# Computational Statistical Physics

## Part II: Interacting particles and molecular dynamics

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# Phase transitions

- 23.02. Introduction to statistical physics and the Ising model
- 02.03. Monte Carlo methods
- 09.03. Finite size methods and cluster algorithms
- 16.03. Histogram methods
- 23.03. Renormalization group
- 30.03. Boltzmann machines

# Molecular dynamics

- 06.04. Molecular Dynamics, Verlet scheme, Leapfrog scheme
- 13.04. Optimization, Linked cell algorithm
- 20.04. ETH vacations
- 27.04. Lagrange multipliers, Rigid bodies, quaternions
- 04.05. Nosé-Hoover thermostat, stochastic method, constant pressure ensemble

# Event-driven dynamics

- 11.05. Event driven, inelastic collisions, friction
- 18.05. Contact dynamics
- 25.05. *Non-equilibrium phase transitions / ab initio MD / Car-Parinello* [TBC]
- 01.06. Advanced topics

# Molecular dynamics

# Molecular dynamics

MD is used in a variety of fields, some examples are:

- Simulation of atoms and molecules,
- Gravitational interactions,
- Flow dynamics,
- Biopolymers,
- Granular materials,
- Dislocations, voids, quasi-particles,
- Electrons (Car-Parrinello),
- Explosions.

