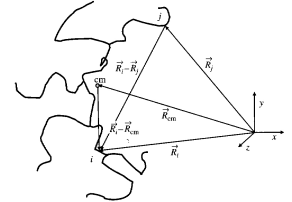# Radius of Gyration

- Complementary measure of the size of chains
  - Separate and distinct from the end-to-end distance
- Succeeds where the end-to-end distance fails
  - e.g. in branched and circular polymers that have no well-defined ends
  - Applicable to all polymer architectures

Radius of Gyration

- Defined as the average square distance between monomers and the center of mass of the polymer (take equal monomer masses)

$$R_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{R}_i - \vec{R}_{cm})^2 \text{ where } \vec{R}_{cm} \equiv \frac{1}{N} \sum_{j=1}^{N} \vec{R}_j$$

Radius of Gyration

$$R_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\vec{R}_i - \vec{R}_{cm})^2$$

Can be expressed in terms of the inter-monomer distances

$$\langle R_g^2 \rangle = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=i}^{N} \langle (\vec{R}_i - \vec{R}_j)^2 \rangle$$

where the average is taken over the ensemble or over many realizations of the same polymer conformation

Radius of Gyration

- Special case of the <u>ideal linear chain</u>
  use

$$\sum_{i=1}^{N} \rightarrow \int_0^N du \quad \text{and} \quad \sum_{j=i}^{N} \rightarrow \int_u^N dv$$

  where du and dv are the continuous coordinates of monomers
- Now

$$\langle R_g^2 \rangle = \frac{1}{N^2} \int_0^N \int_u^N \langle (\vec{R}(u) - \vec{R}(v))^2 \rangle \, dv \, du$$

  where **R**(u) position vector of coordinate u

Radius of Gyration

- Special case of the <u>ideal linear chain</u>

  Can be shown to give in terms of the end-to-end distance

$$\langle R_g^2 \rangle = \frac{b^2 N}{6} = \frac{\langle R^2 \rangle}{6}$$

notes

Temperature Effects

- Polymers can undergo the **coil-globule** transition as a function of temperature
- At high T, the interactions between polymer-solvent are more important → polymer expands to more volume (coil)
- At low T, the interactions between monomers take over → polymer contracts to a compact structure (globule)
- At the θ-temperature, both interactions are balanced
- A real chain at θ-temperature behaves as an ideal chain (i.e. $<R_g^2>$ scales as N)

Temperature Effects

- The graph of $<R_g^2>$ vs T is sigmoidal
- The sharpness of the graph depends on N
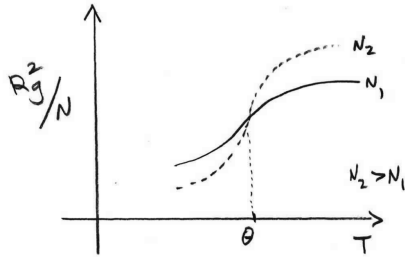
Flexible Polymers

Challenges:

- Time and length scales needed to explore conformational space is quite big
  - Time scale ranges from 10^{-14} (bond vibrations) to hours or more
  - Length scales range from 1-2Å to the diameter of a full-length coiled polymer of thousands of angstroms
- Most simulations use empirical energy models
- Simplifications abound:
  - Use a lattice
  - Use beads
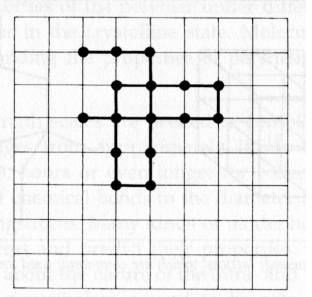 - Use all-atoms with/without hydrogens

