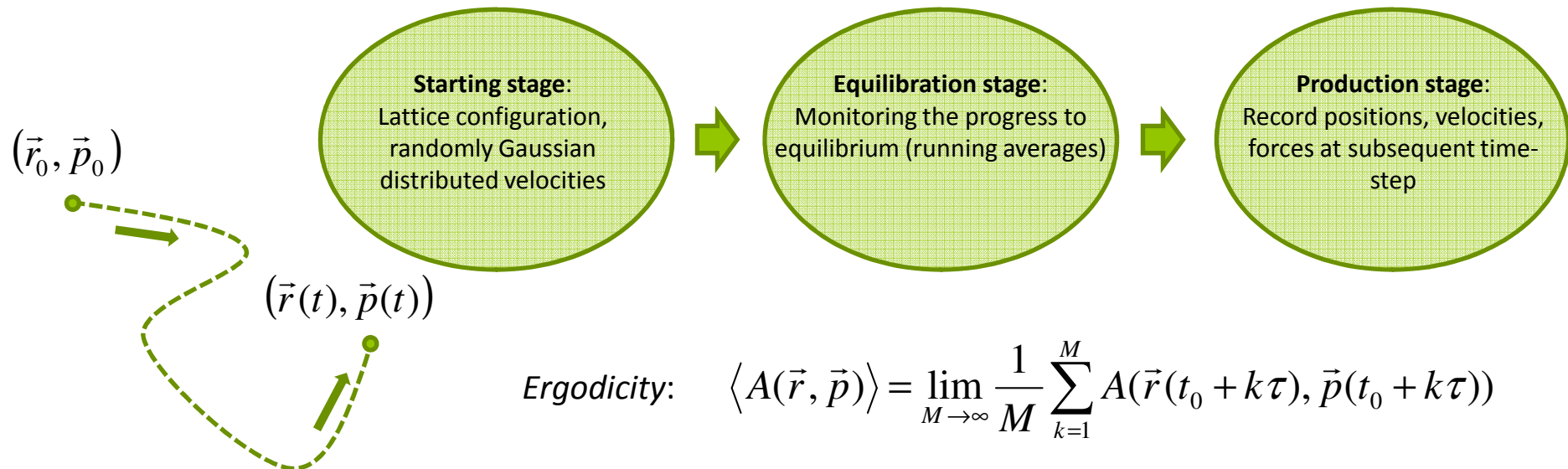
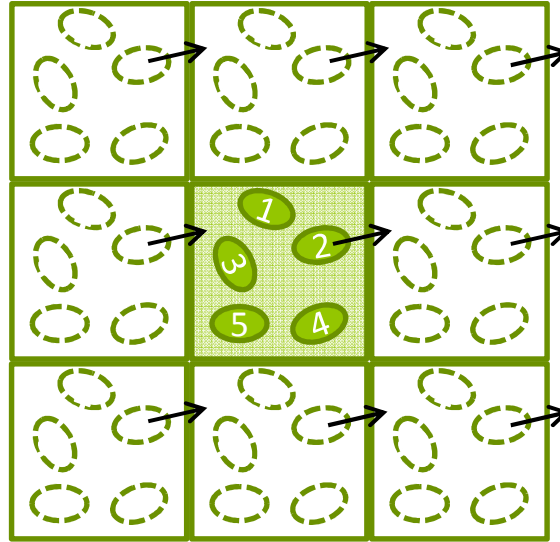


