A study of the effects of polymer entanglement on material properties

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Joint work with

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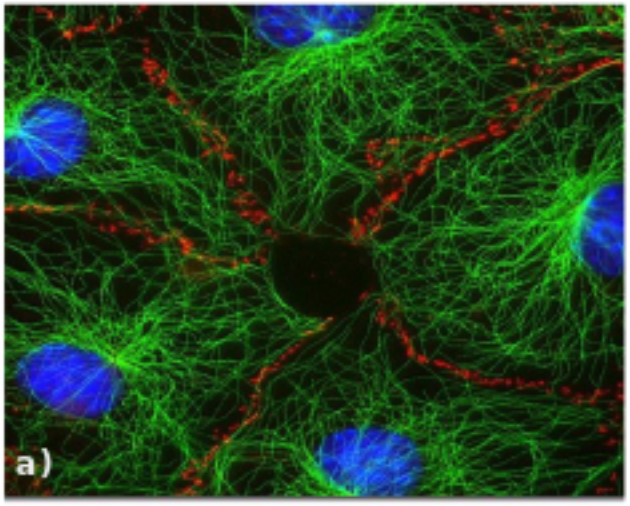
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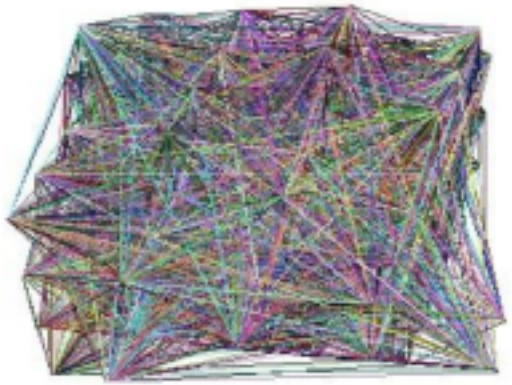
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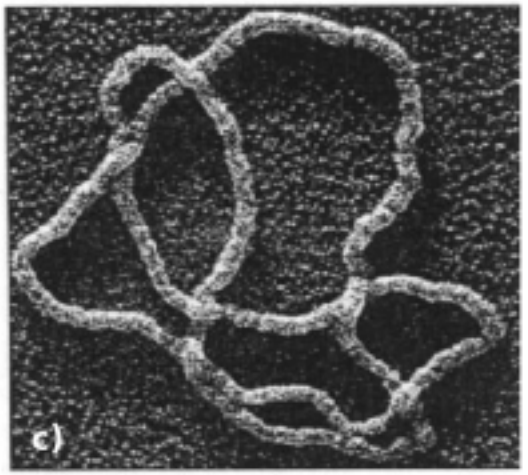
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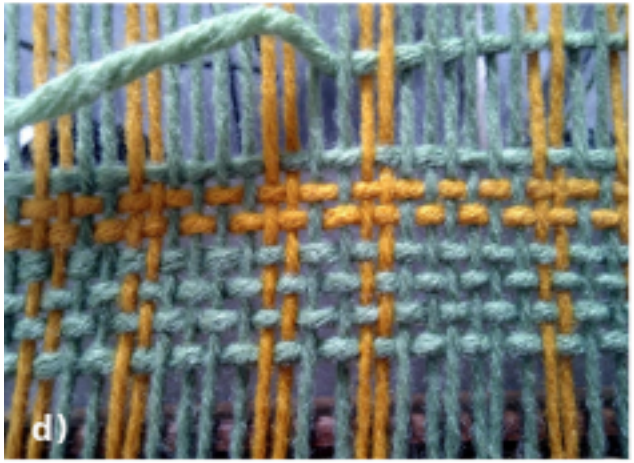
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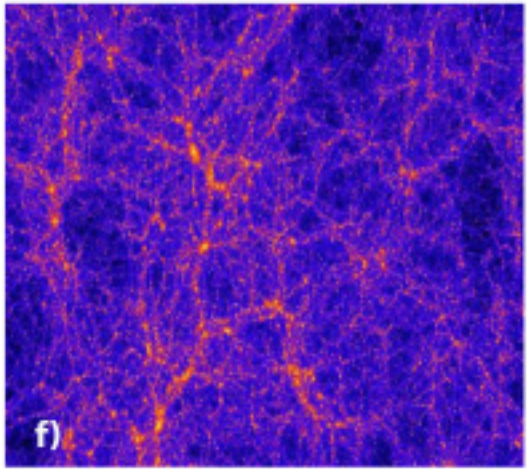

f)

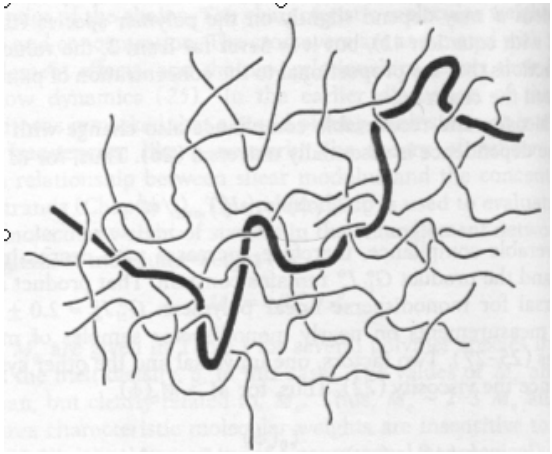
Polymers: material with big range of mechanical properties

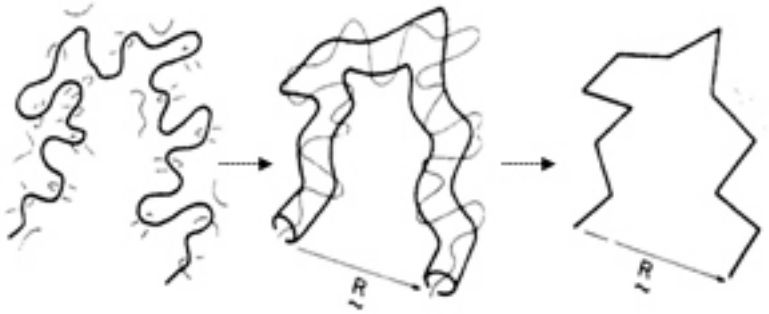
Example: Silly Putty

Solid-like response in one time scale

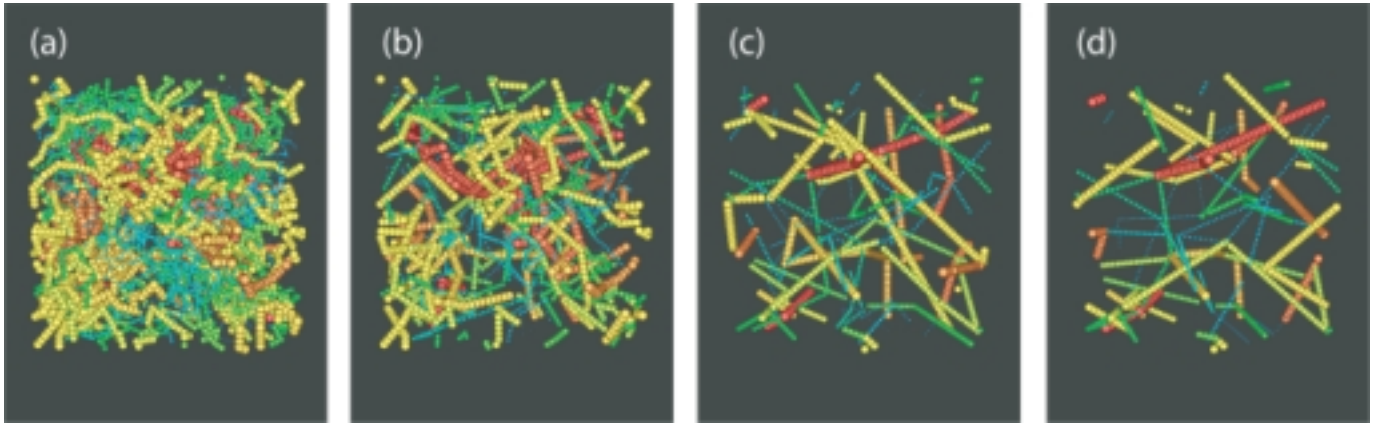
Liquid-like response in a longer time scale

Polymer motion seen as diffusion in an array of obstacles





Entanglement seen as a network of contacts



Z1 algorithm by M. Kroeger

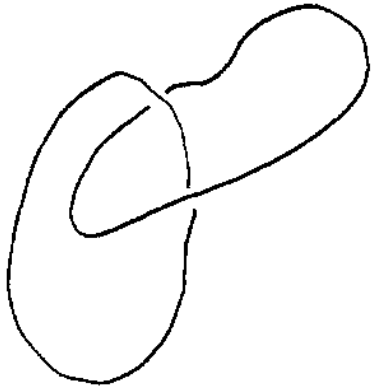
Nr of contacts
+
Distance between contacts

Successful attempts to include in theories of polymer entanglement

Nr of contacts
+
Distance between contacts

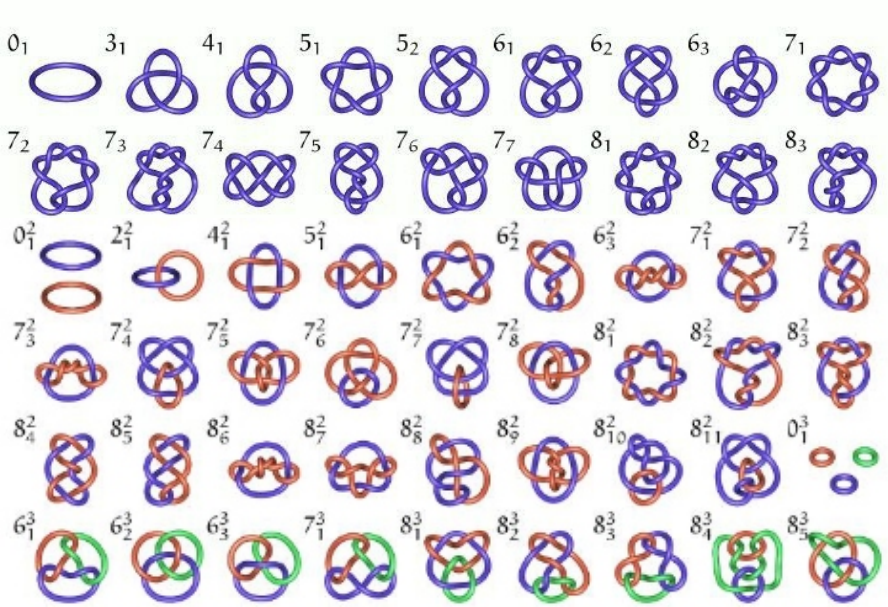
Local Entanglement
Small Length Scale Information

What about other length scales?



S F Edwards 1968 *J. Phys. A: Gen. Phys.* **1** 15

Knots and Links



A knot is a simple closed curve in space

A link is a collection of simple closed curves in space that do not intersect each other.

