LAMMPS and Polymer models

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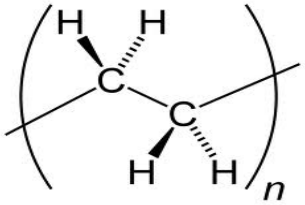
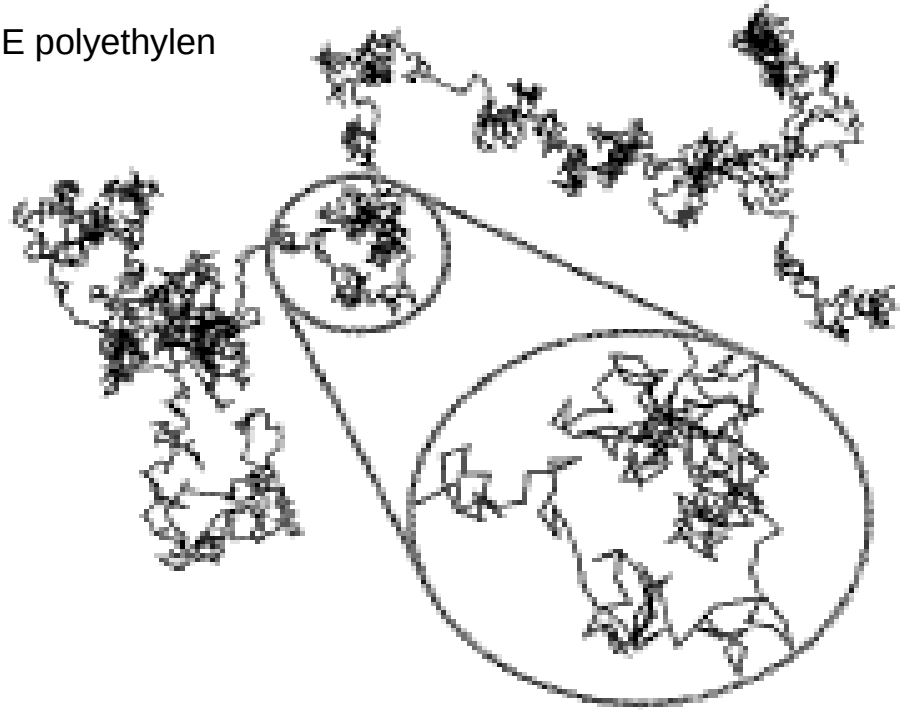
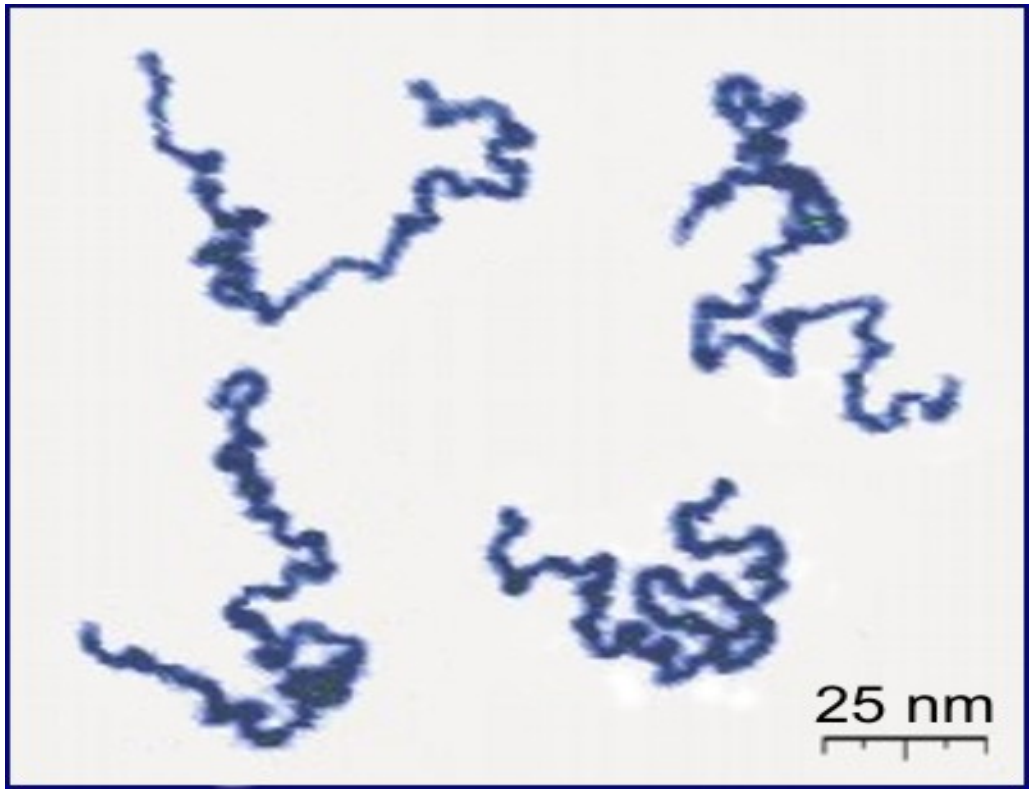
Polymers



