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 $h\omega/kT$?)
- 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.

SHAKE algorithm

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- 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 $\sigma(R) = |r_i - r_{j+1}|^2 - a^2$

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

- 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:

  $R_{new}(t+h) = 2R(t) - R(t-h) + h^2 F(t)/m - h^2 \lambda(t) \nabla\sigma(R,t)$
- Determine $\lambda(t)$ so that $\sigma[R(t+h)]=0$.
- This is a non-linear equation we solve by iteration.

$$R \equiv R(t+h) = R_0 - \lambda G_0 \quad \text{where } R_0 = 2R(t) - R(t-h) + h^2 F(t)/m$$

$$\text{and } G_0 \equiv h^2 \nabla\sigma(R(t))$$

$$\text{Constraint } 0 = \sigma(R_0 - \lambda G_0)$$

$$\text{Expand about } \lambda_n: \quad 0 = \sigma(R_0 - \lambda_n G_0) - (\lambda_{n+1} - \lambda_n) \nabla\sigma(R_0 - \lambda_n G_0) G_0$$

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

$$\text{Iterate until } \sigma_n \equiv \sigma(R_0 - \lambda_n G_0) = 0$$

$$\sigma = r_{ij}^2 - a^2 \quad \text{then} \quad \nabla_i \sigma = 2\left(r_i - r_j\right) = -\nabla_j \sigma$$

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

Multiple constraints

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

$r_i(t+h) = -r_i(t-h) + 2r_i(t) + h^2 F_i(t)/m_i$ Initialize step

Loop over constraints σ_k until $\sigma_k(r(t+h) < \varepsilon$

$$r^{new}{}_i(t+h) = r_i(t+h) - \frac{\nabla_i \sigma_k(r(t)) \sigma_k(r(t+h))}{\sum_j \frac{m_i}{m_j} \nabla_j \sigma_k(r(t+h)) \nabla_j \sigma_k(r(t))}$$

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.

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.

$$S_{ij} = <\phi_j | \phi_i> = \delta_{ij}$$

$$\phi_j(r) = \sum_{\alpha} c_{j\alpha} f_{\alpha}(r)$$

c is an NxM matrix

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

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

Iterate: $$\phi_i = \phi_i - \frac{1}{2}\sum_{j \neq i} \phi_j <\phi_j | \phi_i>$$