MD problems we will deal with

① real interactions are more complicated.

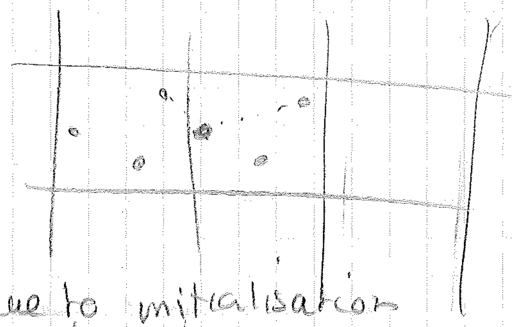
Quantum Mechanics: electron clouds of atoms interact
too much work if you want to do many particles

⇒ - realistic effective classical force fields / potentials
- combination: Quantum MD (still pretty expensive)

⇒ unlike in previous examples usually smooth interaction

② $N \leq N_A$, $t \leq 1s$ $d << 1m$

periodic boundary conditions
(nearest image convention)
be careful if correlation length $> d$



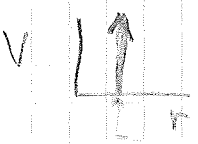
finite-size effects

averaging over finite time ⇒ errors due to initialisation & statistical errors

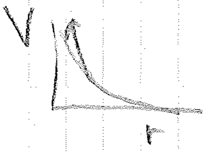
③ Integration algorithms have finite accuracy

Example: smooth interactions in a gas

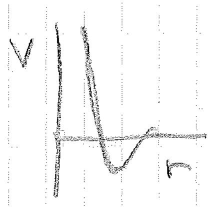
hard spheres & instantaneous coll ⟷ low density.
(no 3-particle interactions)

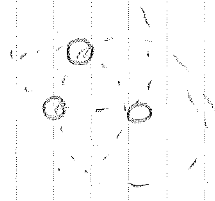


more realistic
soft repulsion



attractive interaction
(i.e. van der Waals)





3 particles close together interact

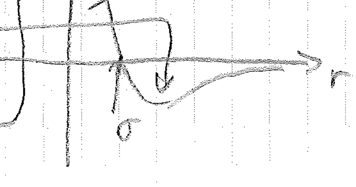
Your first simulation project: Argon liquid
dense, and can actually solidify

Lennard-Jones $V(\vec{r}_1,\vec{r}_2) = U_{LJ}(|\vec{r}_1-\vec{r}_2|)$

$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

↑ weak attractive part

↑ strong repulsive part



(LJ continued)

$U_{LJ} = 0$ at σ.

Minimum at

$$\frac{\partial U_{LJ}}{\partial \vec{r}} = 0 = 4\epsilon\left[12\left(\frac{\sigma}{r}\right)^{11} - 6\left(\frac{\sigma}{r}\right)^{5}\right]\frac{\partial}{\partial \vec{r}}\left(\frac{\sigma}{r}\right)$$

$$\Rightarrow 2\left(\frac{\sigma}{r}\right)^{6} = 1 \quad \Rightarrow r_{min} = \sigma\, 2^{1/6}$$

$$U_{LJ}(r_{min}) = -\epsilon$$

LJ very common; good for argon too

$$\epsilon = 1.654 \cdot 10^{-21}\,\mathrm{J} \quad \sigma = 3.405\,\text{Å}$$

+ minimum image convention + integration = your simulation

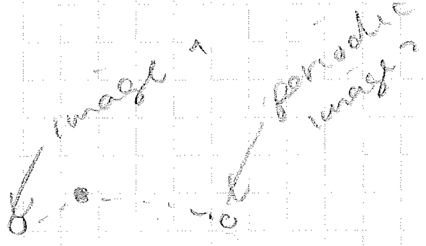
Note on efficiency when you calculate forces

$$F_{LJ} = -\frac{\partial U}{\partial r} = 4\epsilon\left[12\frac{\sigma^{11}}{r^{11}} - 6\frac{\sigma^{5}}{r^{5}}\right]\sigma\frac{\vec{r}}{r^{3}}$$

$$= 4\epsilon\left[12\frac{\sigma^{12}}{r^{14}} - 6\frac{\sigma^{6}}{r^{8}}\right]\vec{r}$$

even powers, no expensive $\mathrm{sqrt}((r_i - r_j)^2)$

Note: You can now get in trouble with periodic boundaries, and interact with several images of 1 particle.



sometimes that's ok, but not here

Nearest image convention:

interact only with nearest image.