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MC on Lattice Models

- Simplest is a 2D lattice
- Let chain grow like a 'random walk' – allow crossings
- Basic results on the size (end-to-end) measure (3D)
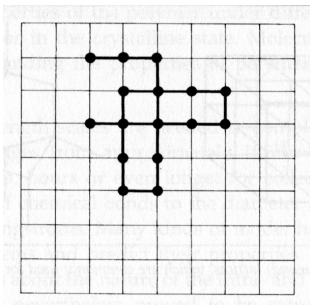
$$\langle R_n^2 \rangle = nl^2$$

n – number of bonds; l – length of each bond

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Lattice Models

- Basic results on the radius of gyration

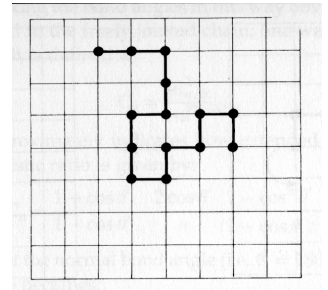$$\langle R_g^2 \rangle = \frac{1}{6} \langle R_n^2 \rangle$$

- Can be compared with experiments:
  - Static light scattering
  - Small angle neutron scatt.
  - X-ray scatt.
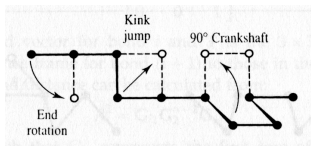
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Lattice Models

- Self-avoiding random walk
- All states can be enumerated, thus can get partition function
- Use appropriate interaction energy to calculate energy of each state (e.g. # of nn)
- End-to-end distance

$$\langle R_n^2 \rangle = Cn^{1.18}$$

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Motion of Polymers - 1

- Done with growing, now move them
- One possibility is to do trial moves of 'units' within the polymer

(Verdier-Stockmayer algorithm)

Kink jump   90° Crankshaft

End rotation

3D 'unit' moves for lattice polymers

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Motion of Polymers - 2

- Usual problems are that for high density polymer melts, moves are very difficult (low acceptance ratio)
- Do the "slithering snake" model where the polymer wiggles around obstacles
  - Called reptation
- Identify 'head' and 'tail' and move either forward or backwards

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Motion of Polymers - 2

- Choose a 'head' at random
- "pull" the rest of the chain by the 'head' to one randomly chosen lattice position
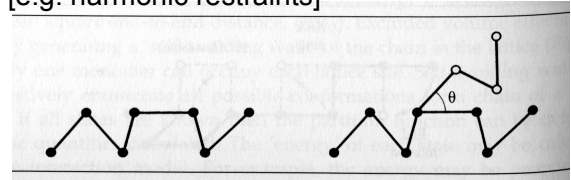- If cannot move, stay and count anyway
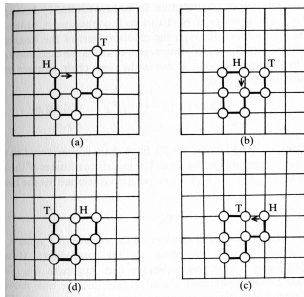
Motion of Polymers - 3

Movement in continuous space

- String of freely-jointed beads in space
- Have them interact by U(r) [e.g. LJ]
- Bonds may be taken either fixed or variable [e.g. harmonic restraints]

'Pivot' algorithm

Motion of Polymers - 3

- Cons:
  - Large polymers have high rate of rejected moves at high density
  - Continuous values for angles between the joints is unrealistic
- Soln:
  - Restrict to small molecules
  - Can rotate around bond, but keep angle fixed
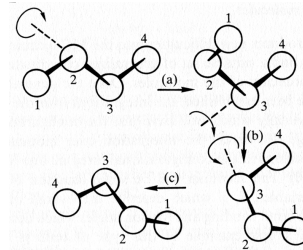 - In one move, keep constraints fixed while move free coordinates
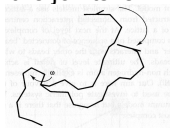
Motion of Polymers - 3

e.g. Butane

- Mix of bond constraints plus freely moving degrees of freedom
- Angles change [$-\pi,\pi$]
- Translate and rotate whole molecule around *cm*

Motion of Polymers - 3

Typical MC move:

- 1 is moved by rotating around the 2-3 bond
- 1 & 2 are moved simultaneously by rotating around the 3-4 bond
- 4 is moved by rotating around the 2-3 bond
- Move and rotate *cm*
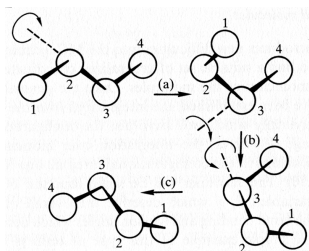
Motion of Polymers - 4

