Course 02/2

Classical molecular dynamics

- Scope
- Setting up a molecular dynamics simulation
- Issues to be considered
- Requirements
- Newtonian dynamics: Lagrangian vs Hamiltonian
- Considerations for integration algorithms

Scope

Definition

In classical molecular dynamics a number of particles are evolved in time on the computer to investigate the effect of the adopted interactions.

The adjective “classical” indicates that the particles are subject to the law of classical mechanics.

Two major scopes

1. Establish the equilibrium properties of a physical quantity $A(\{ \mathbf{p}_i \},\{ \mathbf{r}_i \})$ (ensemble averages) – *static properties*

2. Calculation of time correlation functions – *dynamic properties*

Setting up a molecular dynamics simulation

- Definition of variables, e.g. *x*, *y* and *z* coordinates of the particles
- Definition of interactions, force field

} Definition of the physical system

- Initial configuration – velocities – temperature

$$\frac{3}{2} kT = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^{\,2}$$

Equipartition theorem

- Boundary conditions – periodic boundary conditions

Periodic boundary conditions

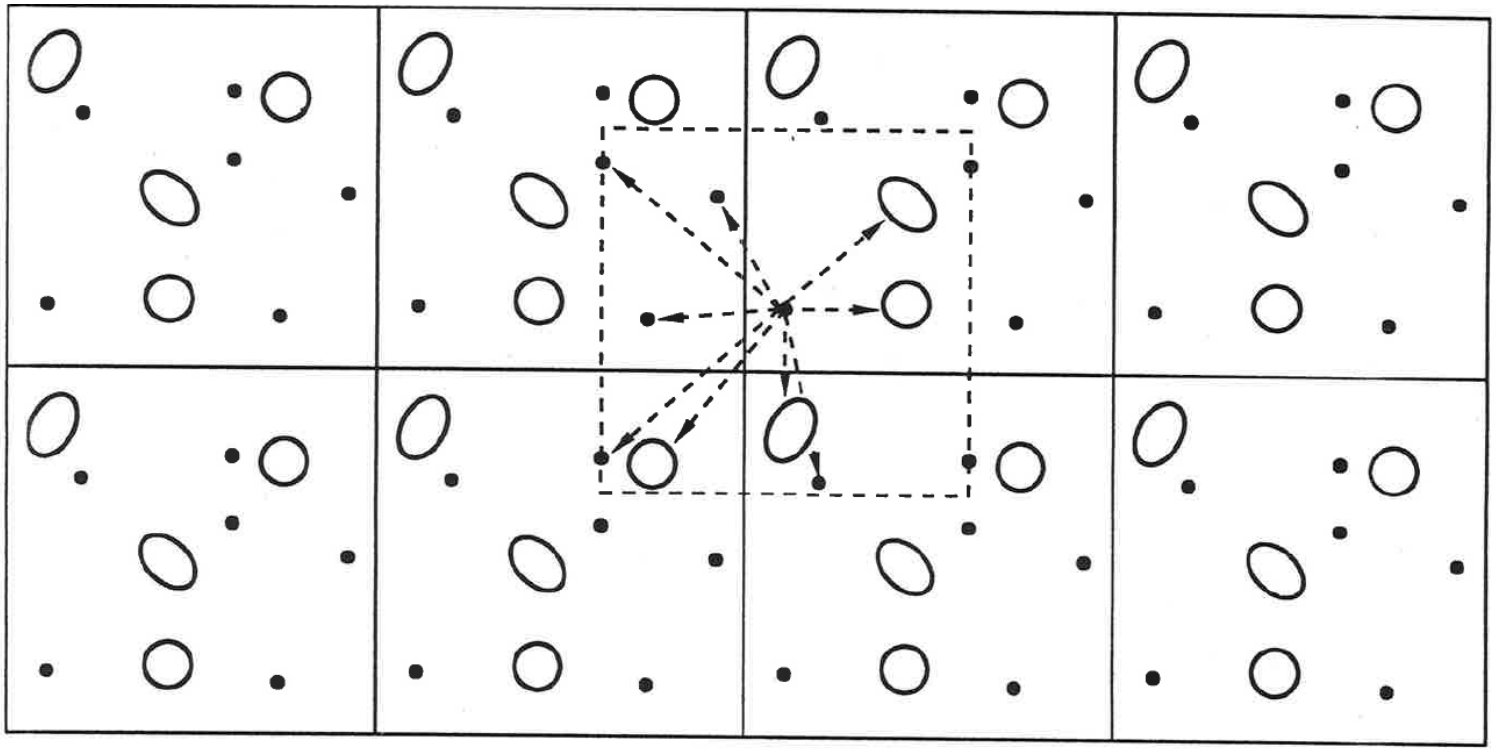


Figure 3.2: Schematic representation of periodic boundary conditions