Two knots/links are equivalent if we can deform one to the other with out cutting and pasting.

Can tools from knot theory provide information relevant to mechanics?

Mathematical measures of entanglement complexity

How to deal with open curves?

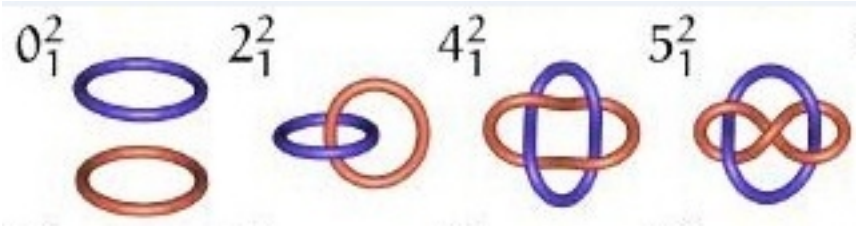
How to account for Geometry?

The Linking Number
of two oriented simple closed curves

Lk(I,J) = algebraic sum of intercrossings in a diagram

= nr of times one curve intersects the surface bounded by the other

Lk Is a topological invariant
(with respect to intercrossings)



Lk=0 Lk=1 Lk=2 Lk=0 !!

The Gauss linking integral

$$L(l_1, l_2) = \frac{1}{4\pi} \int_{[0,1]} \int_{[0,1]} \frac{(\dot{\gamma}_1(t), \dot{\gamma}_2(s), \gamma_1(t) - \gamma_2(s))}{||\gamma_1(t) - \gamma_2(s)||^3} dtds$$

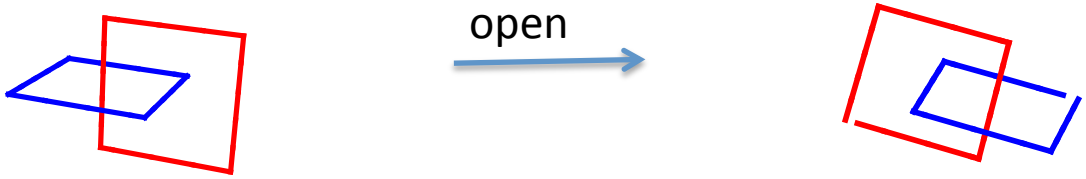
= average algebraic sum of crossings over all possible projection directions

It can be applied to open chains

Is a continuous function of the chain coordinates

Is sensitive on the geometry

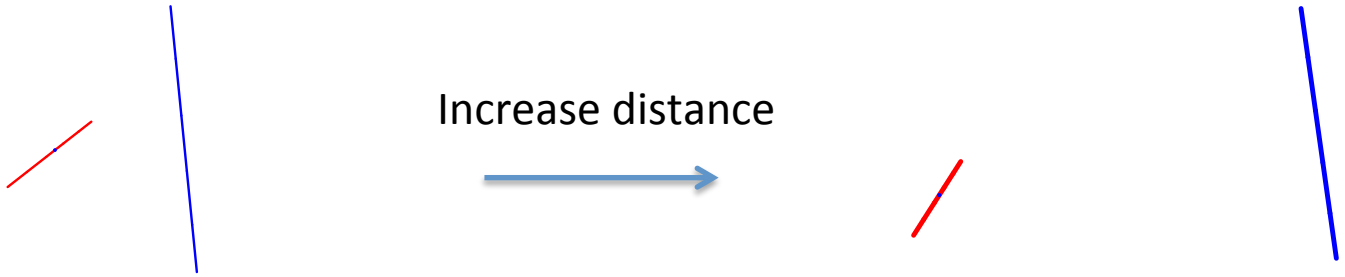
The Gauss linking integral



Lk=1

Lk=0.985497

Not zero even for two straight segments !



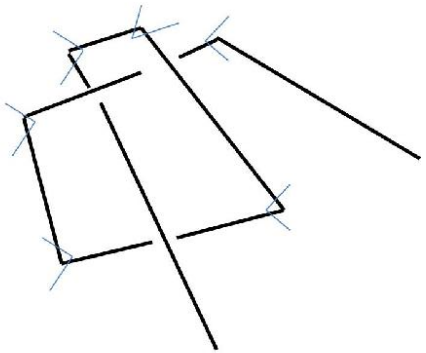
L=-0.166667

L=-0.0318843

The writhe of a chain

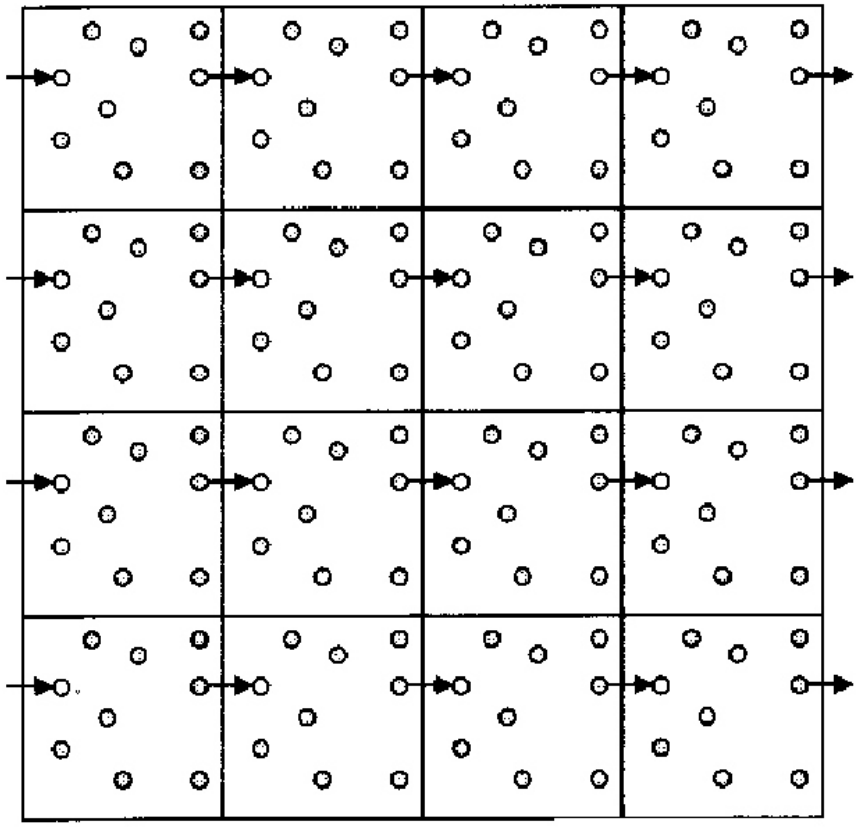
$$Wr(l) = \frac{1}{4\pi} \int_{[0,1]} \int_{[0,1]} \frac{(\dot{\gamma}(t), \dot{\gamma}(s), \gamma(t) - \gamma(s))}{||\gamma(t) - \gamma(s)||^3} dtds$$

Z=6,Wr=0.007

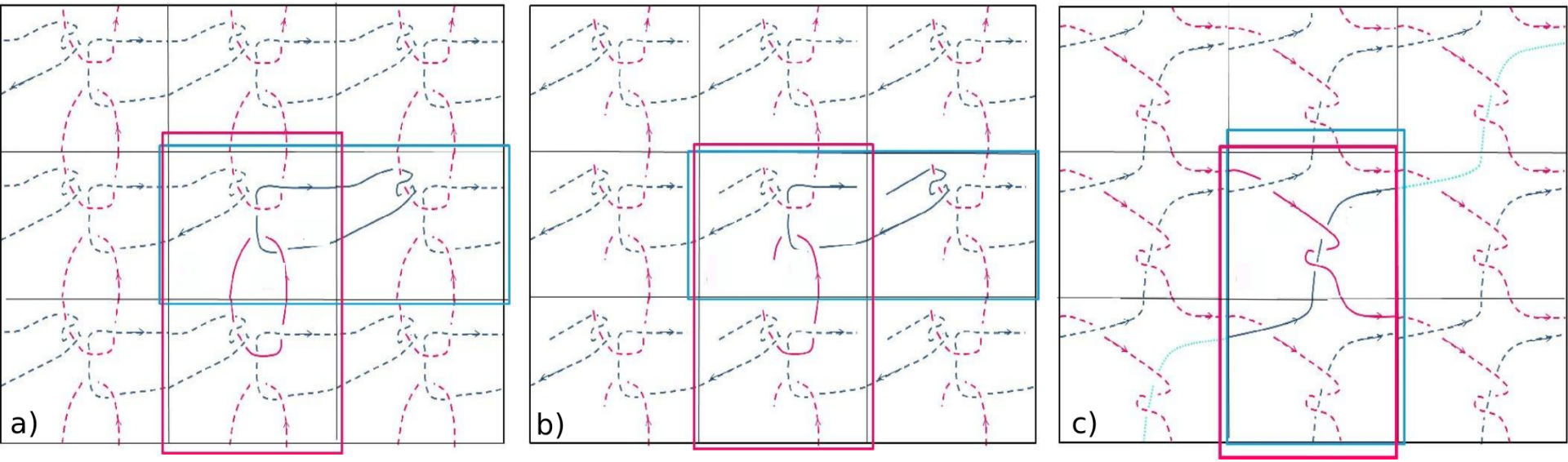


Z=6,Wr=2.78

Polymer Simulation:
Periodic Boundary Conditions are used to avoid boundary effects



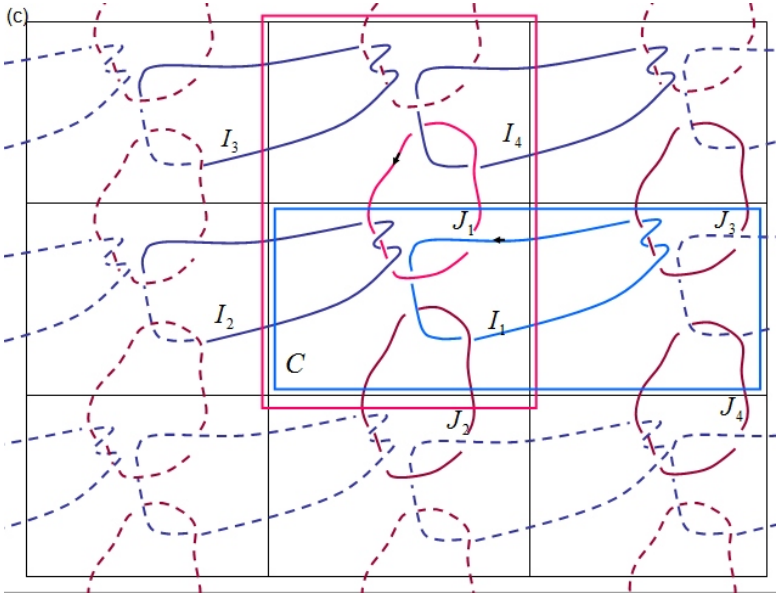
Entanglement in systems employing Periodic Boundary Conditions



