \vec{F}_i$$

3. Conservation of Linear momentum

Eqns. of motion invariant w/ respect to $\vec{p}' = \vec{p} + \vec{c}$

4. Angular momentum? Box is a square; No rotational invariance; Angular momentum not conserved

So far, We have considered simulations at constant NVE - not typical experimental conditions, i.e. at NPT. We will have to change equations of motion to simulate at NPT.

...rlet Algorithms

(Taylor expansions in terms of small finite timesteps away from t) AKA Finite-Difference Methods

A. Regular Verlet (Position)

$f = m \frac{d^2 r}{dt^2}$ Eqn. of motion Important!

(1) $$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{6}\dddot{r} + \ldots O(\Delta t^4)$$

(2) $$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{6}\dddot{r} + \ldots O(\Delta t)^4$$

Similar expressions for x, y, z components for all particles

Add Eqns. (1) and (2) to obtain

requires $r(t)$, $r(t-\Delta t)$, not $v(t)$

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2 + \ldots O(\Delta t^4)$$

Not self-starting : How do we know $r(t-\Delta t)$ at $t=0$?

Subtract (2) from (1) to obtain

need $r(t+\Delta t)$ to calculate $v(t)$

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + O(\Delta t^2)$$

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2$$

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$$

- time reversible $\Delta t \rightarrow -\Delta t$ invariant
- reasonable energy conservation for moderate Δt
- Inaccurate estimate of $v(t)$; velocities known at previous timestep
- simple to implement

B. Velocity Verlet (workhorse)

(1) $r(t+\Delta t+\Delta t) = r(t+\Delta t) + \Delta t\, v(t+\Delta t) + \frac{\Delta t^2}{2} a(t+\Delta t) + \dots$

(2) $r(t+\Delta t-\Delta t) = r(t+\Delta t) - \Delta t\, v(t+\Delta t) + \frac{\Delta t^2}{2} a(t+\Delta t) + \dots$

Add Eqns. (1) and (2)

(3) $r(t+2\Delta t) + r(t) = 2r(t+\Delta t) + \Delta t^2 a(t+\Delta t) + \dots$

$$r(t+2\Delta t) = r(t+\Delta t) + \Delta t\, v(t+\Delta t) + a(t+\Delta t)\frac{\Delta t^2}{2}$$

(5) $$r(t) = r(t+\Delta t) - v(t)\Delta t - a(t)\frac{\Delta t^2}{2}$$

Taylor expansion

Add Eqns. (4) and (5)

(6) $$r(t+2\Delta t) + r(t) = 2r(t+\Delta t) + (v(t+\Delta t) - v(t))\Delta t + (a(t+\Delta t) - a(t))\Delta t^2/2$$

Compare Eqns. (3) and (6)

$$2r(t+\Delta t) + \Delta t^2 a(t+\Delta t) = 2r(t+\Delta t) + (v(t+\Delta t) - v(t))\Delta t + (a(t+\Delta t) - a(t))\Delta t^2/2$$

$$v(t+\Delta t) = v(t) + \frac{a(t+\Delta t) + a(t)}{2}\Delta t$$

$r(0)$
$v(0)$

$r(1)$
$v(1)$

$$\boxed{\begin{aligned} r(t+\Delta t) &= 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2 \\ v(t+\Delta t) &= v(t) + (a(t+\Delta t) + a(t))\frac{\Delta t}{2} \end{aligned}}$$

- both positions and velocities known at time $t+\Delta t$
- more accurate measurement of velocity
- calculate $r(t+\Delta t)$ from previous timesteps, calculate $a(t+\Delta t)$, then calculate $v(t+\Delta t)$
- not time reversible

C. Leap Frog Verlet

$$r(t+\Delta t) = r(t) + \Delta t\, v(t+\Delta t/2) \qquad (1)$$
$$v(t+\Delta t/2) = v(t-\Delta t/2) + \Delta t\, a(t) \qquad (2)$$

Velocities stored at half-timesteps; Eqns. (1) and (2) are different versions of Taylor expansion

Plug (2) into (1)

$$r(t+\Delta t) = r(t) + \Delta t\left(v(t-\Delta t/2) + \Delta t\, a(t)\right)$$
$$= r(t) + \Delta t\left(v(t) - \frac{\Delta t}{2} a(t) + \Delta t\, a(t)\right)$$
$$r(t+\Delta t) = r(t) + \Delta t\, v(t) + \frac{\Delta t^2}{2} a(t)$$

Velocities at time t obtained using

$$v(t) = \frac{1}{2}\left(v(t+\Delta t/2) + v(t-\Delta t/2)\right) \qquad (3)$$

Eqn. (3) is consistent with Taylor expansion

$$v(t-\Delta t/2) = 2v(t) - v(t+\Delta t/2) \qquad (4)$$

Plug (4) into (2) $\quad v(t+\Delta t/2) = v(t) + \frac{\Delta t}{2} a(t) \qquad (5)$

Plug (5) into (1) $\quad r(t+\Delta t) = r(t) + \Delta t\, v(t) + \frac{\Delta t^2}{2} a(t)$

$$m\ddot{x}_i = F_{x_i}$$

$$\vec{F} = \frac{\varepsilon}{\sigma_{ij}}\left(1-\frac{r_{ij}}{\sigma_{ij}}\right)\hat{r}_{ij}$$

$$F_{x_i} = \frac{\varepsilon}{\sigma_{ij}}\left(1-\frac{r_{ij}}{\sigma_{ij}}\right)\frac{x_{ij}}{r_{ij}}$$

$$m\frac{\ddot{x}_i}{\sigma} = \frac{F_{x_i}}{\sigma}$$

$$= \frac{\varepsilon}{\sigma^2}\left(1-\frac{r_{ij}}{\sigma_{ij}}\right)\frac{x_{ij}/\sigma}{r_{ij}/\sigma}$$

$$\frac{m\sigma^2}{\varepsilon}\frac{\ddot{x}_i}{\sigma} = \left(1-\frac{r_{ij}}{\sigma_{ij}}\right)\frac{x_{ij}/\sigma}{r_{ij}/\sigma}$$

$$mv^2 = \varepsilon$$

$$v^2 = \frac{\varepsilon}{m}$$

$$\frac{\sigma^2}{t^2} = \frac{\varepsilon}{m}$$

$$t^2 = \sigma^2\frac{m}{\varepsilon}$$

$$t = \sigma\sqrt{\frac{m}{\varepsilon}}$$

$$\frac{m\sigma^2}{\varepsilon}\frac{d^2 x_i/\sigma}{dt^2} = \left(1-\bar{r}_{ij}\right)\frac{\bar{x}_{ij}}{\bar{r}_{ij}}$$

$$\boxed{\frac{d^2\bar{x}_i}{d\bar{t}^2} = \left(1-\bar{r}_{ij}\right)\frac{\bar{x}_{ij}}{r_{ij}}}$$

$$\bar{t} = \frac{t}{\sigma\sqrt{\frac{m}{\varepsilon}}}$$