# Molecular dynamics

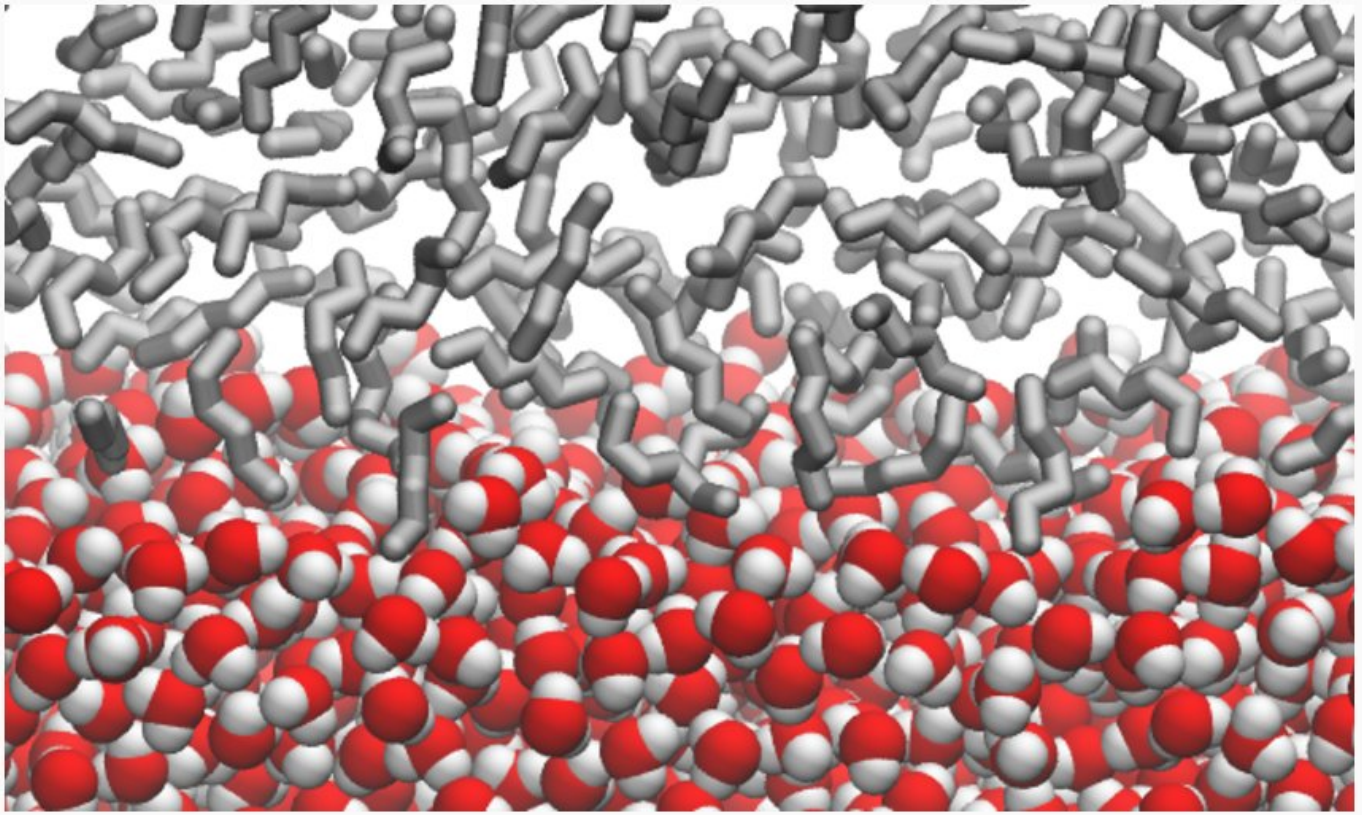

**Figure 1:** Water hexane interface. The figure is taken from `https://commons.wikimedia.org/wiki/File:Simulated_structure_of_the_water_hexane_interface.png`