Molecular Dynamics

➤ Periodic boundary conditions



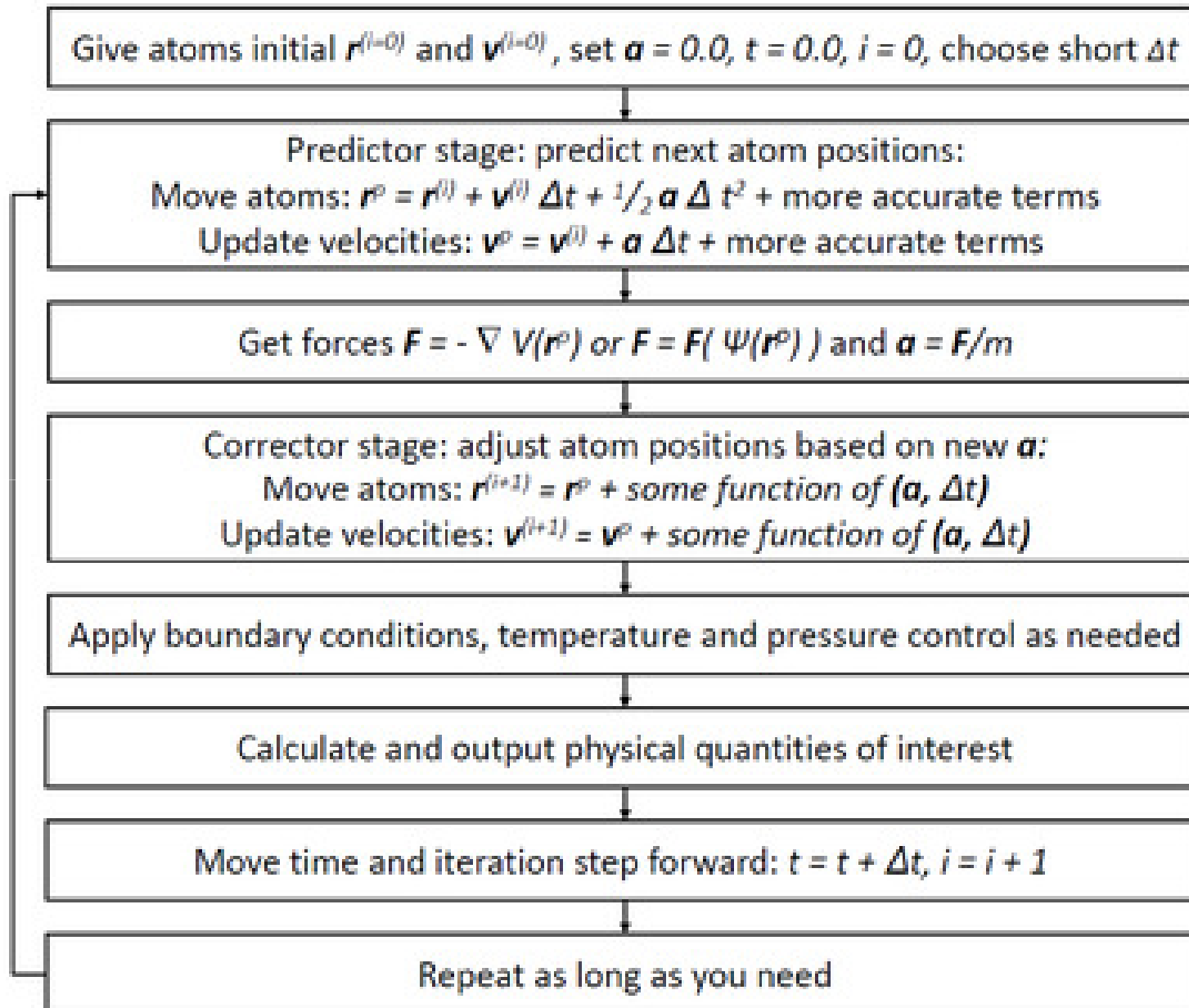
- Put N particles in a box and impose periodic boundary conditions
- Choose a force field (ex. LJ) to make particles interact with each other and a force cut-off
- Select an initial configuration (ex. lattice) and assign random velocities ($\langle \mathbf{v}^2 \rangle = 3k_B T/m$)
- Integrate Newton's equations to make the system evolve in the microcanonical (NVE) ensemble towards equilibrium

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j \neq i} \mathbf{f}(r_{ji})$$

