Rheology Simulator

PASTA

(Polymer rheology Analyzer with Slip-link model of enTAnglement)

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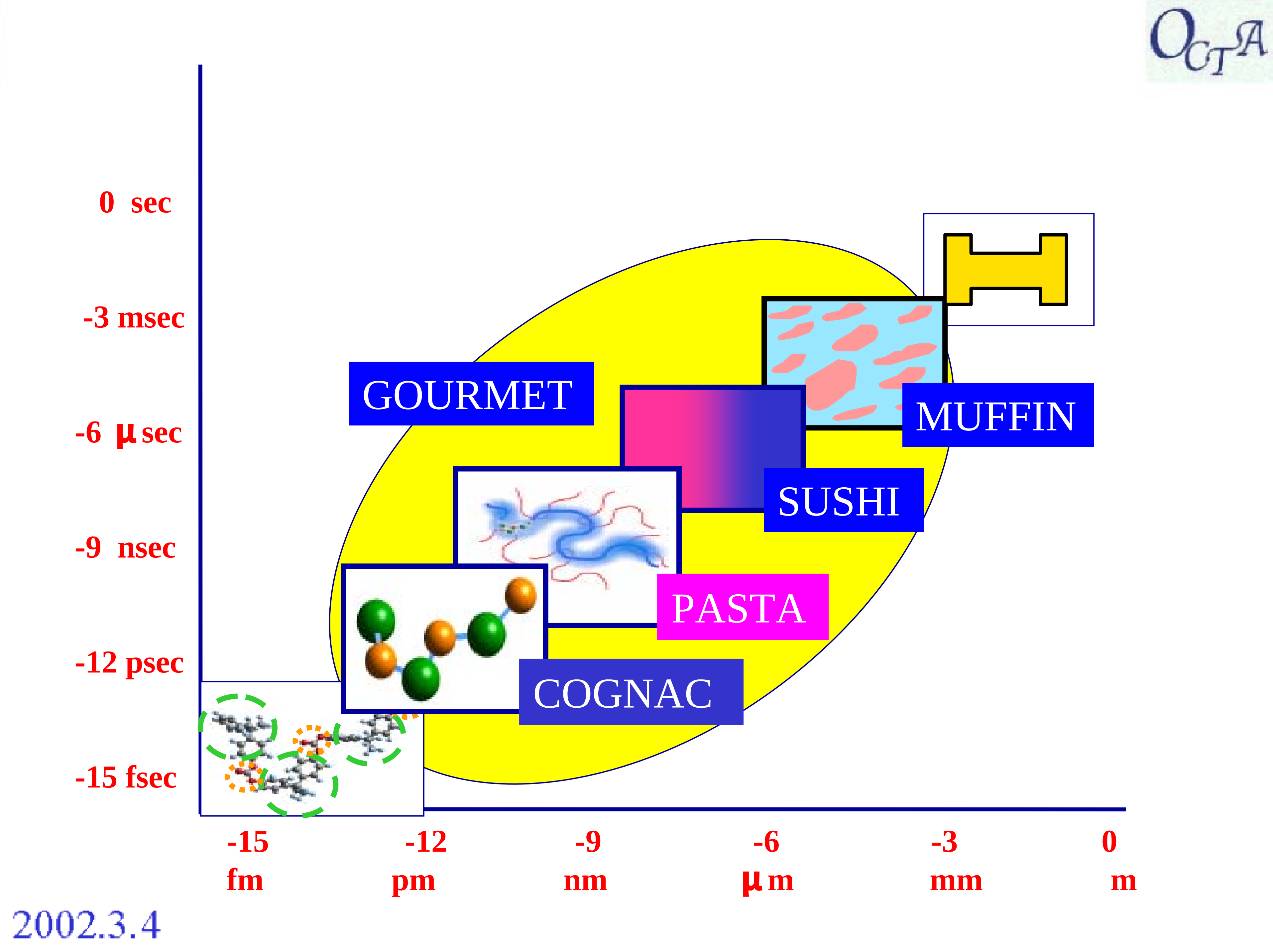
JCII, Doi Project

2002.3.4



OCTA
0 sec
-3 msec
-6 μsec
-9 nsec
-12 psec
-15 fsec
GOURMET
MUFFIN
SUSHI
PASTA
COGNAC
-15
fm
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pm
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nm
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m
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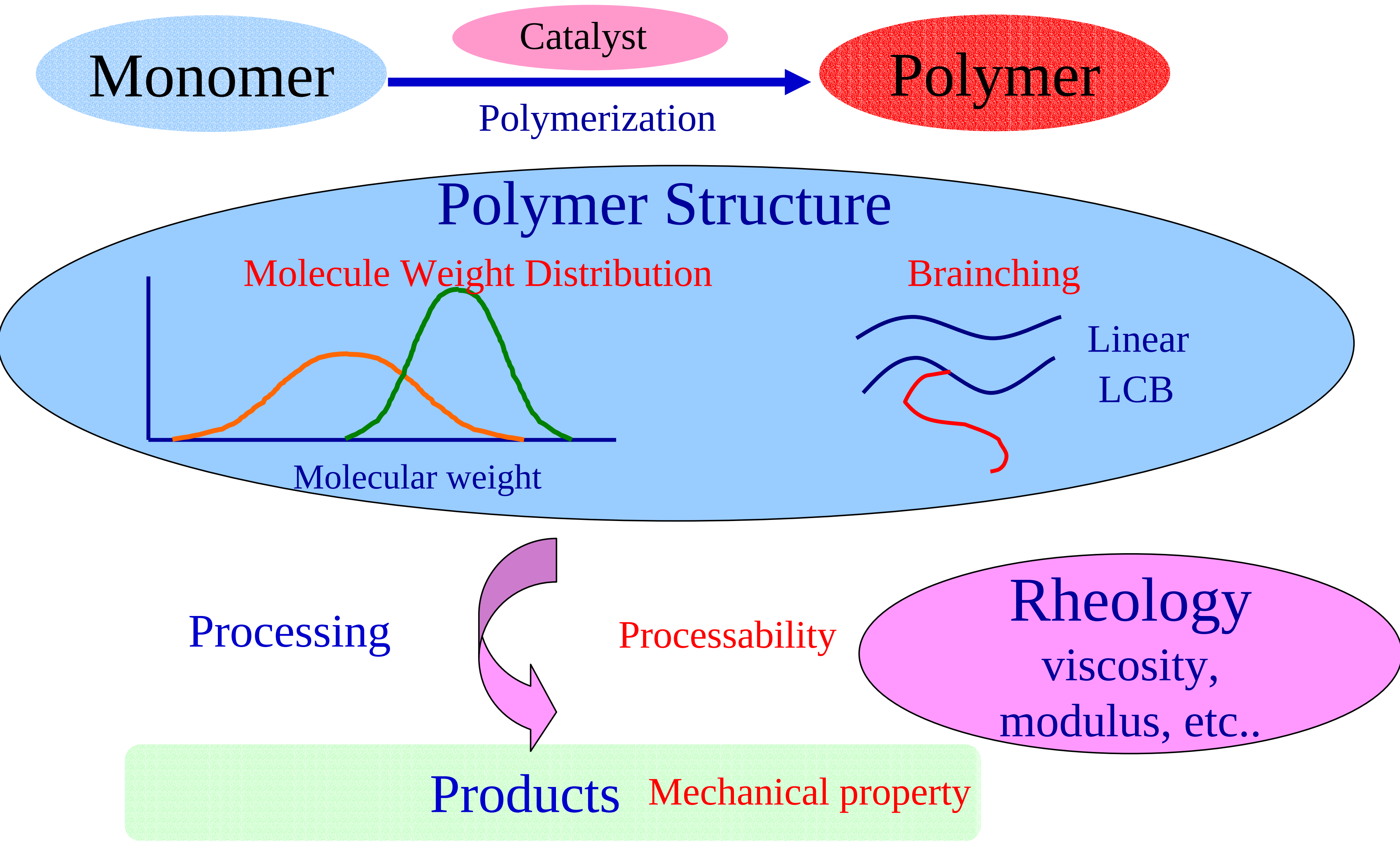
Introduction



Objectives

Prediction of the rheological properties from the knowledge of the structure of polymer

It is not feasible to simulate the rheological properties of polymer by MD simulations.

