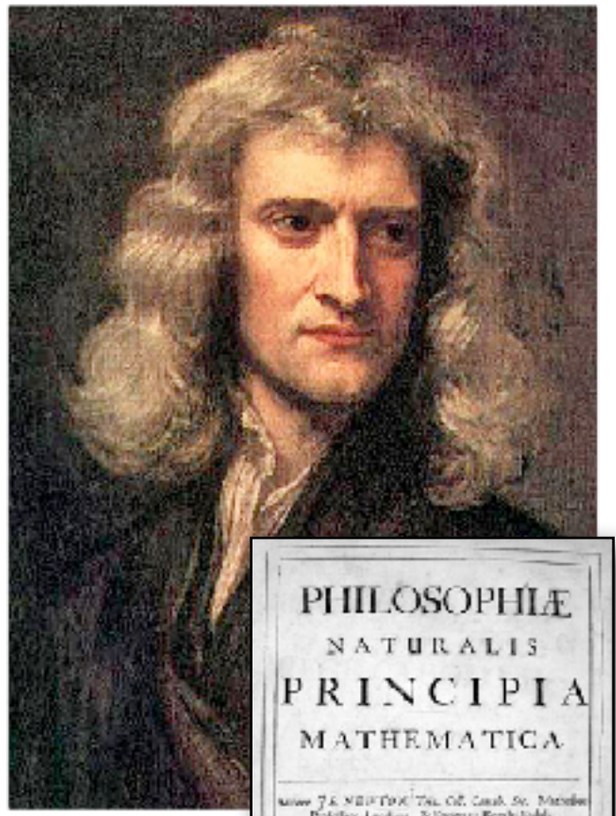
Molecular Dynamics

Goal: trajectories *x(t)* that sample the different conformations of the system so that we can calculate correct **thermodynamic observables**.

Molecular Dynamics Algorithm



source: Wikipedia

- equations of motion for *N* particles

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2\mathbf{r}}{dt^2} = m_i \ddot{\mathbf{r}}_i$$

- potential energy

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = U_{\text{bonded}}(\{\mathbf{r}_i\}) + U_{\text{nonbonded}}(\{\mathbf{r}_i\})$$

$$U_{\text{bond}}(\mathbf{r}_j, \mathbf{r}_k) = \frac{K}{2}(|\mathbf{r}_j - \mathbf{r}_k| - b_0)^2$$

$$U_{\text{angles}}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \qquad U_{\text{dih}}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l)$$

$$U_{\text{elec}}(\mathbf{r}_j, \mathbf{r}_k) = \frac{1}{4\pi\epsilon_0} \frac{q_j q_k}{|\mathbf{r}_j - \mathbf{r}_k|}$$

$$U_{\text{vdW}}(\mathbf{r}_j, \mathbf{r}_k) = 4\varepsilon \left[\left(\frac{\sigma}{r_{jk}}\right)^{12} - \left(\frac{\sigma}{r_{jk}}\right)^{6} \right]$$

- forces

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

Basic MD program

initialize()

t=0

while $t < t_{max}$

$\mathbf{f} = forces(\mathbf{r})$

$\mathbf{r} = integrate(\mathbf{r}, \mathbf{f})$

write_trajectory($\mathbf{r}$)

$t = t + dt$

Basic workflow

1. prepare starting conformation
2. run equilibration
3. run production
    - compute estimators for observables $a(\mathbf{r}, \mathbf{v})$
    - save trajectory ($\mathbf{r}$, maybe $\mathbf{v}$ and $\mathbf{F}$)
4. analyse trajectory/output files

Force calculation

initialize()

t=0

while $t < t_{max}$

f = *forces*(**r**)

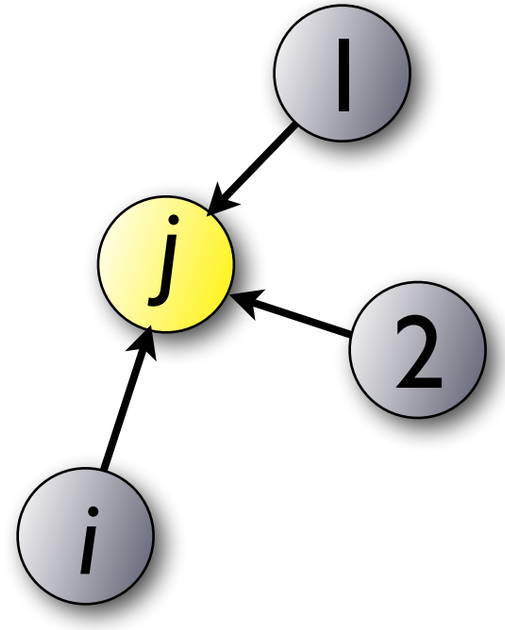
r = *integrate*(**r**, **f**)

write_trajectory(**r**)

$t = t + dt$

Force calculation

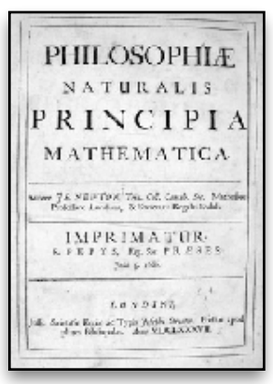
$$\mathbf{F}_i = -\nabla_i U(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N)$$



For pair-potentials $v(|\mathbf{r}_j - \mathbf{r}_i|) = v(r_{ij})$

$$\mathbf{F}_j = \sum_i \underbrace{[-\nabla_i v(r_{ij})]}_{\mathbf{f}_{ij}} = -\sum_i \frac{\mathbf{r}_{ij}}{r_{ij}} \frac{\partial}{\partial r_{ij}} v(r_{ij})$$