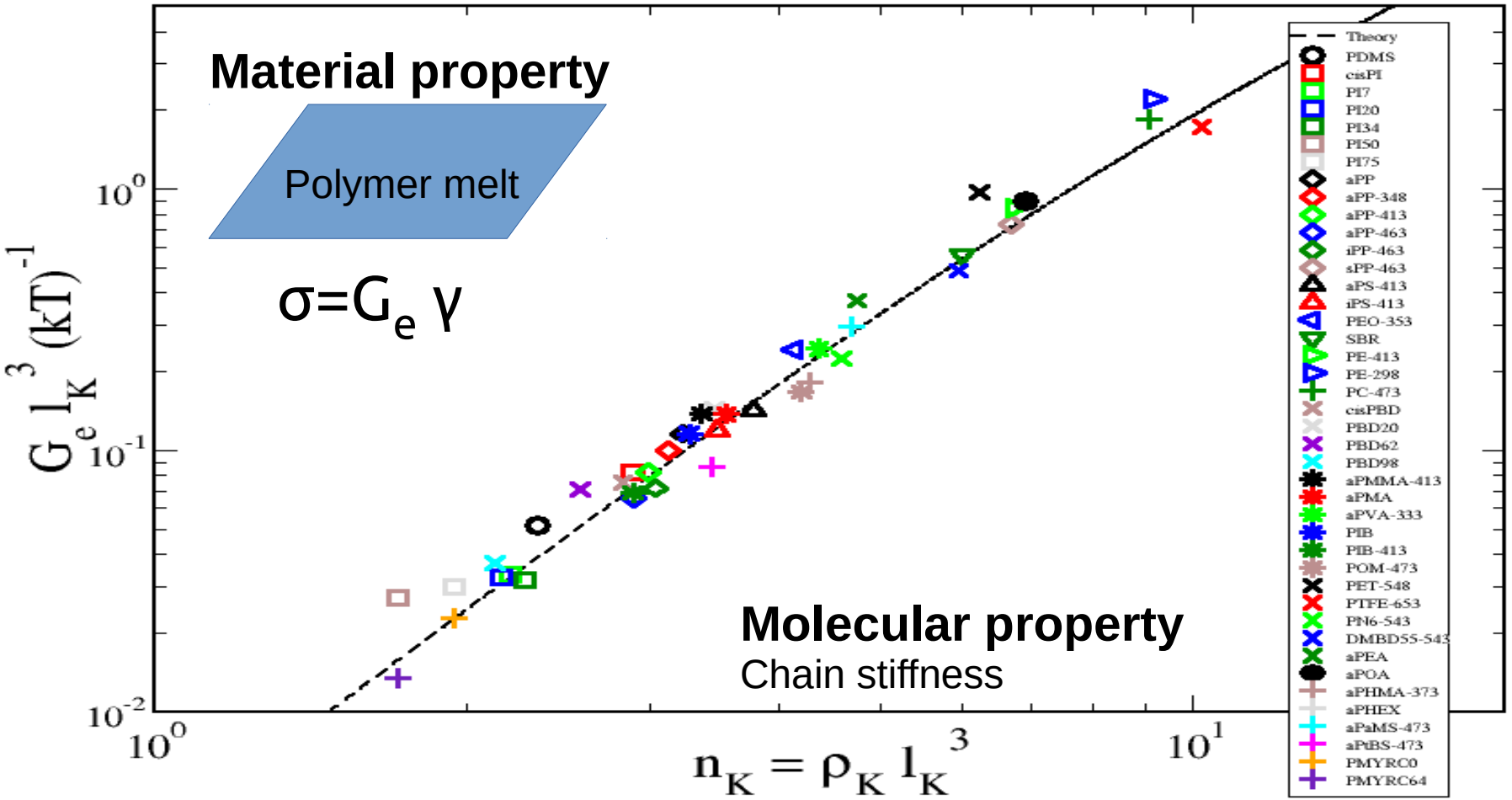
PE polyethylen



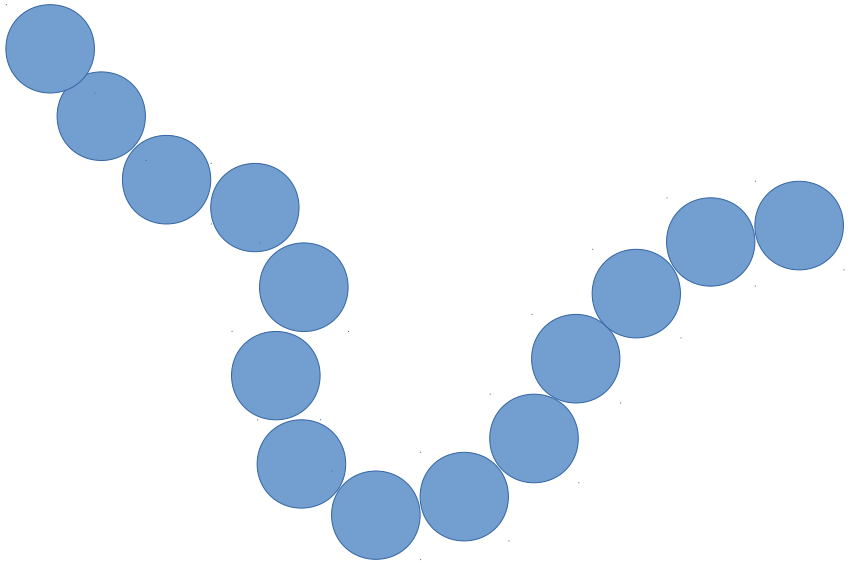


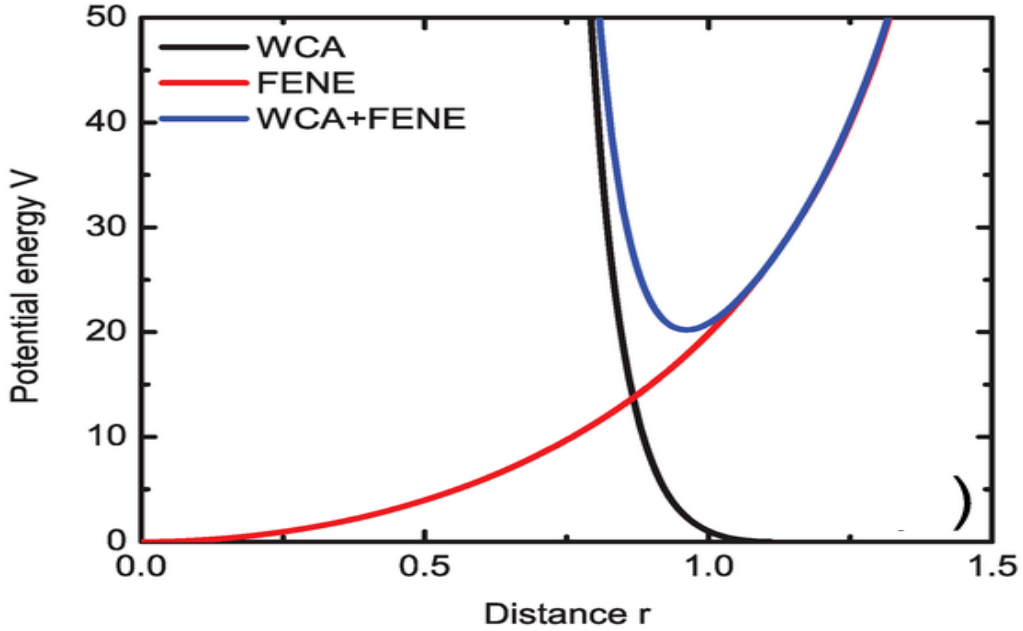
Atomic-Force mikroskop billed
af polymere på en overflade.
Bredde ~ 0.4nm, længde 204nm
(Kilde: Wikipedia)

Kuhnification of polymers



Kremer-Grest model





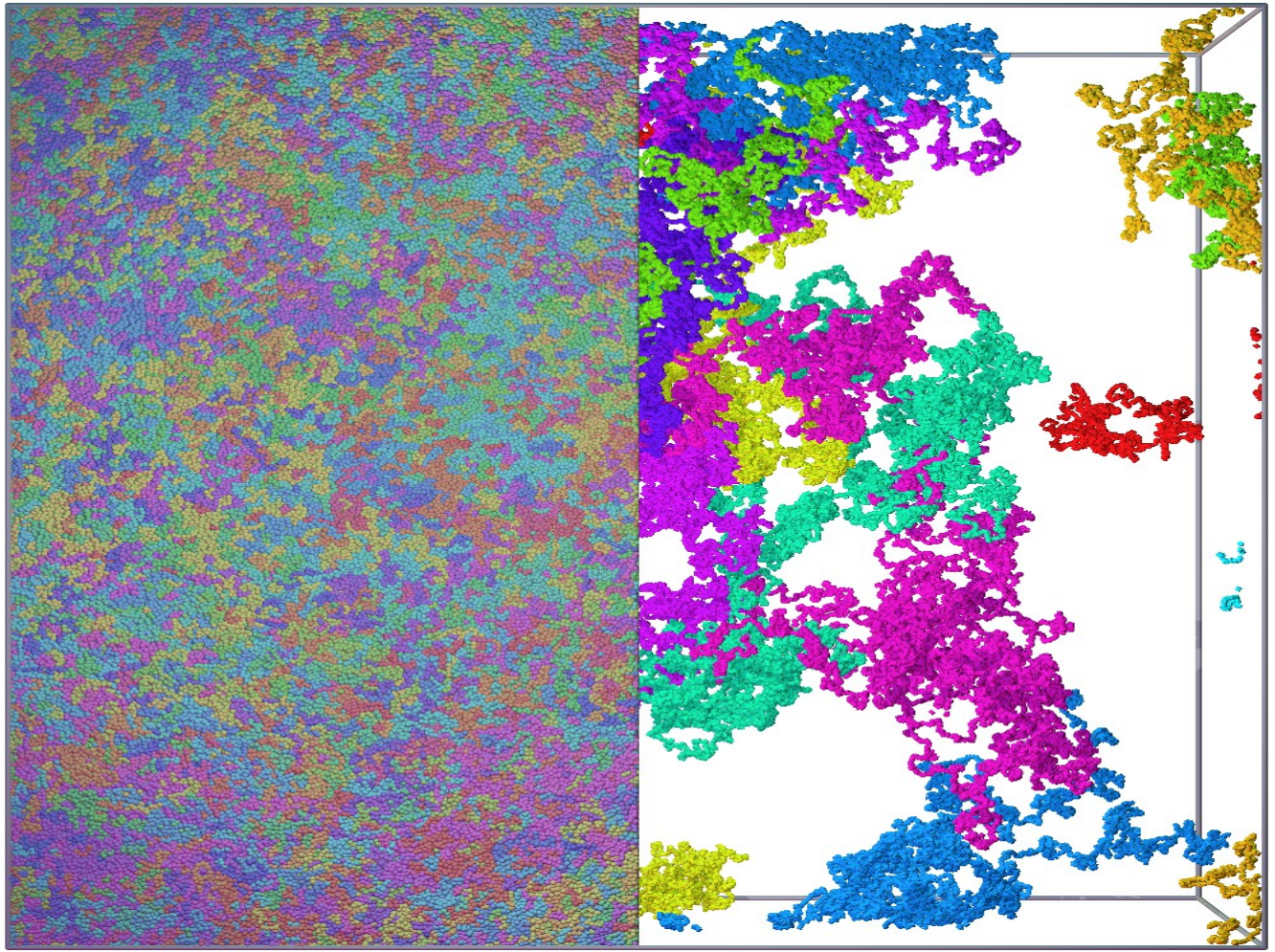
$$U_{WCA}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right)$$