- For high density of polymers, such as in a melt:
  - Use the 3D MC reptation model
    - Start with N non-overlapping chains with n_a monomers each
    - All monomers interact via the repulsive part of the LJ potential $v^{repul}_{LJ}(r) \sim 1/r^{12}$ (considering the excluded volume)
    - Adjacent atoms in the same chain interact via a modified harmonic potential

$$v^H(r) = \begin{cases} -0.5\,k\,\sigma_1^2 \ln[1-(r/\sigma_1)^2] & 0 \le r \le \sigma_1 \\ \infty & r > \sigma_1 \end{cases}$$

    - Typically, $\sigma_1 = 1.95\sigma$ and k = 20.

Motion of Polymers - 4

- After choosing one end at random, "move" (reptate) by choosing new position
  - Suppose chain i with positions $(r_{i1}, r_{i2}, ..., r_{ina})$
    - Choose to move monomer n_a to $\boldsymbol{r}' = \boldsymbol{r}_{ina} + \delta\boldsymbol{r}$
      - Direction chosen at random from the surface of a sphere
      - Magnitude chosen according to $\exp(-\beta v^H(r))$ [i.e. using the bond energy as the deciding factor]
    - Final configuration is $(r_{i2}, ..., r_{ina}, r')$
    - Change in energy to use in the Metropolis criteria

$$\delta V_{nm} = \sum_{a=2}^{n_a} v_{LJ}^R (|\boldsymbol{r}_{ia} - \boldsymbol{r}'|) - v_{LJ}^R (|\boldsymbol{r}_{ia} - \boldsymbol{r}_{i1}|) \qquad \text{Subtracting contribution from the now missing } r_{i1}$$
$$+ \sum_{j \neq i} \sum_{a=1}^{n_a} v_{LJ}^R (|\boldsymbol{r}_{ja} - \boldsymbol{r}'|) - v_{LJ}^R (|\boldsymbol{r}_{ja} - \boldsymbol{r}_{i1}|)$$

Note: there are no geometrical constraints; all atoms are free to move under the influence of the potentials!

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MD of polymers

Constraint dynamics:

- Conformational behavior is a mixture of fast (e.g. bond vibrations) and slow (e.g. conformational change) motion

- Because MD uses the fastest modes as the time scale, it would benefit from ignoring the fast modes to focus on conformation (more important)

- Solution: constrain internal motions and run with the bigger time step
  - Fix all bonds as unchangeable
  - Equations of motion will now include extra forces (internal)
  - Use Langrange's formalism

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MD of polymers

- Lagrange multipliers

$$\frac{d}{dt}(\partial L/\partial \dot{q}_k)-(\partial L/\partial q_k)=\Sigma_l \lambda_l a_{lk}$$

Term on the right are the generalized forces, equivalent to the imposed constraints

- Constraints are holonomic, i.e. can be written as

$$g_l(\{q_k\},t)=0$$

with $\quad a_{lk}=\dfrac{\partial g_l}{\partial q_k}$

- These equations couple the dynamics of particles, no longer independent

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MD of polymers

- Equations of motion will involve the regular intermolecular interactions (e.g. LJ)

- Will also involve the constraint forces, that e.g. keep bonds as a <u>fixed</u> distance with forces (along the axis of the bond)

$$F_{lk}^c=\lambda_l \frac{\partial g_l}{\partial q_k}$$

and with constraints

$$g_l=(\boldsymbol{r}_i-\boldsymbol{r}_j)^2-d_{ij}^2=0$$

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MD of polymers

- Because forces act on each atom in the bond (and opposite to each other - Newton's 3rd), these forces do no work on the system

  e.g. atoms i and j
  - Constraint force on i:
    $$\partial g_l/\partial \boldsymbol{r}_i=2(\boldsymbol{r}_i-\boldsymbol{r}_j)\quad so\quad F_i^c=2\lambda(\boldsymbol{r}_i-\boldsymbol{r}_j)$$
  - Constraint force on j:
    $$\partial g_l/\partial \boldsymbol{r}_j=-2(\boldsymbol{r}_i-\boldsymbol{r}_j)\ and\ F_j^c=-2\lambda(\boldsymbol{r}_i-\boldsymbol{r}_j)$$

