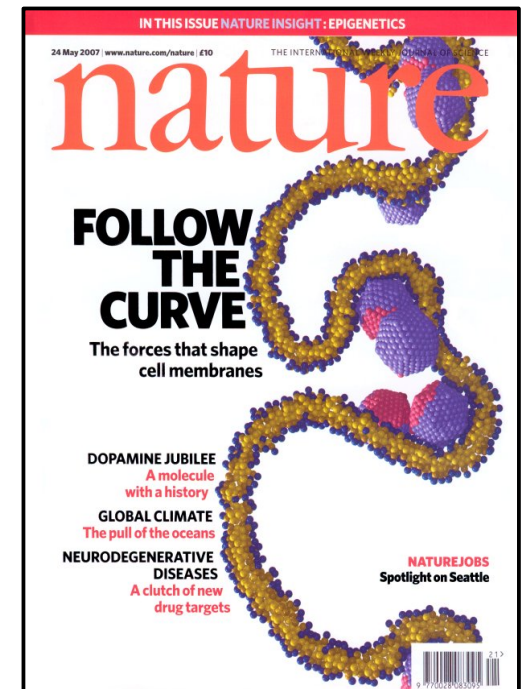
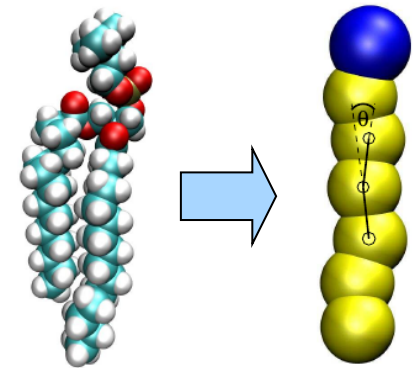
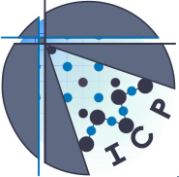


Coarse-Grained Models

- Large and complex molecules (e.g. long polymers) can not be simulated on the all-atom level
- Requires coarse-graining of the model
- Coarse-grained models are usually also particles (beads) and interactions (springs, ...)
- A bead represents a group of atoms
- Coarse-graining a molecule is highly non-trivial, see systematic coarse-graining, VOTCA, AdResS



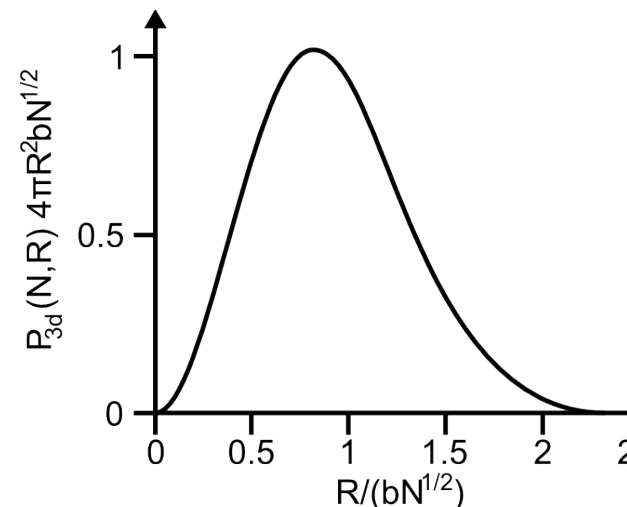
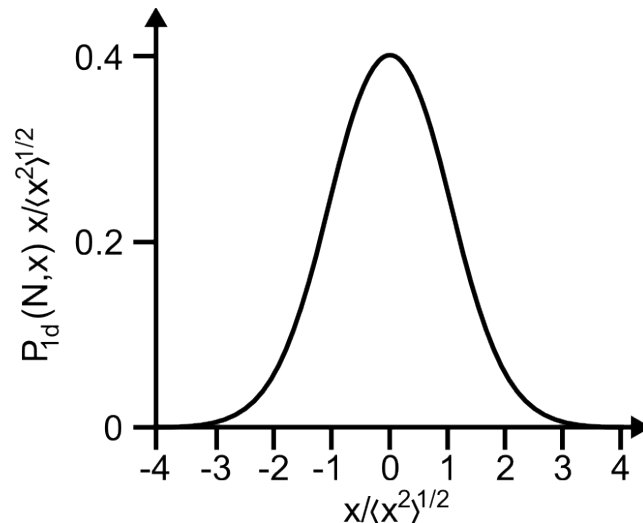


End-to-End Distance Distribution

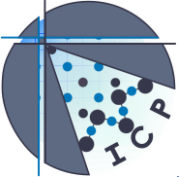
$$P(\vec{R}, N) = \left(\frac{2\pi N b^2}{3} \right)^{-3/2} \exp \left(- \frac{3R^2}{2N b^2} \right) \quad \text{equivalent to a RW distribution}$$

In spherical coordinates it can be written as: here $|\vec{R}| = R$

$$P_{3D}(R, N) 4\pi R^2 dR = 4\pi \left(\frac{2\pi N b^2}{3} \right)^{-3/2} \exp \left(- \frac{3R^2}{2N b^2} \right) R^2 dR$$



Be aware: For $R > R_{max}$ the Gaussian approximation predicts a finite probability, which is unphysical



Free Energy of an Ideal Chain

Entropy $S = k_B \ln \Omega$

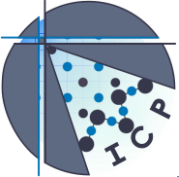
$\Omega(N, \vec{R})$: number of conformations of a freely jointed chain with N monomers and \vec{R}

$$\hookrightarrow P_{3D}(N, \vec{R}) = \frac{\Omega(N, \vec{R})}{\int \Omega(N, \vec{R}) d\vec{R}}$$

$$\begin{aligned}\hookrightarrow S(N, \vec{R}) &= k_B \ln P_{3D}(N, \vec{R}) + k_B \ln \left[\int \Omega(N, \vec{R}) d\vec{R} \right] \\ &= -\frac{3}{2} k_B \frac{R^2}{Nb^2} + \underbrace{\frac{3}{2} k_B \ln \left(\frac{3}{2\pi Nb^2} \right) + k_B \ln \left[\int \Omega(N, \vec{R}) d\vec{R} \right]}_{+ S(N, 0)} \\ &= -\frac{3}{2} k_B \frac{R^2}{Nb^2} + S(N, 0)\end{aligned}$$