Setting up a molecular dynamics simulation

- Definition of variables, e.g. x, y and z coordinates of the particles
- Definition of interactions, force field

} Definition of Hamiltonian

- Initial configuration – velocities – temperature

$$\frac{3}{2} kT = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^{\,2}$$

Equipartition theorem

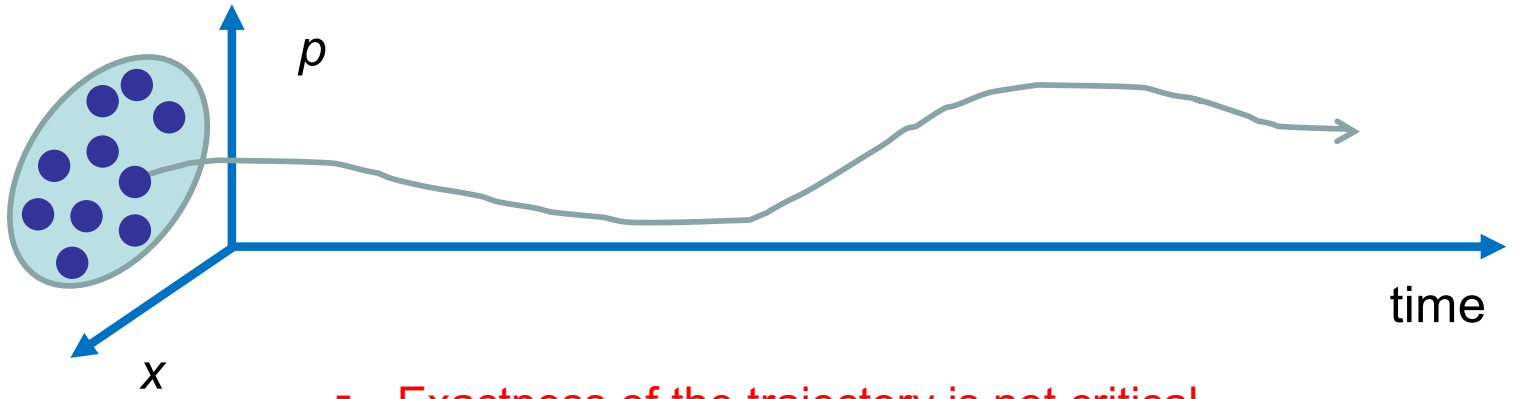
- Boundary conditions – periodic boundary conditions
- Force calculation (most cpu time consuming part)
  - Pair-interactions: $N \cdot (N - 1) / 2$ terms.
  - Or many-body interactions or …
  - Extent of the interaction, cutoff radius r_c, minimum cell convention.
- Integration algorithm

Issues to be considered

- Quality of the interactions: classical, electronic structure, nuclear quantum effects
- Size of the system
- Time limitations
- Accuracy of integration algorithm (energy conservation)
- Statistical noise

Requirements

Ensemble averages – static properties



- Exactness of the trajectory is not critical
- For a microcanonical ensemble, energy conservation is important

Time correlation function – dynamic properties

- Exactness of the trajectory over the correlation times of interest is critical in this case.
- Deviations from exact time trajectories go exponentially with time.