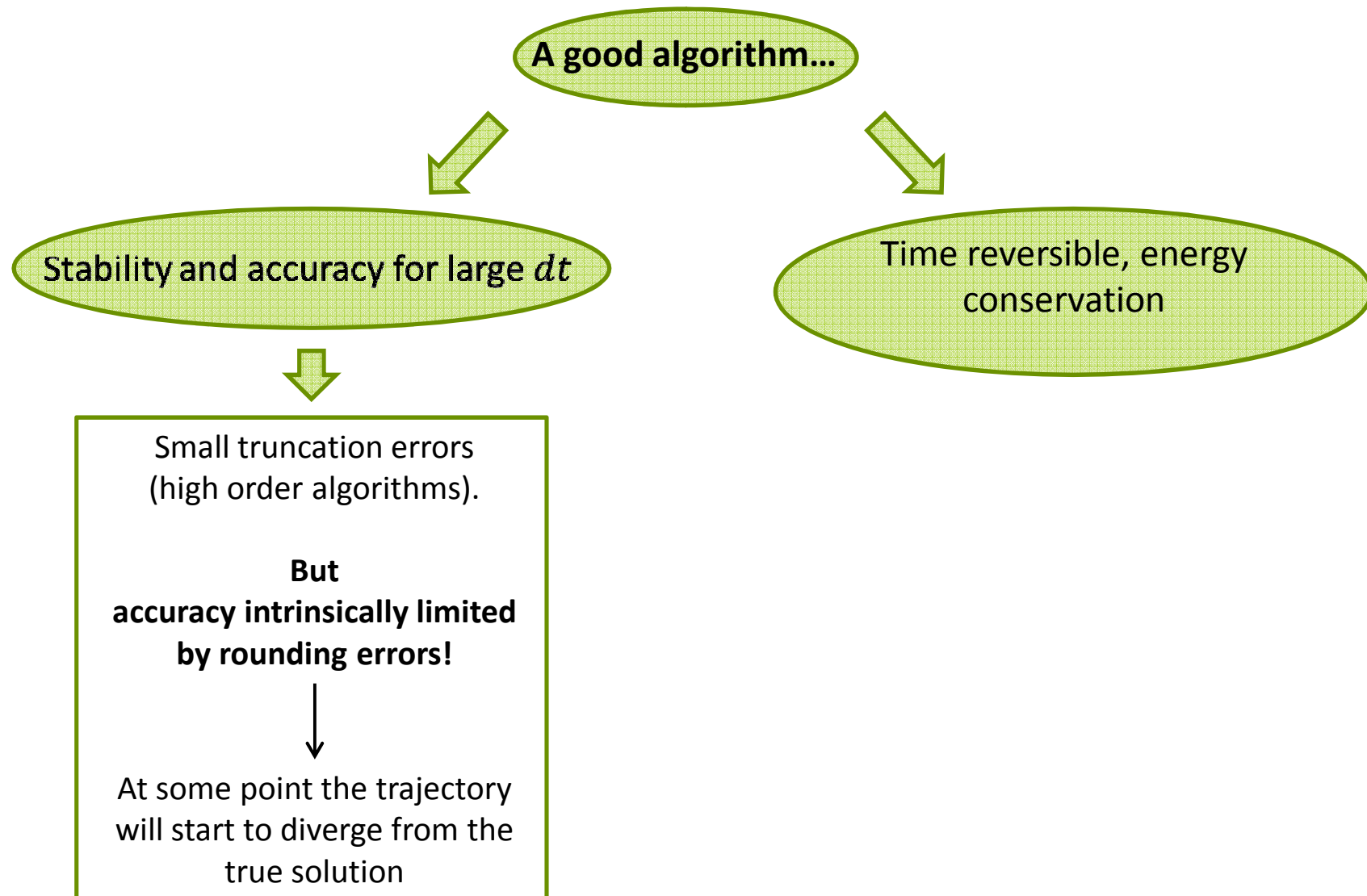
- When the system is equilibrated, generate a (sufficiently) long **trajectory** to calculate the desired autocorrelation function (the ergodic hypothesis is assumed)

$$Z_j = \frac{1}{N} \sum_{i=1}^N \left(\frac{1}{k_{\max}} \sum_{k=1}^{k_{\max}} \mathbf{v}_k \cdot \mathbf{v}_{k+j} \right) \quad t = j * dt$$