$$\mathbf{f}_{ij} = -\mathbf{f}_{ji}$$ (Newton's 3rd law)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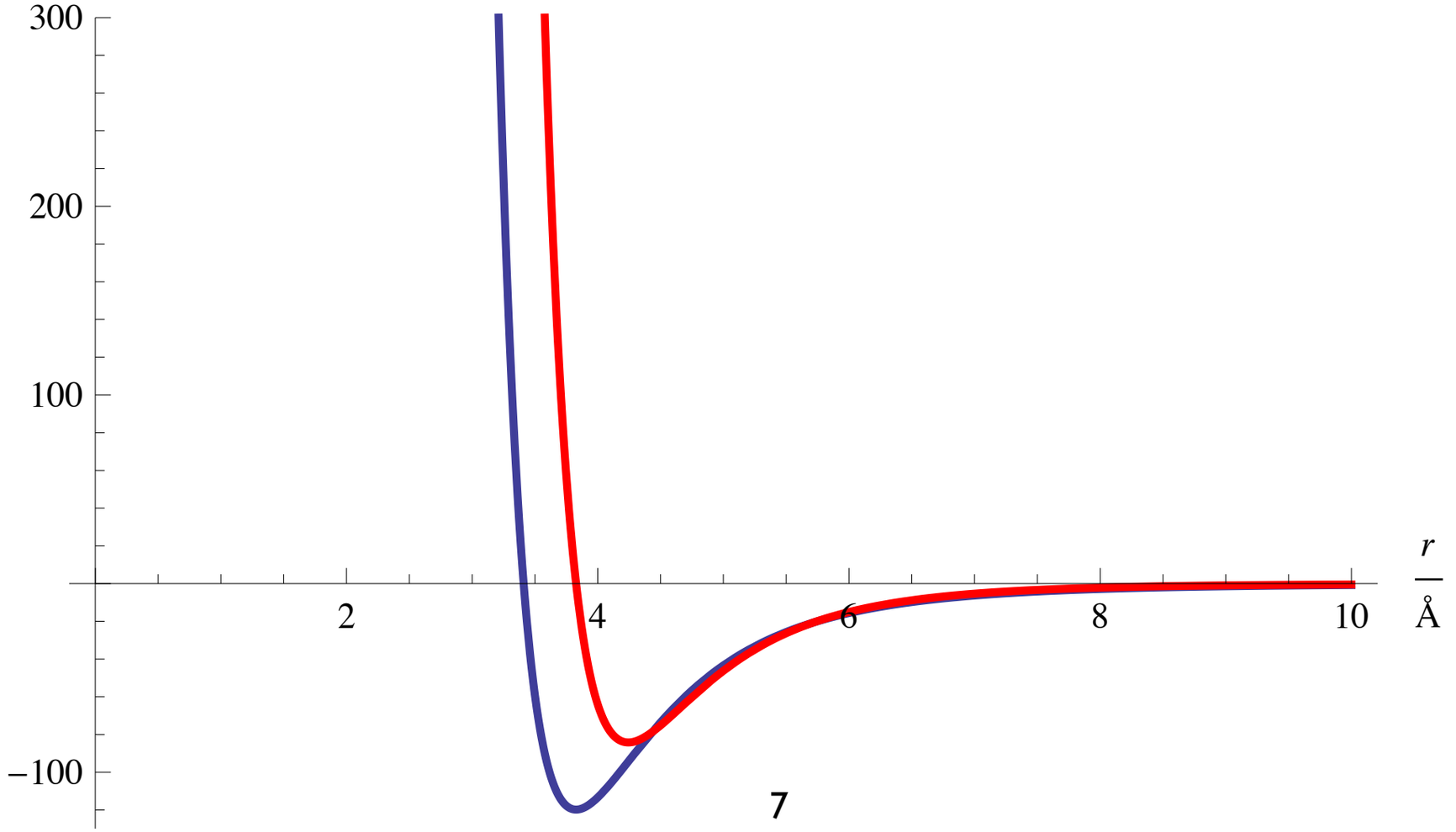
Lennard-Jones Potential

$$v(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$\mathbf{f}(r_{ij}) = -24\epsilon\frac{\mathbf{r}_{ij}}{r_{ij}^2}\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$



Integrating the Equations of Motion

initialize()

t=0

while $t < t_{max}$

$\mathbf{f} = forces(\mathbf{r})$

$\mathbf{r} = integrate(\mathbf{r}, \mathbf{f})$

write_trajectory($\mathbf{r}$)

$t = t + dt$

Integrating the Equations of Motion

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$$

- have forces $\mathbf{F}_i$ and current positions $\mathbf{r}_i(t)$
- want: positions $\mathbf{r}_i(t+\Delta t)$

Velocity Verlet Integrator

$$\mathbf{v}(t + \tfrac{\Delta t}{2}) = \mathbf{v}(t) + \frac{\Delta t}{2}\frac{\mathbf{F}(t)}{m} \tag{1}$$

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \Delta t\, \mathbf{v}(t + \tfrac{\Delta t}{2}) \tag{2}$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t + \tfrac{\Delta t}{2}) + \frac{\Delta t}{2}\frac{\mathbf{F}(t + \Delta t)}{m} \tag{3}$$

- gives both positions and velocities
- one force evaluation per time step
- see Module 10 ODEs

Good integrators

- speed? – not very relevant
- accuracy for large time steps Δt
- **energy conservation** (for $\partial H/\partial t = 0$)
  - short term
  - long term (more important)
- time reversible (Newton's EOMs!)
- phase-space area preserving (Hamiltonian dynamics!)
- accurately predict the trajectories of all particles for short and long times?

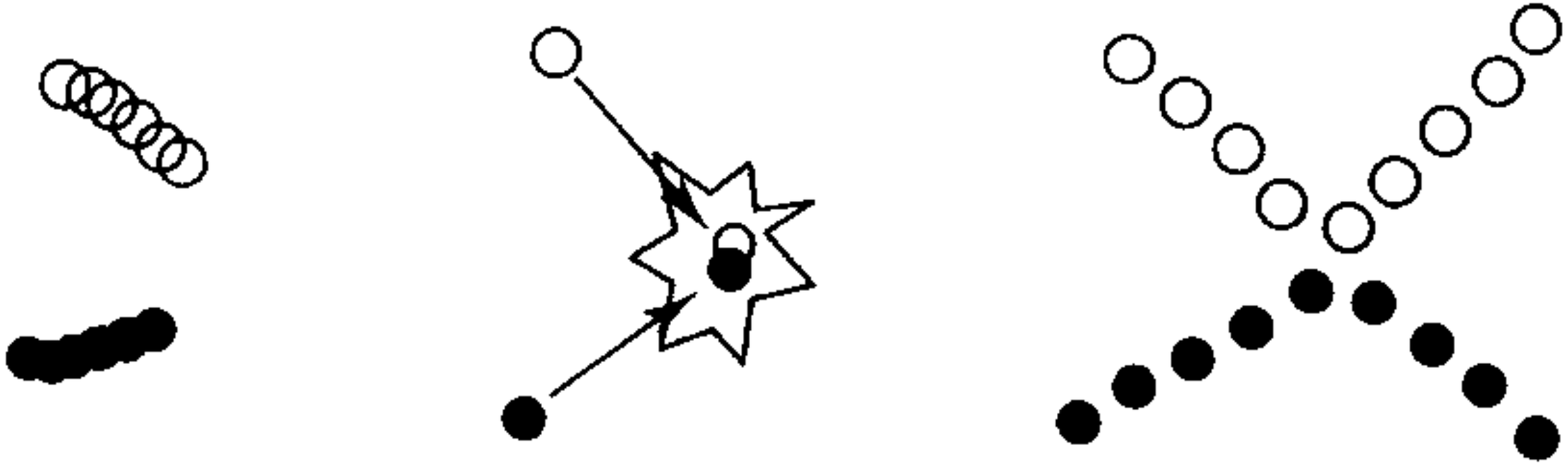
Good integrators

- speed/memory? – not very relevant
- accuracy for large time steps Δt
- energy conservation (for $\partial H/\partial t = 0$)
  - short term
  - long term (more important)
- time reversible (Newton's EOMs!)
- phase-space area preserving (Hamiltonian dynamics!)
- accurately predict the trajectories of all particles for short and long times?