$\hookrightarrow \max(S(N, \vec{R})) = S(N, 0)$ Helmholtz-Free energy:

$$F(N, \vec{R}) = \underbrace{U(N, \vec{R})}_{\substack{\text{ideal chain has no long range} \\ \text{interaction, independent of } \vec{R}}} - TS(N, \vec{R}) = \frac{3}{2} k_B T \frac{R^2}{Nb^2} + \underbrace{F(N, 0)}_{U(N, 0) - TS(N, 0)}$$



Free Energy of an Ideal Chain

Ideal chain free energy increases $\sim \vec{R}^2$

Hooke's law of a spring!

To stretch the chain ends by a distance R_x in x-direction requires a force

$$f_x = \frac{\partial F(N, R_x)}{\partial x} = \frac{3k_B T}{Nb^2} R_x, \text{ or in general}$$

$$\vec{f} = \underbrace{\frac{3k_B T}{Nb^2}} \vec{R}$$

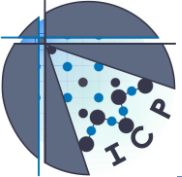
entropic spring constant

For large N , large b , lower T a polymer becomes easier to stretch

Entropic elasticity

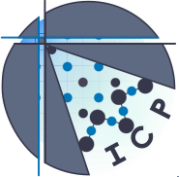
Metals and ceramics become soft as T is raised energetic elasticity

→ Rubber contracts if one raises T [or heats up when one extends it!]



www.youtube.com/watch?v=GUY1w2WX2tc



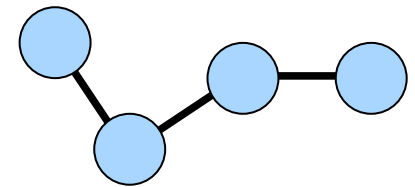


Ex: Gaussian Polymer in a Θ -Solvent

- Conformational properties of a Gaussian polymer in a Θ -solvent are that of a random walk

→ Basis for bead-spring model of a polymer!

- Use a harmonic potential for the bonds:

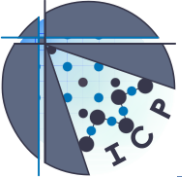


$$V_h(r) = \frac{k}{2} (r - r_0)^2$$

- We can compute the partition function exactly

$$H_0 = \frac{1}{2} \underbrace{\frac{3k_B T}{b^2}}_k \sum_{i=0}^{N-1} |\vec{r}_i - \vec{r}_{i+1}|^2$$

- Random walk and bead-spring model generate the same partition function!



Polymer Chains in Good Solvent

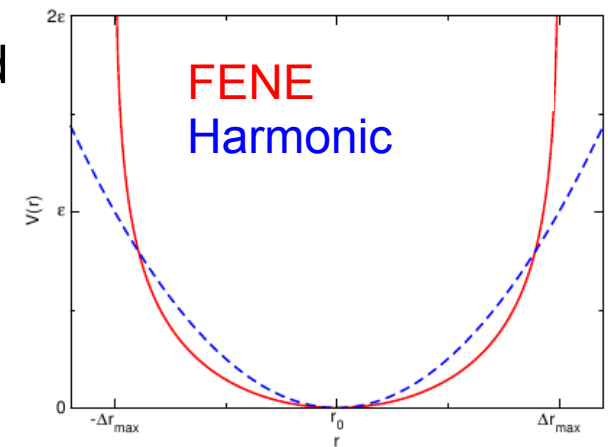
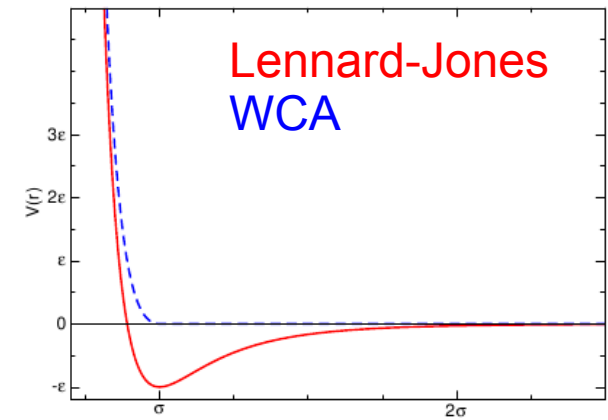
- Θ -solvent is a special case!
- Solvents are good or poor w.r. to the polymer
- Good solvent can be modeled via a repulsive potential
 - Use the repulsive part of Lennard-Jones (aka Weeks-Chandler-Anderson)

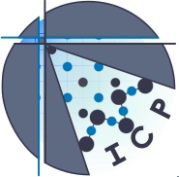
$$V_{\text{WCA}}(r) = \begin{cases} V_{\text{LJ}}(r) + \varepsilon & , \text{if } r < 2^{1/6}\sigma \\ 0 & , \text{otherwise} \end{cases}$$

- FENE (Finite Extensible Nonlinear Elastic) bond

$$V_{\text{FENE}}(r) = -\frac{1}{2}\epsilon(\Delta r_{\text{max}})^2 \log\left(1 - \frac{r - r_0}{\Delta r_{\text{max}}}\right)^2$$

