Course 14/1

Constraints in MD (1/2): introduction

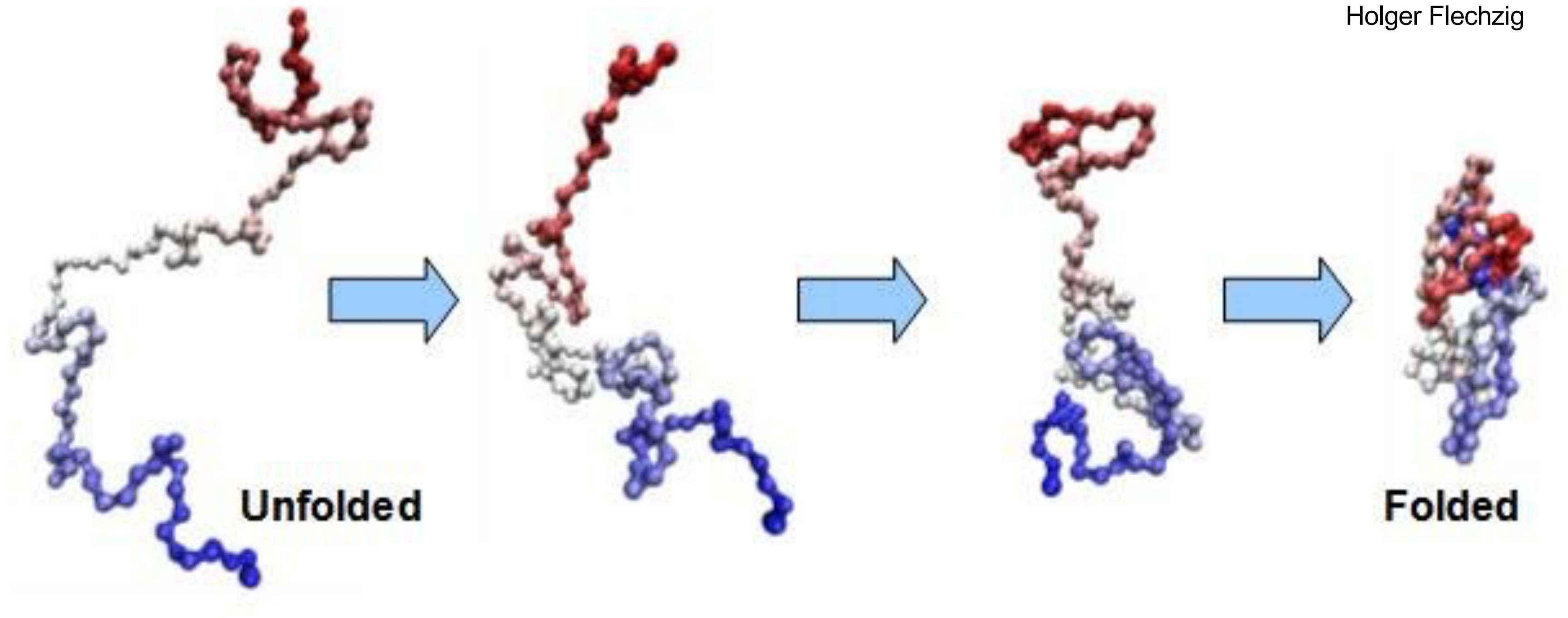
- Motivation
- Formal theory
- Method enforcing constraints explicitly

Motivation

1. The timescale of the fastest motions determines the MD timestep.
   By “freezing” the fast vibrations, we can use longer timesteps in the MD and thus follow physical phenomena over longer timescales.