Verlet

- fast, small memory requirements
- not very high accuracy for long time steps
- fair short- and good long term energy conservation
- time reversible and area preserving ("symplectic")

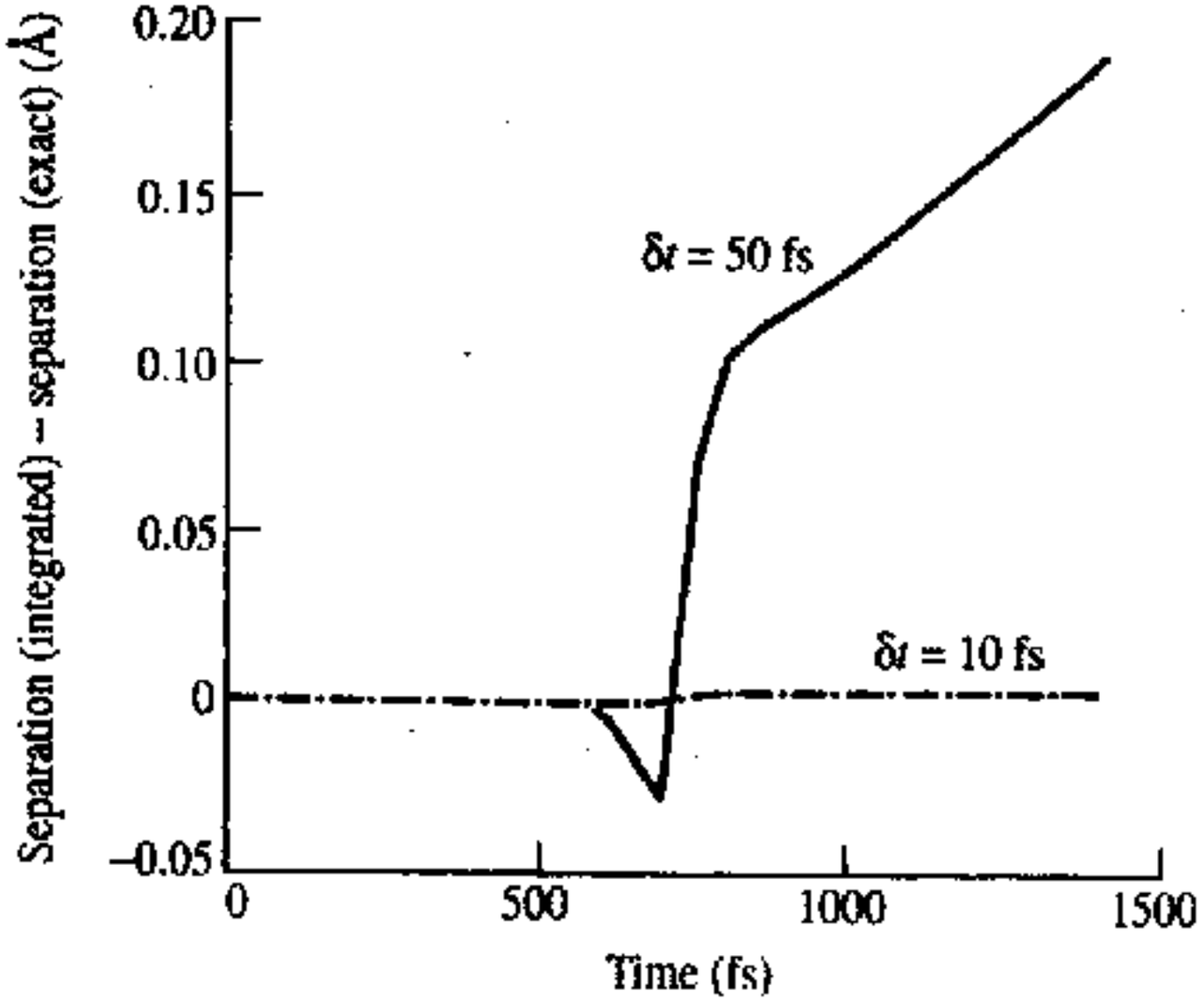
Time step

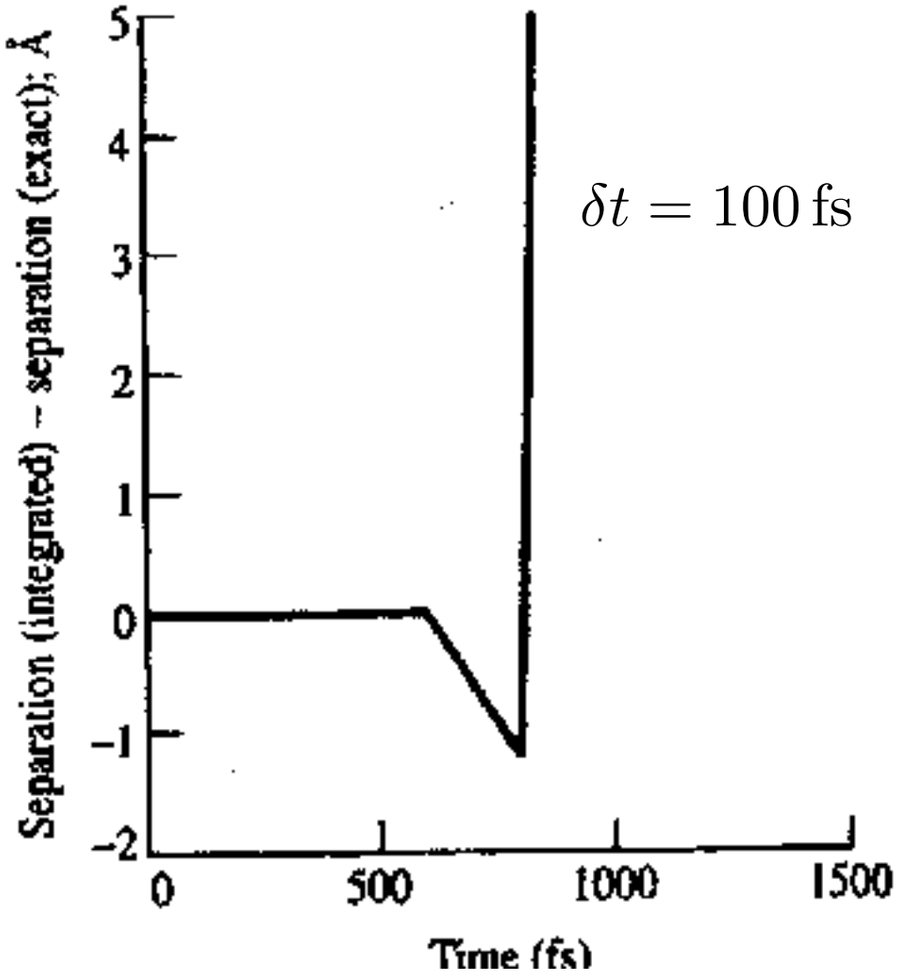


from Leach, 2001

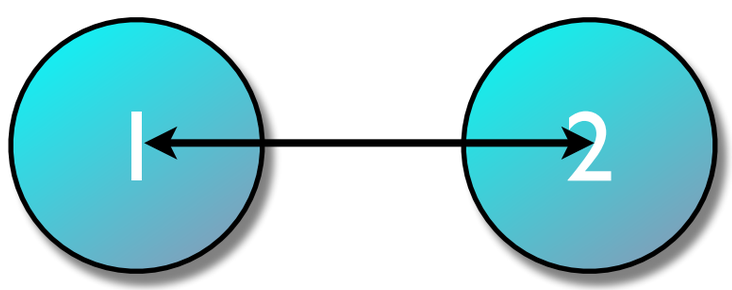
- *rule of thumb for Verlet-type integrators: 5 steps per period*
  (typically 1-2 fs in biomolecular systems)

Time step





$\delta t = 100\,\mathrm{fs}$



from Leach, 2001

Thermodynamic observables

- Macroscopic thermodynamic quantities (temperature T, pressure P, volume V, particle number N, heat capacities, dipole moments, magnetization, …) can be written as **averages** over functions that depend on microscopic positions and velocities ("estimator").

$$A = \langle a \rangle$$

$$A = \langle a(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N, \mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N \rangle$$

$$A = \langle a\big(\mathbf{x}_1(t), \mathbf{x}_2(t), \ldots, \mathbf{x}_N(t), \mathbf{v}_1(t), \mathbf{v}_2(t), \ldots, \mathbf{v}_N(t)\big) \rangle_t$$

$$A = \frac{1}{N_t} \sum_{i=1}^{N_t} a\big(\mathbf{x}_1(t), \mathbf{x}_2(t), \ldots, \mathbf{x}_N(t), \mathbf{v}_1(t), \mathbf{v}_2(t), \ldots, \mathbf{v}_N(t)\big)$$

Energy E

$$E = \langle \mathcal{H} \rangle$$