# Molecular dynamics

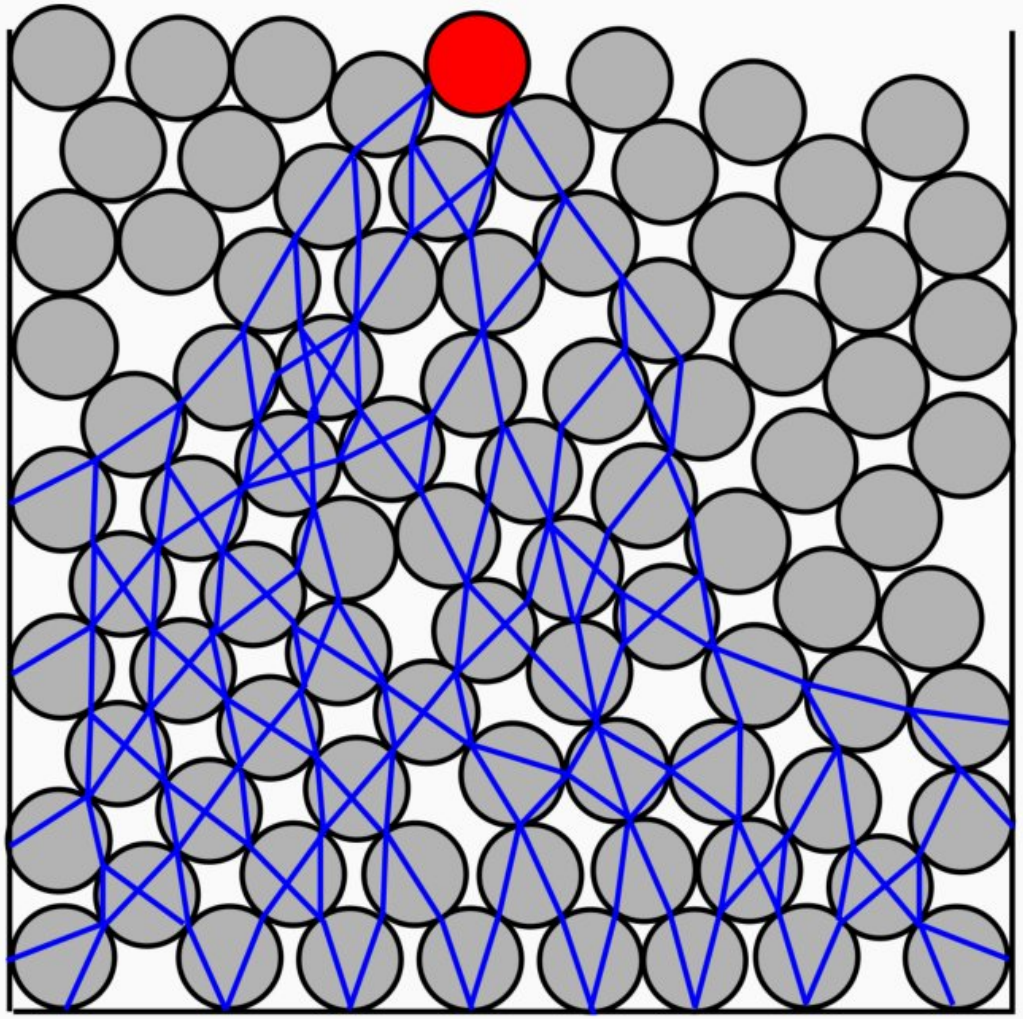

**Figure 2:** Granular matter. The figure is taken from `https://commons.wikimedia.org/wiki/File:Stress_transmision.svg`

# Molecular dynamics

To model interacting particle systems, we use generalized coordinates

$$\mathbf{q}_i = \left(q_i^1, \ldots, q_i^d\right) \quad \text{and} \quad \mathbf{p}_i = \left(p_i^1, \ldots, p_i^d\right). \tag{1}$$

in a system where each particle has $d$ degrees of freedom.

# Molecular dynamics

The system of $N$ particles is then described by

$$Q = (\mathbf{q}_1, \ldots, \mathbf{q}_N) \quad \text{and} \quad P = (\mathbf{p}_1, \ldots, \mathbf{p}_N), \tag{2}$$

using the Hamiltonian

$$\mathcal{H}(P, Q) = K(P) + V(Q) \tag{3}$$

with $K(P) = \sum_{i,k} \frac{\left(p_i^k\right)^2}{2m_i}$ being the kinetic energy, $m_i$ the mass of the $i^{\text{th}}$ particle and $V(Q)$ the potential energy. The sum over $k \in \{1, ..., d\}$ accounts for the d degrees of freedom.

# Molecular dynamics

The potential (e.g., an attractive or repulsive electromagnetic potential) determines the mutual interactions of all particles and therefore their dynamics. An expansion of the potential energy yields:

$$V(Q) = \sum_i v_1(q_i) + \sum_i \sum_{j>i} v_2(q_i, q_j) + \sum_i \sum_{j>i} \sum_{k>j} v_3(q_i, q_j, q_k) + \ldots. \tag{4}$$

# Molecular dynamics

Typically three or more body interactions are neglected and their effect is considered in an effective two body interaction described by

$$v_2^{\text{eff}}(q_i, q_j) = v^{\text{attr}}(r) + v^{\text{rep}}(r) \quad \text{with} \quad r = |\mathbf{q}_i - \mathbf{q}_j|, \qquad (5)$$

where $v^{\text{attr}}(r)$ and $v^{\text{rep}}(r)$ represent attractive and repulsive part of the effective potential, respectively.

# Molecular dynamics

For now, we only consider potentials that depend on distance, not particle orientation. Analytically, the simplest potential is the hard sphere interaction potential

$$v^{\text{rep}}(r) = \begin{cases} \infty & \text{if } r < \sigma, \\ 0 & \text{if } r \geq \sigma. \end{cases} \tag{6}$$