$$U_{FENE}(r) = \frac{-k R_0^2}{2}\ln\left(1 - \frac{r^2}{R_0^2}\right)$$

$$U_{bend}(\Theta) = \kappa(1 + \cos\Theta)$$

K. Kremer G. S. Grest “Molecular dynamics simulation for polymers in the presence of a heat bath” Phys. Rev. A 33, 3628 (1986).

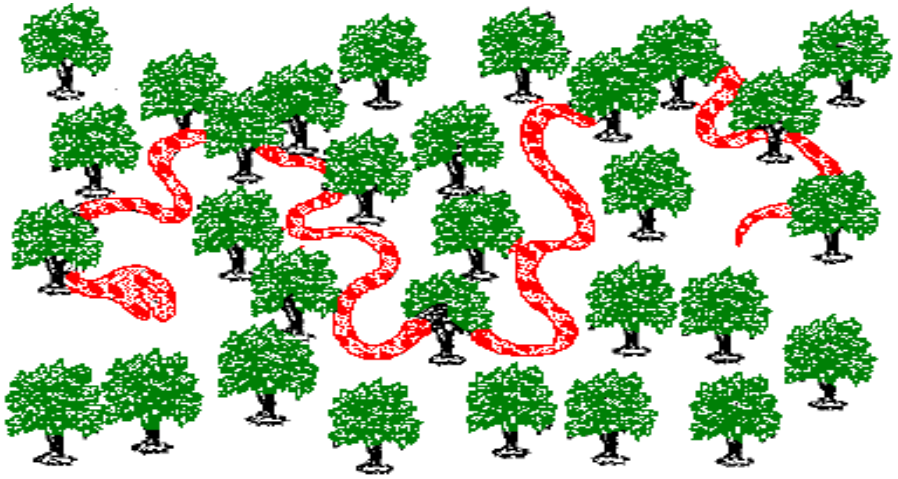
KG polymer melt



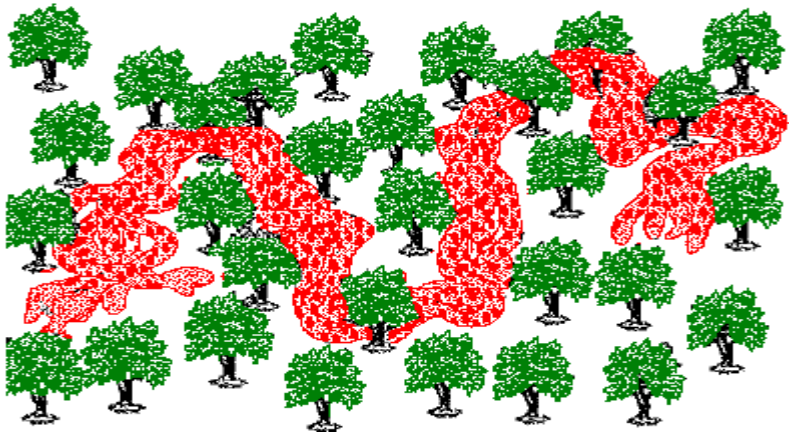
LAMMPS
Modification:
force
capped LJ

CS, RE
Multiscale
Equilibration
Phys.Rev. E
2016

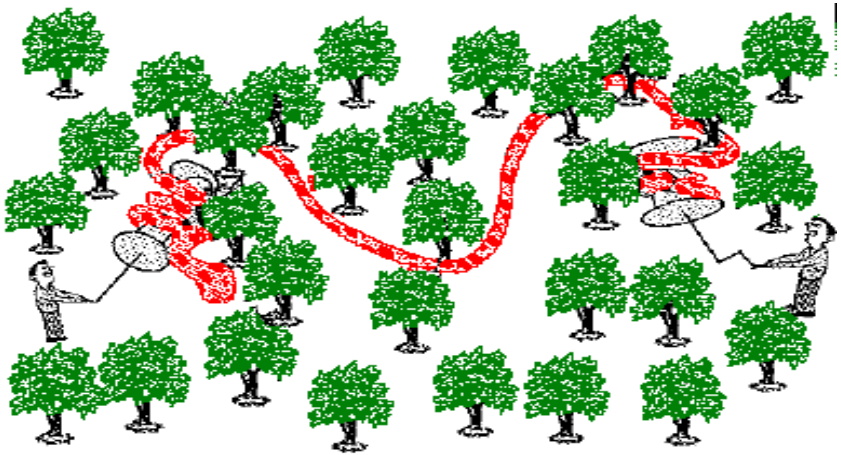
Fluctuations



Polymer + obstacles (other chains)