$$\mathcal{H} = T_{\mathrm{kin}}(t) + U(t)$$

$$= \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 + \sum_{i<j}^{N-1} U_{\mathrm{LJ}}(r_{ij})$$

$$r_{ij} := |\mathbf{r}_j - \mathbf{r}_i|$$

$\mathcal{H}$:"Hamiltonian" (total instantaneous energy)

Energy conservation: $\frac{d\mathcal{H}}{dt} = 0$

Temperature *T*

$$T_{\mathrm{kin}}(t) = \frac{1}{2}\sum_{i=1}^{N} m_i\,\mathbf{v}_i(t)^2 \qquad \langle T_{\mathrm{kin}}\rangle = N\frac{3}{2}k_B T$$

1/2 *kT* per degree of freedom

$$T = \frac{2\langle T_{\mathrm{kin}}\rangle}{3k_B N}$$

$$\mathcal{T}(t) = \frac{2T_{\mathrm{kin}}(t)}{3k_B N}$$

$$T = \langle \mathcal{T}(t)\rangle_t$$

Boltzmann's constant

$k_B = 1.38064852 \times 10^{-23}\,\mathrm{J}\cdot\mathrm{K}^{-1}$

$$A = \frac{1}{N_t}\sum_{i=1}^{N_t} a\big(\mathbf{x}_1(t), \mathbf{x}_2(t), \ldots, \mathbf{x}_N(t), \mathbf{v}_1(t), \mathbf{v}_2(t), \ldots, \mathbf{v}_N(t)\big)$$

Pressure *P*

- pressure can be derived from a version of the *virial theorem* (… another time)

$$PV = Nk_BT + \frac{w}{3}$$

"virial" $\quad w := \left\langle \sum_{i<j}^{N-1} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle \qquad \mathbf{F}_i = \sum_{j \neq i} \mathbf{f}_{ij}$

$$\mathcal{P}(t) = V^{-1} \left[Nk_B\mathcal{T}(t) + \frac{1}{3} \sum_{i<j}^{N-1} \mathbf{r}_{ij}(t) \cdot \mathbf{f}_{ij}(t) \right]$$