# Molecular dynamics

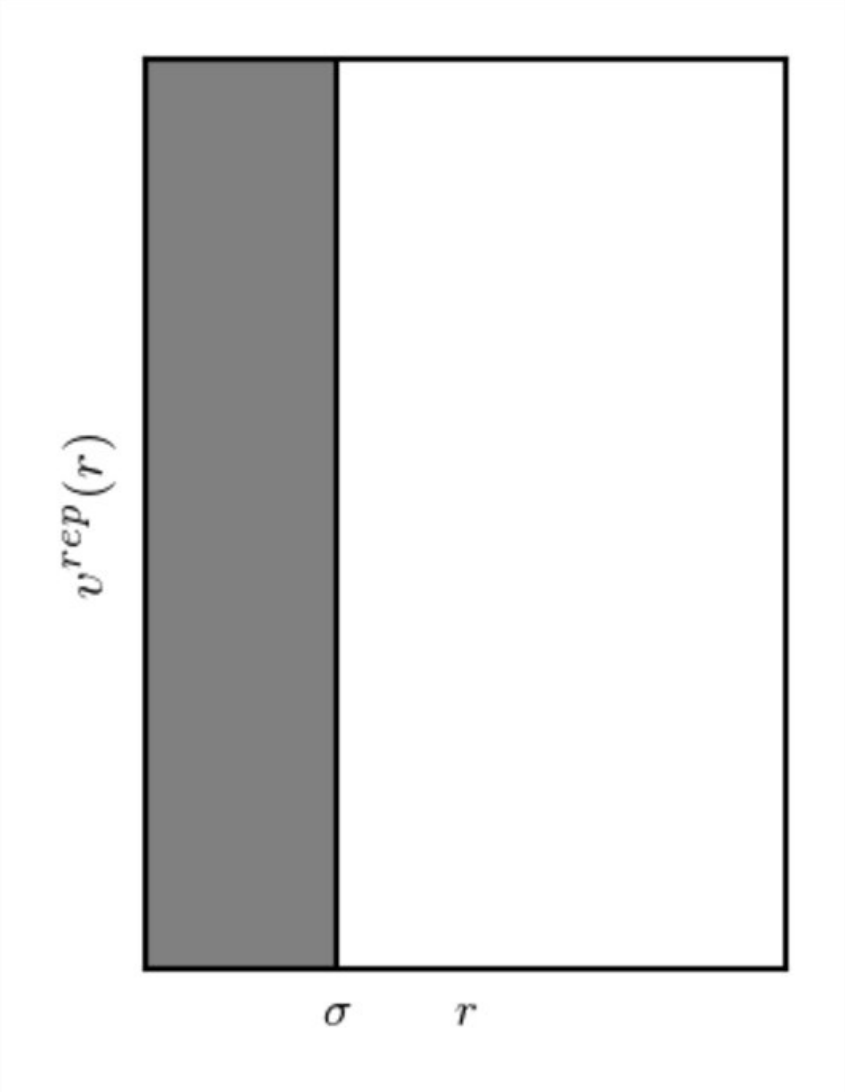


**Figure 3:** An example of a hard sphere potential.

# Equations of motion

The first order Taylor approximation of a symmetric attractive or repulsive potential is given by an elastic potential. For two particles with radii $R_1$ and $R_2$, the potential is given by

$$v^{\text{rep}}(r) = \begin{cases} \frac{k}{2}(R-r)^2 & \text{if } r < R \\ 0 & \text{if } r > R \end{cases} \quad \text{with} \quad R = R_1 + R_2, \qquad (7)$$

where $k$ is the elastic spring constant.

# Equations of motion

Another very important form of potential typically used to describe the interaction between molecules is the *Lennard-Jones* potential

$$v^{\mathrm{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \tag{8}$$

where $\epsilon$ is the attractive energy and $\sigma$ the interaction range.

LJ potential approximates the spherical symmetric interaction between a pair of neutral atoms or molecules.