The Periodic Linking Number

Free chain i: all the red curves

Free chain J: all the blue curves

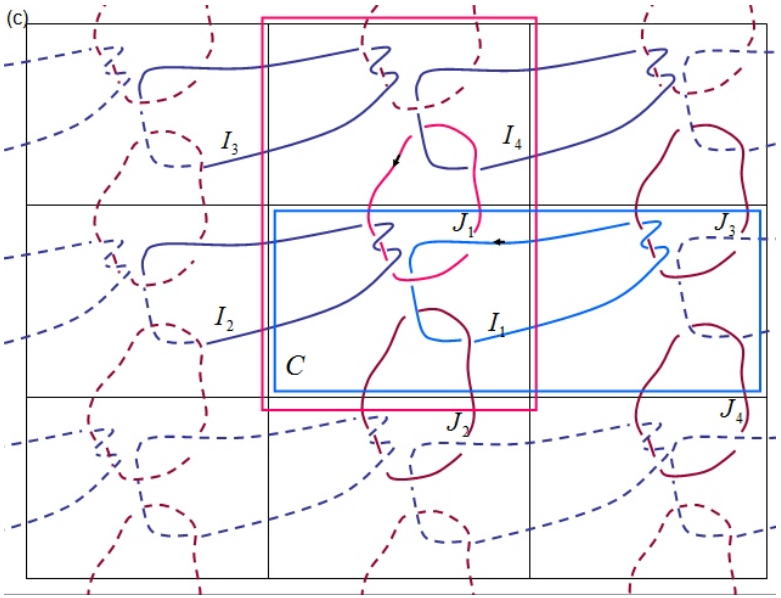


LK_P = sum of Gauss linking numbers between an image of I and all the images of J

The Periodic Linking Number

Free chain i: all the red curves

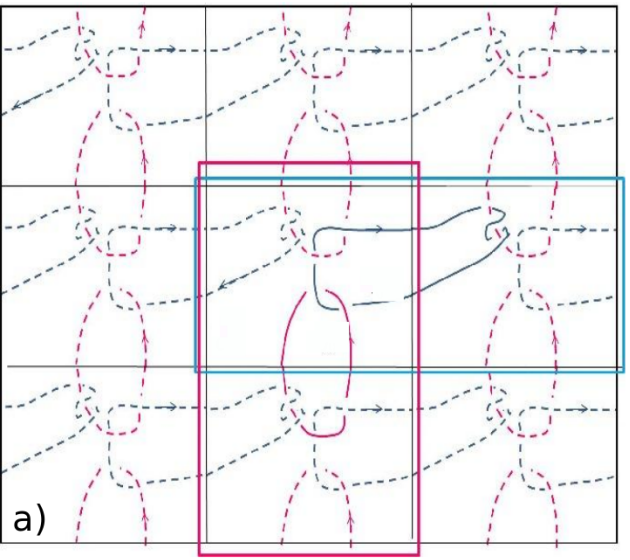
Free chain J: all the blue curves

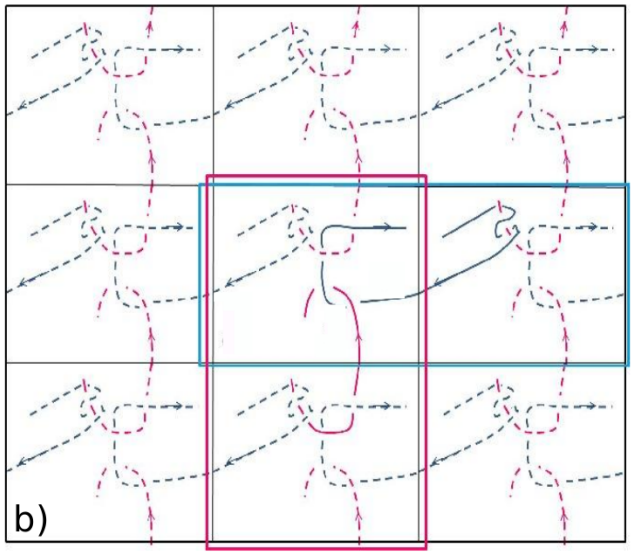


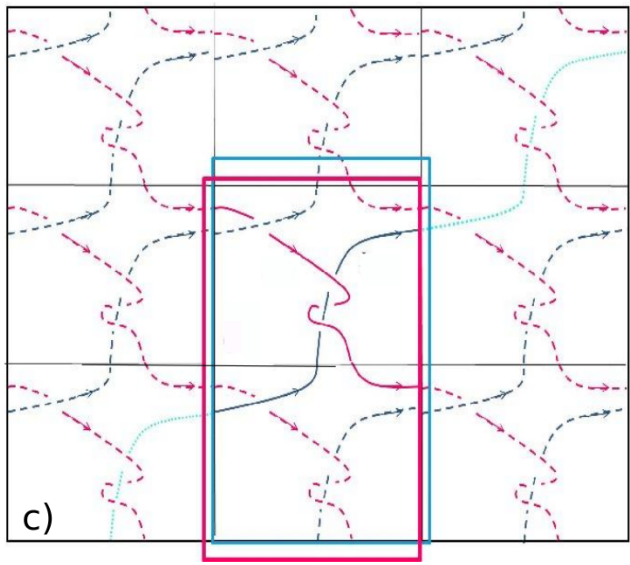
$$LK_P(I,J)=L(I_0,J_0)+L(I_0,J_1)+L(I_0,J_2)+L(I_0,J_3)+L(I_0,J_4)+.....$$

The Periodic Linking Number

LK_P = sum of Gauss linking numbers between an image of I and all the images of J







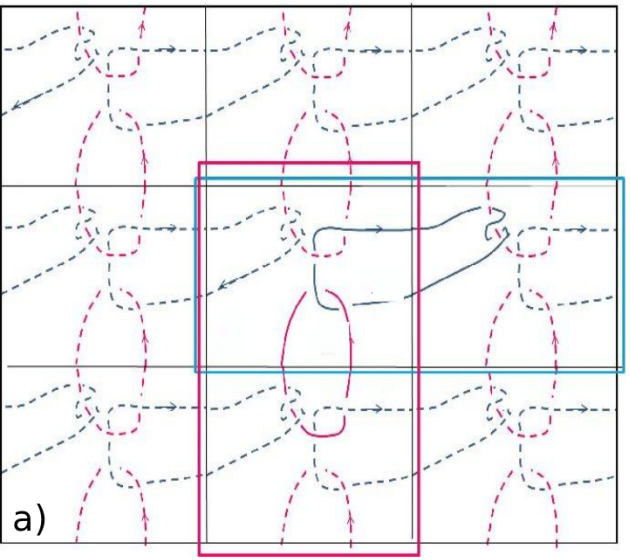
Closed chains:
LK_P is a finite sum

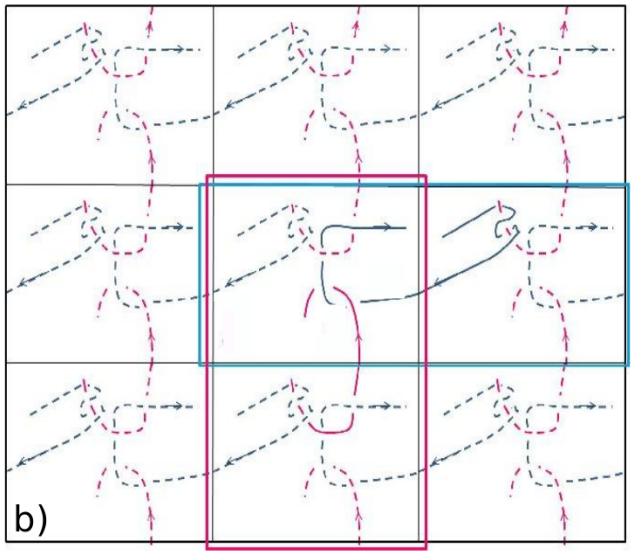
Open chains:
LK_P is an infinite sum!

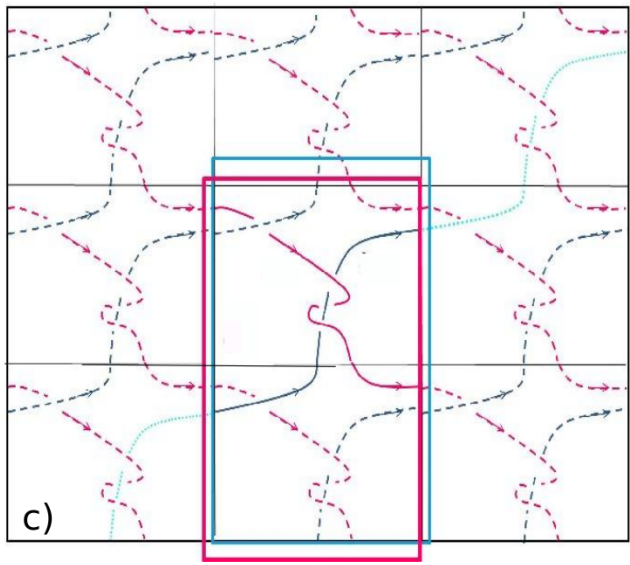
Infinite chains:
LK_P is an infinite sum!

The Periodic Linking Number

LK_P = sum of Gauss linking numbers between an image of I and all the images of J







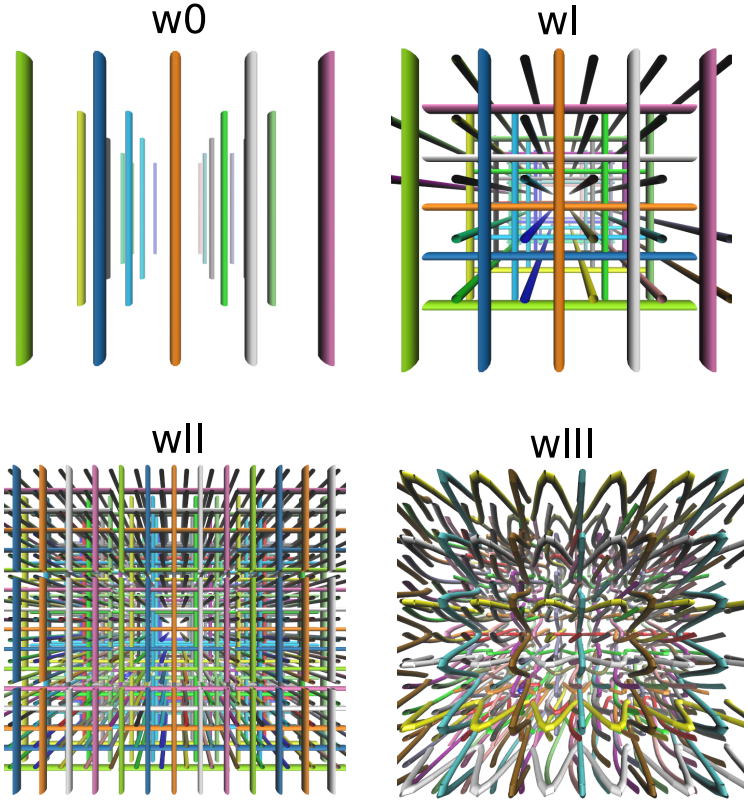
Closed chains:
LK_P is a finite sum

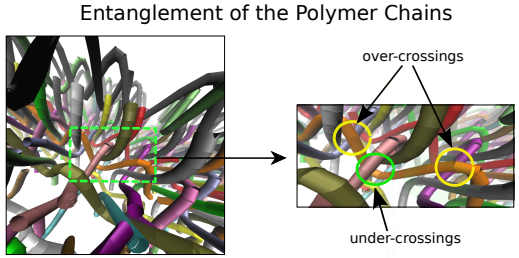
Open chains:
LK_P converges*

Infinite chains:
LK_P converges*

*Panagiotou E. 2015, *J. Comp. Phys.* **300** 533-573

Weave Topologies





Weave	**Topology**	**Density**	**MW (open)**
Weave 0 (w0)	parallel, non-interlaced	0.0625 (15 amu/nm^3)	20 m_0
Weave I (wI)	orthogonal (non interlaced)	0.1875 (45 amu/nm^3)	20 m_0
Weave II (wII)	orthogonal (non interlaced)	0.33 (80 amu/nm^3)	15 m_0
Weave III (wIII)	alternating interlaced	0.35 (84 amu/nm^3)	21 and 17 m_0