$$P = \langle \mathcal{P}(t) \rangle_t$$

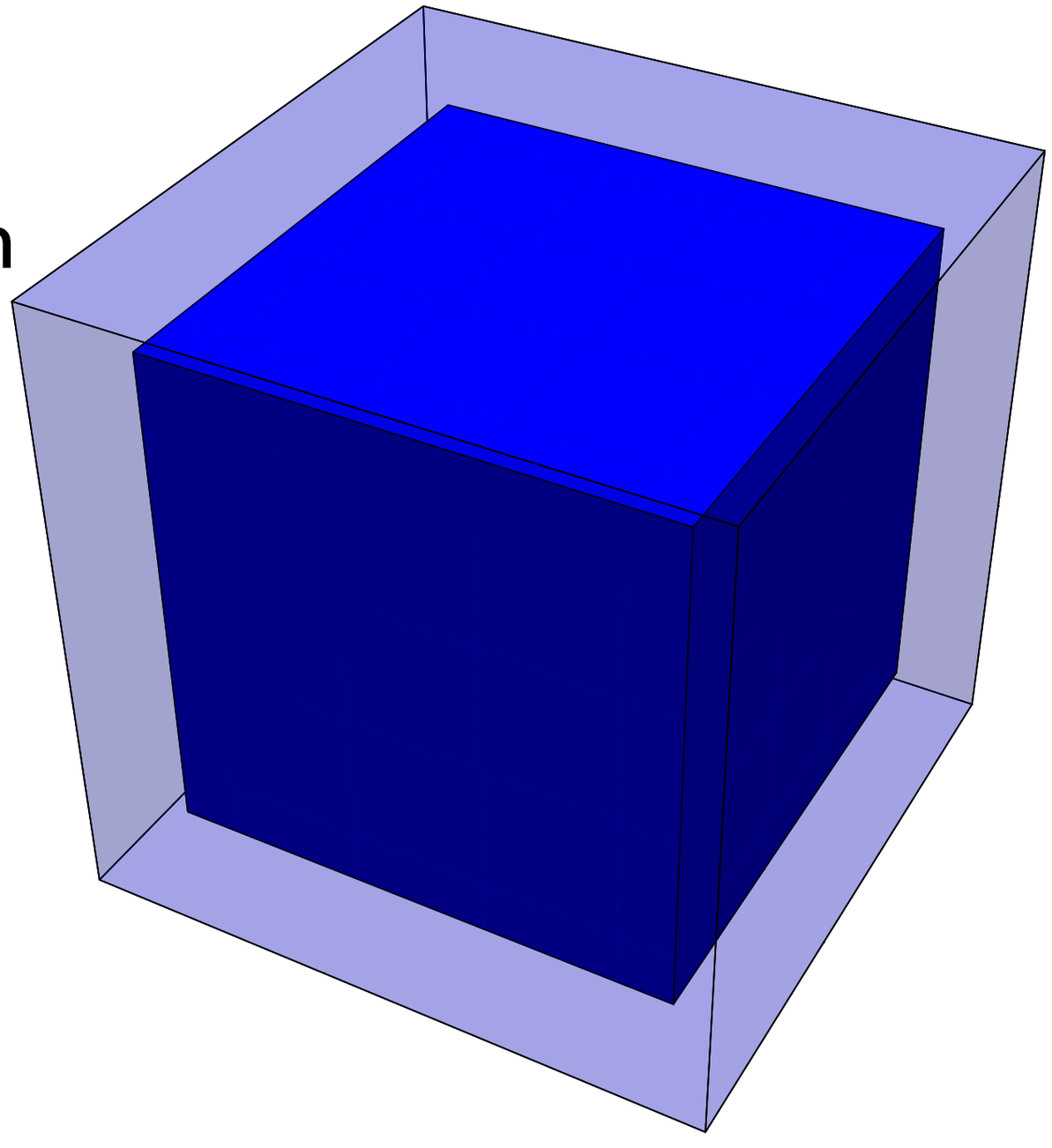
Summary

- outline of the MD algorithm
- use of periodic boundary conditions
- potential truncation
- integrators
- calculating macroscopic observables from microscopic estimators

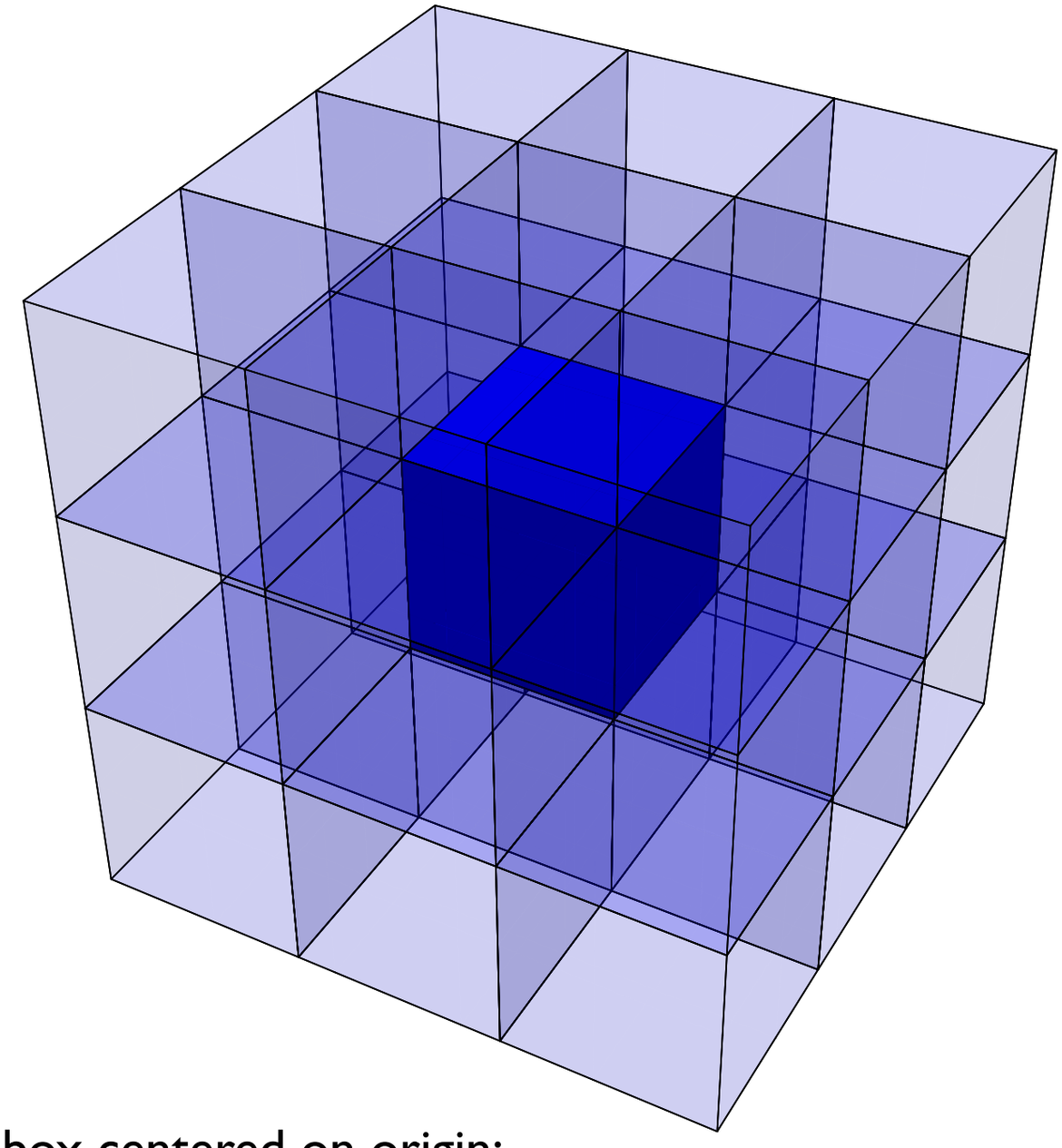
Appendix

Small systems: Surface effects

- In a small system, "most" particles are "near: the surface.
- "near" = typical interaction distance $d \sim 3\sigma$
- $N_{surf}/N \sim N^{-1/3}$
- *Problem* when we are interested in **bulk properties**.