Argon liquid model: LJ, N atoms, periodic boundaries

variables $(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots \vec{r}_N, \vec{v}_1, \vec{v}_2, \ldots \vec{v}_N) = \gamma \longleftarrow$ dynamical system

$$\downarrow$$

$$\dot{\gamma} = f(\gamma, t)$$

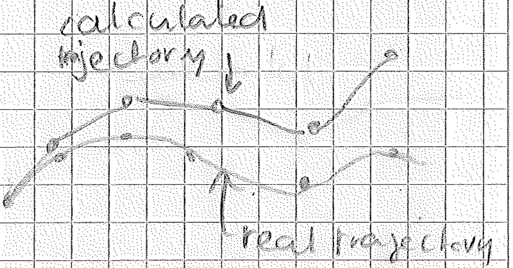
eqs of motion

$$\dot{\vec{r}}_i = \vec{v}_i$$

$$\dot{\vec{v}}_i = -\sum_j \frac{\partial V(\vec{r})}{m_i \partial \vec{r}}\Big|_{\vec{r} = \vec{r}_i - \vec{r}_j} = \vec{a}_i$$

How to solve? Small time steps h

Naive approach (Euler)



$$\gamma(t+h) = \gamma(t) + h\, f(\gamma, t) + O(h^2)$$

$$\begin{cases} r(t+h) = r(t) + h\, v(t) \quad (+\,O(h^2)) \\ v(t+h) = v(t) + h\, a(r(t)) \,(+\,O(h^2)) \end{cases}$$

$$E(t+h) = \tfrac{1}{2}m\left[v(t) + h\, a(r(t))\right]^2 + V(r(t) + h\, v(t))$$

$$= \tfrac{1}{2}\, m\, v(t)^2 + m\, h\, a(r(t)) + \tfrac{1}{2} m\, h^2\, a(r(t))^2$$

$$+ V(r(t)) + h\, v(t)\, V'(r(t)) + \tfrac{1}{2}(h\, v(t))^2\, V''(r(t))$$

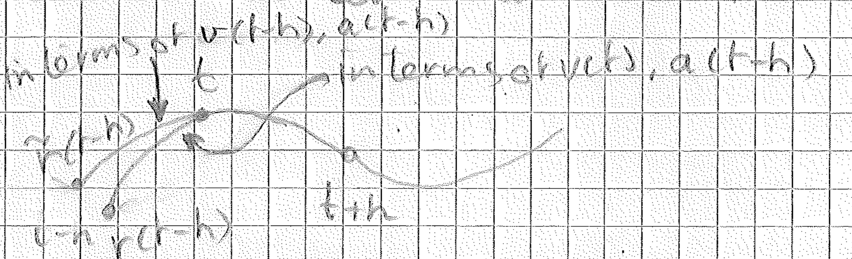
$$= E(t) + O(h^2)$$

also error in γ is ht

This is terrible and very unstable

DO NOT USE

We can do better than Euler; Verlet



backwards ≠ inverse (forwards)

$$r(t+h) = r(t) + h\,v(t) + \tfrac{1}{2}h^2 a(t) + \tfrac{1}{6}h^3 \dot{a}(t) + O(h^4)$$

$$\underline{+}\ r(t-h) = r(t) - h\,v(t) + \tfrac{1}{2}h^2 a(t) - \tfrac{1}{6}h^3 \dot{a}(t) + O(h^4)$$

(addition)

$$r(t+h) = -r(t-h) + 2r(t) + h^2 a(t) + O(h^4) \qquad \textcircled{1}$$

(subtraction)