MD simulation
System parameters*

$$E = K_b(r - r_0)^2,\ K_b = 250$$ Bond rest length =1

$$E = K_\theta(1 - \cos(\theta - \theta_0))\ K_\theta = 8$$ Bond rest angle = pi

Semiflexible chains with persistence length 1/5 of the length of the Simulation box

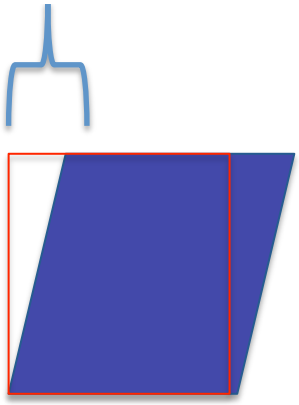
$$E = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$ Lennard-Jones potential to impose uncrossability

$$m\frac{dV}{dt} = -\gamma V - \nabla\Phi(X) + \sqrt{2k_BT\gamma}\frac{dB_t}{dt}$$ Langevin Theormostat

*Panagiotou E., Millett K. C. and Atzberger, P. J., 2017,(submitted)

Oscillatory shear

$$L(t) = L_0 + A\sin(2\pi\frac{t}{T_p})$$



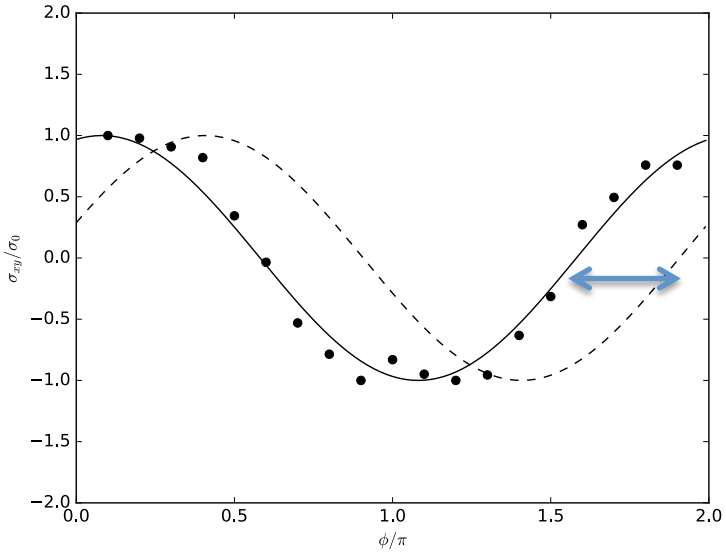
Lees-Edwards boundary conditions

$$\sigma_{l,k} = \frac{1}{V}\sum_{n}\sum_{j=1}^{n-1}\left\langle f_j^{(l)} \cdot (x_{q_n}^{(k)} - x_{q_j}^{(k)})\right\rangle$$

Irving-Kirkwood Method

Do this for increasing frequency of oscillations
Average over many frequencies of oscillation

$\sigma_{xy}(t)$



Phase lag
- = 0 solid
- = pi/2 liquid

Least squares fit to the function:

$$g(t) = G_2(\omega)\gamma_0 \cos(\omega t) + G_1(\omega)\gamma_0 \sin(\omega t)$$

Loss modulus

(Liquid-like)

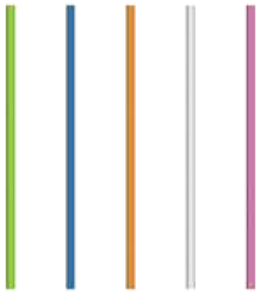
Storage modulus

(Sollid-like)

w0

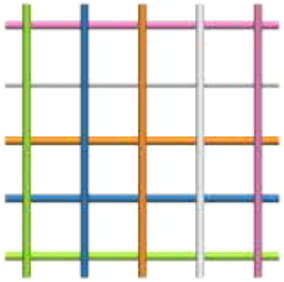
infinite

open

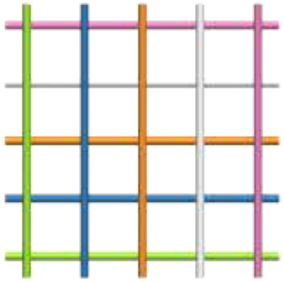


wl

infinite

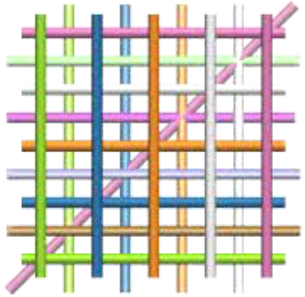


open

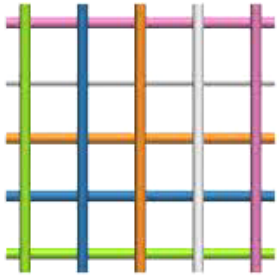


wll

infinite

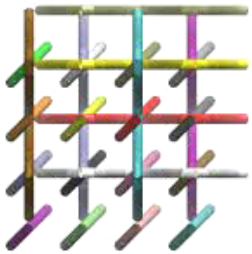


open

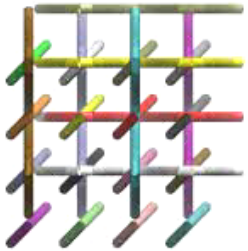


wlll

infinite



open

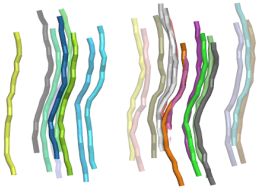


w0

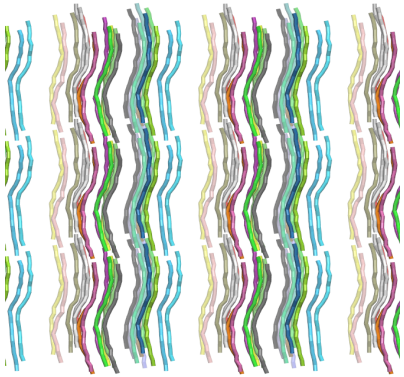
(period *T=16 tau_D*)

infinite

(*t=6T*)



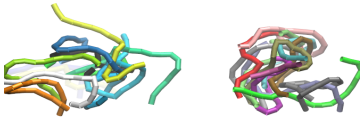
unit cell



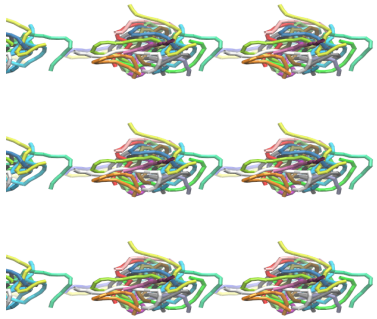
periodic system

open

(*t=16T*)



unit cell



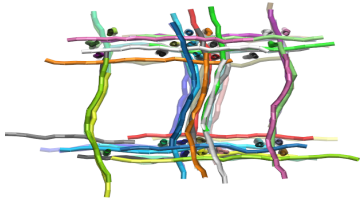
periodic system

wl

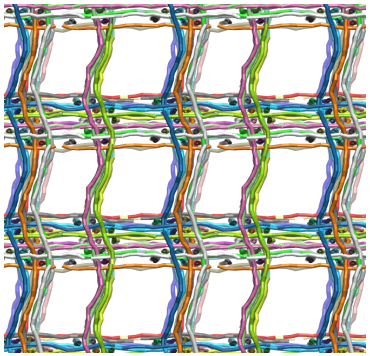
(period *T=16 tau_D*)

infinite

(*t=6T*)



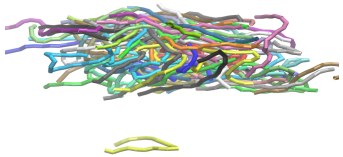
unit cell



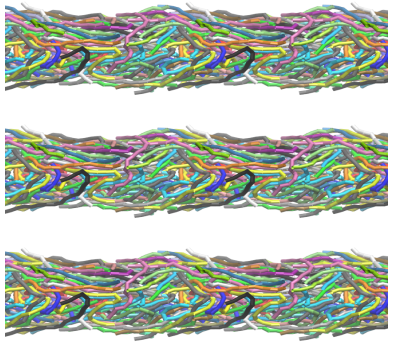
periodic system

open

(*t=16T*)



unit cell



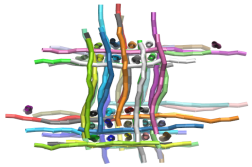
periodic system

wII

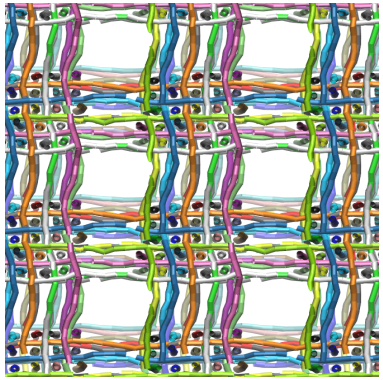
(period *T=16 tau_D*)

infinite

(*t=6T*)