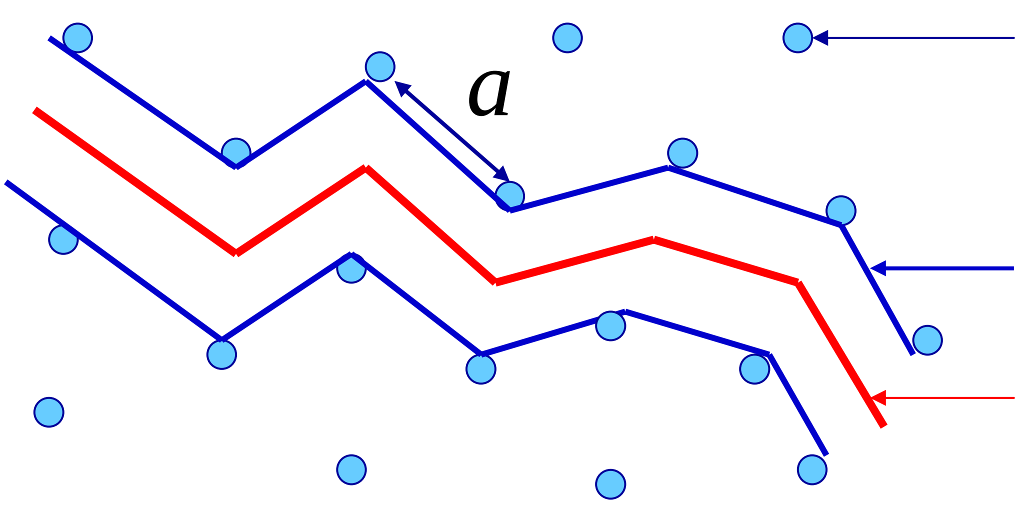
↓

coarse-grained model for polymer ← the Doi-Edwards theory(tube model)

↓

New stochastic simulation method (PASTA)

Classical tube model



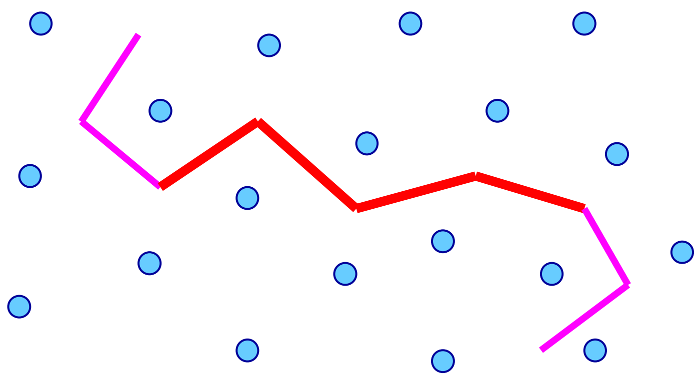
Assumption

- The length of primitive path is constant
- Obstacles are permanent

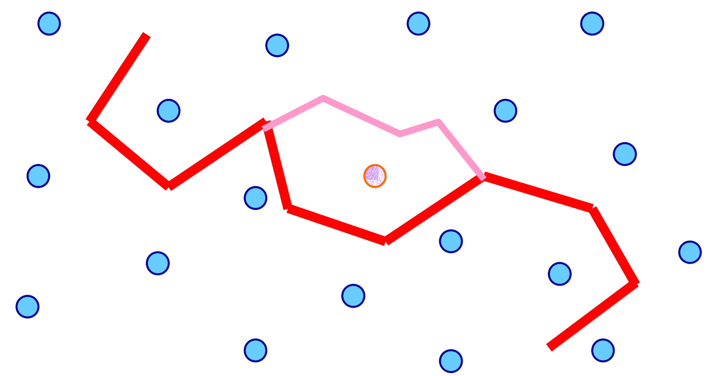
Reptation is the only mechanism of the relaxation

Important Extensions of the tube model -1-

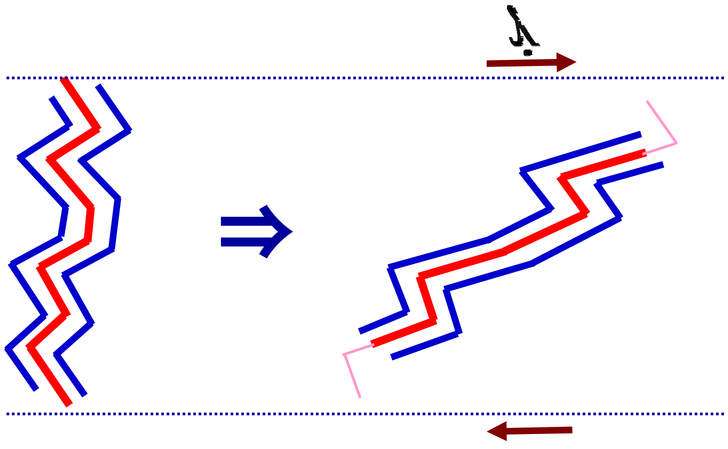
Contour Length Fluctuation



Constraint Release



Convective Constraint Release (CCR)



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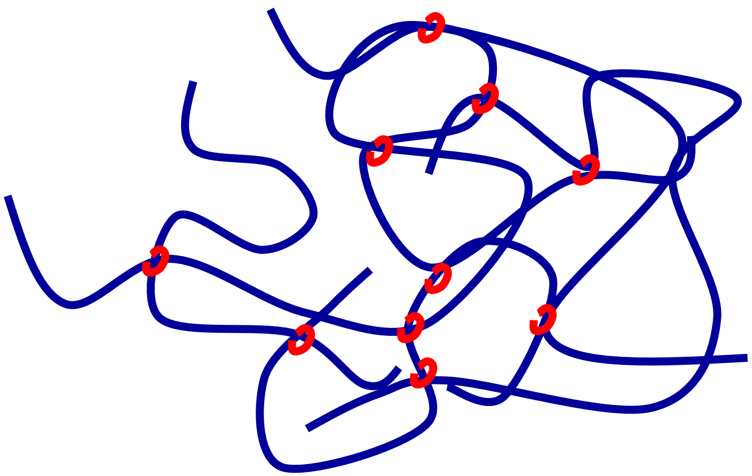
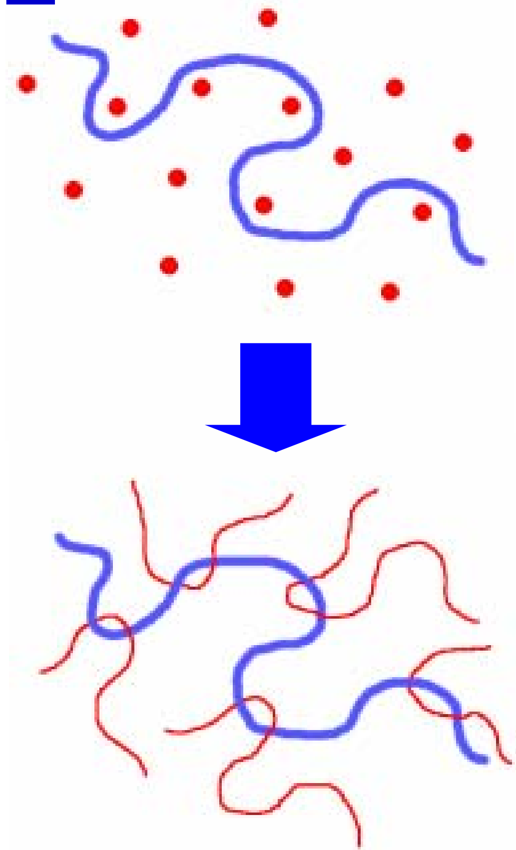
Important Extensions of the tube model -2-

