Constraints

Today we will learn how one handles constraints within molecular dynamics.

• Why constraints?
• Effects on the ensemble
• Non-Cartesian coordinate systems
• SHAKE method
• Constraints in *ab initio* MD

Constraints in MD

• In simulations of molecular systems there are various time scales:
  – Vibrational frequencies (energies greater than 300K)
  – Rotations
  – Internal molecular reorientation (i.e. torsional motions)
  – Diffusion
  – Melting, ....
• The vibrational dynamics sets the time step but are decoupled and not interesting for the longer scales.
• Vibrations are not classical but quantum. (What is $\hbar \omega / kT$?)
• Constraints simplify construction of potential and allow more efficient dynamics

• WARNING: constraints change the ensemble (Gibbs).
  If you take the limit as a spring constant gets large you get a different answer than if you do dynamics on a constrained surface (for some constraints) because constraints are non-linear in Cartesian coordinates.
**Constrained coordinates**

- Simplest example: a linear molecule.
  - Need center of mass and a unit vector (5 coord./molecule)
  - C.O.M. moves in the usual fashion.
  - The angle moves by application of a torque.
- Can treat rigid molecules using Euler angles or quaternions.
- You have to watch out for singular places of the coordinates (i.e., the north pole—along the z-axis—where angles are undefined.)
- For partially rigid molecules the equation of motion in generalized coordinates is difficult as the number of degrees of freedom increases.
- Putting constraints in “by hand” is difficult (e.g., polar coords.)
- Reduction in number of D.O.F. does not per se save computer time.

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**SHAKE algorithm**

- Work directly with Cartesian atomic coordinates.
- Dynamics move forward without constraints
- Algorithm then readjusts to satisfy the constraints.

- Suppose equation for a single constraint is: \( \sigma(R) = 0 \)
  - e.g. a bond constraint is \( \sigma(R) = |r_{ij} - r_{ij_{0}}|^2 - a^2 \)

- Equation of motion with constraint is determined from Hamiltonian's principle: \( m \ddot{a}(t) = F - \lambda(t) \nabla \sigma(R,t) \)

- Do not determine EOM for \( \lambda(t) \) because numerical errors will cause a drift of the trajectory away from the constraint.
- Instead \( \lambda(t) \) is fixed so that the constraint is satisfied.
• Verlet algorithm:
  \[ \mathbf{R}_{\text{new}}(t+h) = 2\mathbf{R}(t) - \mathbf{R}(t-h) + h^2 \mathbf{F}(t)/m - h^2 \lambda(t) \nabla \sigma(\mathbf{R},t) \]
  
  • Determine \( \lambda(t) \) so that \( \sigma(\mathbf{R}(t+h)) = 0 \).
  
  • This is a non-linear equation we solve by iteration.

\[
R = R(t + h) = R_0 - \lambda G_0 \quad \text{where} \quad R_0 = 2R(t) - R(t-h) + h^2 \mathbf{F}(t)/m \\
\text{and} \quad G_0 = h^2 \nabla \sigma(R(t))
\]

Constraint \( 0 = \sigma(R_0 - \lambda G_0) \)

Expand about \( \lambda_0 \) :
\[
0 = \sigma(R_0 - \lambda_0 G_0) - (\lambda_{n+1} - \lambda_n) \nabla \sigma(R_0 - \lambda_n G_0) G_0
\]

\[
\lambda_{n+1} = \lambda_n - \frac{\sigma_n}{G_0 \nabla \sigma_n}
\]

Iterate until \( \sigma_n = 0 \equiv \sigma(R_0 - \lambda_n G_0) = 0 \)

\[\sigma = r_0^2 - \rho^2 \quad \text{then} \quad \nabla \sigma = 2\left(r_i - r_j\right) = -\nabla f \]

Actually we have many constraints. So we need to generalize. b

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**Multiple constraints**

One MD step: determine \( r_i(t+h) \)

\[
r_i(t+h) = -r_i(t-h) + 2r_i(t) + h^2 F_i(t)/m_i \quad \text{Initialize step}
\]

Loop over constraints \( \sigma_k \) until \( \sigma_k(r(t+h)) \leq \varepsilon \)

\[
\mathbf{r}^{\text{new}}(t+h) = \mathbf{r}_i(t+h) - \frac{\nabla \sigma_i(r(t)) \sigma_i(r(t+h))}{\sum_j \frac{m_j}{m_i} \nabla \sigma_j(r(t+h)) \nabla \sigma_j(r(t))}
\]

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**Advantages of SHAKE**

- Typically one must iterate the Newton cycle about 25 times - but because the intermolecular force is not re-evaluated--only the constraints, this only takes 25% of the total CPU time. (vs. a non-constrained system).

- Constrained dynamics have a much larger time step so it is much more efficient. (anyway vibrations are often quantum.)

- SHAKE algorithm allows great flexibility

- Easier than inventing appropriate coordinate systems. Generalized coordinates are ok for completely rigid molecules but an iterative method is needed when molecules are partially rigid/partially constrained.

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**Ab Initio (Car-Parrinello) MD**

- Do QM for electrons (DFT), classical MD for ions.
- At each step solve a wave eq. for electrons also using MD.
- Constraints enter in: we must keep (single-particle) electronic wave functions orthogonal.

\[
S_{ij} = \langle \phi_j | \phi_i \rangle = \delta_{ij}
\]

\[
\phi_j(r) = \sum_{\alpha} c_{j\alpha} \hat{f}_{\alpha}(r)
\]

- Use the SHAKE to satisfy these \(N(N+1)/2\) constraints.

\[
\phi_i = \phi_i - \frac{1}{2} \sum_{j \neq i} \phi_j < \phi_j | \phi_i >
\]

Hence, \(c^Tc=I\), where \(T_{ab} = \int dr \hat{f}_a^*(r) \hat{f}_b(r)\) = overlap matrix.