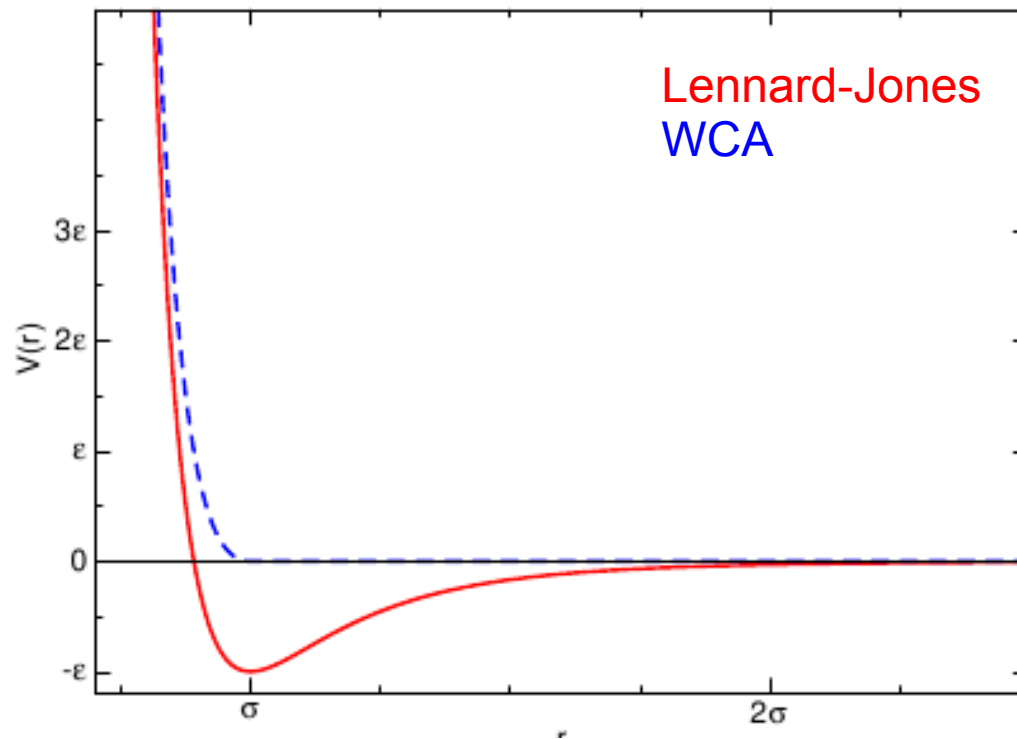
- Has a maximal extension/compression
- Very similar to harmonic potential at r_0





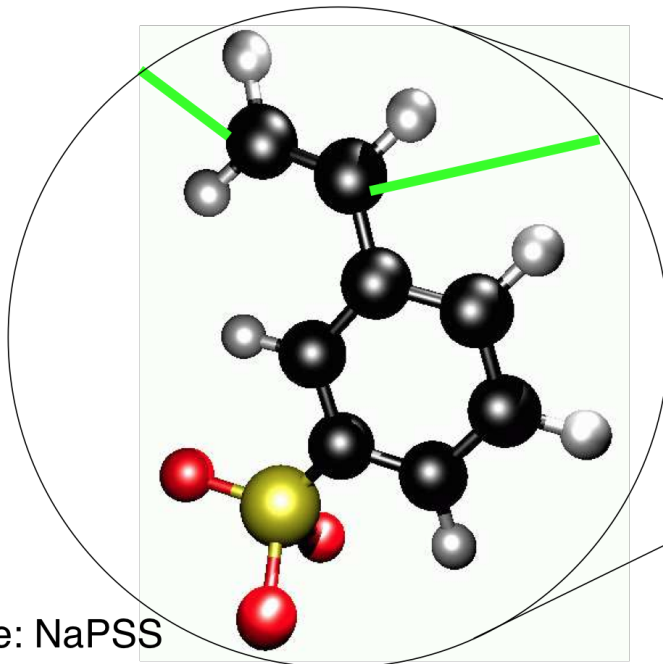
Polymer Chains in Poor Solvent

- Poor solvent can be modeled via a full
 - Lennard-Jones potential
 - Polymer monomers experience an attraction,
 - since they want to minimize contact with solvent
 - the quality of the solvent can be changed by
 - varying the attraction via the interaction parameter ϵ and the cut-off