Slip links



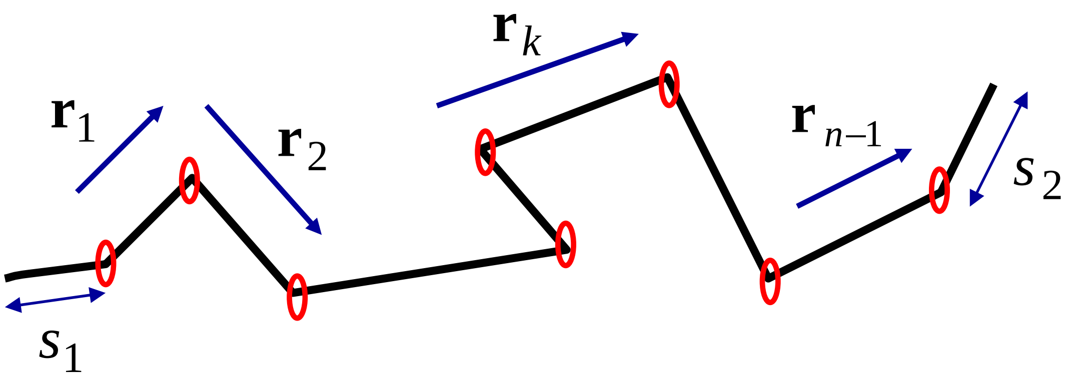


(1) Each chain obeys the reptation dynamics.

(2) Each slip link constrains a pair of chains, and disappears when eithe one of the chain moves away from the slip link.

Simulation method

1) Each polymer chain is modeled by a primitive path and slip links along it.



Subchain vector $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_{n-1}$

Length of the tube $L_t = \sum_k |\mathbf{r}_k|$

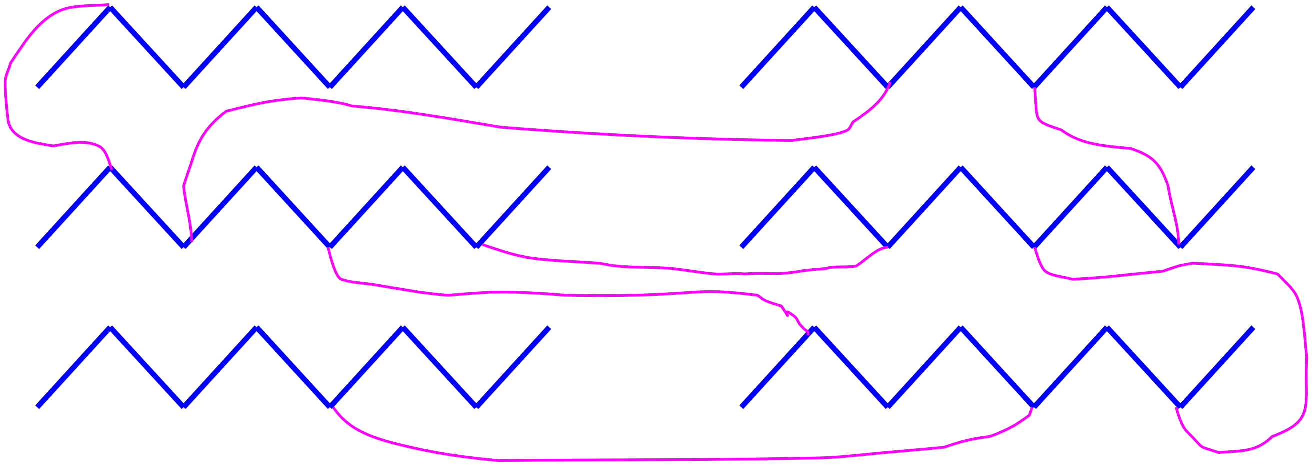
Length of the tail at each end s_1, s_2

Length of the primitive path $L = L_t + s_1 + s_2$

Simulation method

2) A collection of many chains (ex. 10^2〜10^4)

3) The interaction among the chains is taken into account through the "pairing" of the slip links



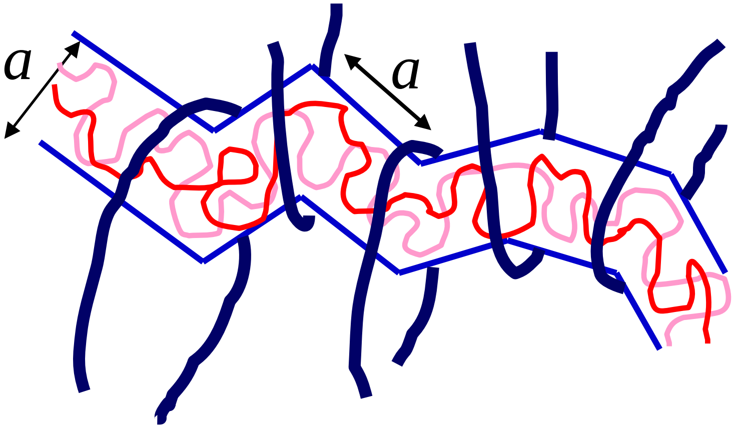
Pairing of the slip links

(Each slip link has its partner, but only representative pairs are shown)

Simulation method

4 operations in each time step

1. Affine deformation of the tubes
2. Contour length fluctuation
3. Reptation
4. Constraint release / creation



Unit of length a

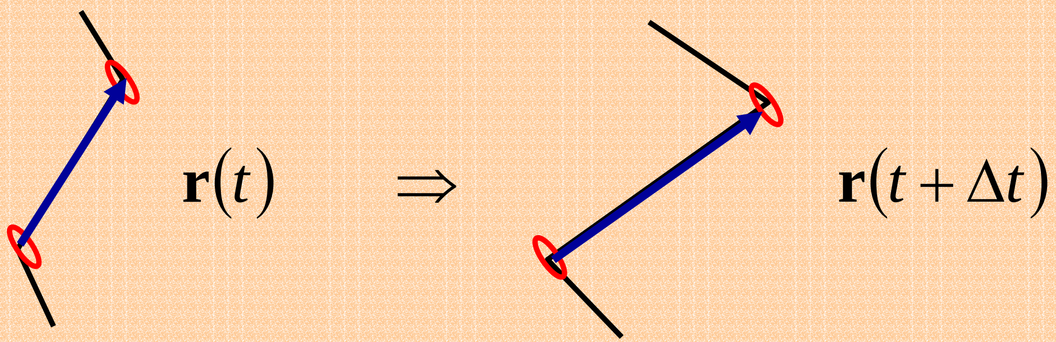
Unit of time $\tau_e = \tau_R(M = M_e)$

M_e : Entanglement molecular weight

Operation-1

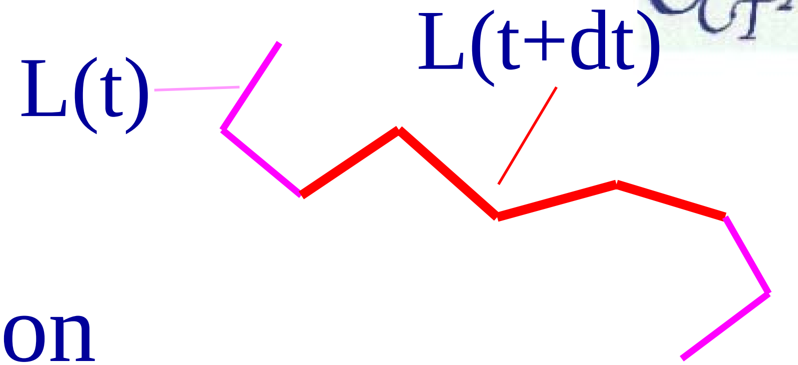
Affine deformation of the primitive path