Example: slow motions of protein branches vs fast atomic stretching vibrations

Holger Flechzig

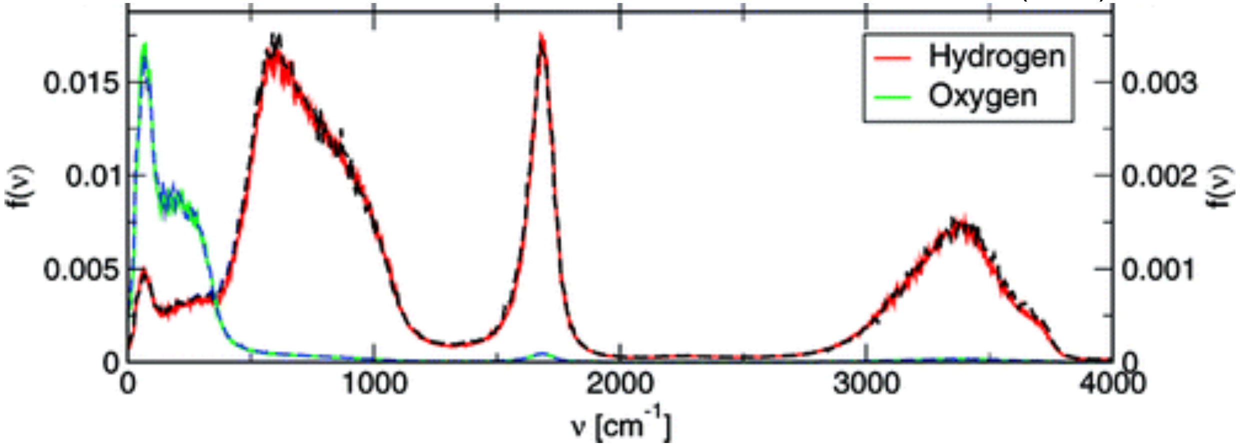


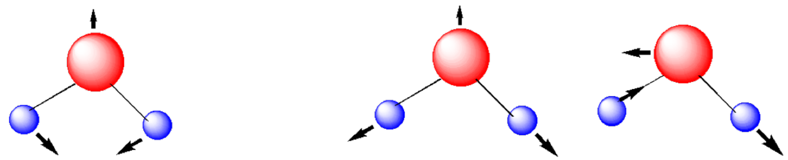
Motivation

2. Decoupling between fast and slow motions can lead to severe thermalization problems.

Example: vibrational density of states of liquid water

Kühne, Krack & Parrinello, *JCTC* **5**, 235 (2009)





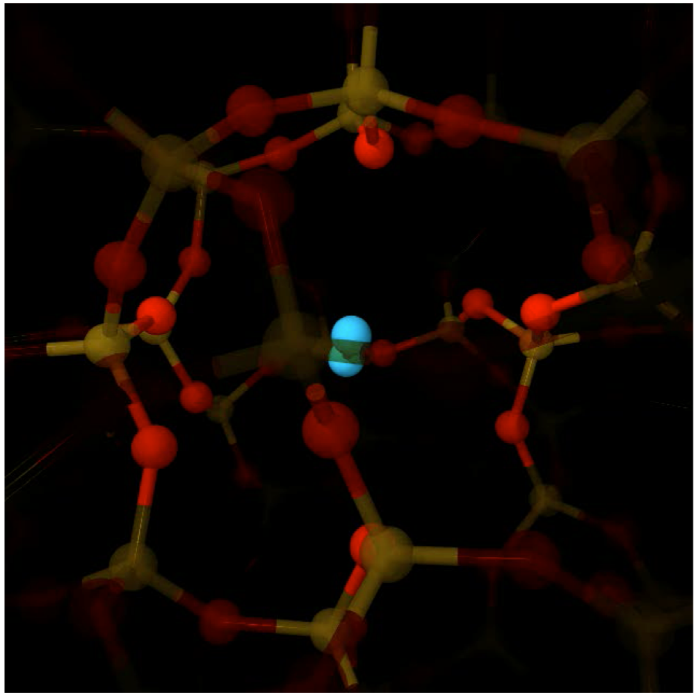
bending modes

stretching modes

Motivation

3. To study constrained motions and minimum energy paths.

Example: motion of diffusing O_2 molecule through amorphous SiO_2



Bongiorno & Pasquarello, *J. Phys. Condens. Matter* **17**, S2051 (2005)

Formal theory

Holonomic constraints (do not depend on velocities)

$$\sigma_k(\vec{r}^{\,N}) = 0 \qquad k = 1,\ldots M$$

Equation of motion

The equation of motion is obtained through the minimization of the action:

$$\text{Min}\left\{ \int_{t_1}^{t_2} \left[\ \tfrac{1}{2} m v^2 - U(\vec{x})\ \right] dt \right\} \Longrightarrow \vec{F} = -\frac{\partial U}{\partial \vec{x}}$$

Through the use of a Lagrange multiplier λ_k for each of the M constraints, this gives:

$$m_i \ddot{\vec{r}}_i = \vec{F}_i - \sum_{k=1}^{M} \lambda_k \frac{\partial \sigma_k}{\partial \vec{r}_i} \qquad i = 1, \ldots N$$

where the holonomic constraints enter in the same way as the potential.

