NPT

- Volume change pseudo code

```
SUBROUTINE mcvol                        attempts to change
                                        the volume
call toterg(box,eno)                    total energy old conf.
vo=box**3                               determine old volume
lnvn=log(vo)+(ranf()-0.5)*vmax          perform random walk in ln V
vn=exp(lnvn)
boxn=vn**(1/3)                          new box length
do i=1,npart
  x(i)=x(i)*boxn/box                    rescale center of mass
enddo
call toterg(boxn,enn)                   total energy new conf.
arg=-beta*((enn-eno)+p*(vn-vo)
+ -(npart+1)*log(vn/vo)/beta)           appropriate weight function!
if (ranf().gt.exp(arg)) then            acceptance rule (5.2.3)
  do i=1,npart                          REJECTED
    x(i)=x(i)*box/boxn                  restore the old positions
  enddo
endif
return
end
```


Other Ensembles

- Grand Canonical (μVT)
  - e.g. in adsorption problems.
    - Could use MD to see how gas adsorbs to surface. However, this takes seconds in real experiments (impractical in simulations)
    - Could use MC in grand canonical. Equating chemical potential in and out (close and far) of the surface can be simulated by "creating" and "destroying" particles

notes

Molecular Liquids

- Rigid non-spherical molecules:
  - Move positions
  - Move orientations
- Typical to move and rotate as a single step
- various ways to rotate

Rotations – method #1

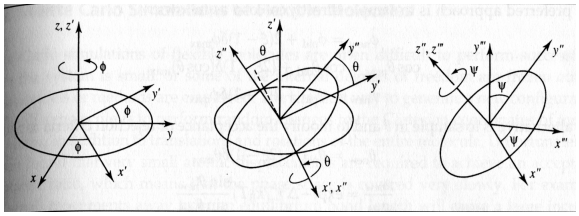
- Choose one Cartesian axis and rotate by δω from a range of $\delta\omega_{max}$
- Apply usual trigonometry: suppose rotate around x-axis

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & cos\delta\omega & sin\delta\omega \\ 0 & -sin\delta\omega & cos\delta\omega \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

- Where (x**i**, y**j**, z**k**) and (x'**i**, y'**j**, z'**k**) are vectors before and after rotation

Rotations – Method #2

- Use Euler angles



Rotations – Method #2

- Given φ, θ, and ψ get new configuration by changing by δφ, δθ, and δψ
- Given orientation vector $\mathbf{v}_{old}$

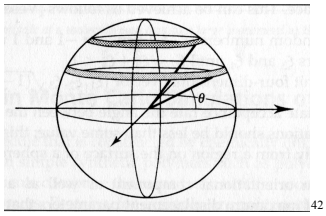
$$\mathbf{v}_{new} = \mathbf{A}\mathbf{v}_{old}$$

- where A is given by

$$\begin{pmatrix} cos\delta\phi cos\delta\psi - sin\delta\phi cos\delta\theta sin\delta\psi & sin\delta\phi cos\delta\psi + \cos\delta\phi cos\delta\theta sin\delta\psi & sin\delta\theta sin\delta\psi \\ -cos\delta\phi sin\delta\psi - sin\delta\phi cos\delta\theta cos\delta\psi & -sin\delta\phi sin\delta\psi + \cos\delta\phi cos\delta\theta cos\delta\psi & sin\delta\theta cos\delta\psi \\ sin\delta\phi sin\delta\theta & -cos\delta\phi sin\delta\theta & cos\delta\theta \end{pmatrix}$$

Rotations – Method #2

- A note on sampling: when generating changes by δφ, δθ, and δψ this will <u>not</u> generate a uniform distribution in θ
- Explored area is smaller for angles close to 90
- Soln: sample from cos(θ) instead



Rotations – Method #2

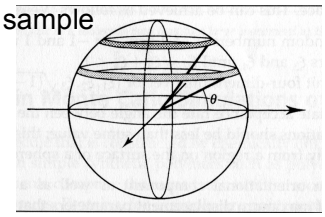
- Sampling from cos(θ) new trial angles are:

$$\phi_{new} = \phi_{old} + (2\xi - 1)\delta\phi_{max}$$
$$cos\ \theta_{new} = cos\ \theta_{old} + (2\xi - 1)\delta(cos\ \theta)_{max}$$
$$\psi_{new} = \psi_{old} + (2\xi - 1)\delta\psi_{max}$$