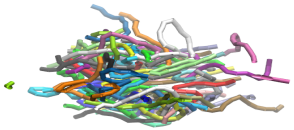
unit cell



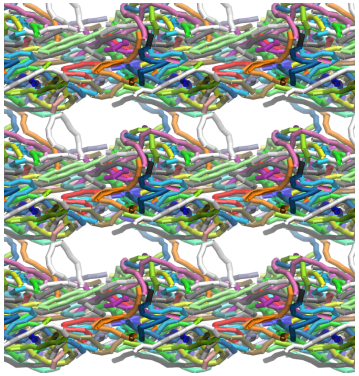
periodic system

open

(*t=16T*)



unit cell



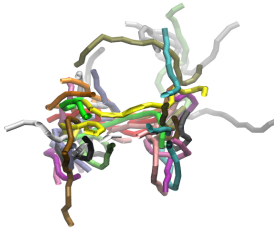
periodic system

wIII

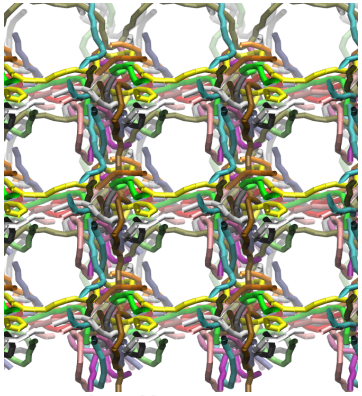
(period *T=16 tau_D*)

infinite

(*t=16T*)



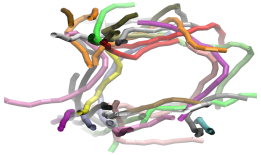
unit cell



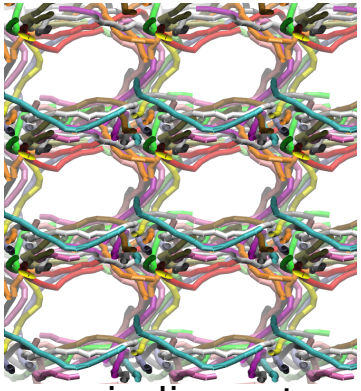
periodic system

open

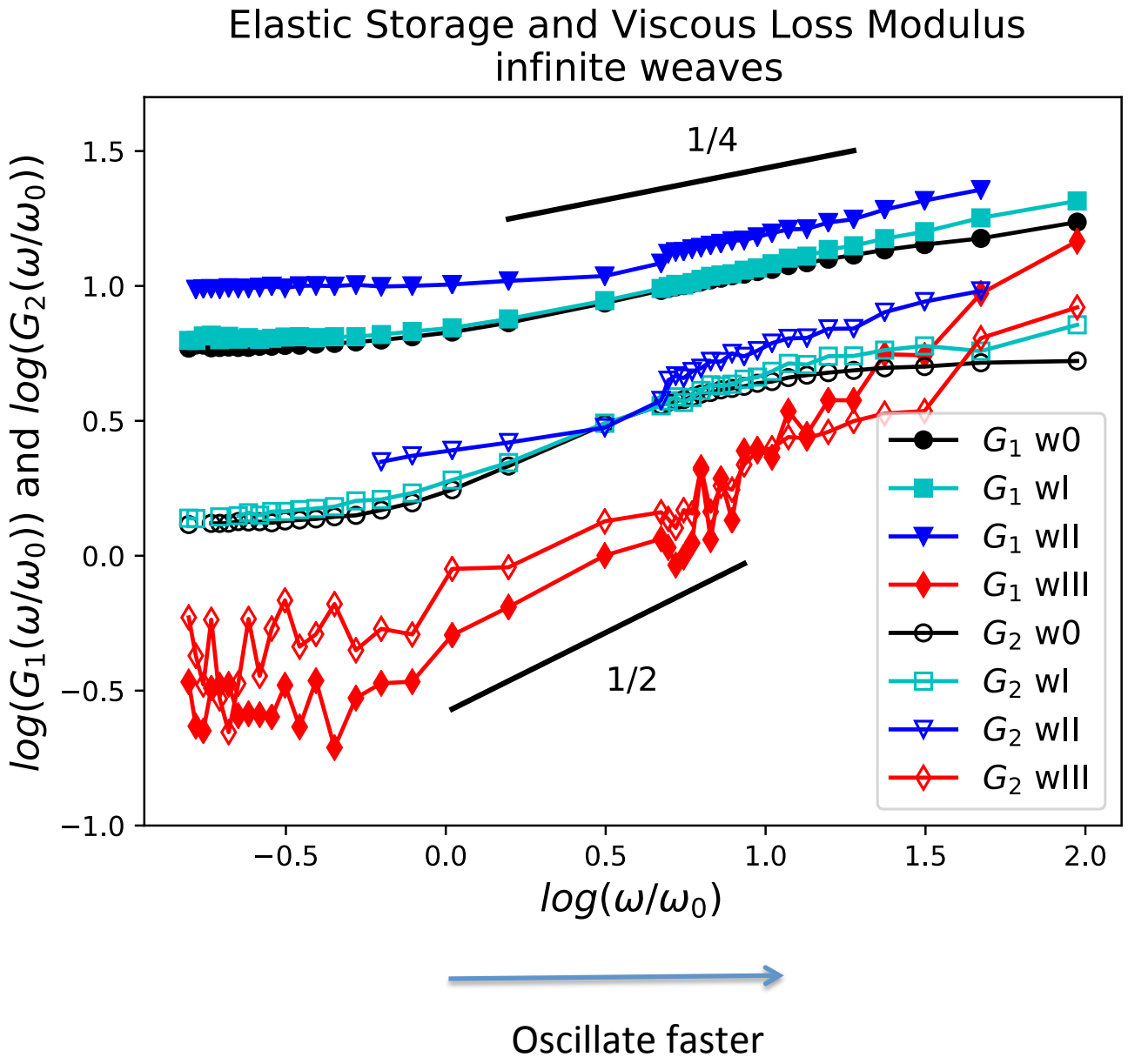
(*t=16T*)