Each slip link is moved according the macroscopic flow of the sample.



$$x(t+\Delta t) = x(t) + \dot{\gamma}\Delta t \cdot y(t)$$

$$y(t+\Delta t) = y(t)$$



Operation-2

Contour length fluctuation

$$\frac{dL}{dt} = -\frac{1}{\tau_R}\left(L(t) - L_{eq}\right) + \dot{L}_{affine} + g(t)$$

Variation rate of *L* by the affine deformation

Gaussian random force

$L_{eq} = Za$	Equilibrium length
$\tau_R = \tau_e Z^2$	Rouse relaxation time
$Z \equiv M / M_e$	Average number of slip links

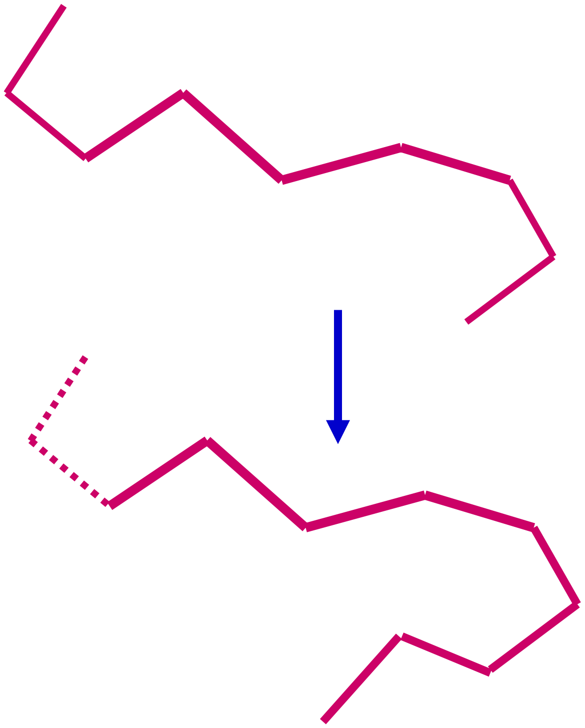
Operation-3

Reptation

The center of mass of each primitive path is randomly moved by Δs along the path with diffusion constant D_c