Thermal fluctuations of polymer

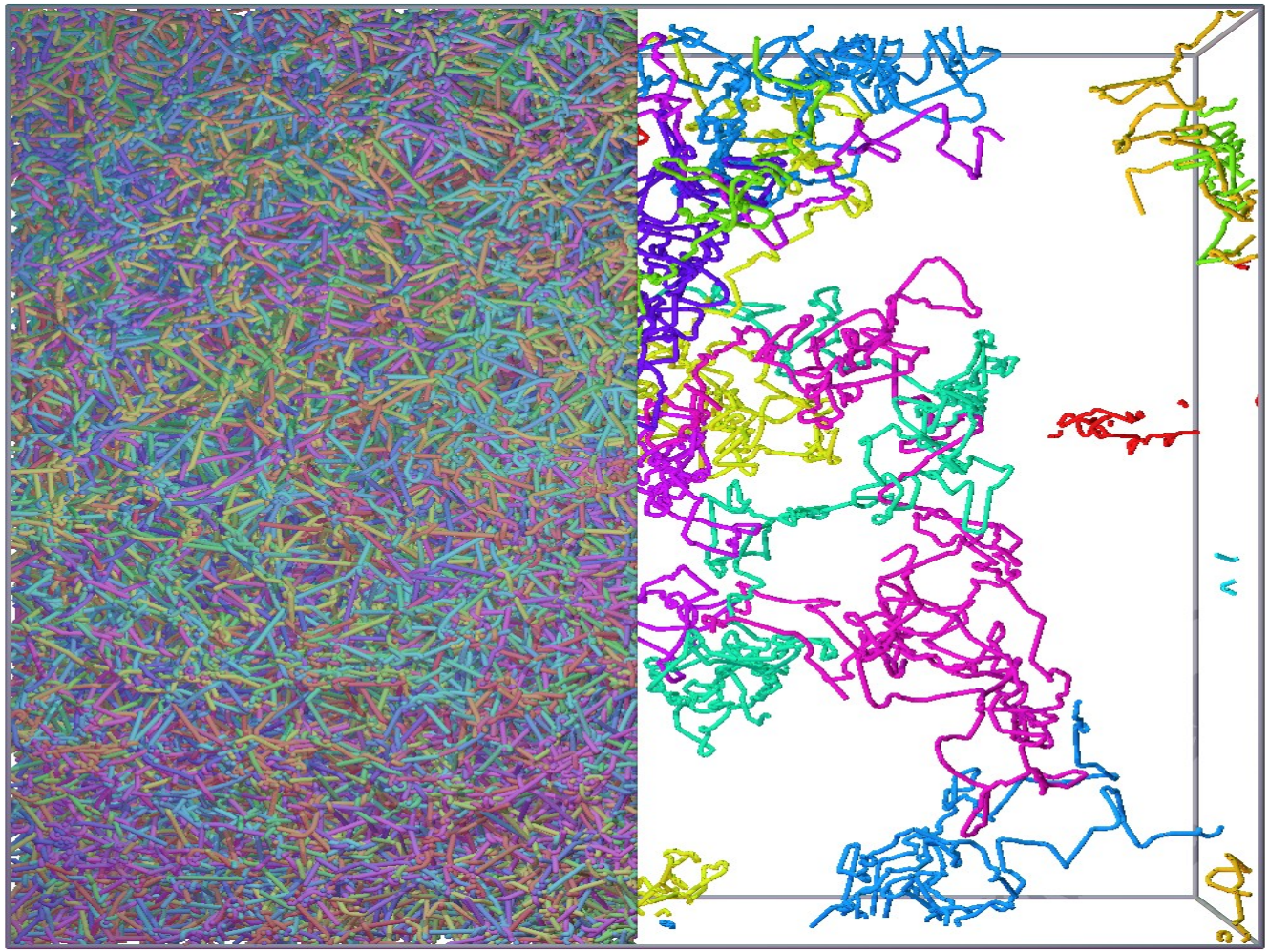


Topological state =

Ne monomers between entanglement points

Rubinstein Colby
Polymer physics

Topological analysis => Ge



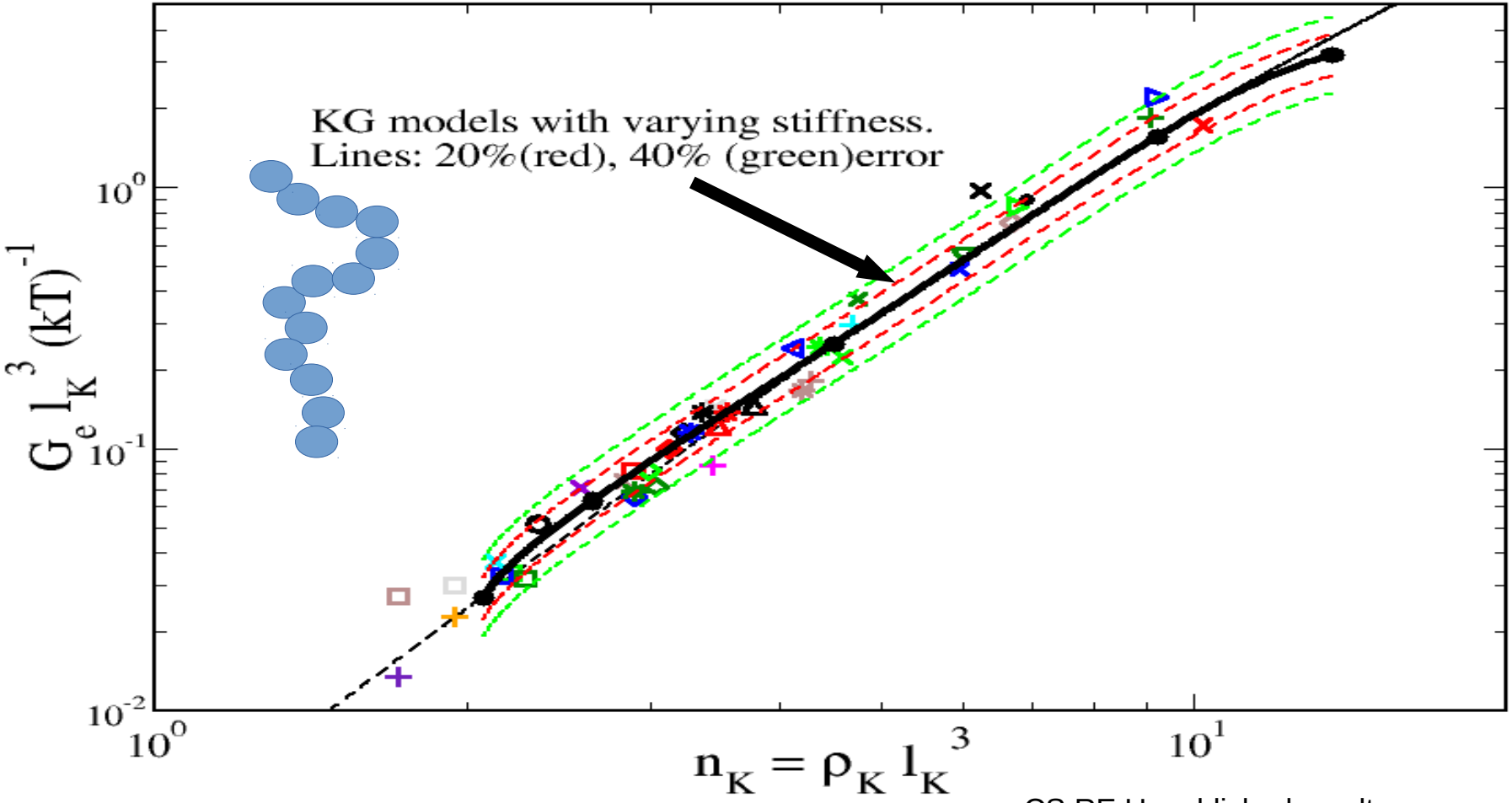
$$G_e = \frac{n k_B T}{N_e}$$

LAMMPS modification
1) Remove intramolecular pair interactions up to certain chemical distance