- If want nonetheless to sample in θ have to change:

$$\theta_{new} = \theta_{old} + (2\xi - 1)\delta\theta_{max}$$
$$\frac{\rho_{new}}{\rho_{old}} = exp(-\Delta V/k_B T)\frac{sin\ \theta_{new}}{sin\ \theta_{old}}$$

But notice problems at $\theta_{old} = 0$



Rotations – Method #3

- Problem with Euler angles – too many (6) trigonometric function evaluations
- Soln: use the four-dimensional vectors called *quaternions*
  - Property: $q_0^2+q_1^2+q_2^2+q_3^2 = 1$
  - equivalence:

$$q_0 = cos\ \tfrac{1}{2}\theta\ cos\ \tfrac{1}{2}(\phi+\psi)$$
$$q_1 = sin\ \tfrac{1}{2}\theta\ cos\ \tfrac{1}{2}(\phi+\psi)$$
$$q_2 = sin\ \tfrac{1}{2}\theta\ sin\ \tfrac{1}{2}(\phi+\psi)$$
$$q_3 = cos\ \tfrac{1}{2}\theta\ sin\ \tfrac{1}{2}(\phi+\psi)$$

Rotations – Method #3

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  - Rotation matrix A:

$$\mathbf{A} = \begin{pmatrix} q_0^2+q_1^2-q_2^2-q_3^2 & 2(q_1q_2+q_0q_3) & 2(q_1q_3-q_0q_2) \\ 2(q_1q_2-q_0q_3) & q_0^2-q_1^2+q_2^2-q_3^2 & 2(q_2q_3+q_0q_1) \\ 2(q_1q_3+q_0q_2) & 2(q_2q_3-q_0q_1) & q_0^2-q_1^2-q_2^2+q_3^2 \end{pmatrix}$$

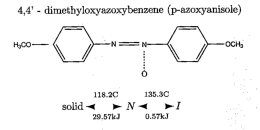
Rotations – Method #3

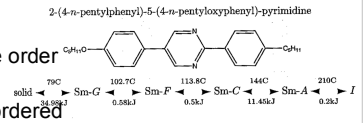
- Implementation: obtain a new orientation in four-dimensional space
- For this, follow recipe:
  - Generate pairs of random number (ξ_1 , ξ_2) between -1 and 1 until $S_1 = \xi_1^2+\xi_2^2 < 1$
  - Do the same for pairs ξ_3 and ξ_4 until $S_2 = \xi_3^2+\xi_4^2 < 1$.
  - Form the random unit four-dimensional vector:

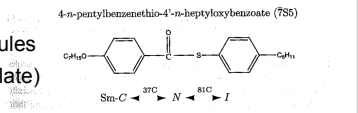
$$\left(\xi_1, \xi_2, \xi_3\sqrt{((1-S_1)/S_2)}, \xi_4\sqrt{((1-S_1)/S_2)}\right)$$

Liquid Crystals

- MC can be applied with relative ease to simulate Liquid Crystal transitions
- Liquid Crystals:
  - Materials with long-range order in orientation
  - Centers of mass are disordered and mobile
  - Many liquid crystal molecules are rod-shaped (some oblate)

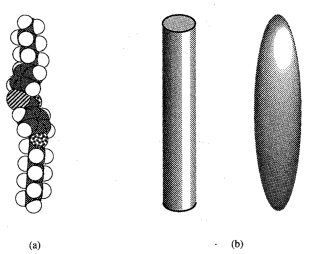






Liquid Crystals

- … are molecularly complicated. Site-site models would need several connected spheres
- Better with models that only deal with orientation
- Can be modeled by rods or cylinders
- Can use angle-dependent LJ

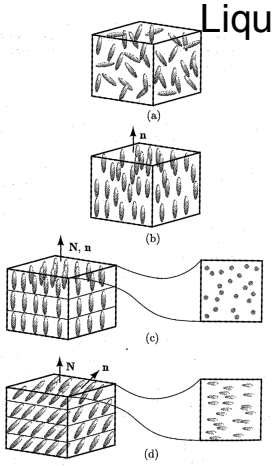


Liquid Crystals

Phases:

- At high temps are disordered in all degrees of freedom
- At lower temps can form a nematic phase

Liquid Crystals



a) Isotropic phase (angles and cm are disordered)

b) Nematic phase (cm are disordered, not angles)

c) Smectic-A phase

d) Smectic-C phase

Liquid Crystals

- Simple models could use

$$v(r_{ij}, \Omega_i, \Omega_j) = AP_2(cos\gamma_{ij})$$

  restricted to a lattice.
- Next level of complication frees CoM to move as LJ particles with the orientations on top.
  - Angle-dependent LJ