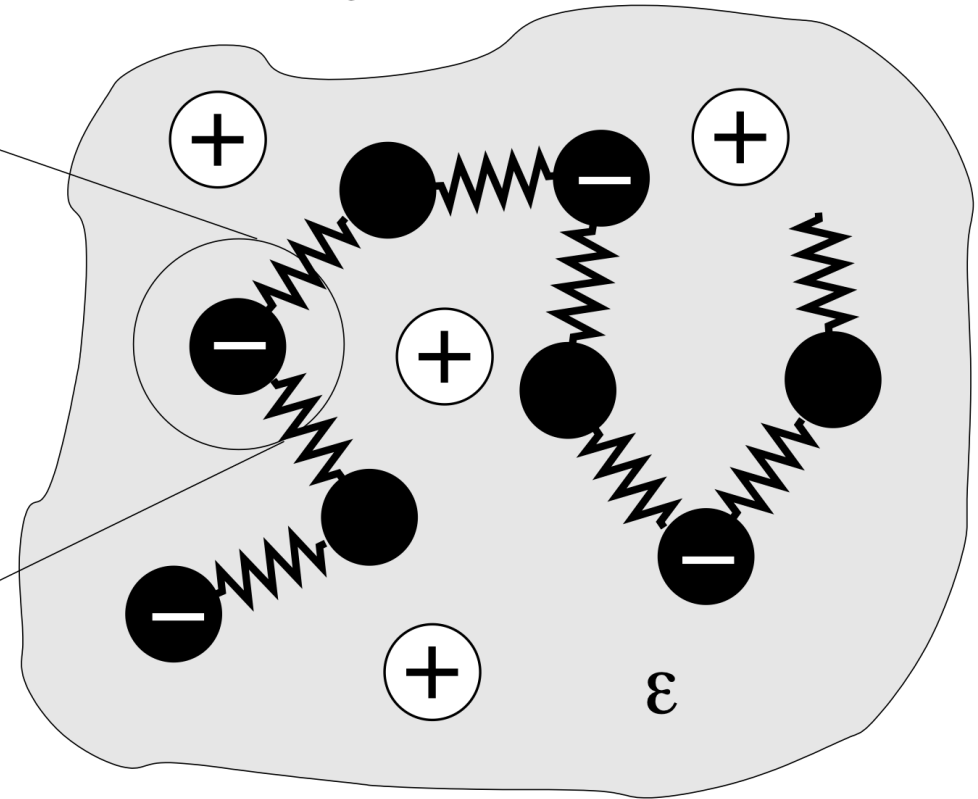


Charged Polymers

Mapping onto a bead-spring model



Example: NaPSS
sulfonated polystyrene



monomers, ions

bond potential

solvent

solvent quality τ

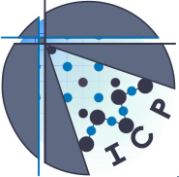


beads with charge fraction f

nonlinear springs

dielectric background ϵ

effective bead-bead interaction



Kremer-Grest Model