# Equations of motion

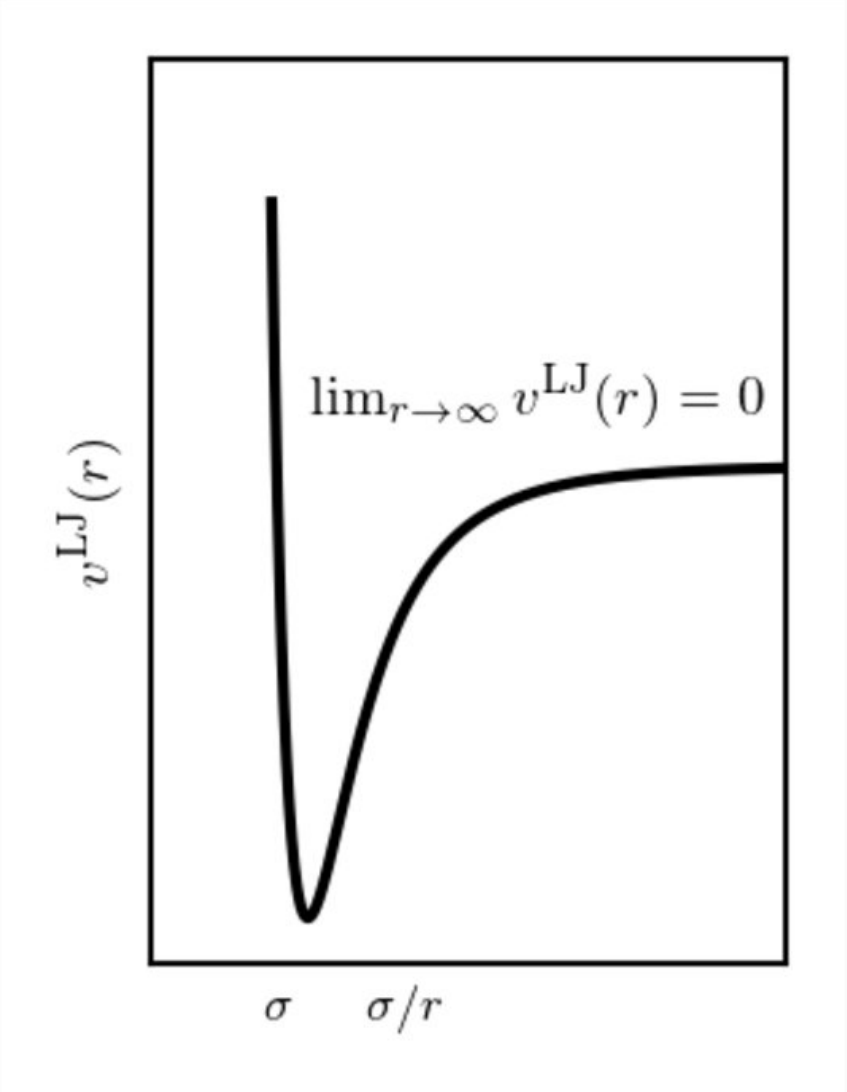


**Figure 4:** An example of a Lennard-Jones potential, cf. `http://www.atomsinmotion.com/`.

# Equations of motion

Once the interaction potential has been defined, we can easily derive the equations of motion using the Hamilton equations

$$\dot{q}_i^k = \frac{\partial \mathcal{H}}{\partial p_i^k}, \quad \dot{p}_i^k = -\frac{\partial \mathcal{H}}{\partial q_i^k}, \tag{9}$$

where $k \in \{1, \ldots, d\}$ and $i \in \{1, \ldots, N\}$.

# Equations of motion

For every particle, we identify $q_i$ with the position vector $x_i$ and $\dot{\mathbf{q}}_i = \dot{\mathbf{x}}_i$ with the velocity vector $\dot{\mathbf{v}}_i$. Due to $\dot{\mathbf{x}}_i = \mathbf{v}_i = \frac{\mathbf{p}_i}{m}$ and $\dot{\mathbf{p}}_i = -\nabla V(Q) = \mathbf{f}_i$, the equations of motion are:

$$m_i \ddot{\mathbf{x}}_i = \mathbf{f}_i = \sum_j \mathbf{f}_{ij}, \tag{10}$$

where $\mathbf{f}_{ij}$ is the force exerted by particle $j$ on particle $i$.