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

$\uparrow$ from $\frac{1}{3}h^3 \dot{a}(t) \frac{1}{2h}$

velocity is byproduct, not in expression for $r(t+h)$

What happens to errors after long time?

use induction for error in r $\left(n = \frac{t}{h}\right)$

$err(0) = 0$

$err(1) = O(h^4)$

$$err(n+1) = -err(n-1) + 2\,err(n) + h^2\,err(n) + O(h^4)$$

Solution: $err(n) \propto n(n+1)$

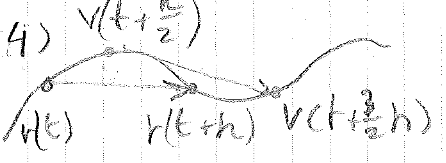
$\Rightarrow$ error after time $t = \left(\frac{t}{h}\right)^2 O(h^4) \sim t^2 h^2$

Other Verlet incarnations

leap-frog

$$v(t+h/2) = v(t-h/2) + h\,a(t) \quad (3)$$

$$r(t+h) = r(t) + h\,v(t+h/2) \quad (4)$$



(4) is similar to (2) with $h \to 2h$

(3) is reformulation of (1)

Velocity verlet

$$r(t+h) = r(t) + h\,v(t) + h^2\,a(t)/2$$

$$v(t+h) = v(t) + \underbrace{h[\underline{a(t+h)} + a(t)]/2}$$

use this for programming — average of forward & backward

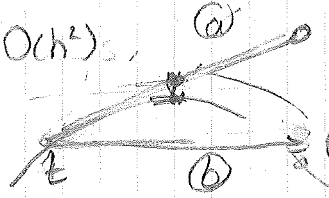
Implement as
$\tilde{v}(t) = v(t) + h\,a(t)/2$
$r(t+h) = r(t) + h\,\tilde{v}(t)$
$v(t+h) = \tilde{v}(t) + h\,\frac{a(t+h)}{2}$

This was for simple eqs of motion with Hamiltonian dynamics.

Can include in Verlet $\dot{v}(t) = a(r(t)) - \eta v(t)$ viscous friction
(common addition in models, for instance Langevin thermostat)

Problem: other non-Hamiltonian terms not always easy. $\dot{\gamma} = f(\gamma, t)$ ← for time dependence, see appendix

(a) $\gamma(t+h) = \gamma(t) + h\,f(\gamma(t))$ error $O(h^2)$



(b) $\gamma(t+\frac{1}{2}h) = \gamma(t) + \overbrace{\frac{1}{2}h\,f(\gamma(t))}^{k_1}$

$\gamma(t+h) = \gamma(t) + h f(\gamma(t+\frac{1}{2}h))$ midpoint rule

$= \gamma(t) + k_2 + O(h^3)$, $k_2 = h f(\gamma(t) + \frac{1}{2}k_1)$

Taylor expansion:

$$\gamma(t+h) = \gamma(t) + h f(\gamma(t) + \tfrac{1}{2}h\,f(\gamma(t)))$$
$$= \gamma(t) + h[f(\gamma(t)) + \frac{\partial f}{\partial \gamma}\,\tfrac{1}{2}h f(\gamma(t))]$$
$$= \gamma(t) + h\,\dot{\gamma}(t) + \tfrac{1}{2}h^2\,\ddot{\gamma}(t)$$

error is $O(h^3)$

(c) Even more midpoints:

$k_1 = h\,f(\gamma(t))$ $\quad k_2 = h\,f(\gamma(t) + \frac{1}{2}k_1)$

$k_3 = h\,f(\gamma(t) + \frac{1}{2}k_2)$ $\quad k_4 = h\,f(\gamma(t) + k_3)$

$\gamma(t+h) = \gamma(t) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) + O(h^5)$

4th order Runge-Kutta.
(you can take this further)

big advantage! efficient with variable time step (so that you can save computation time in intermittent systems like dilute gasses)

RK-Fehlberg compare RK4, RK5

very general method
more work than Verlet

end lecture 2.