K. Kremer, G. Grest, J. Chem. Phys. **92**, 5057 (1990)

- Bead-Spring model: FENE bonds plus WCA potential for beads

Idea of Reptation

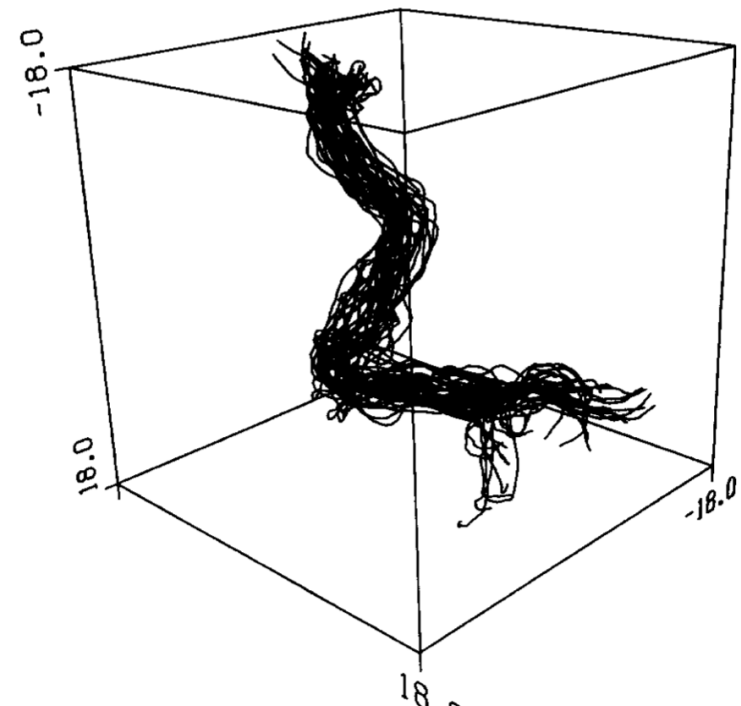
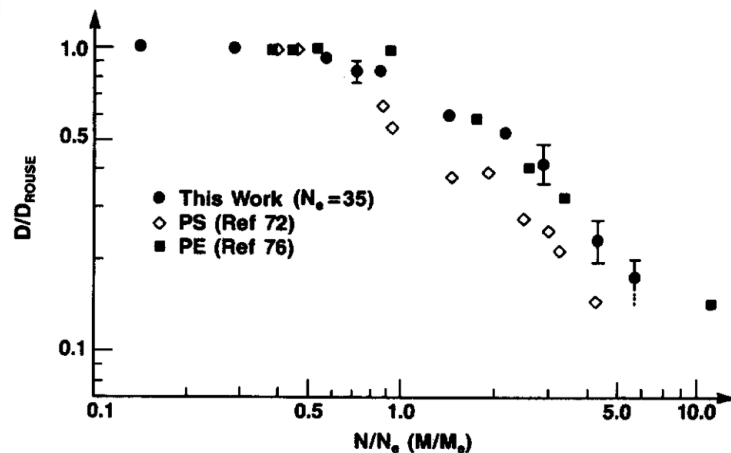
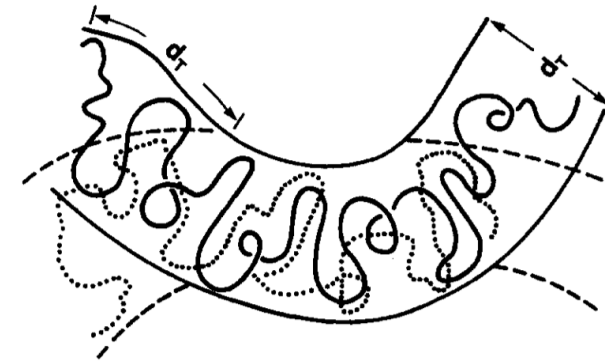
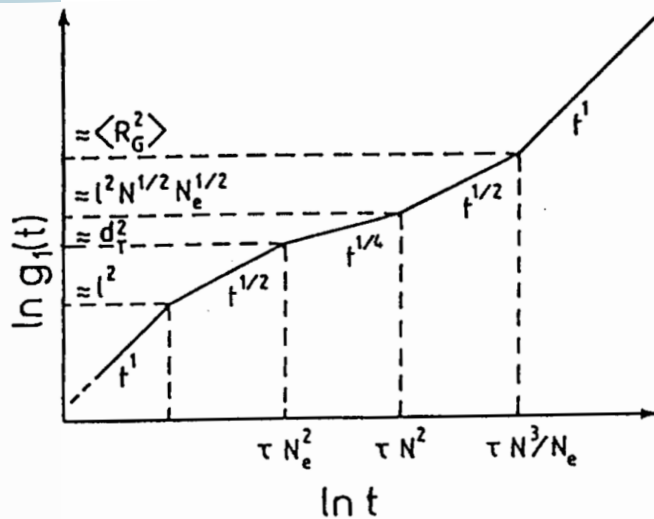
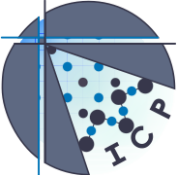
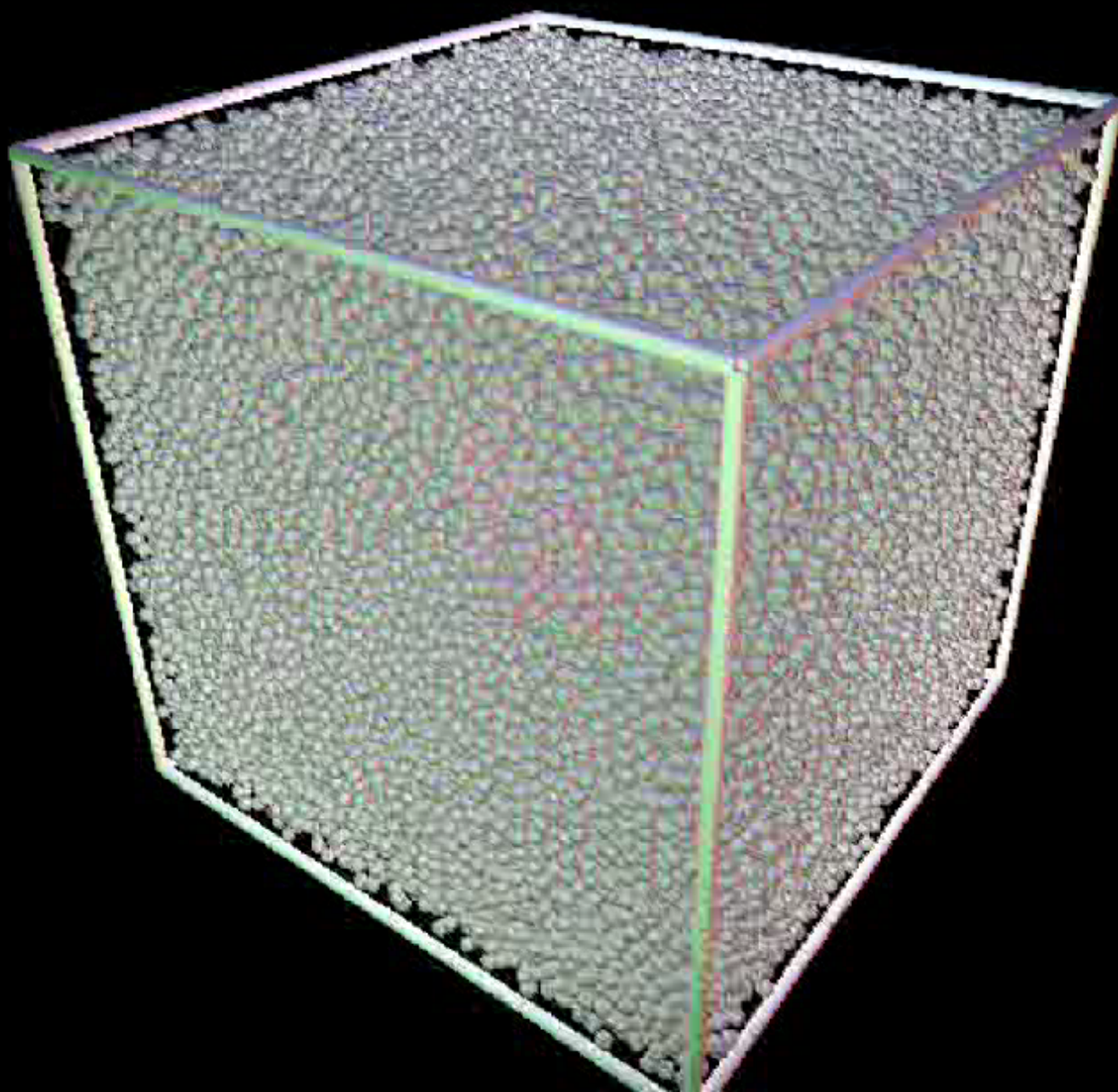
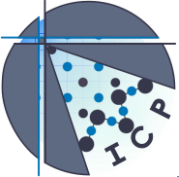