# Contact time

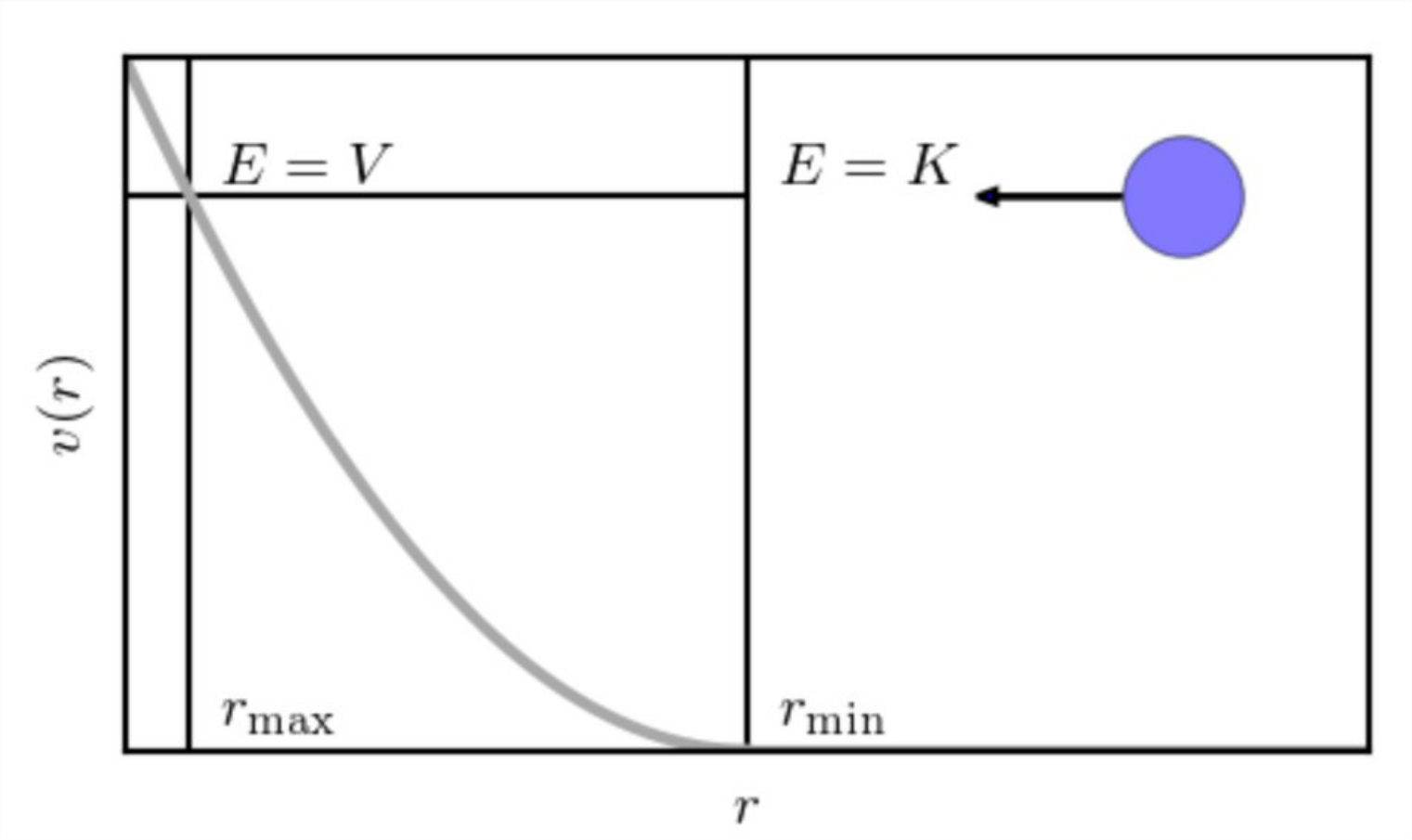


**Figure 5:** Derivation of the contact time.

# Contact time

Using the equations for energy

$$E = \frac{1}{2} m \dot{r}^2 + V(r) = \text{const.} \tag{11}$$

and radial velocity

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \left[ \frac{2}{m} \left( E - V(r) \right) \right]^{\frac{1}{2}}, \tag{12}$$

we derive the contact time

$$t_c = 2 \int_0^{\frac{1}{2} t_c} \mathrm{d}t = 2 \int_{r_{\min}}^{r_{\max}} \frac{\mathrm{d}t}{\mathrm{d}r} \mathrm{d}r = 2 \int_{r_{\min}}^{r_{\max}} \left[ \frac{2}{m} \left( E - V(r) \right) \right]^{-\frac{1}{2}} \mathrm{d}r, \tag{13}$$

where $r_{\min}$ and $r_{\max}$ are the range of the potential and the turning point of a colliding particle, respectively.

## Contact time

We expect reasonable results only if the time step is not larger than the smallest contact time. The time integration of the equations of motion is then possible using an integration method such as

- Euler's method,
- Runge-Kutta methods,
- Predictor-corrector methods,
- Verlet methods,
- Leap-frog methods.