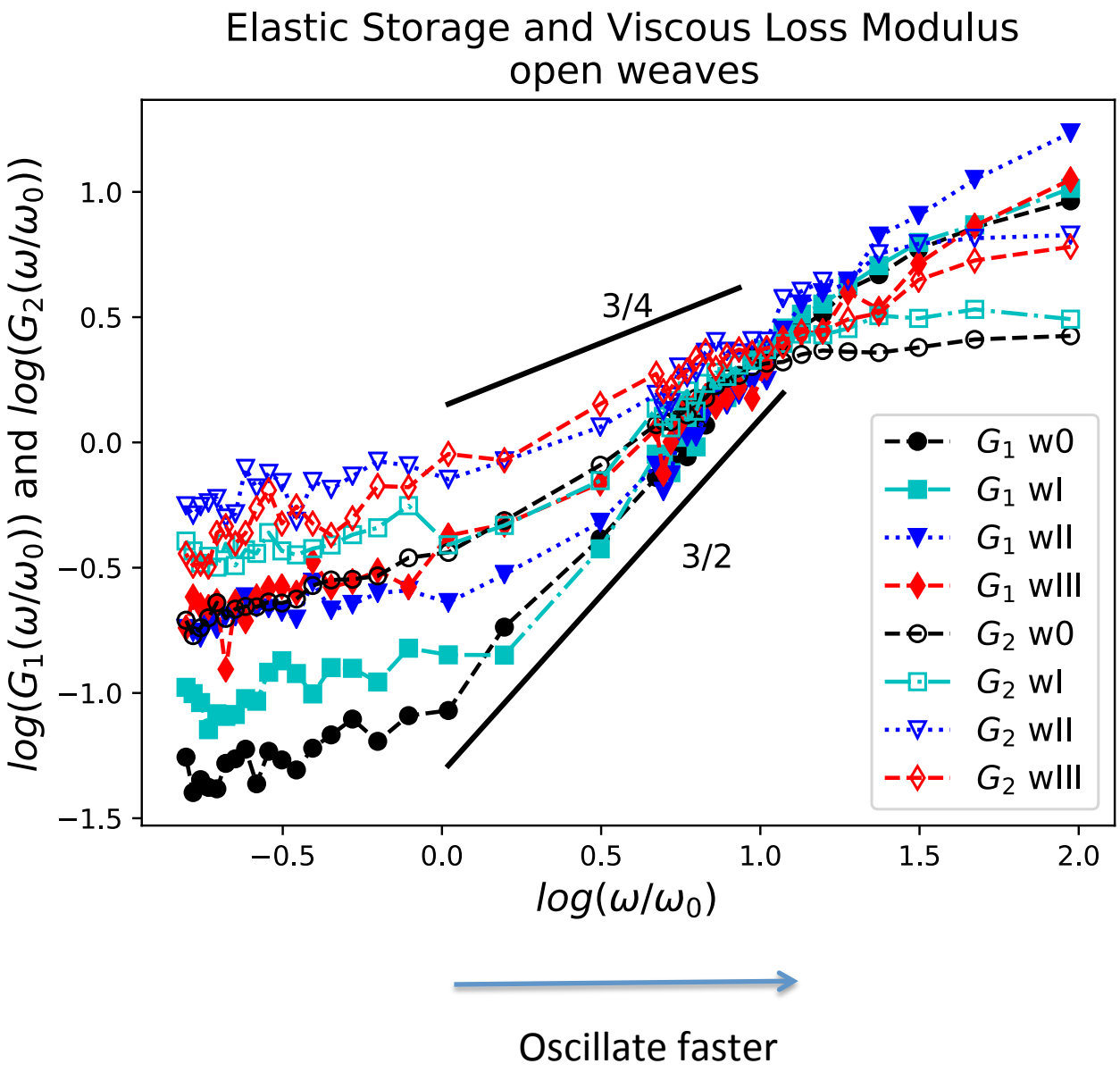


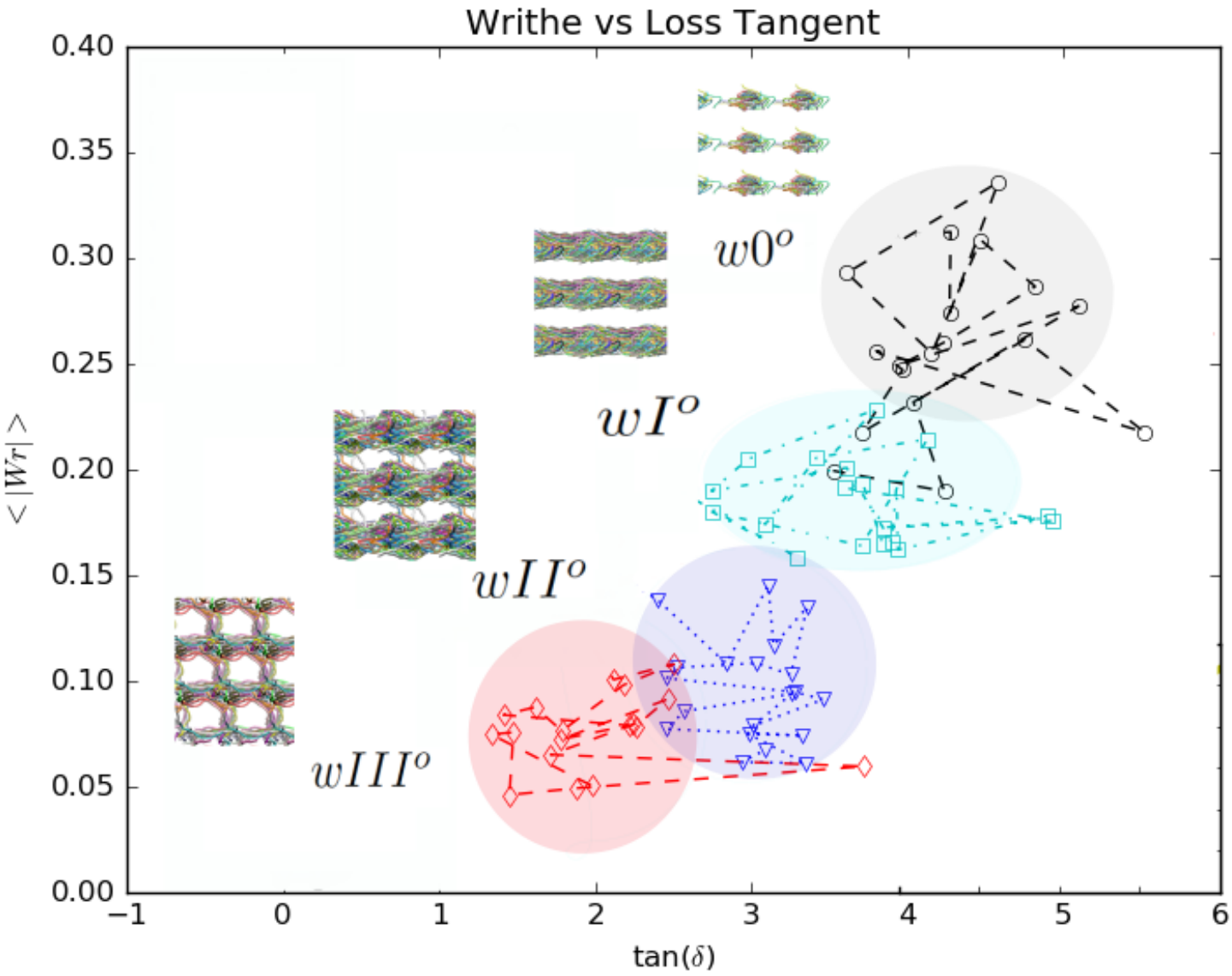
unit cell



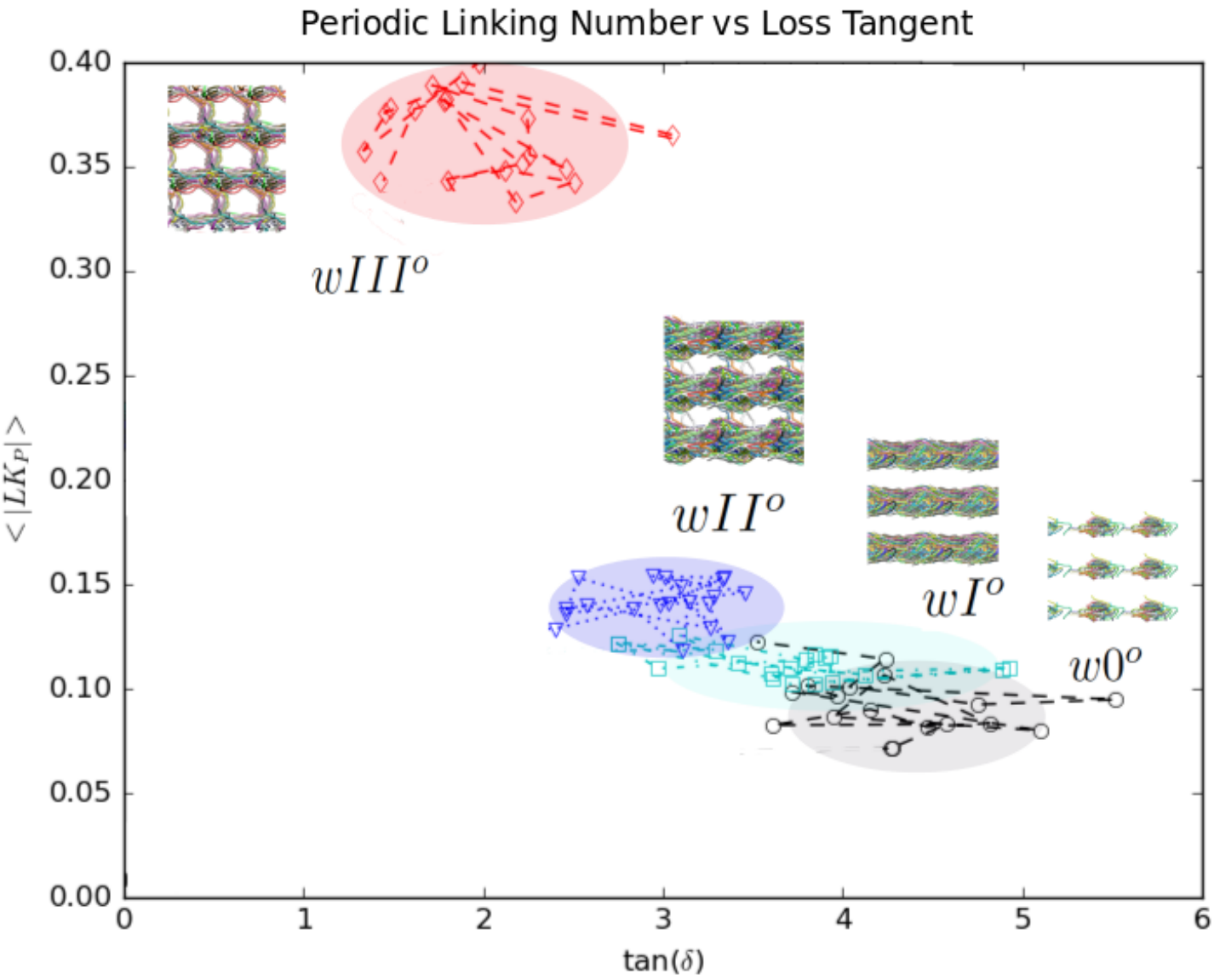
periodic system


Elastic Storage and Viscous Loss Modulus
infinite weaves
1/4
1/2
G_1 w0
G_1 wI
G_1 wII
G_1 wIII
G_2 w0
G_2 wI
G_2 wII
G_2 wIII
$log(G_1(\omega/\omega_0))$ and $log(G_2(\omega/\omega_0))$
$log(\omega/\omega_0)$
1.5
1.0
0.5
0.0
−0.5
−1.0
−0.5
0.0
0.5
1.0
1.5
2.0
Oscillate faster


Elastic Storage and Viscous Loss Modulus
open weaves
log(G1(ω/ω0)) and log(G2(ω/ω0))
log(ω/ω0)
3/4
3/2
G1 w0
G1 wI
G1 wII
G1 wIII
G2 w0
G2 wI
G2 wII
G2 wIII
Oscillate faster



Solid like → Liquid like



Solid like

Liquid like

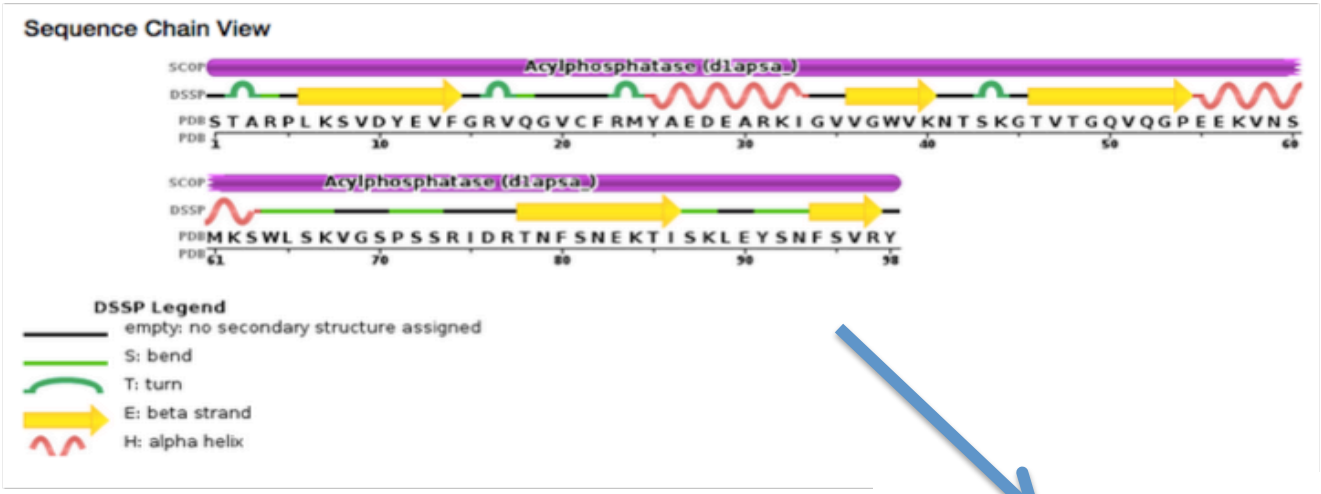
Next: What is the role of the solvent?

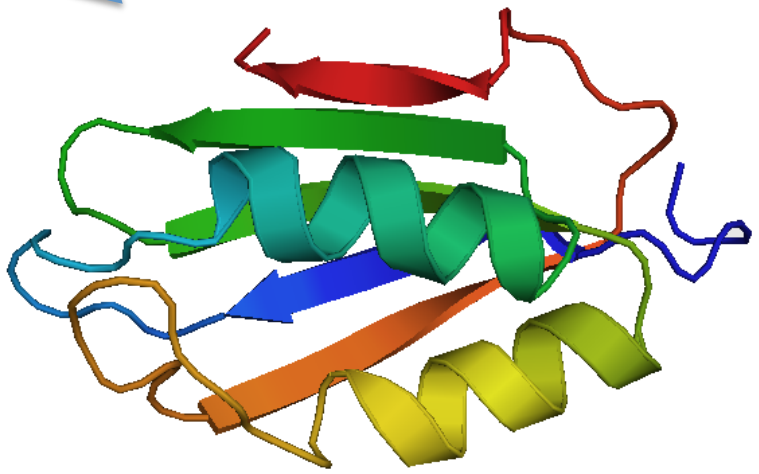
$$m\frac{dV}{dt} = -\gamma V - \nabla\Phi(X) + \sqrt{2k_BT\gamma}\frac{dB_t}{dt}$$