FIG. 22. Diffusion data for several polymeric liquids compared to the simulation results.

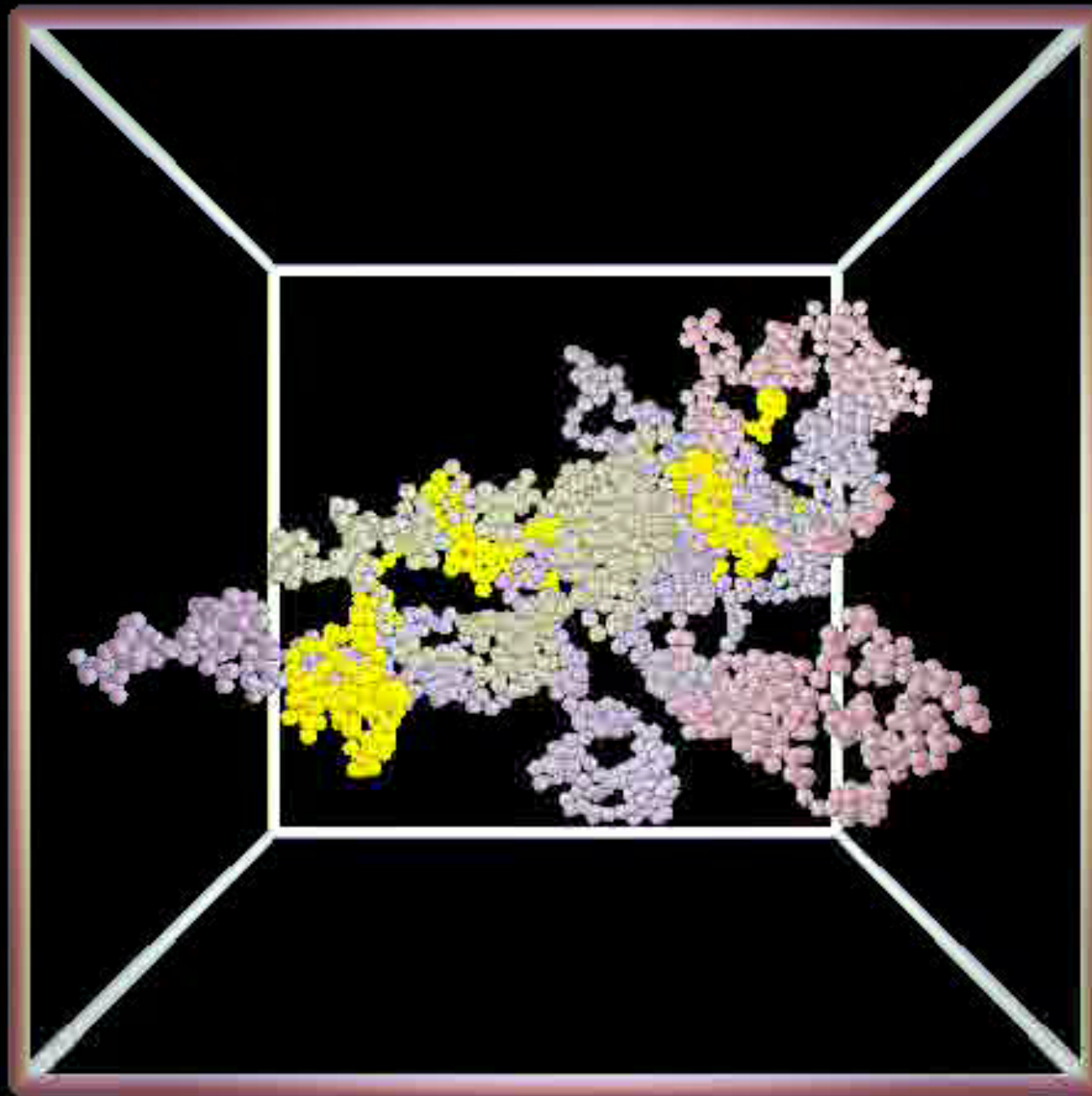


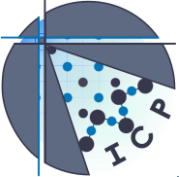
Kremer-Grest Polymer Melt



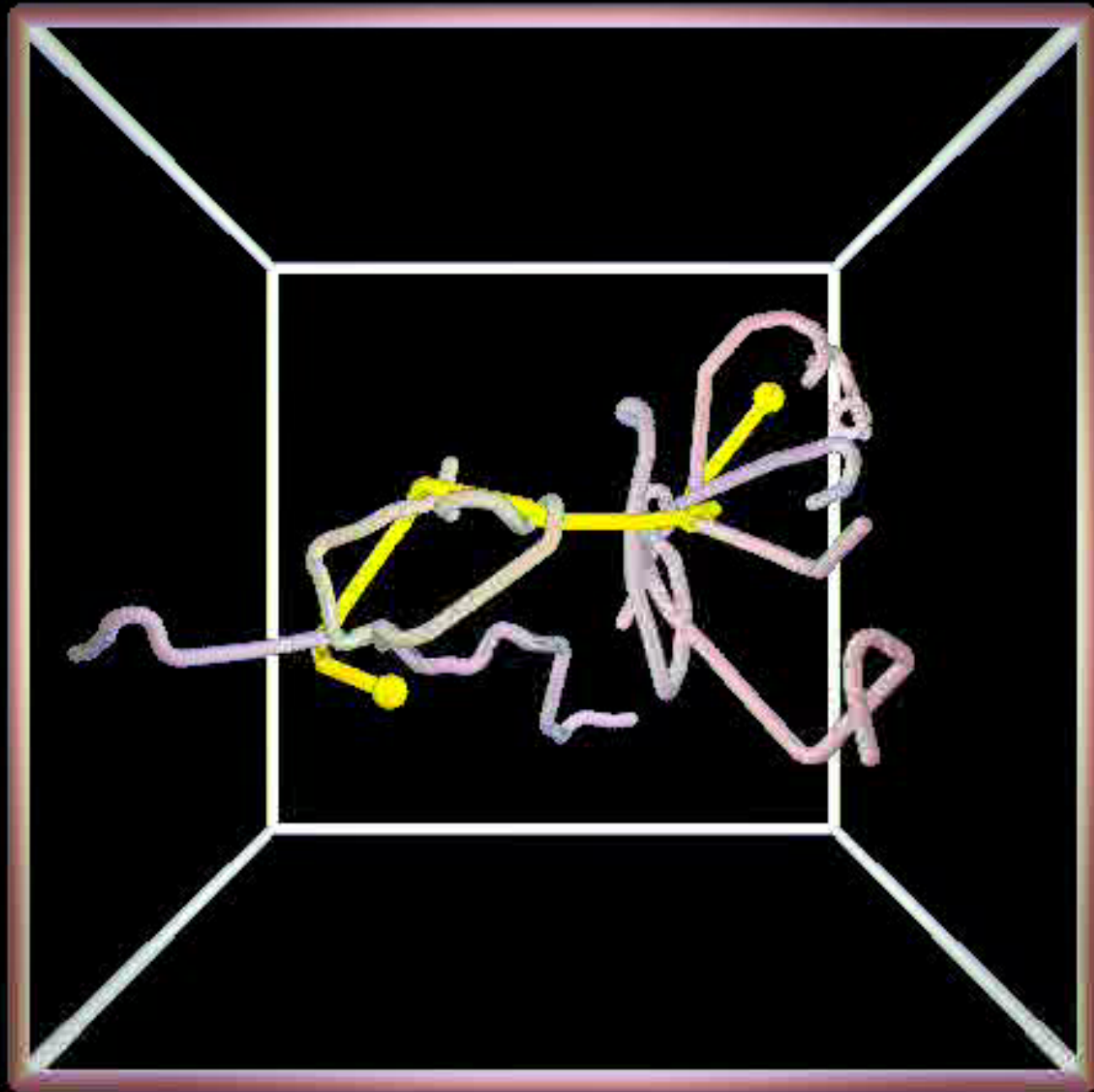


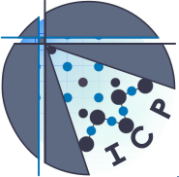
Primitive Path Analysis ->





Entanglements

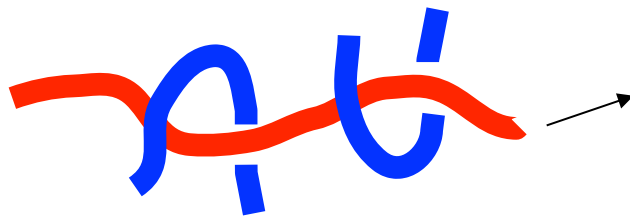




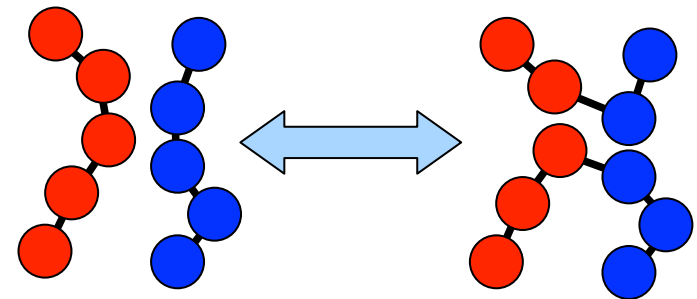
MC moves in polymer simulations

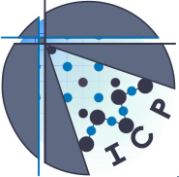
- Single particle moves ensure irreducibility
- Other moves can be invented to faster sample the possible states
- Examples for polymer simulations: pivot, double pivot, or...

Reptation moves



Crossover moves



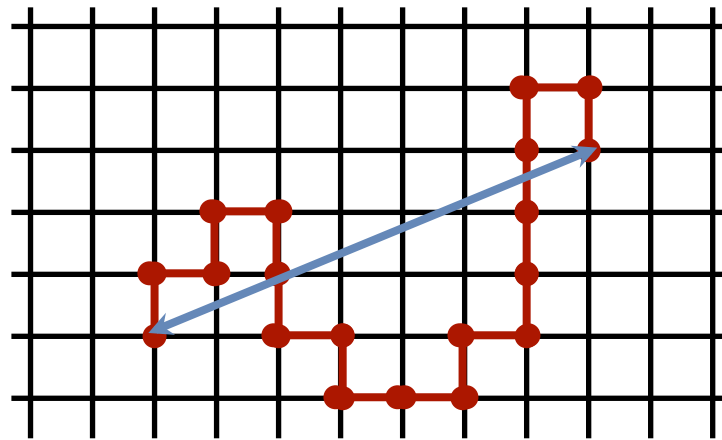


Lattice Models for Polymers

Scaling of the end-to-end distance (= length of RW):

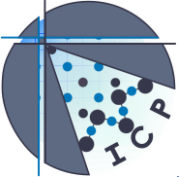