# Verlet method [Verlet '67]

We begin with a Taylor expansion of $x(t + \Delta t)$ for sufficiently small time steps $\Delta t$ so that

$$\begin{aligned} \mathbf{x}\,(t + \Delta t) &= \mathbf{x}\,(t) + \Delta t\,\mathbf{v}\,(t) + \frac{1}{2}\Delta t^2\,\dot{\mathbf{v}} + \mathcal{O}(\Delta t^3), \\ \mathbf{x}\,(t - \Delta t) &= \mathbf{x}\,(t) - \Delta t\,\mathbf{v}\,(t) + \frac{1}{2}\Delta t^2\,\dot{\mathbf{v}} - \mathcal{O}(\Delta t^3). \end{aligned} \tag{14}$$

Adding the latter two expressions yields

$$\mathbf{x}\,(t + \Delta t) = 2\mathbf{x}\,(t) - \mathbf{x}\,(t - \Delta t) + \Delta t^2\,\ddot{\mathbf{x}}\,(t) + \mathcal{O}(\Delta t^4). \tag{15}$$

# Verlet method

Newton's second law enables us to express $\ddot{\mathbf{x}}(t)$ as

$$\ddot{\mathbf{x}}_i(t) = \frac{1}{m_i} \sum_j \mathbf{f}_{ij}(t) \quad \text{with} \quad \mathbf{f}_{ij}(t) = -\nabla V(r_{ij}(t)). \tag{16}$$

The particle trajectories are then computed by plugging in the latter results in Eq. (15). Typically, we use a time step of approximately $\Delta t \approx t_c/20$, with $t_c$ a contact time defined in Eq. (13).

# Verlet method

Some general remarks about the Verlet method:

- Two time steps need to be stored ($t$ and $t - \Delta t$).
- Velocities can be computed with $\mathbf{v}(t) = \frac{\mathbf{x}(t+\Delta t)-\mathbf{x}(t-\Delta t)}{2\Delta t}$.
- The local numerical error is of order $\mathcal{O}\left(\Delta t^4\right)$, i.e. it is globally a third order algorithm.
- The numbers which are added are of order $\mathcal{O}\left(\Delta t^0\right)$ and $\mathcal{O}\left(\Delta t^2\right)$.
- Improvable by systematical inclusion of higher orders (very inefficient).
- The method is time reversible, which allows to estimate the error accumulation by reversing the process and comparing it to the initial conditions.

# Leapfrog Method

For the derivation of the Leapfrog method, we consider velocities at intermediate steps:

$$\mathbf{v}\left(t+\frac{1}{2}\Delta t\right) = v(t) + \frac{1}{2}\Delta t\,\dot{\mathbf{v}}(t) + \mathcal{O}(\Delta t^2), \tag{17}$$

$$\mathbf{v}\left(t-\frac{1}{2}\Delta t\right) = v(t) - \frac{1}{2}\Delta t\,\dot{\mathbf{v}}(t) + \mathcal{O}(\Delta t^2). \tag{18}$$

Taking the difference of the two equations leads to

$$\mathbf{v}\left(t+\frac{1}{2}\Delta t\right) = \mathbf{v}\left(t-\frac{1}{2}\Delta t\right) + \Delta t\,\ddot{\mathbf{x}}\,(t) + \mathcal{O}(\Delta t^3) \tag{19}$$

and we then update the positions according to

$$\mathbf{x}\,(t+\Delta t) = \mathbf{x}\,(t) + \Delta t\,\mathbf{v}\left(t+\frac{1}{2}\Delta t\right) + \mathcal{O}(\Delta t^4). \tag{20}$$

# Leapfrog Method

The analogies and differences between the Leapfrog method

$$\begin{aligned} \dot{\mathbf{v}}\left(t+\Delta t\right) &= \frac{f\left(\mathbf{x}\left(t\right)\right)}{m}, \\ \mathbf{v}\left(t+\Delta t\right) &= \mathbf{v}\left(t\right) + \Delta t\, \dot{\mathbf{v}}\left(t+\Delta t\right), \\ \mathbf{x}\left(t+\Delta t\right) &= \mathbf{x}\left(t\right) + \Delta t\, \mathbf{v}\left(t+\Delta t\right) \end{aligned} \tag{21}$$