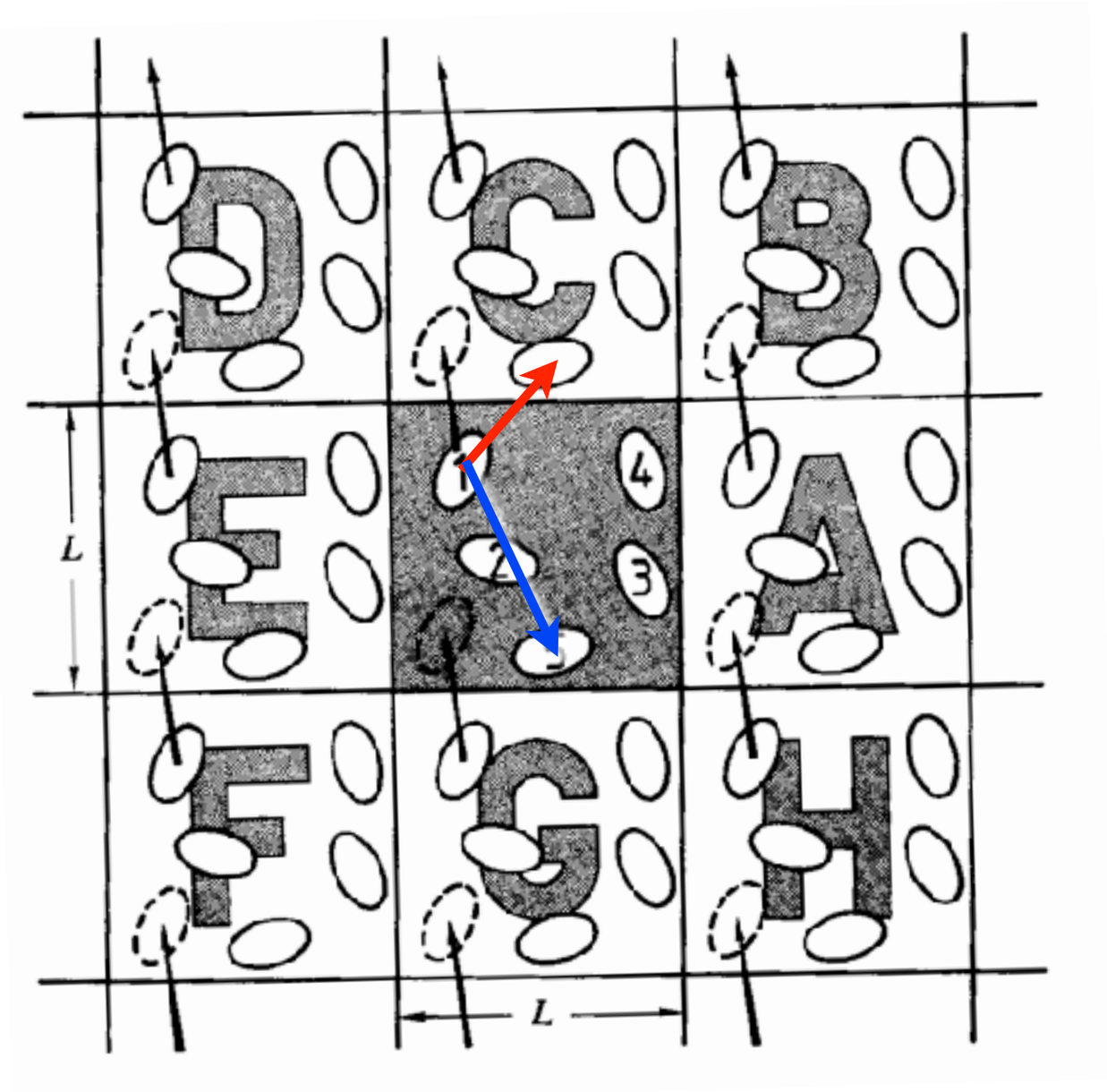
Small systems: Periodic boundaries



box centered on origin:

$$\mathbf{r}_i \leftarrow \mathbf{r}_i - L\,\mathrm{rint}\left(\frac{\mathbf{r}_i}{L}\right)$$

$$\mathbf{r}_{ij} \leftarrow \mathbf{r}_{ij} - L\,\mathrm{rint}\left(\frac{\mathbf{r}_{ij}}{L}\right)$$



from Allen & Tildesley, 1987

Periodic boundaries: Potential Issues

- simulate *infinite* system so must handle an infinite amount of interactions (though often truncation is permissible)
- spurious correlations/ordering
- only fluctuations allowed with lattice periodicity, and max wavelength $\lambda = L$

  ➡ phase transitions with long wavelength fluctuations problematic
- non-isotropic pair distribution function

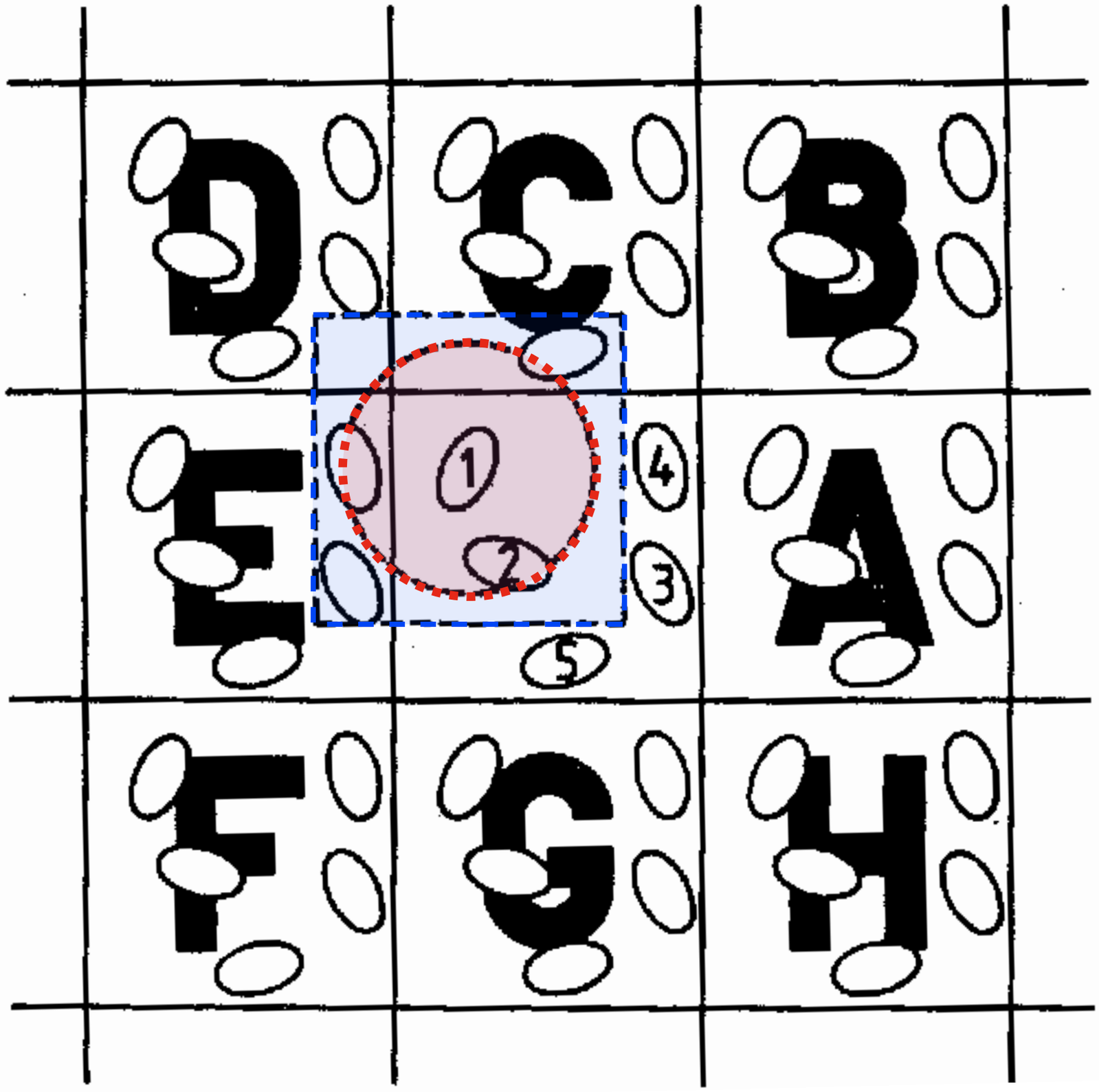
... but generally works rather well!