Newtonian dynamics

Lagrangian

$$\mathcal{L}(x, \dot{x}) = \frac{1}{2} m \dot{x}^2 - U(x)$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{x}} = \frac{\partial \mathcal{L}}{\partial x}$$

$$m\ddot{x} = -\frac{\partial U}{\partial x}$$

one 2nd order equation

Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + U$$

$$\begin{cases} \dot{p} = -\dfrac{\partial U}{\partial x} \\ \dot{x} = \dfrac{p}{m} \end{cases}$$

two 1st order equations

Considerations for integration algorithms

1. One force calculation per time step.

   The force calculation is the most expensive part.

2. Accuracy of $o(\Delta t^4)$.

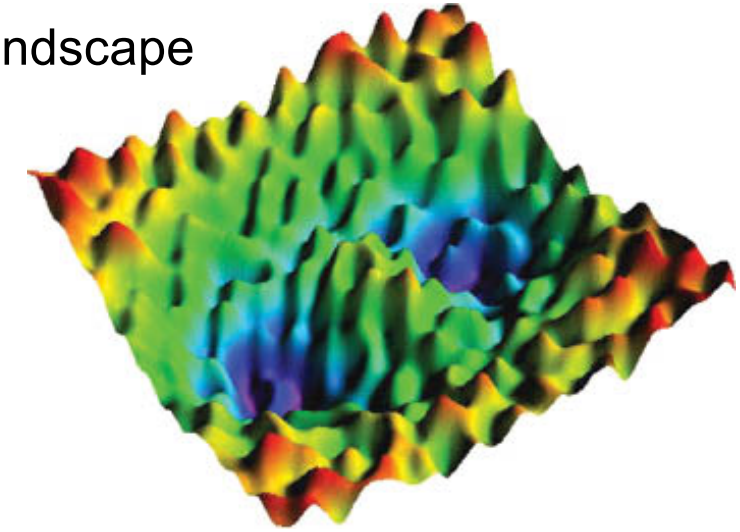
$$x(t+\Delta t) = x(t) + \dot{x}\,\Delta t + \frac{\ddot{x}}{2}\Delta t^2 + \frac{\dddot{x}}{6}\Delta t^3 + o(\Delta t^4)$$

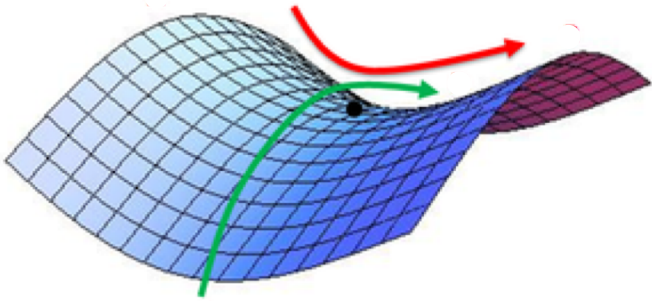
velocity force

$$\frac{\partial U}{\partial x} \qquad \frac{\partial^2 U}{\partial x^2}$$

Why caring about 2nd derivative of the potential?

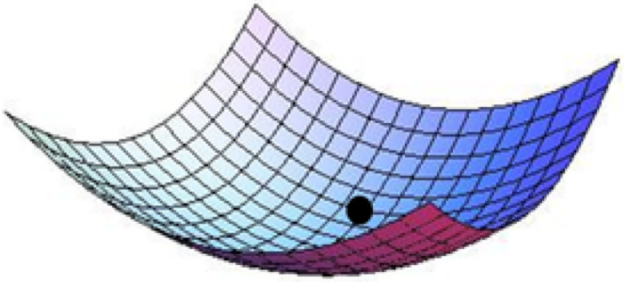
Potential energy landscape





$$\frac{\partial^2 U}{\partial x^2} < 0$$

responsible for diffusive motion



$$\frac{\partial^2 U}{\partial x^2} > 0$$

systematically more frequent!

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