2) Minimize energy

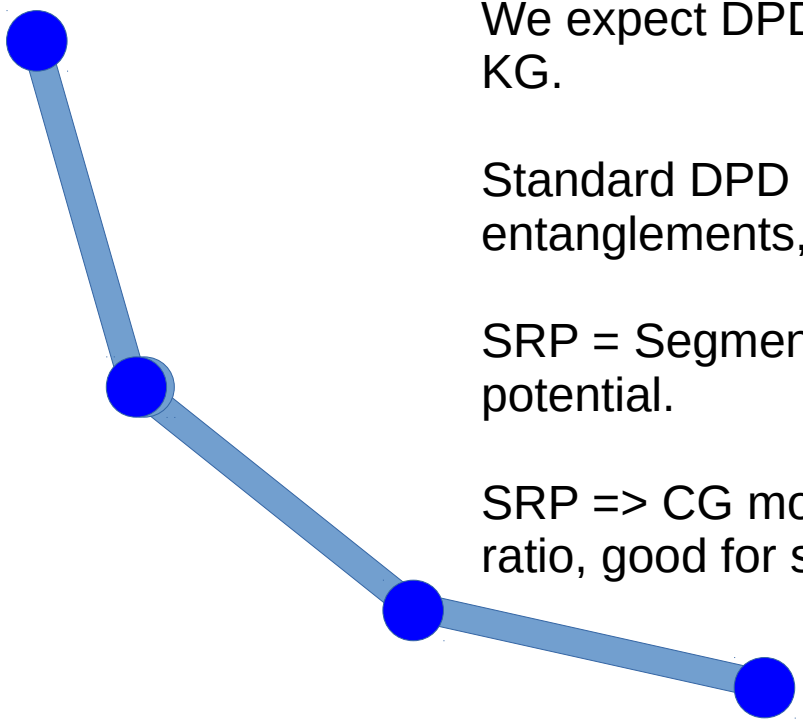
PPA Method
RE et al. Science 2004

Kuhnification of polymers



CS RE Unpublished results

DPD SRP polymer models

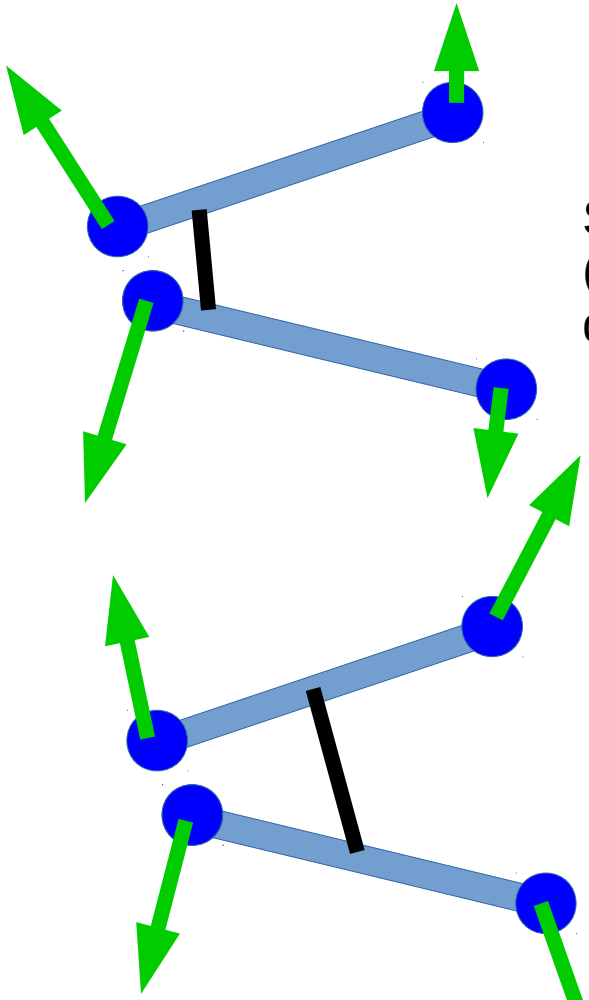


We expect DPD to be faster than KG.

Standard DPD does not preserve entanglements, but DPD+SRP can.

SRP = Segmental repulsive potential.

SRP => CG model with high aspect ratio, good for stiff filaments.

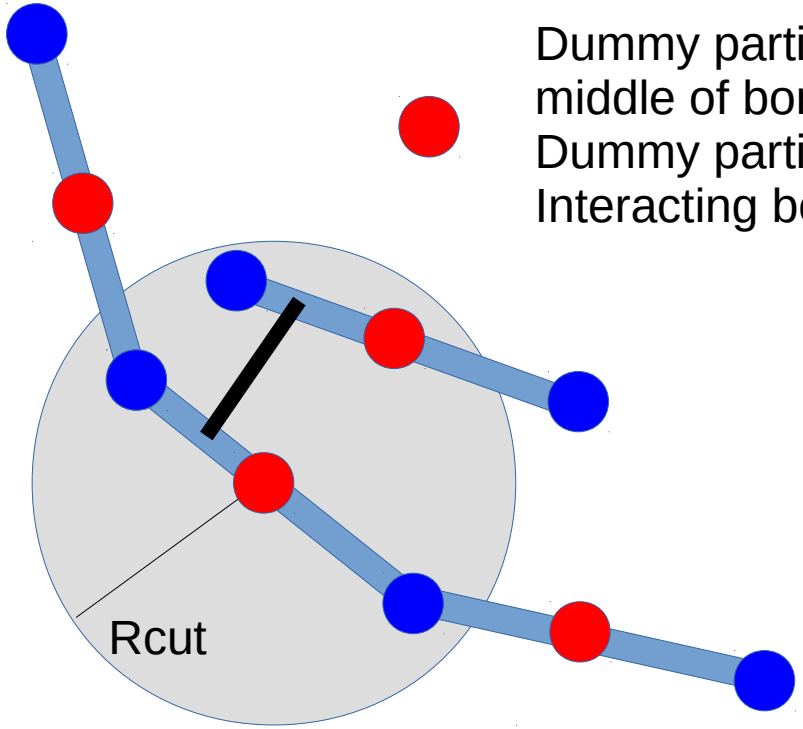


SRP (minimum distance)

mSRP (middle points)

Sirk et al. J. Chem. Phys. 136, 134903 (2012)
Kumar et al. J. Chem. Phys. 114, 6937 (2001)
Goujon et al. J. Chem. Phys. 129, 034902 (2008)

Implementation LAMMPS



Dummy particle always placed in the middle of bonds. Neighbor lists between Dummy particles used to determine Interacting bonds.