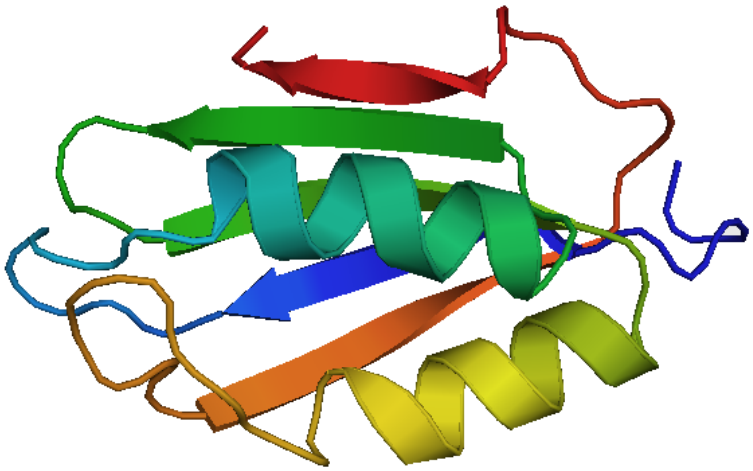
Use the Partitioned Model*

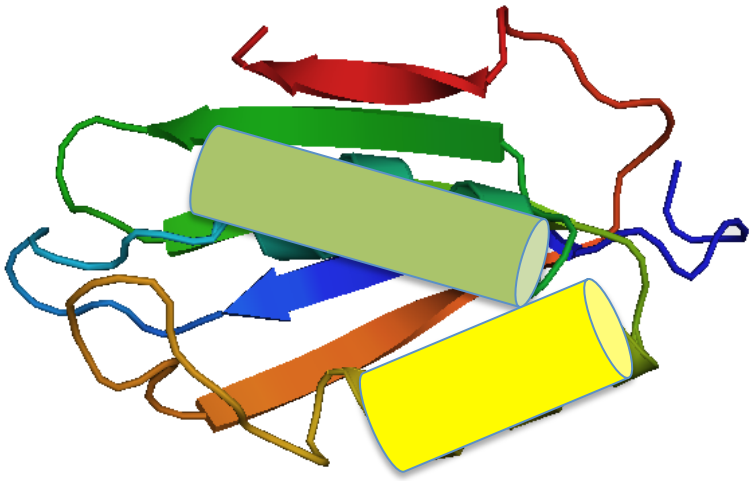
*Timalsina, A., Hou, G. and Wang, J. 2018, *J. Adv. Appl. Math.*. **3: 29**

Protein Folding Kinetics



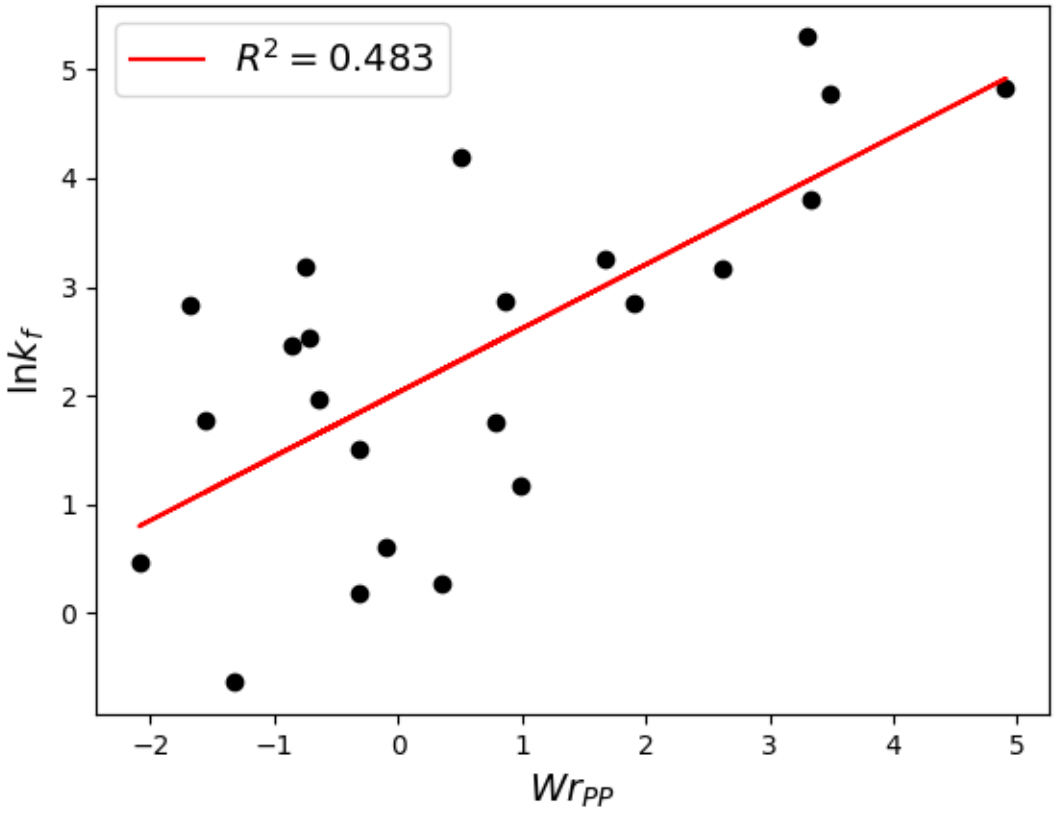






$$Wr(\mathrm{PP}) \approx Wr(\mathrm{protein}) - \sum_{\alpha-\mathrm{helices}} Wr_{\alpha-\mathrm{helix}} - \sum_{\beta-\mathrm{strands}} Wr_{\beta-\mathrm{strand}}$$

decreasing
folding rate



*Panagiotou, E. and Plaxco, K. W.2018, , (submitted)

Polymer brushes

Aim: design new material (supersoft,super-elastic)

By varying the

Number of side arms

Length of side arms

Field Theoretic Simulation

S. F. Edwards

$$e^{-\frac{1}{2}\rho v \rho} = \frac{\int dw\ e^{i\rho w - \frac{1}{2} w v^{-1} w}}{\int dw\ e^{-\frac{1}{2} w v^{-1} w}}$$

w: an “auxiliary field”

A Hubbard-Stratonovich-Edwards transformation is used to convert the many-body Problem into a statistical field theory

$$Z(n, V, T) = \int \mathcal{D}w\ \exp(-H[w])$$

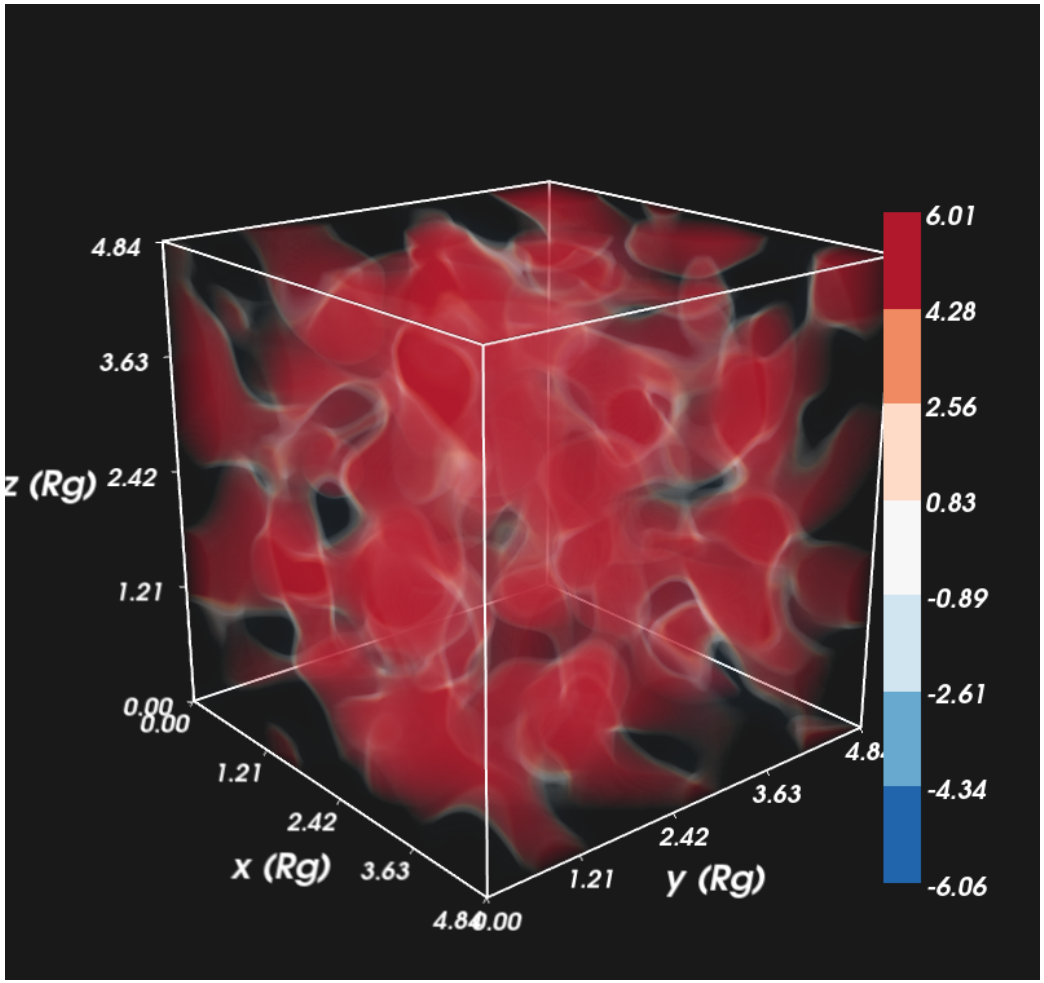
$$H[w] = \frac{1}{2v} \int d\mathbf{r}\, w^2 - n \ln Q[iw]$$

The effective hamiltonian uses the single chain partition function for a polymer in an imaginary potential field iw

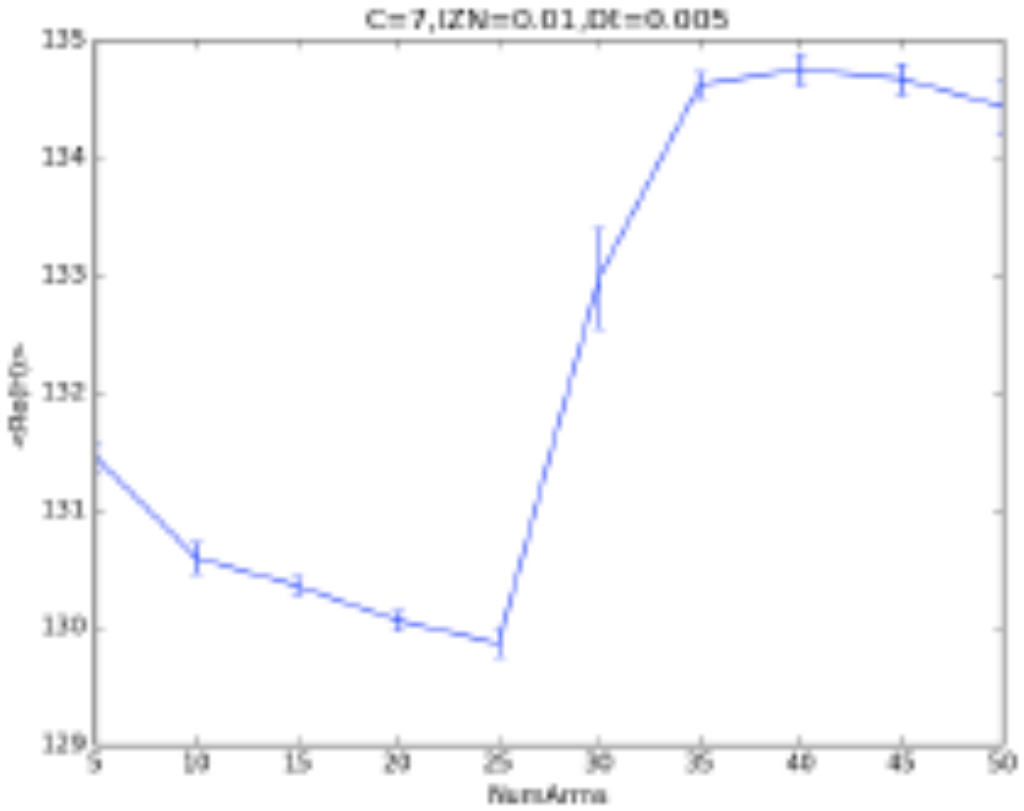
Observables can be expressed as averages of operators Q[w] with complex weight exp(-H[w])