and the forward Euler integration

$$\begin{aligned} \dot{\mathbf{v}}\left(t+\Delta t\right) &= \frac{f\left(\mathbf{x}\left(t\right)\right)}{m}, \\ \mathbf{x}\left(t+\Delta t\right) &= \mathbf{x}\left(t\right) + \Delta t\, \mathbf{v}\left(t\right), \\ \mathbf{v}\left(t+\Delta t\right) &= \mathbf{v}\left(t\right) + \Delta t\, \dot{\mathbf{v}}\left(t+\Delta t\right) \end{aligned} \tag{22}$$

are the following: The update of the variables is done in a different order (both methods rely on explicit forward integration). In the case of the Leapfrog method, the position is not updated using the previous velocity, as it is done in the usual Euler method.

# Leapfrog Method

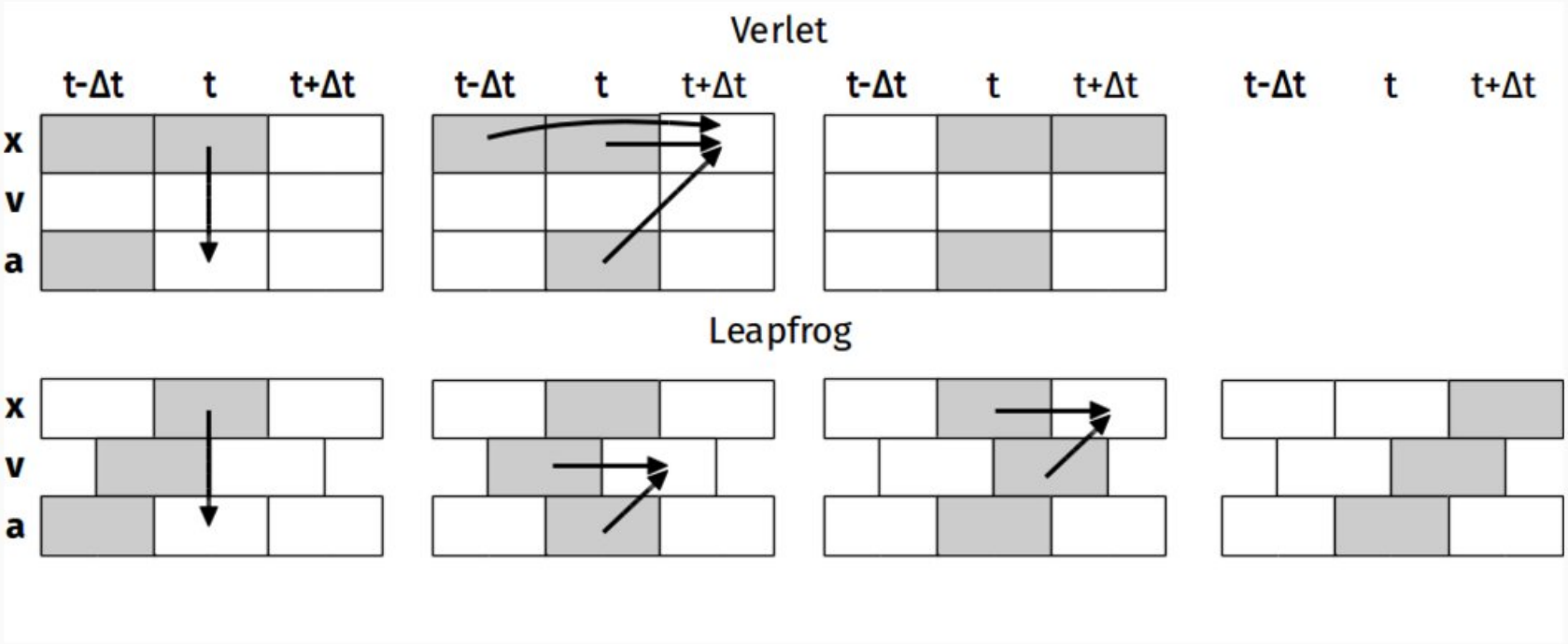


**Figure 6:** A comparison between Verlet and Leapfrog update schemes.