Force: $$F_{ij}^{SRP} = C(1 - r/r_c)\hat{r}_{ij} \qquad r < r_c$$

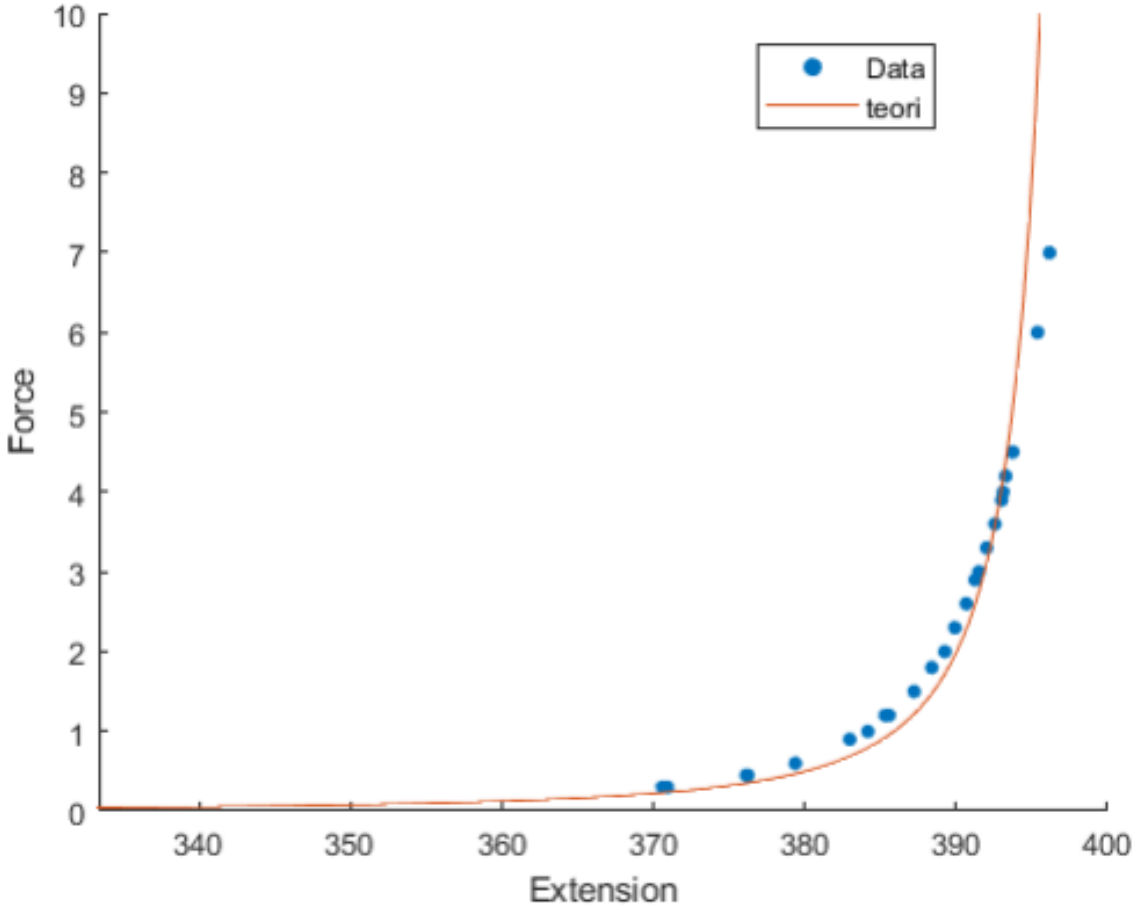
Lever rule for projecting force onto beads. L = 0.5 for mid.

$$F_{i1}^{SRP} = F_{ij}^{SRP}(L)$$
$$F_{i2}^{SRP} = F_{ij}^{SRP}(1 - L)$$

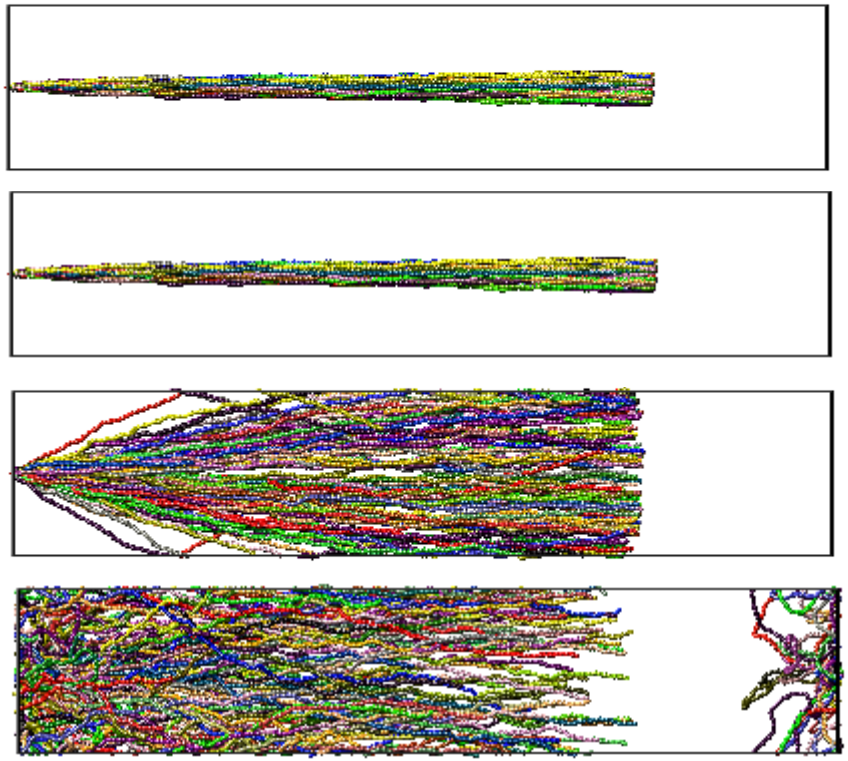
```
pair_style hybrid dpd 1.0 1.0 12345 srp 0.8 1 mid exclude yes
pair_coeff 1 1 dpd 60.0 4.5 1.0
pair_coeff 1 2 none
pair_coeff 2 2 srp 100.0 0.8
```


Sirk et al. J. Chem. Phys. 136, 134903 (2012)
Kumar et al. J. Chem. Phys. 114, 6937 (2001)
Goujon et al. J. Chem. Phys. 129, 034902 (2008)

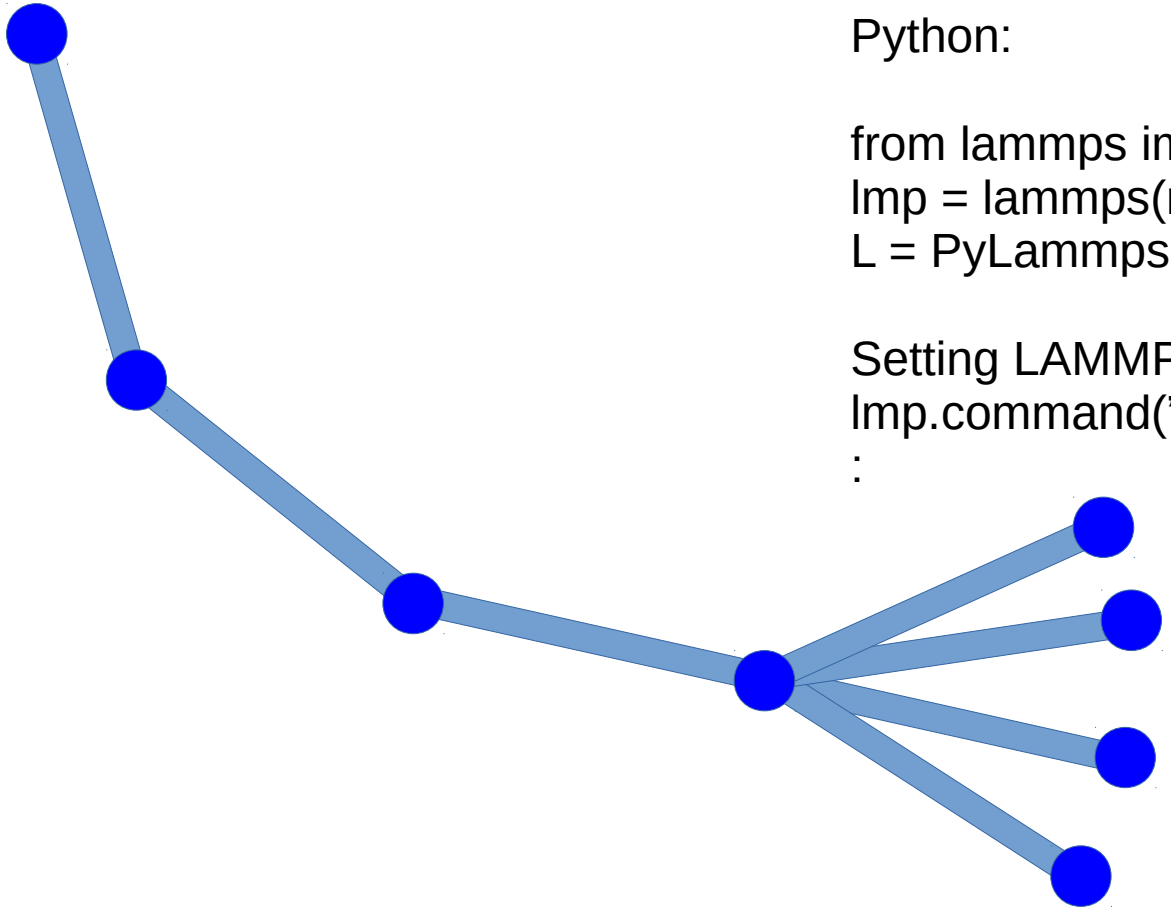
Force extension relation



Theory: Marko-Siggia
Macromolecules 28, 8759 (1995)



Generation of DPD SRP gels of rigid chains



Python:

```
from lammps import lammps,PyLammps
lmp = lammps(name="zqex")
L = PyLammps(ptr=lmp)
```

Setting LAMMPS variable from python variable
lmp.command(”variable box equal %f” % box)
:

Use MC to generate grow chain step by step.