$$\langle \|\mathbf{r}(t) - \mathbf{r}(0)\|^2 \rangle = 6Dt \quad \Rightarrow \quad \langle \|\mathbf{P}(N) - \mathbf{P}(0)\|^2 \rangle \propto N$$

This can be verified with a simple 2D on-lattice model



generating a number of RW (polymers) of fixed length, and taking the average value of $|\mathbf{P}(N) - \mathbf{P}(0)|^2$.

Many static polymeric properties can be predicted (gyration radius, structure factor,...)

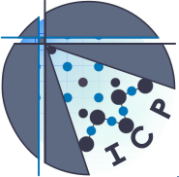


Lattice Models for Polymers

- Original: Random walk for ideal chains
- SAW for good solvent chains
- A simple SAW with local moves is not ergodic for large N , since exceptional trapped configuration like knots can appear

Solutions:

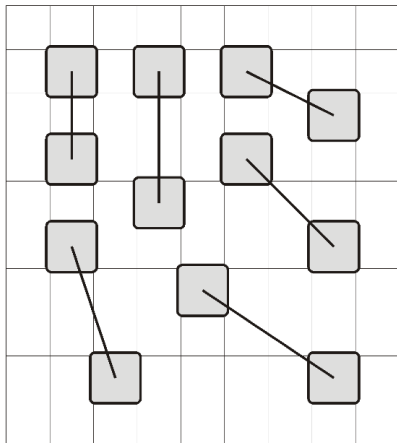
- Bond-fluctuation model
- Prune enriched Rosenbluth sampling



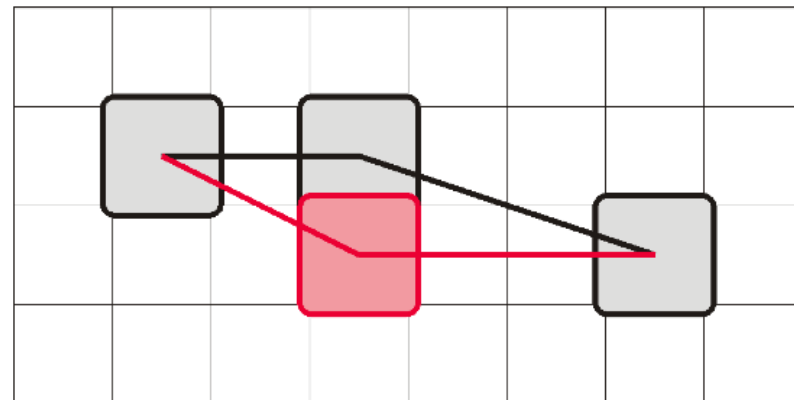
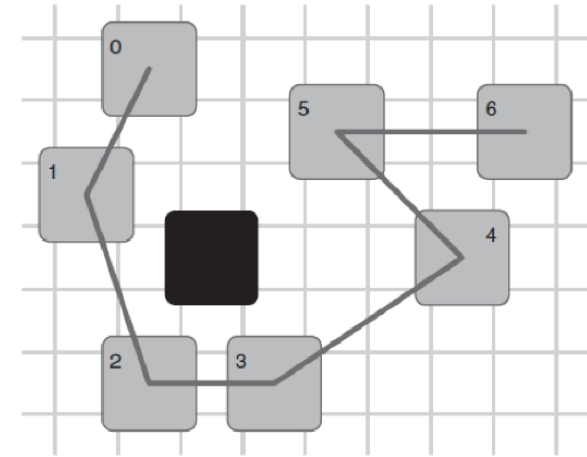
Bond-Fluctuation Model