Full stochastic sampling of the complex field theory (FTS)

An example of a field configuration



The real part of the Hamiltonian as a function of the number of arms for a fixed Length of Arms = 0.25*



*Panagiotou, E., Delaney, K. and Fredrickson, G.,.2018, in preparation

Nematic Order Parameter

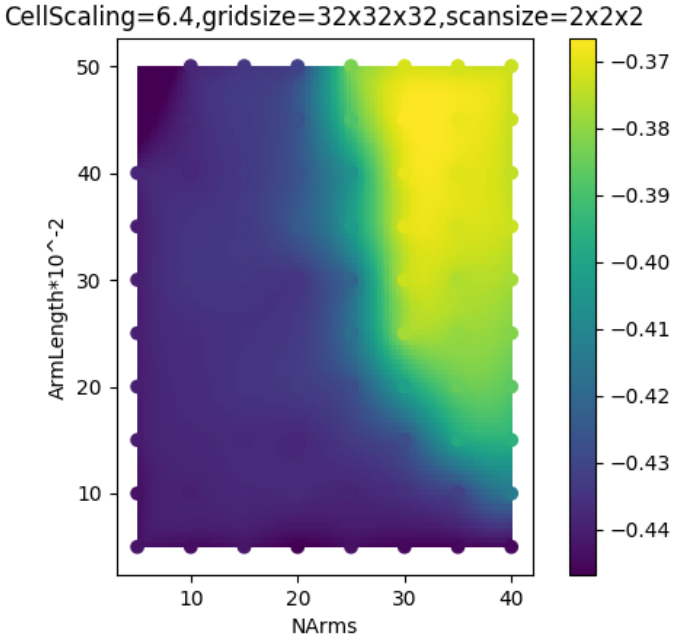
Definition 3.1. . Given a field configuration $w(x, y, z)$, we define the nematic order parameter as the maximum absolute eigenvalue of the tensor:

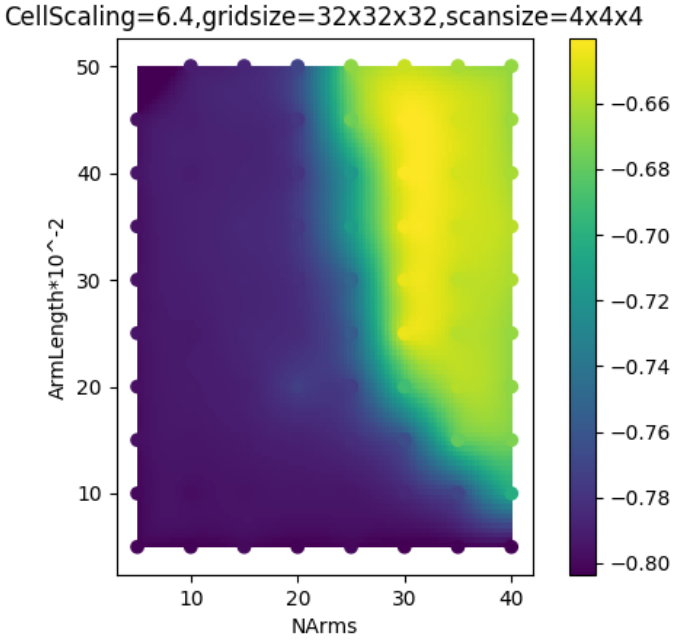
$$Q(x, y, z) = \langle \frac{\nabla w(x, y, z)}{||\nabla w(x, y, z)||} \otimes \frac{\nabla w(x, y, z)}{||\nabla w(x, y, z)||} - \frac{1}{3} I \rangle_{(x,y,z)}$$

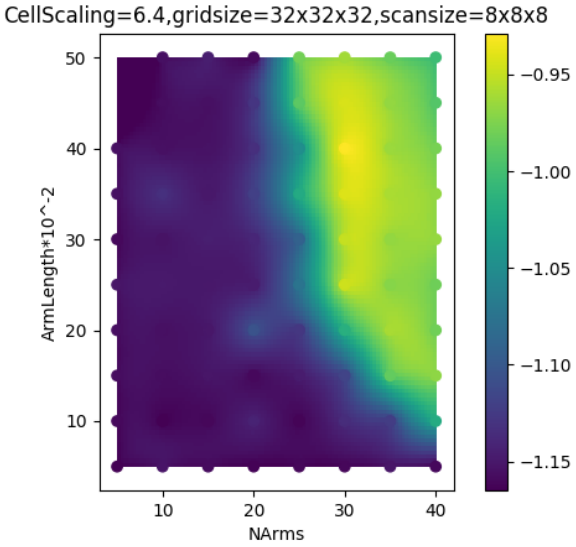
where I is the identity matrix and the average is taken over all grid points

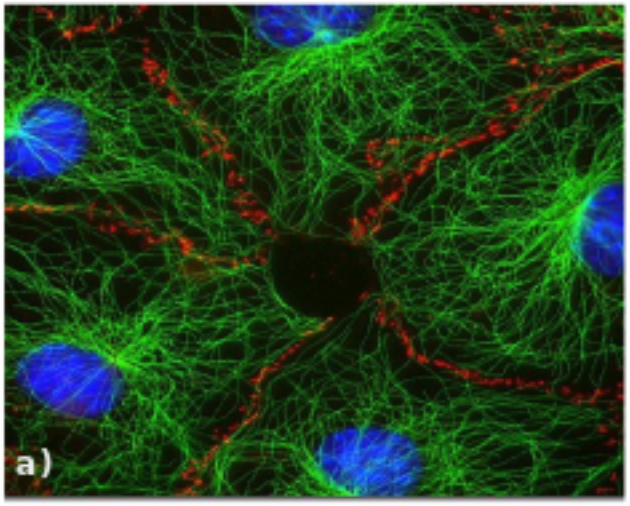
- We subdivide the domain in subsets (cubes) of volume $c_1 \times c_1 \times c_1$, which we call (i, j, k)-cubes, where (i, j, k) is the coordinate of one vertex of the cube.
- We compute $Q_{(i,j,k)}$ for the cube (i, j, k) and its maximum eigenvalue, $\lambda_{(i,j,k)}$, for $1 \leq i, j, k \leq CS - c_1$, where CS is the length of an edge of the simulation cell.
- Our proposed order parameter is the average maximum absolute eigenvalue over all subcells $\langle |\lambda_{(i,j,k)}| \rangle_{(i,j,k)}$.

Isotropic to nematic order transition





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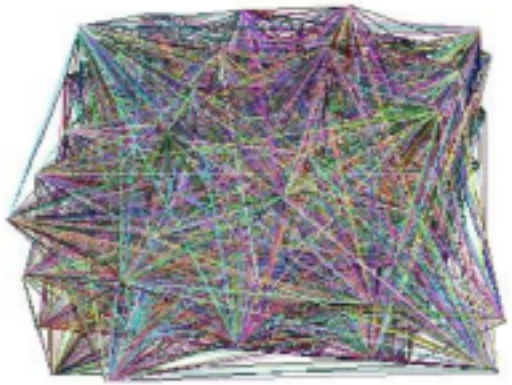
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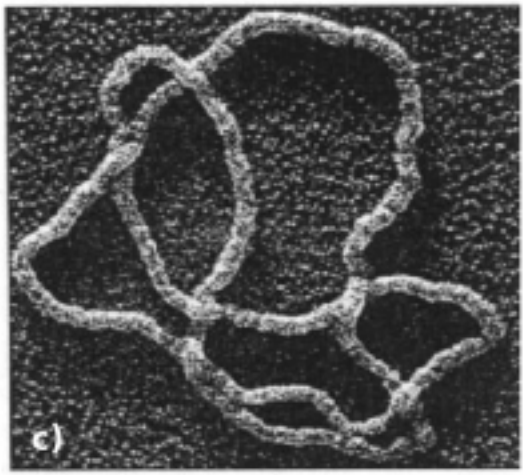
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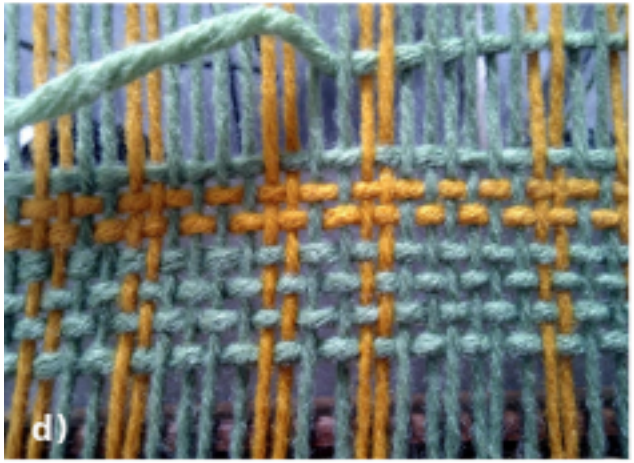
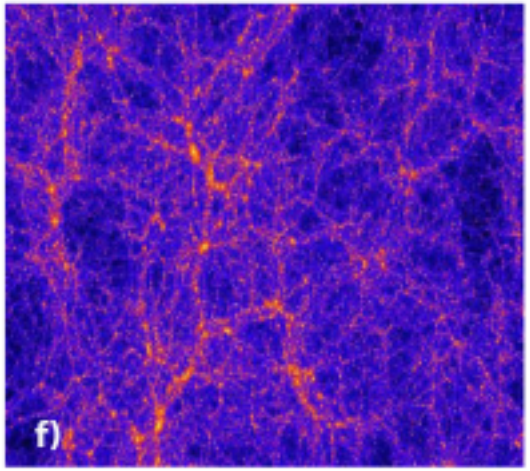

d)


e)


f)