$$\left\langle \Delta s^2 \right\rangle = 2 D_c \Delta t$$

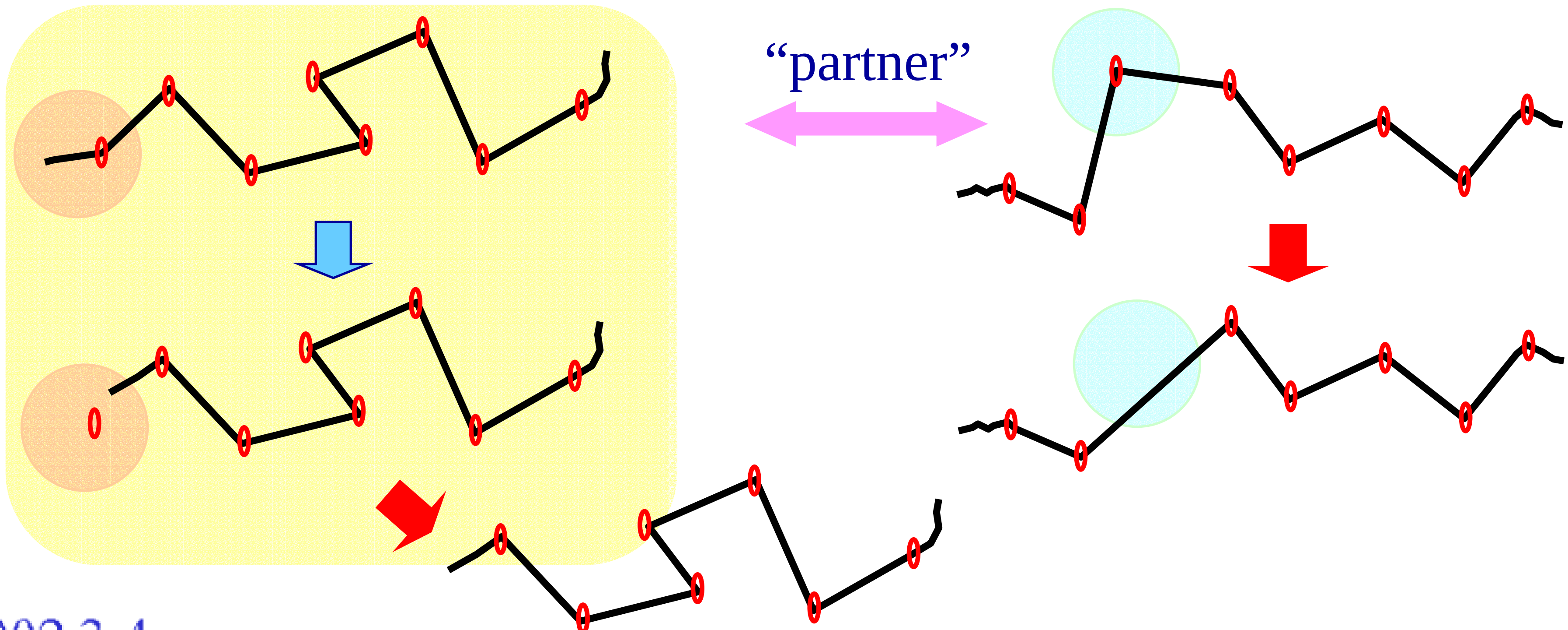
$$D_c \propto \frac{1}{Z}$$



Operation-4

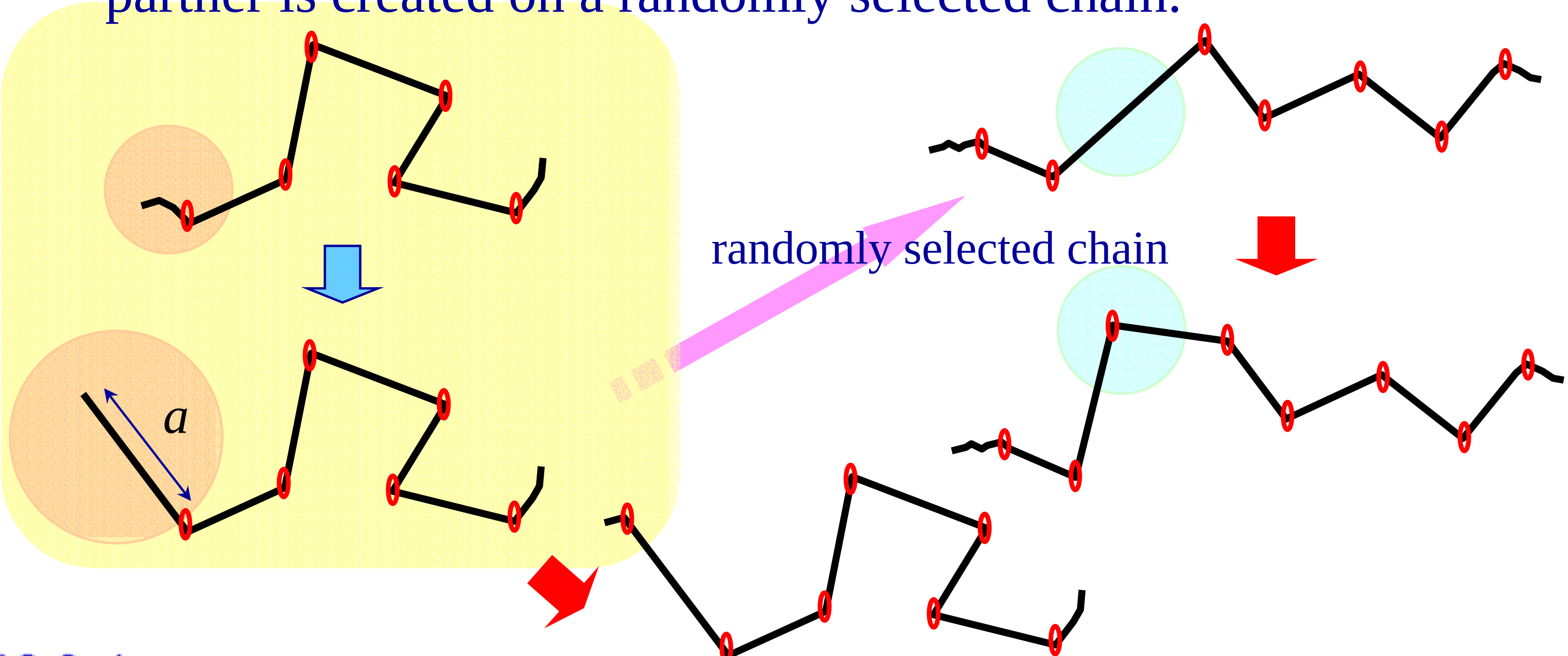
Constraint renewal

If a end of a primitive path passes through the last slip link on the chain, the slip link and its partner are destroyed.



Operation-4
Constraint renewal

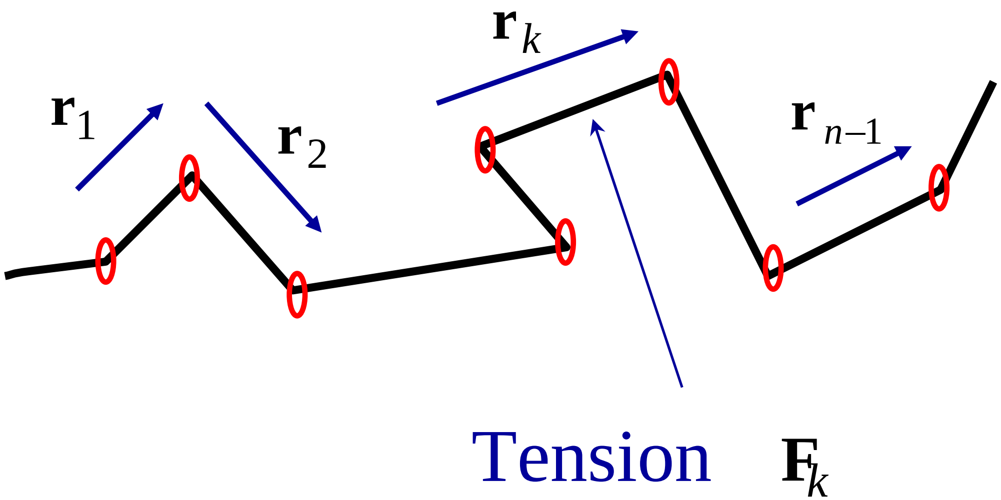
If the length of a tail at the end of the primitive path becomes longer than a , a new slip link is created at the end and its partner is created on a randomly selected chain.



Simulation method

Calculation of the Stress

$$\sigma_{\alpha\beta} = -\sum_k F_{k\alpha} r_{k\beta}$$



$$\mathbf{F}_k = F \frac{\mathbf{r}_k}{r_k}$$

$$F = -\frac{dU(L)}{dL} = -\frac{3k_BT}{a}\frac{L}{L_{eq}}$$

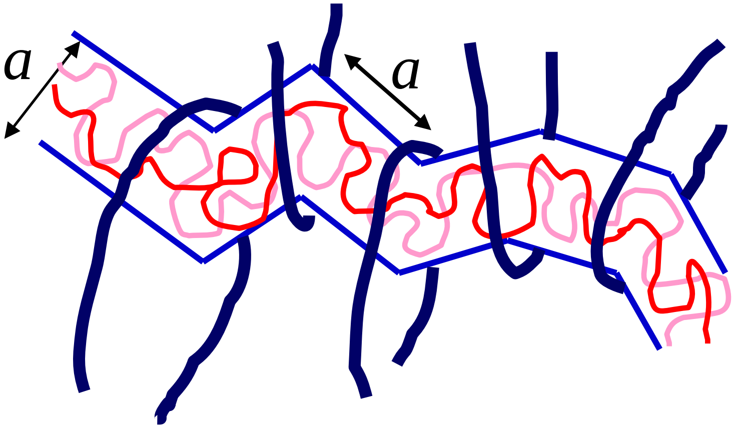
$$U(L) = \frac{3k_BT}{2aL_{eq}}\left(L - L_{eq}\right)^2$$

$$\sigma_{\alpha\beta} = \frac{3k_BT}{Za^2}\sum_k L \frac{r_{k\alpha} r_{k\beta}}{r_k}$$

Simulation method

4 operations in each time step

1. Affine deformation of the tubes
2. Contour length fluctuation
3. Reptation
4. Constraint release / creation

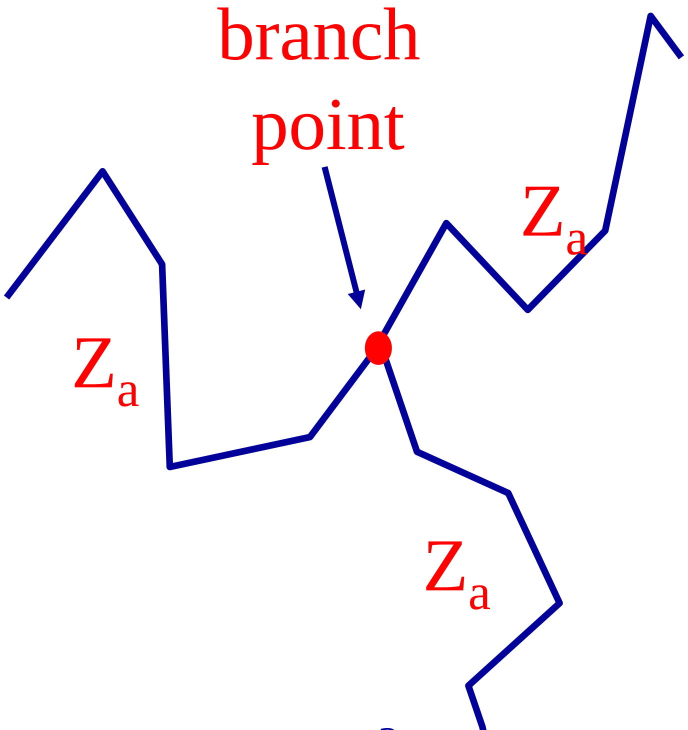


Unit of length a

Unit of time $\tau_e = \tau_R(M = M_e)$

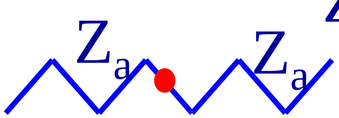
M_e : Entanglement molecular weight

Star Polymer



linear $\tau_R = \tau_e Z^2$

$Z_a = 1/2Z$



star $\tau_R = \tau_e (2Z_a)^2$

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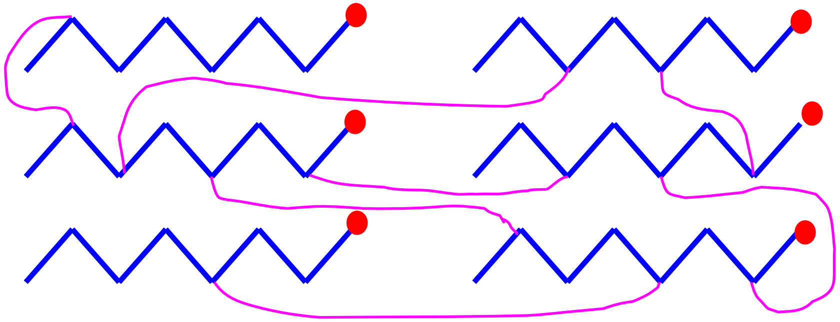