Carmesin/Kremer. 1987

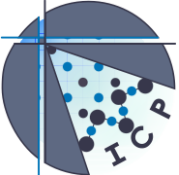
- Every monomer occupies 2^D lattices in D dimensions, no double occupancy.
- There is a maximal bond length
in 2D < 4 ,
in 3D $< \sqrt{10}$



- **Advantage**
- Simple implementation
- Fast CPU times on a lattice

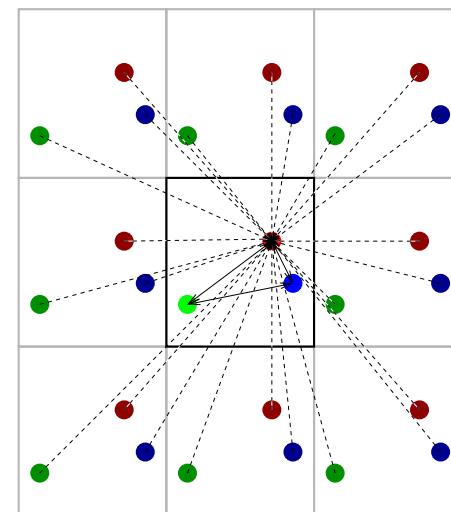


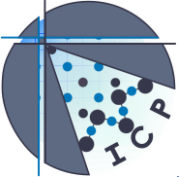
- **Disadvantage**
- Simplistic model
- Still not ergodic (less severe than SAW)



Review:Electrostatics under pbc

- Periodic boundary conditions (pbc) eliminate boundary effects in bulk simulations
- Minimum image convention for short ranged potentials
- Coulomb potential $\approx 1/r$ is long ranged, many images contribute significantly
- Sum is only conditionally convergent
- For fully periodic boundary conditions (pbc) many efficient methods exist:
Ewald ($N^{3/2}$), P³M ($N \log N$), FMM (N)
- Simulation of surface effects: both periodic and nonperiodic coordinates (2d+h / 1d+2h geometries)





Conditionally Convergence

Example: The alternating harmonic series:

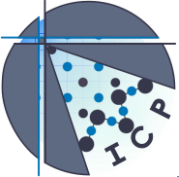
$$\sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \dots = \ln 2$$

but look at this...

$$\left(1 - \frac{1}{2}\right) - \frac{1}{4} + \left(\frac{1}{3} - \frac{1}{6}\right) - \frac{1}{8} + \left(\frac{1}{5} - \frac{1}{10}\right) - \frac{1}{12} + \left(\frac{1}{7} - \frac{1}{14}\right) - \frac{1}{16} - \dots$$

$$= \frac{1}{2} - \frac{1}{4} + \frac{1}{6} - \frac{1}{8} + \frac{1}{10} - \frac{1}{14} - \dots$$

$$= \frac{1}{2} \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \dots \right] = \frac{1}{2} \ln 2$$



Ewald Summation in a Nutshell

$$E = \frac{1}{2} \sum_{i,j=1}^N \sum'_{\mathbf{n} \in \mathbb{Z}^3} \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{n}L|} \quad \text{Trick: } \frac{1}{r} = \frac{\text{erfc}(\alpha, r)}{r} + \frac{1 - \text{erfc}(\alpha, r)}{r}$$

$$E = E^{(r)} + E^{(k)} + E^{(s)} + E^{(d)}$$

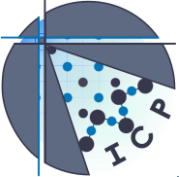
$$E^{(r)} = \frac{1}{2} \sum_{i,j} \sum'_{\mathbf{m} \in \mathbb{Z}^3} q_i q_j \frac{\text{erfc}(\alpha |\mathbf{r}_{ij} + \mathbf{m}L|)}{|\mathbf{r}_{ij} + \mathbf{m}L|}$$

$$E^{(k)} = \frac{1}{2} \frac{1}{L^3} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} e^{-k^2/4\alpha^2} |\tilde{\rho}(\mathbf{k})|^2$$

$$E^{(s)} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2, \quad E^{(d)} = \frac{2\pi}{(1 + 2\epsilon')L^3} \left(\sum_i q_i \mathbf{r}_i \right)^2$$

$\tilde{\rho}(\mathbf{k}) = \int_{V_b} d^3r \rho(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}} = \sum_{j=1}^N q_j e^{-i \mathbf{k} \cdot \mathbf{r}_j}$ is the Fourier transformed charge density.

Suitably truncate \mathbf{m} and \mathbf{k} in the exponentially convergent sums



Methods for Coulomb Sum in 3D

periodicity	3	2	1
+MC	Ewald ($N^{3/2}$)	Ewald (N^2)	Ewald (N^2)
+MC	MMM3D ($N \log N$)	MMM2D ($N^{5/3}$)	MMM1D (N^2)
-	Lekner (N^2)	Lekner (N^2)	Lekner (N^2)
+MD	P ³ M ($N \log N$)	P ³ MLC ($N \log N$)	?
	Tree codes ($N \log N$)	possible	possible
	FMM (N)	possible	possible
+MD	Multigrid ($N \log N$)	possible	possible
+MC, ?	Maggsweilian (N)	possible	possible

- Use the method most applicable to your problem
- MD or MC, N , density, desired accuracy, method familiarity
- know which parameters need to be tuned
- Check accuracy