Formal theory

Equation of motion

$$m_i \ddot{\vec{r}}_i = \vec{F}_i - \sum_{k=1}^{M} \lambda_k \frac{\partial \sigma_k}{\partial \vec{r}_i} \qquad (*)$$

Method of Lagrange multipliers

For $k = 1, \ldots M$:

$$\frac{d}{dt}[\dot{\sigma}_k] = \frac{d}{dt}\left(\sum_{i=1}^{N} \frac{\partial \sigma_k}{\partial \vec{r}_i} \dot{\vec{r}}_i\right) = \sum_{i=1}^{N}\left(\sum_{j=1}^{N} \frac{\partial^2 \sigma_k}{\partial \vec{r}_i \partial \vec{r}_j} \dot{\vec{r}}_i \dot{\vec{r}}_j + \frac{\partial \sigma_k}{\partial \vec{r}_i} \ddot{\vec{r}}_i\right) = 0 \qquad (**)$$

If we substitute $(*)$ into $(**)$, we achieve M linear equations in λ_k , which can be solved and which thus formally determine the Langrange multipliers.

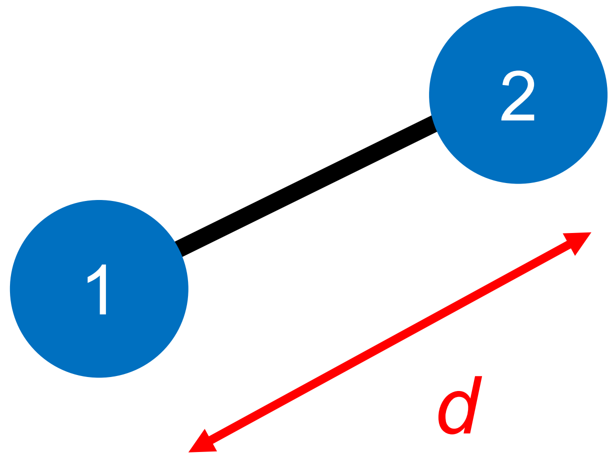
However, when this is implemented in a MD scheme, the constraints $\sigma_k(\vec{r}^N)$ $(k = 1, \ldots M)$ deviate from 0 in a divergent way because of the errors due to the integrator and to the numerical round-offs.

Method enforcing constraints explicitly

J.-P. Ryckaert, G. Ciccotti & H.J.C. Berendsen, *J. Comp. Phys*. **23**, 327 (1977)

- The constraints are satisfied exactly at every step.
- The method depends on the integrator.
- ”Position Verlet” is the preferred integrator because the constraints are holonomic, i.e. position dependent.

Application to simple case



Bond constraint (M = 1)

$$\sigma[\vec{r}_1(t), \vec{r}_2(t)] = |\vec{r}_1(t) - \vec{r}_2(t)|^2 - d^2 = 0$$

Equation of motion

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(t) + \vec{G}_i(t) = -\frac{\partial U}{\partial \vec{r}_i} - \lambda \frac{\partial \sigma_k}{\partial \vec{r}_i}$$

For particle 1: $\vec{G}_1(t) = -2\lambda(\vec{r}_1 - \vec{r}_2)$

For particle 2: $\vec{G}_2(t) = 2\lambda(\vec{r}_1 - \vec{r}_2)$

Position Verlet integrator

$$\vec{r}_i(t + \Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + \frac{\vec{F}_i(t)}{m_i}\Delta t^2 + \frac{\vec{G}_i(t)}{m_i}\Delta t^2$$

Exact enforcement of constraint

$$|\vec{r}_1(t + \Delta t) - \vec{r}_2(t + \Delta t)|^2 = d^2$$

The Lagrange multiplier λ is found through the solution of an equation of 2nd order.

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