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MD of polymers

- A point of concern:
  - In principle, the undetermined coefficients can be found and the constraint forces solved
  - The dilema comes from the fact that positions are solved iteratively (by e.g. Verlet)
  - Inacuracies in the <u>iterative positions</u> plus knowledge of <u>exact constraint forces</u> will cause atoms in bonds to slowly drift away from each other
  - **Solution**: make constraint forces as "inaccurate" as the positions by "forcing" the constraint at every time step (the constraints are adjusted to the inaccurate new positions)
  - This difference will be manifested only in the way that forces are calculated, not in the formalism

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MD of polymers

- Combining everything into the **Verlet** algorithm

$$\vec{r}_i(t+\delta t)=2\vec{r}_i(t)-\vec{r}_i(t-\delta t)+\frac{\delta t^2}{m_i}\vec{F}_i(t)+\sum_j \frac{\lambda_j \delta t^2}{m_i}\vec{r}_{ij}(t)$$

- Note that constraints act as "perturbations" to the unconstrained motion
$$\vec{r}_i(t+\delta t)=\vec{r}_i^0(t+\delta t)+\sum_j \frac{\lambda_j \delta t^2}{m_i}\vec{r}_{ij}(t)$$

  but this final expression needs the λ's

- Get them by:
  constraint
  $$g_l=(\boldsymbol{r}_i-\boldsymbol{r}_j)^2-d_{ij}^2=0$$
  - applying the constraint to $\mathbf{r}_i(t+\delta t)$
  - dropping all non-linear terms in λ
  - solving the linear system for all λ
  - substitute back and repeat

notes on example   33

MD of polymers

Problems in this scheme:

- For large molecules, the iteration involves inverting a $k \times k$ matrix that is very time consuming

An approach: SHAKE algorithm

- Because couplings are only between neighboring atoms,
    - iterate for each constraint separately
    - then repeat cyclically as needed until all constraints are satisfied (moving atoms in one instance can break constraint in neighboring atoms)

MD of polymers

Modified Approach: RATTLE algorithm

- Use **Velocity Verlet** (two step algorithm)
    - Recall: 1st step

$$\vec{r}^{\,0}(t+\delta t) = \vec{r}^{\,0}(t) + \delta t\, \vec{v}^{\,0}(t) + \frac{1}{2}\delta t^2 \vec{a}^{\,0}(t)$$
$$\vec{v}^{\,0}(t+\delta t/2) = \vec{v}^{\,0}(t) + \frac{1}{2}\delta t\, \vec{a}^{\,0}(t)$$

    - 2nd step, calculate new forces and finalize update of velocity

$$\vec{v}^{\,0}(t+\delta t) = \vec{v}^{\,0}(t+\delta t/2) + \frac{1}{2}\delta t\, \vec{a}^{\,0}(t+\delta t)$$

MD of polymers

New Velocity Verlet with constraints

- 1st step:

$$\vec{r}_i(t+\delta t) = \vec{r}_i^{\,0}(t+\delta t) + \sum_k \frac{\lambda_k \delta t^2}{m_i}\vec{r}_{ij}(t)$$

$$\vec{v}_i(t+\delta t/2) = \vec{v}_i^{\,0}(t+\delta t/2) + \sum_k \frac{\lambda_k \delta t}{m_i}\vec{r}_{ij}(t)$$

- Solve first for r(t+δt) as usual [matrix invert or SHAKE], and obtain all λ's
- Plugin to obtain v(t+δt/2)

MD of polymers

2nd step:

- Update velocities by

$$\vec{v}_i(t+\delta t) = \vec{v}_i(t+\delta t/2) + \frac{1}{2}\delta t\, \vec{a}_i(t+\delta t) + \sum_k \frac{\lambda_k^v \delta t}{m_i}\vec{r}_{ij}(t+\delta t)$$

- The lambdas are different and are determined from the time derivative of the constraints

$$g_l = (r_i - r_j)^2 - d_{ij}^2 = 0$$

$$\dot{g}_l = 2(r_i - r_j)\cdot(v_i - v_j) = 0$$

- Iterate in the same manner as before to find the new lambdas