Generating a step

For each chain: start

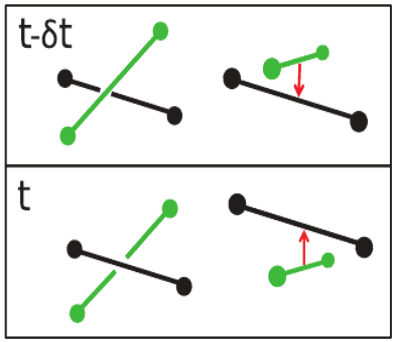
```
    R=randompos(box)
    dR=randomdir(l0)


    atomprev=0
    atomprevprev=0


    L.atoms[atomno-1].position = R
    lmp.command("set atom %d type 1" % atomno)


    for n in range(0,nbond):   #add a bond

        P=tuple(map(lambda x, y: x + y, R, dR))


        atomprevprev=atomprev
        atomprev=atomno
        atomno+=1


        L.atoms[atomno-1].position = PutInBox(*P)
        lmp.command("set atom %d type 1" % atomno)


        if (atomprev>0):
                lmp.command("create_bonds single/bond 1 %d %d" % (atomprev,atomno) )

        if (atomprevprev>0 and atomprev>0):
                lmp.command("create_bonds single/angle 1 %d %d %d" % (atomprevprev,atomprev,atomno) )
```

MC loop

```
O=L.atoms[atomno-1].position                    #store old


dRtrial=rotatedir(dR[0],dR[1],dR[2],angle)      #make trial by rotation of current bond around random vector
P=tuple(map(lambda x, y: x + y, R, dRtrial))
L.atoms[atomno-1].position = PutInBox(*P)       #Set coordinate of bead


lmp.command("run 0")                            #evaluate PE
e = L.eval("pe")


if e <= elast:                                  #Metropolis algorithm for selecting trials
    elast = e
    naccept += 1
    dR=dRtrial
elif random.random() <= math.exp((elast-e)/temp):
    elast = e
    naccept += 1
    dR=dRtrial
else:
    L.atoms[atomno-1].position = O              #reject and reinstate position
    nreject +=1


if saveimage and frameno%everyframe==0:         #Use dump image to generate images of growth dynamics
    lmp.command("group vis type 1")
    lmp.command("reset_timestep %d" % (frameno) )
    lmp.command("dump visualize vis image 1 img/*.png type type adiam 1 bond type 5.5 zoom 1.6 view 0 270")
    lmp.command("dump_modify visualize first yes pad 8")
    lmp.command("run 0")
    lmp.command("undump visualize")
frameno+=1
```

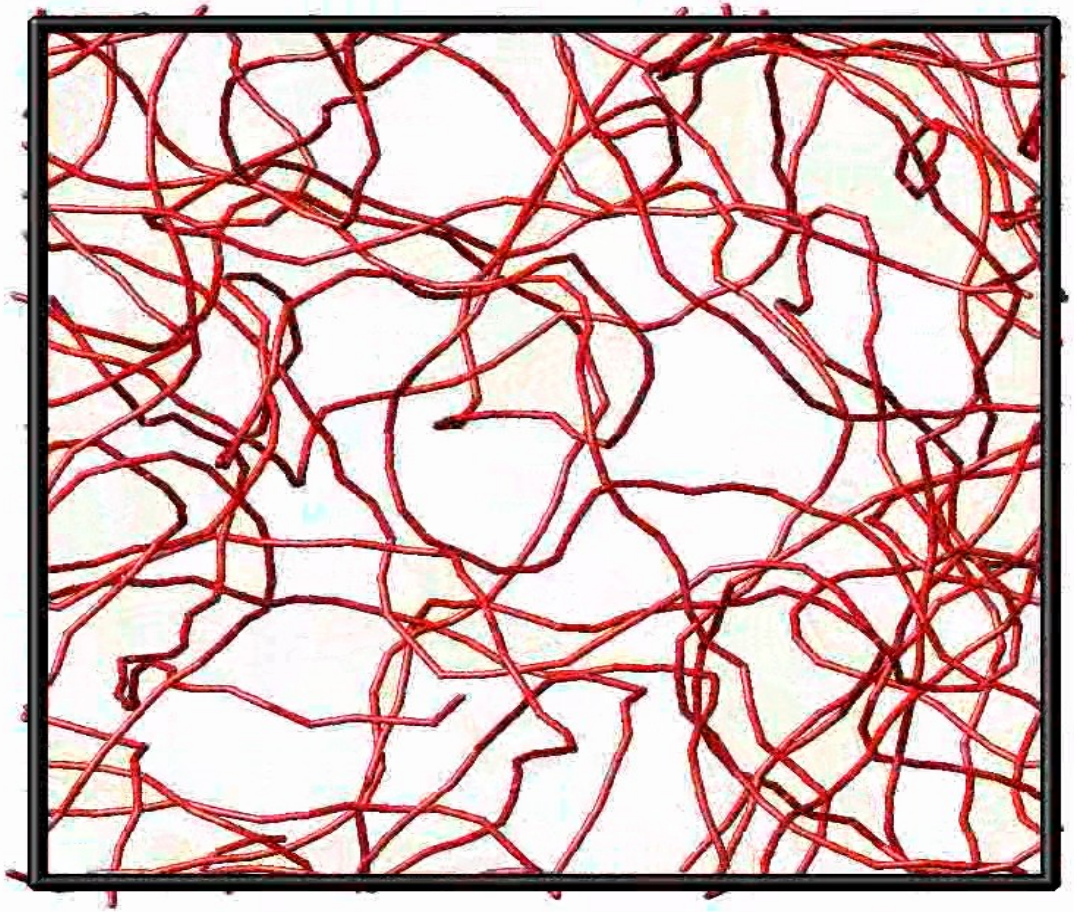
Simulation of gel nK=10

Topology violations?