Periodic boundaries: Interactions

- pair wise $v(r_{ij})$ ~N^2
- minimum image convention
- truncation at cutoff R_c

  $v(r)$ must fall off faster than r^{-3}

  $R_c < L/2$



from Allen & Tildesley, 1987

Truncation of potentials

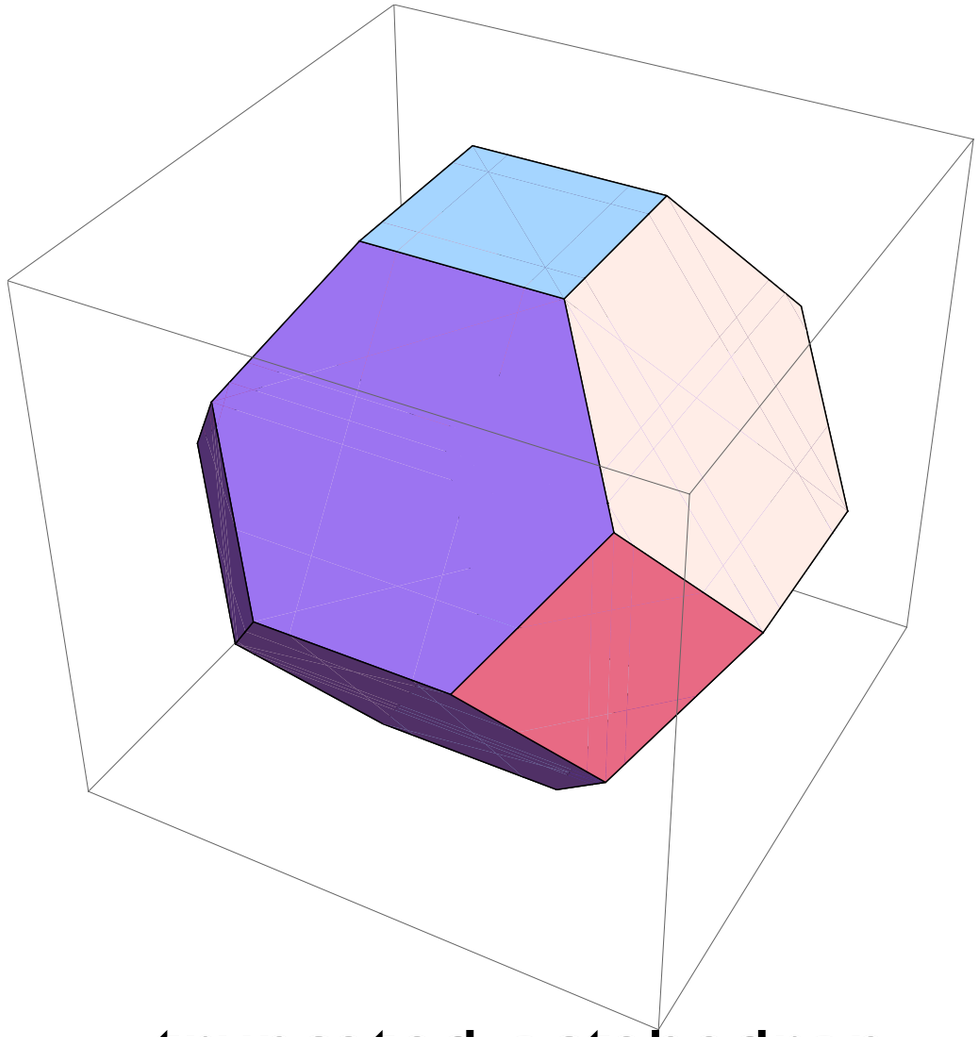
(proper periodic treatment: advanced topic)

- simple truncation $$u^{\mathrm{trunc}}(r) = \begin{cases} u(r) & r \leq R_c \\ 0 & r > R_c \end{cases}$$

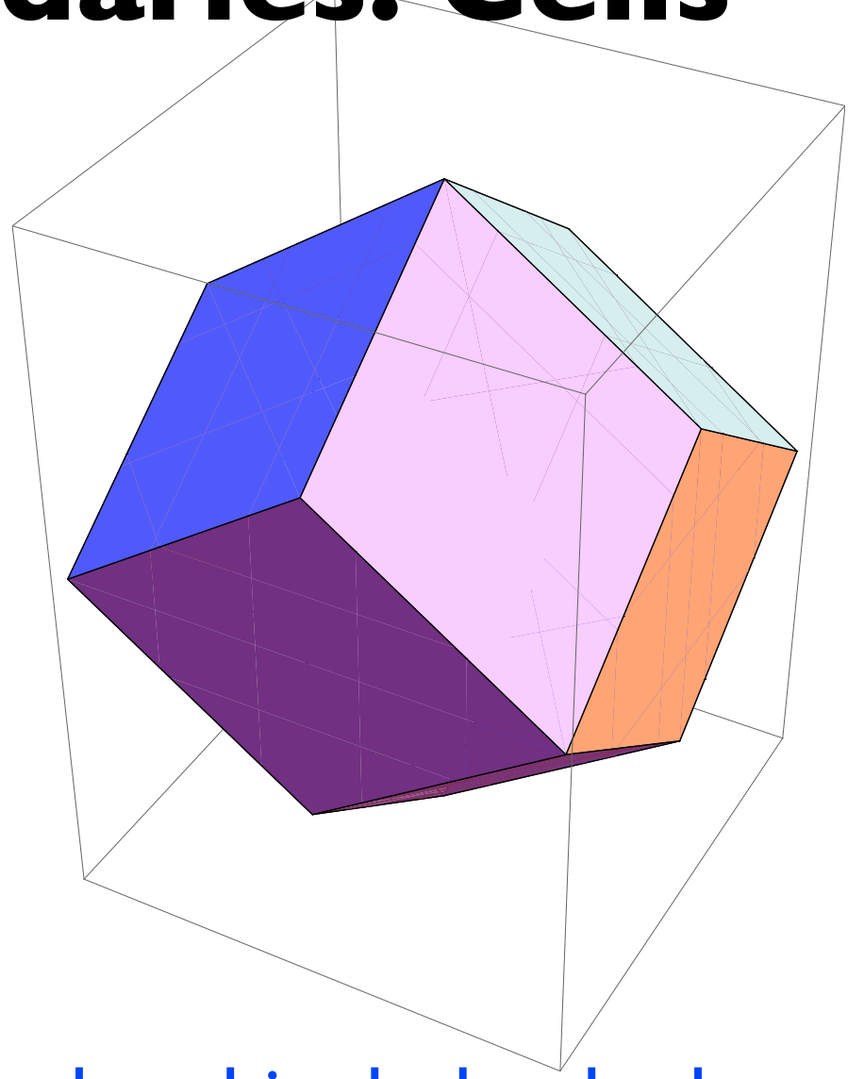
- truncation and shift $$u^{\mathrm{shift}}(r) = \begin{cases} u(r) - u(R_c) & r \leq R_c \\ 0 & r > R_c \end{cases}$$