3 operations in each time step

1\. Affine deformation of the tubes

2\. Contour length fluctuation

~~3. Reptation~~

3\. Constraint release / creation

FUNCTION of PASTA

Target Sample

- linear polymer
  - monodisperse
  - polydisperse
- star polymer
  - monodisperse
  - polydisperse
- linear/star mixture

Flow type

- steady flow
- step strain
- noflow

→thermalization, stress relaxation

Deformation type

- shear
- uniaxial elongation
- biaxial elongation
- planar elongation

Simulation results

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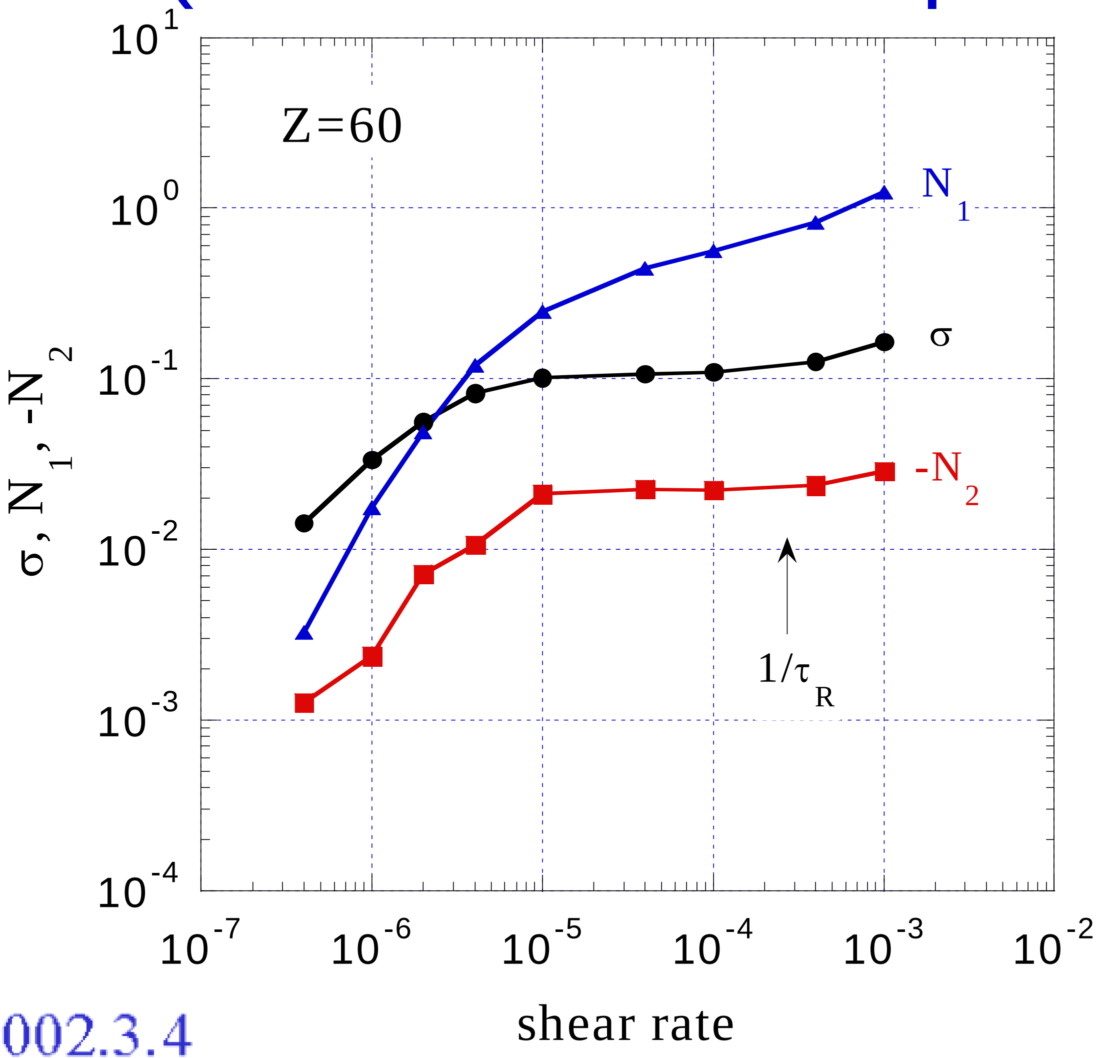
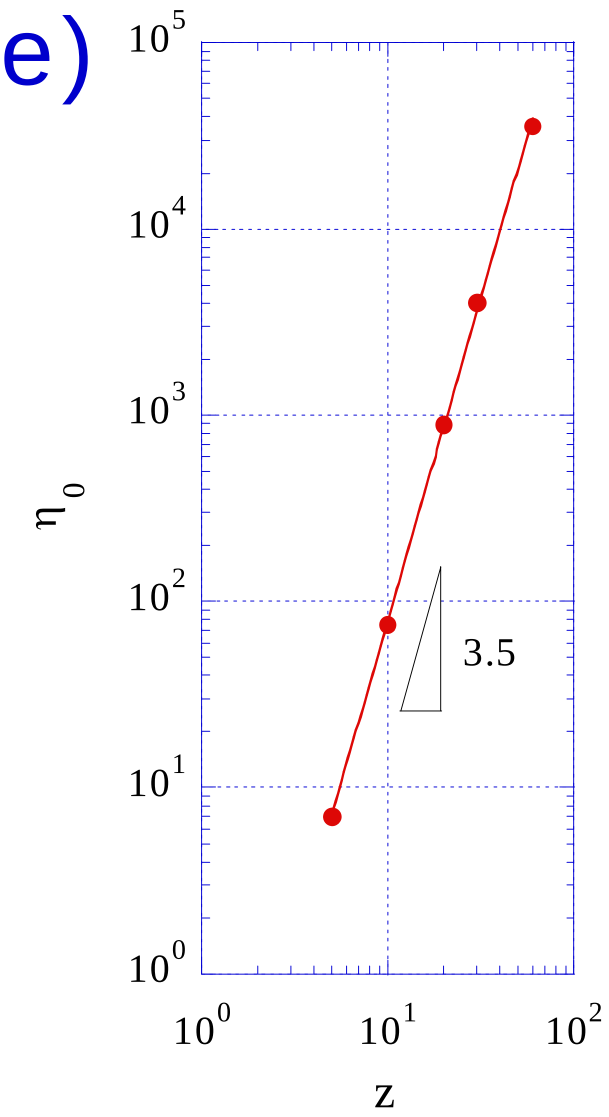
Steady shear flow (z=60 monodisperse)