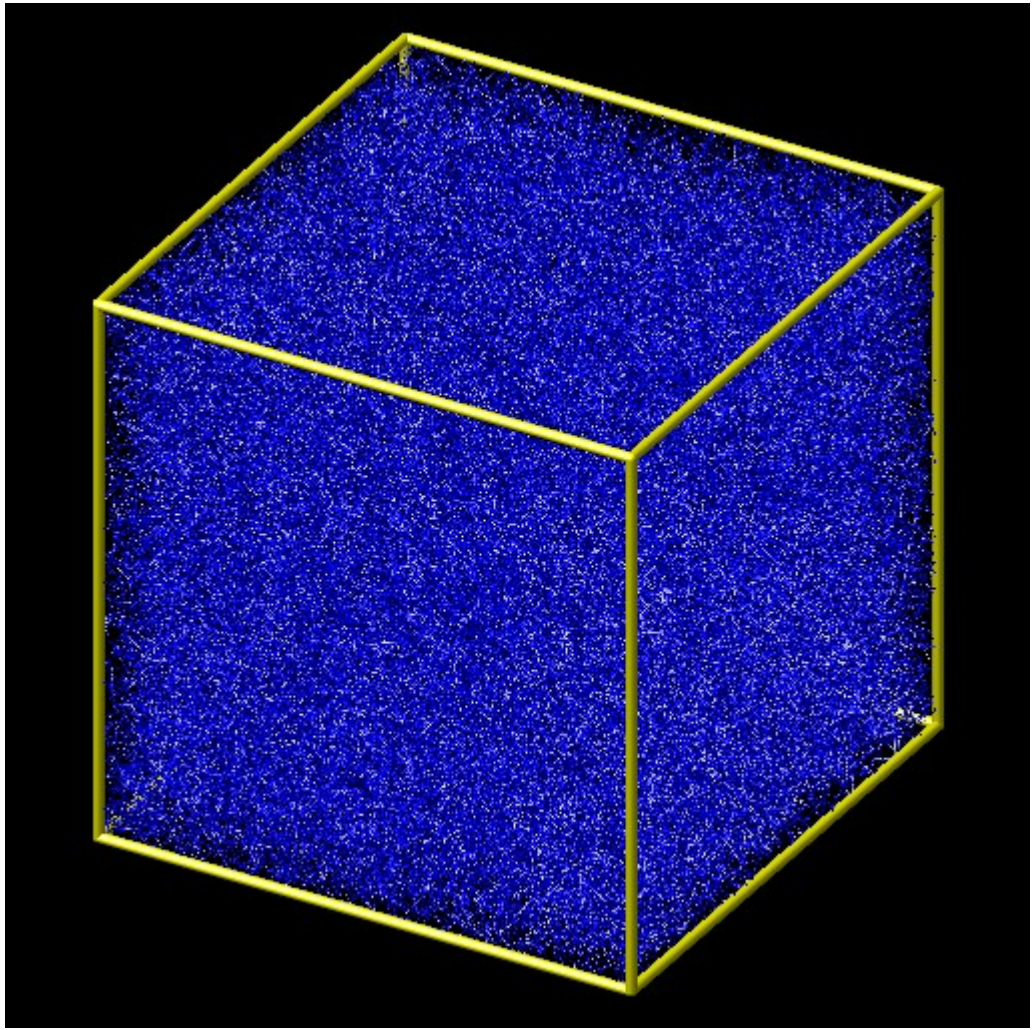


Implemented in LAMMPS.

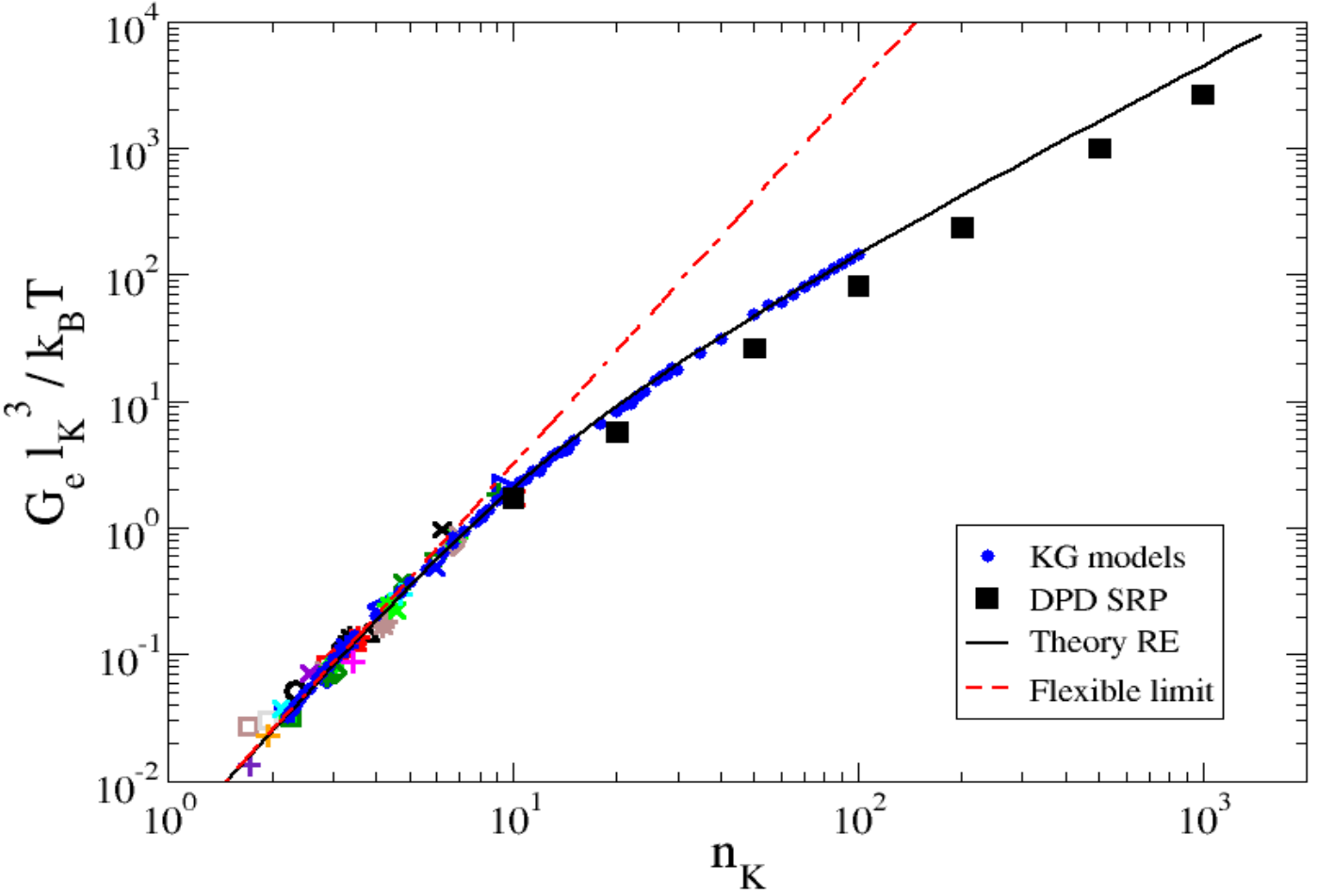
None detected.



nK=1000 gel



KG + DPDSRP Ge moduli (WIP)



Summary

- Used LAMMPS for many years.
- Here presented some ideas towards modelling polymer systems.

- Contributed pair, bond, angle, dihedral, improper styles zero, and bond, angle harmonic shift

Implemented a few fixes, computes, pair and bond styles, e.g.:

- Fix_bond_swap_srp Bond swapping equilibration method for SRP
- fix_quake to identify quakes in glassy colloidal systems.
- fix_network. Add springs between particles within cutoff distance
- fix_nve_constraint: NVE dynamics with fixed chunk CMs.
- Compute to tally interchunk pair and bond forces.
- pair_lj_cut with force cap
- bond_fene_break / fix_bond_breakcount Breakable FENE bonds with accounting.
- bond poly04 4th order polynomium bond potential
- compute_reduce.cpp do various moments e.g. <cos(theta)>
- npair.cpp excluding intramolecular interactions in chemical distance window
- error.cpp Saves error msg to file .final.