Simplified schematic of the molecular dynamics algorithm



Integrating the equation of motion



Integrating the equation of motion

Verlet algorithm

$$x(t_0 + h) = x(t_0) + hv(t_0) + \frac{h^2}{2} a(t_0) + \frac{h^3}{6} \dot{a}(t_0) + O(h^4)$$

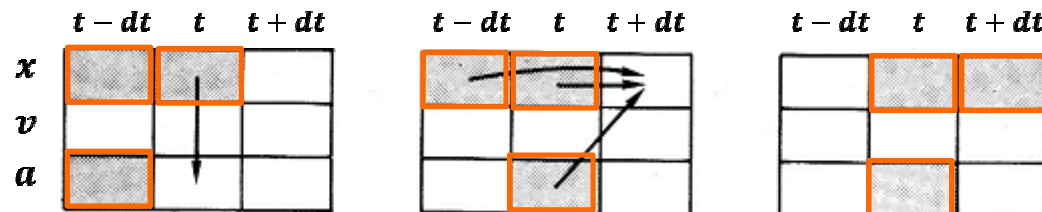
$$x(t_0 - h) = x(t_0) - hv(t_0) + \frac{h^2}{2} a(t_0) - \frac{h^3}{6} \dot{a}(t_0) + O(h^4)$$

$$x(t_0 + h) = 2x(t_0) - x(t_0 - h) + h^2 a(t_0) + O(h^4)$$

← + - →

$$v(t_0) = \frac{x(t_0 + h) - x(t_0 - h)}{2h} + O(h^2)$$

Algorithm steps



What do we calculate by means of MD?

➤ Thermodynamic functions:

- Entropy

$$S(B) - S(A) = \int_A^B dT \frac{1}{T(E)} \left(\frac{\partial T}{\partial E} \right)^{-1}$$

- Pressure (through *Virial equation*)

$$pV = Nk_B T + \frac{1}{d} \left\langle \sum_i \vec{F}_i \cdot \vec{r}_i \right\rangle$$

➤ Structural quantities:

- Pair correlation function

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle$$

- Orientational correlation function ($g(r_{ij}, \mathbf{\Omega}_i, \mathbf{\Omega}_j)$)

➤ Time (auto)correlation functions:

$$C_{AB}(t) = \langle \delta A(0) \delta B(t) \rangle$$

- Picture of the dynamics

- Time integrals related to macroscopic transport coefficient

$$\gamma = \int_0^{\infty} dt \langle \dot{P}(0) \dot{P}(t) \rangle$$

- Diffusion coefficient, Shear viscosity, Thermal conductivity

- Fourier transforms $\hat{C}_{AA}(\omega)$ related to experimental spectra

$$\circ S(Q, \omega) = FT(F(Q, t)) = \frac{1}{N} \langle \rho(-k, 0) \rho(k, t) \rangle$$

Estimating errors

Two sources of errors:

- Systematic (size-dependence, random number generator, interaction cut-off, numerical integration,...)
- Statistical (averages over runs of finite length)

Errors in equilibrium averages:

$$\langle A \rangle_{run} = \frac{1}{N} \sum_{n=1}^N A(n) \qquad \sigma^2(A) = \langle \delta A^2 \rangle_{run} = \frac{1}{N} \sum_{n=1}^N (A(n) - \langle A \rangle_{run})^2$$

Statistically independent configurations: $\sigma^2(\langle A \rangle_{run}) = \frac{\sigma^2(A)}{N}$