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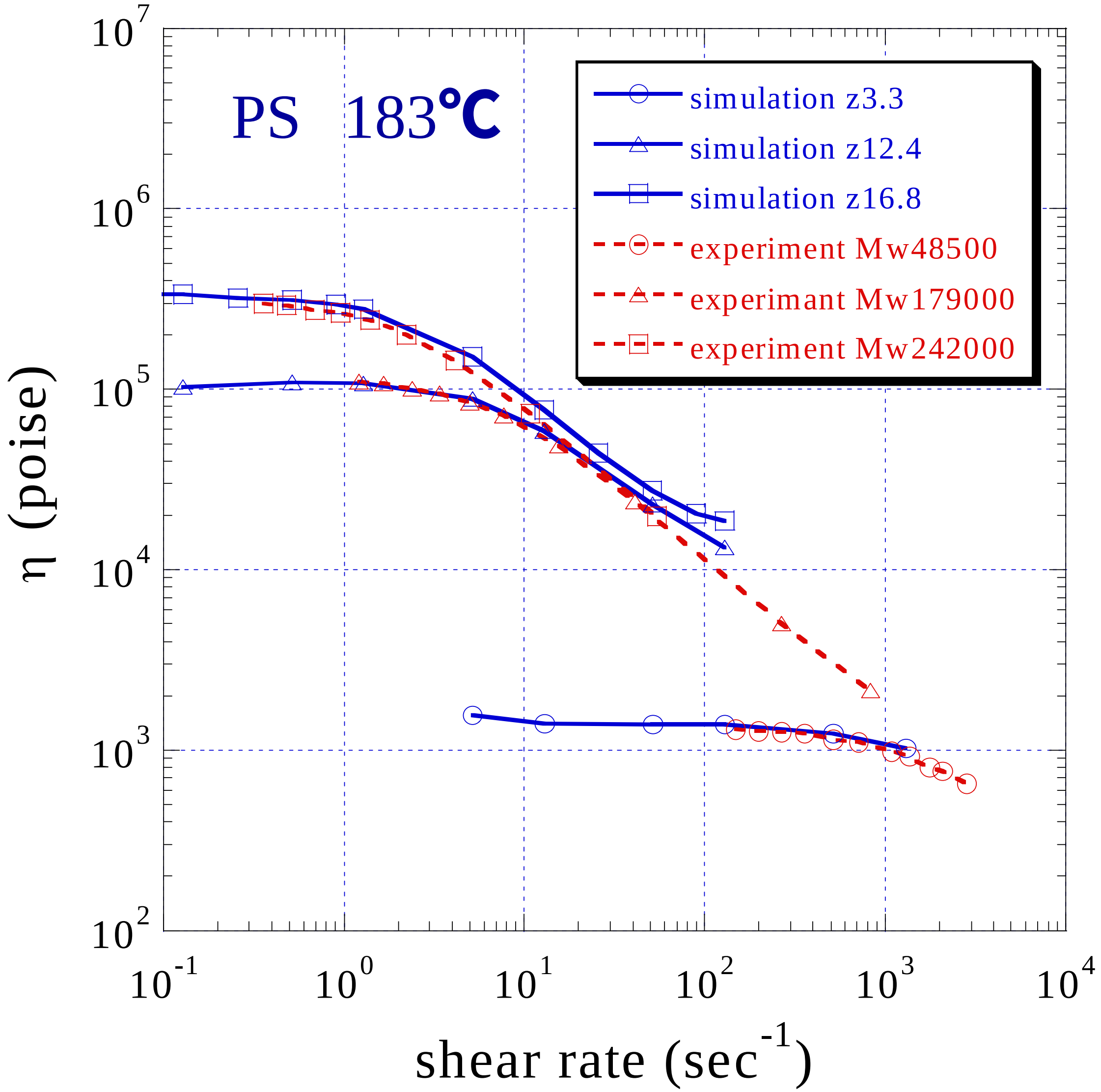
Steady shear viscosity Monodisperse Polystyrene

Vertical shift: $(15/4)\, G_N^0 \tau_e$
Horizontal shift: τ_e^{-1}

$M_e = 14400$
$G_N^0 = 2 \times 10^6$ dyn/cm^2



R. A. Stratton,
J. Colloid Interfac. Sci.,
22, 517 (1966)

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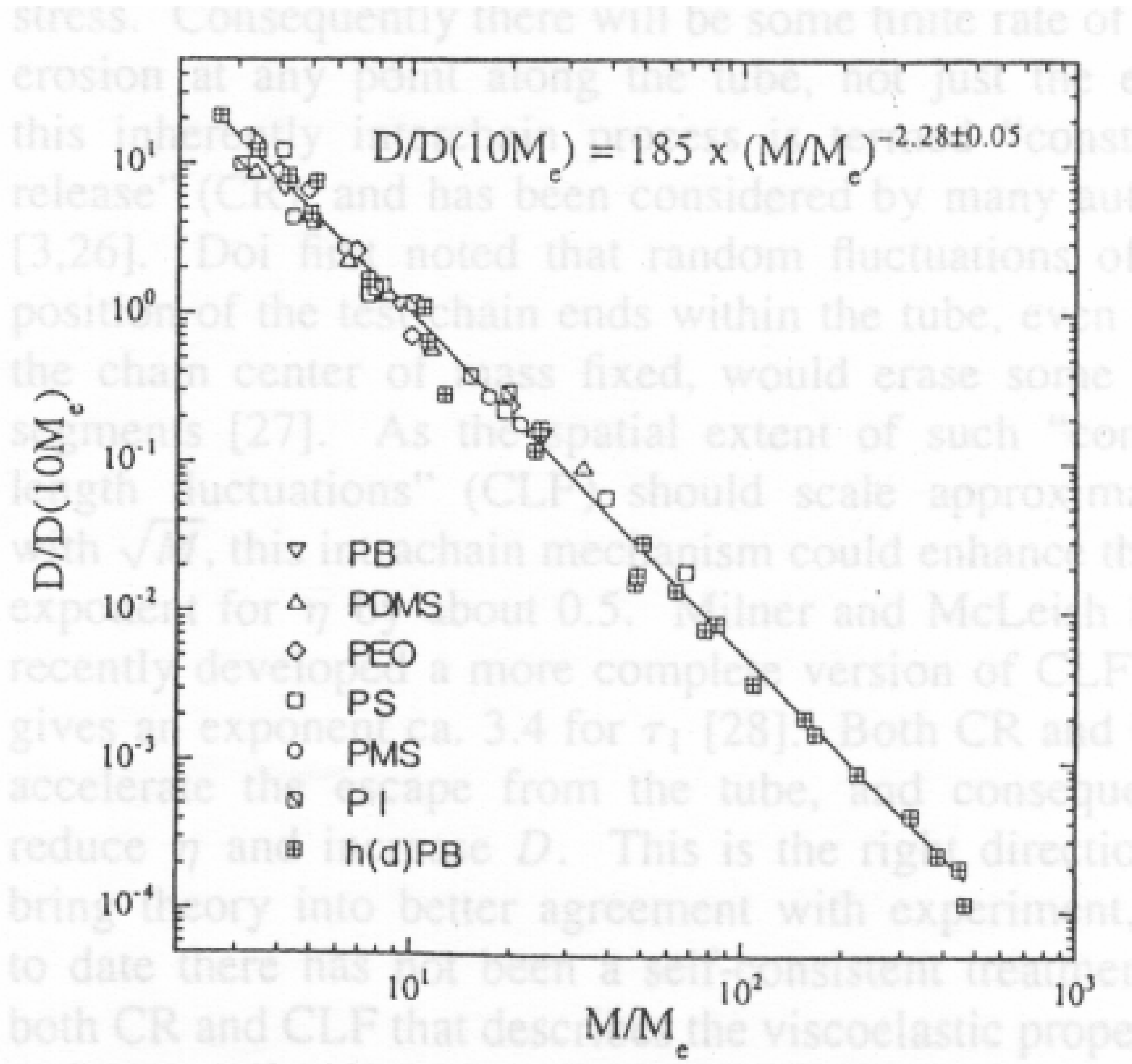
Self diffusion coefficient



