

Constraints and Langevin dynamics

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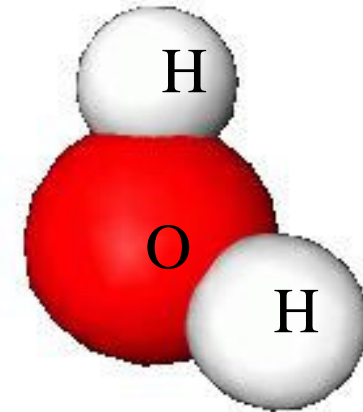
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Constraints

Recall from last lecture:

Molecular Systems



- *E. g.* Water. Extended Simple Point Charge (SPC/E) model
- OH distance : 1 \AA ; HOH angle : 109.47°
- $q_H = 0.4238 e$; $q_O = -2q_H$
- O-O interaction *via* LJ $\sigma = 3.166 \text{ \AA}$, $\epsilon = 0.6502 \frac{KJ}{mol}$.
- Rigid molecule model. Bond distances cannot change. Introduce constraint forces, that act along the bond directions.

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$$F_{i\alpha} = F_{i\alpha}^{free} + F_{i\alpha}^{constraint}$$

- Dynamics satisfying constraints using Lagrange multipliers.

Constraints

- If angles and bonds are fixed (say, we have a rigid molecule), one possibility is to work with COM and rotational degrees of freedom. **Too messy.**
- Other alternative: Add constraint forces to keep specified distances constant:

$$F_{i\alpha} = F_{i\alpha}^{free} + F_{i\alpha}^{constraint}$$

where i indexes molecules, and α atoms

With H-O-H labeled as 1, 2, 3 define constraint parameter χ_{12} to keep distance between atoms 1 and 2:

$$\chi_{12} = r_{12}^2 - d_{12}^2 = 0$$

Constraints (cont)

The force on atom 1 will be

$$F_1 = F_1^{free} + \frac{1}{2} \lambda_{12} \nabla_{r_1} \chi_{12}$$

etc. the λ are the Lagrange multipliers to be determined.

The constraint forces are:

$$F_1^c = \lambda_{12} \vec{r}_{12} - \lambda_{31} \vec{r}_{31}$$

NB: we have included the bond angle constraint here.

$$F_2^c = \lambda_{23} \vec{r}_{23} - \lambda_{23} \vec{r}_{23}$$

$$F_3^c = \lambda_{31} \vec{r}_{31} - \lambda_{23} \vec{r}_{23}$$

Constraints (contd)

The equations of motion can be integrated as:

$$r_{\alpha}(t + \delta t) = r'_{\alpha}(t + \delta t) + \frac{\delta t^2 F_{\alpha}^c}{m_{\alpha}}$$

And the distances (' indicated unconstrained updates) are:

$$r_{12}(t + \delta t) = r'_{12}(t + \delta t) + \delta t^2(m_1^{-1} + m_2^{-1})\lambda_{12}r_{12}(t) - \delta t^2 m_2^{-1} \lambda_{23}(t) - \delta t^2 m_1^{-1} \lambda_{31}r_{31}(t)$$

Imposing condition: $|r_{12}(t + \delta t)|^2 = |r_{12}(t)|^2 = d_{12}^2$

Quadratic equations for λ which have to be solved and positions updated accordingly.

Constraints (contd)

Instead, better to linearize update equations (λ^2 terms quartic in time step):

$$r_{i\alpha}(t + \delta t) = r_{i\alpha}(t + \delta t) + \left(\frac{1}{2}\right)\left(\frac{m_\beta}{m_\alpha + m_\beta}\right)\left(\frac{r_{\alpha\beta}^2(t + \delta t) - d_{\alpha\beta}^2}{r_{\alpha\beta}(t + \delta t) \cdot r_{\alpha\beta}(t)}\right)$$

$$r_{i\beta}(t + \delta t) = r_{i\beta}(t + \delta t) - \left(\frac{1}{2}\right)\left(\frac{m_\alpha}{m_\alpha + m_\beta}\right)\left(\frac{r_{\alpha\beta}^2(t + \delta t) - d_{\alpha\beta}^2}{r_{\alpha\beta}(t + \delta t) \cdot r_{\alpha\beta}(t)}\right)$$

Iterate while $\delta r_{\alpha\beta}^2(t + \delta t) - d_{\alpha\beta}^2 > \Delta$

Δ is the tolerance specified.

Langevin Dynamics: Brownian motion

The original Langevin equation written to describe the effect of the solvent on a “Brownian” particle.

Liquid exerts a friction force, described by a friction coefficient γ

Many collisions of the atoms in the solvent resulting in many “random forces” acting on Brownian particle.

$$\dot{p}(t) = -\gamma p(t) + R(t)$$

Delta correlated random forces: $\langle R(t)R(0) \rangle = C\delta(t)$

Requiring $\langle \frac{p^2}{2m} \rangle = \frac{1}{2}k_B T$ yields $C = 2mk_B T \gamma$

Thermalization at temperature T. Velocity correlation decays exponentially with time constant $1/\gamma$

Langevin Dynamics

Inclusion of the intermolecular interaction leads to:

$$\dot{p}(t) = -\nabla V(x(t)) - \gamma p(t) + R(t)$$

A physical choice of γ may be made from Stoke's law:

$$\gamma = 6\pi\eta a/m$$

or Einstein's relation $\gamma = k_B T/mD$

η is the viscosity of the medium and D the diffusion coefficient of the solute.

$\gamma \sim 50 \text{ ps}^{-1}$ typical Choice.

Langevin dynamics: Integration

A generalized Verlet algorithm can be written as:

$$p^{n+1/2} = p^n + (\Delta t/2)[- \nabla V(x^n) - \gamma p^n + R^n]$$

$$x^{n+1} = x^n + \Delta t p^{n+1/2} / m$$

$$p^{n+1} = p^{n+1/2} + (\Delta t/2)[- \nabla V(x^{n+1}) - \gamma p^{n+1} + R^{n+1}]$$

Last equation implicit for p^{n+1} but linear.

Generalized Langevin equation: Mori-Zwanzig formalism

Although the Langevin equation earlier was written as a phenomenological equation, this can also be derived formally as the general equation of motion.

Starting with:

$$\dot{A}(t) = i\mathcal{L}A(t) = \mathcal{P}i\mathcal{L}A(t) + (1 - \mathcal{P})i\mathcal{L}A(t)$$

Projection operator \mathcal{P} : $\mathcal{P}B \equiv \langle AB \rangle \langle AA \rangle^{-1} A$

One obtains:

$$\dot{A}(t) = i\mathbf{\Omega}A(t) - \int_0^t dt' M(t')A(t-t') + R(t)$$

M - Memory function

Mori-Zwanzig formalism (contd)

Frequency:

$$i\Omega \equiv \langle \dot{A}A \rangle \langle AA \rangle^{-1}$$

Random force: orthogonal to A, also in evolution.
“Fast degrees of freedom”

$$R(t) = \exp[(1 - \mathcal{P})i\mathcal{L}t](1 - \mathcal{P})i\mathcal{L}A(0)$$

Memory function: Autocorrelation function of R

$$M(t) = \langle R(t)R(0) \rangle \langle AA \rangle^{-1}$$