- minimum image convention

Periodic boundaries: Cells

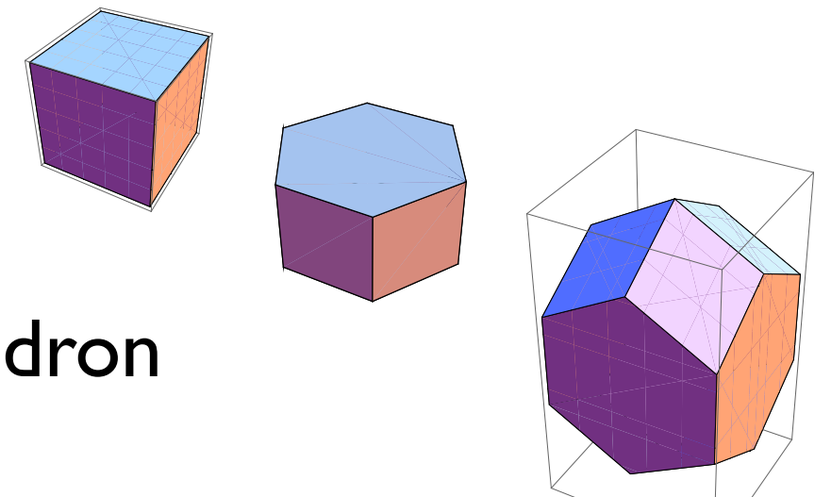


truncated octahedron
(0.77 d^3)



rhombic dodecahedron
(0.71 d^3)

+ cube/parallel epiped (d^3)
+ hexagonal prism
+ elongated rhombic dodecahedron



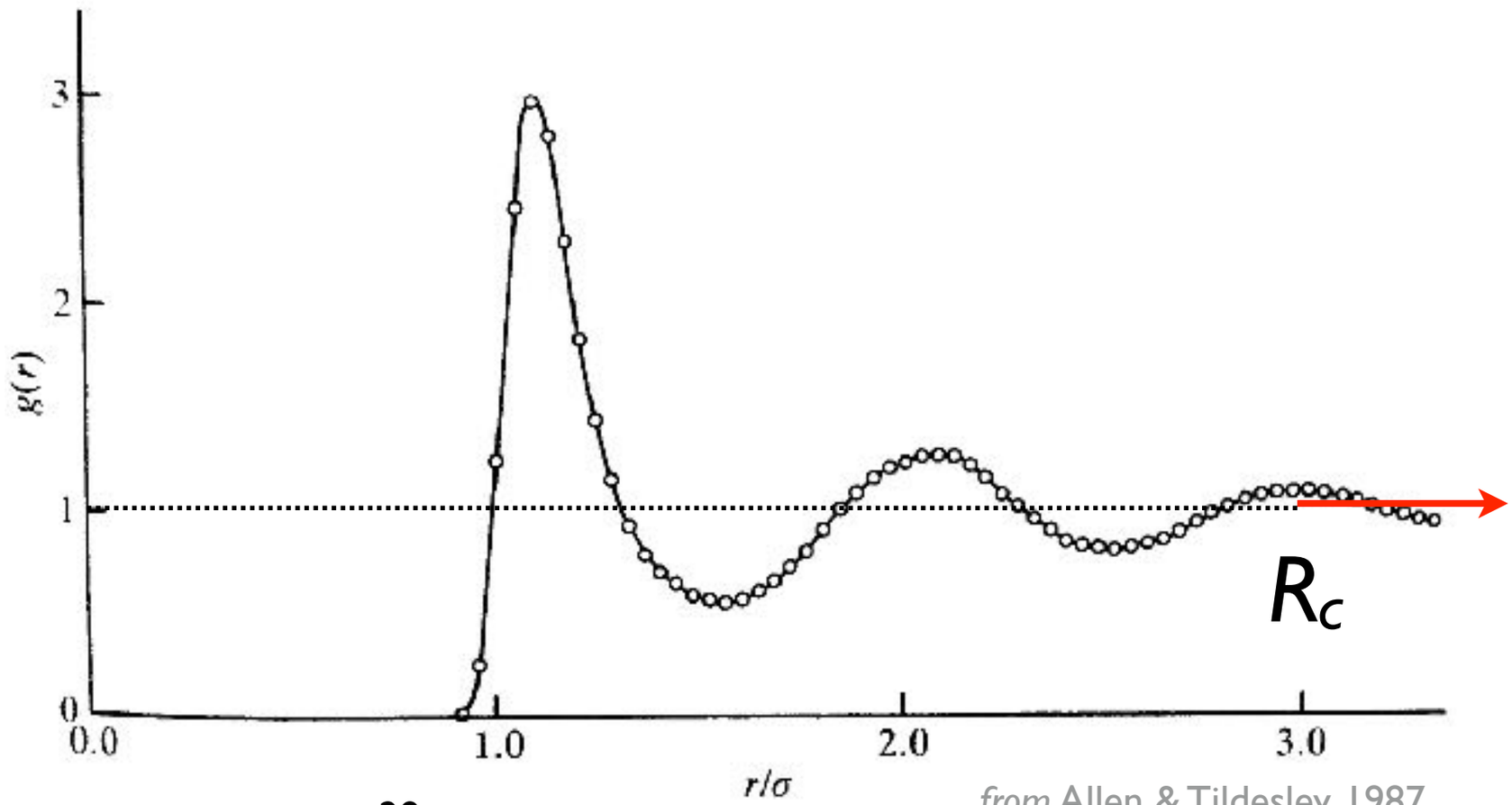
Periodic boundaries: Tail correction

$$U_{\text{tot}} = \tfrac{1}{2} N \rho \int_0^\infty u(r)\, g(r)\, 4\pi r^2 dr$$

$$U_{\text{tot}} = \sum_{i<j} u_c(r_{ij}) + \tfrac{1}{2} N \rho \int_{R_c}^\infty u(r)\, 4\pi r^2 dr$$

$$g(r) \approx 1 \quad \text{for } r > R_c$$

$$u_c(r) = \begin{cases} u(r) & r \le R_c \\ 0 & r > R_c \end{cases}$$



from Allen & Tildesley, 1987

Verlet Integrator

$$\mathbf{r}(t+\Delta t) \approx 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) + \frac{\mathbf{F}(t)}{m}\Delta t^2$$

- no velocities needed
- same accuracy as velocity Verlet
- velocities can be computed (but $\mathcal{O}(\Delta t^2)$)

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