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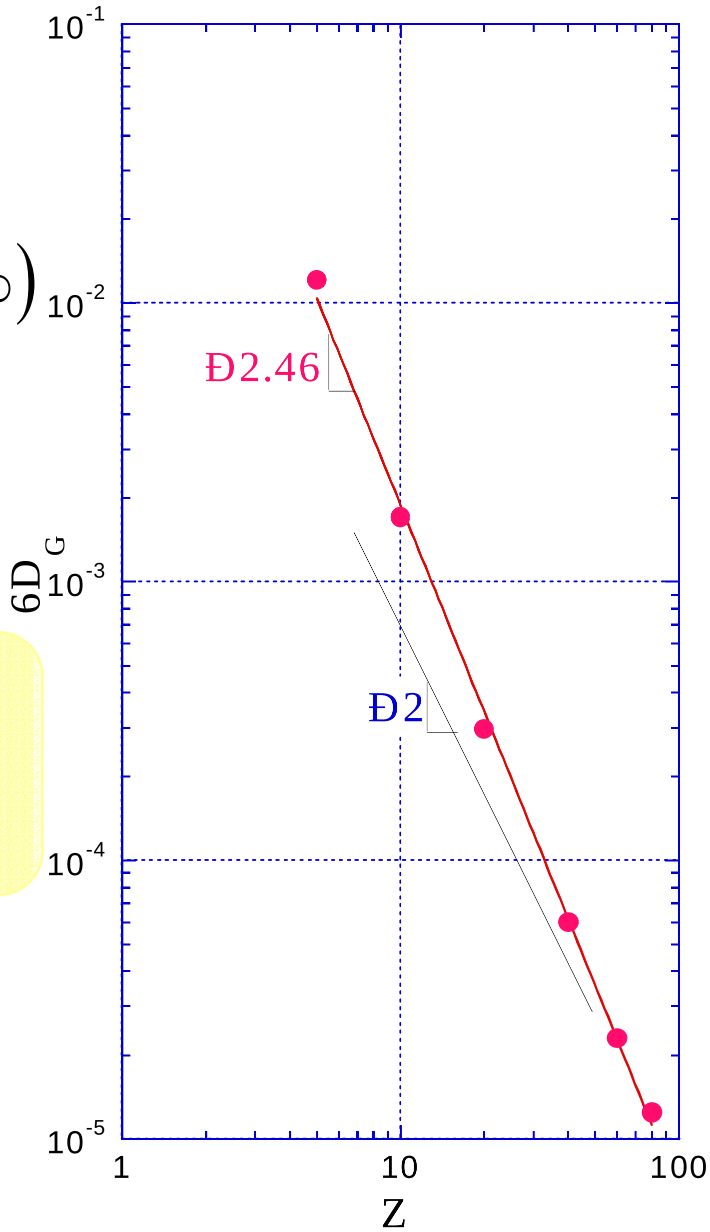
T.P. Lodge, Phys. Rev. Lett. **83**, 3218 (1999)

Self diffusion coefficient (monodisperse)

$$\left\langle \left(\mathbf{R}_G(t) - \mathbf{R}_G(0) \right)^2 \right\rangle = 6 D_G t \quad \left(t \to \infty \right)$$

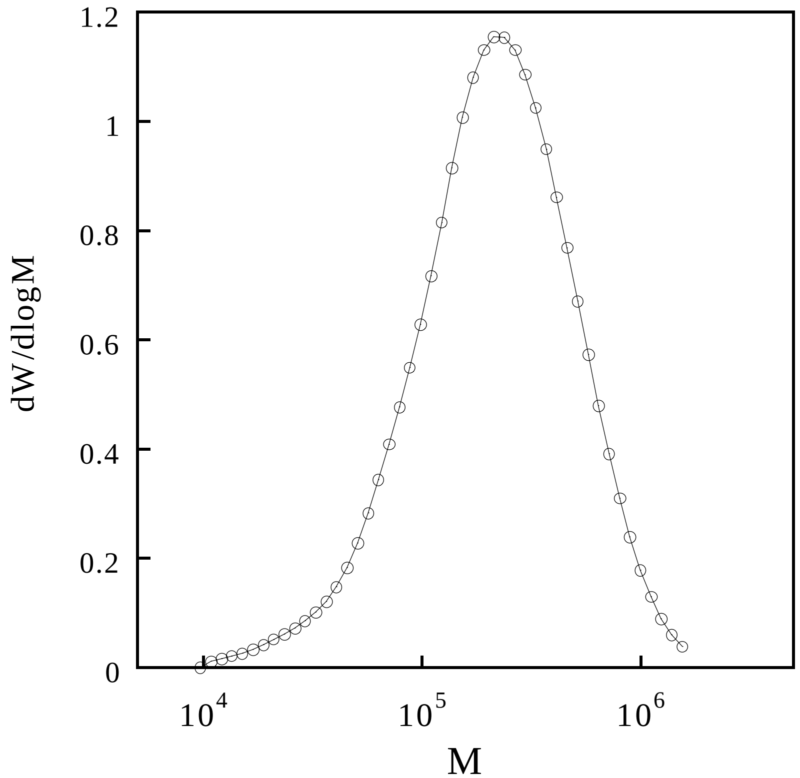
$10 < Z < 80$

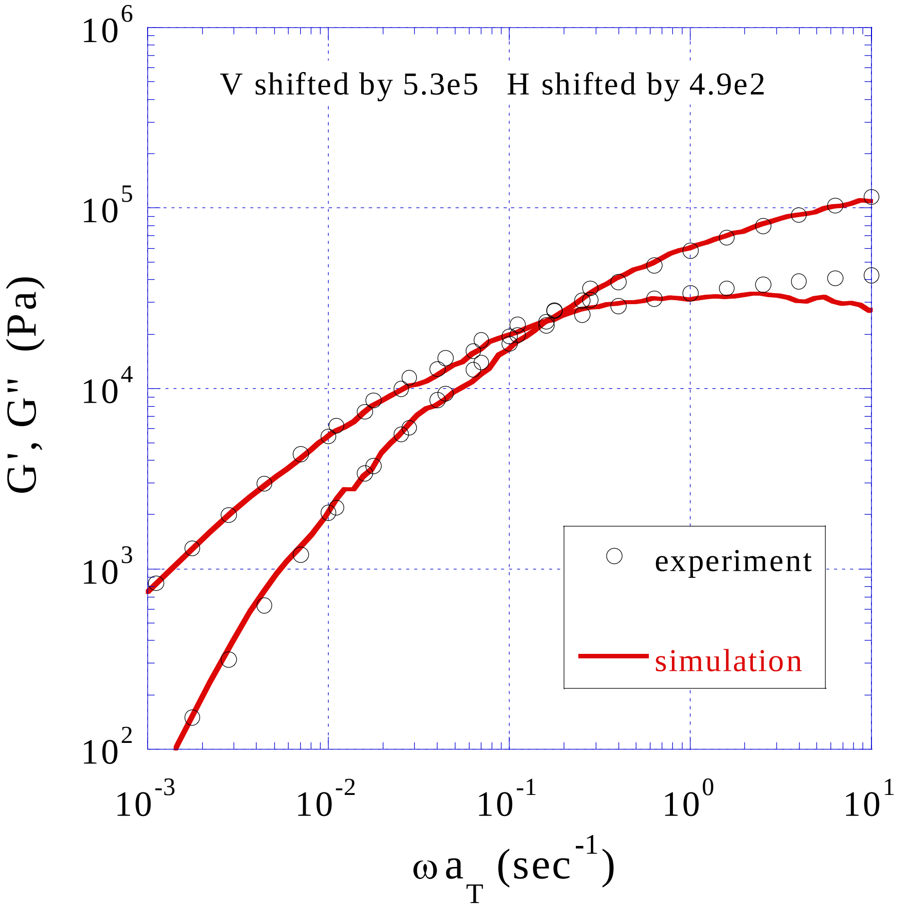
$$D_G \propto Z^{-2.4-2.5}$$
$$\left(c.f. \quad \eta_0 \propto Z^{-3.5} \right)$$



Elongational viscosity
Polydisperse Polystyrene

$Mw = 2.85 \times 10^5$
$Mw/Mn = 2.0$





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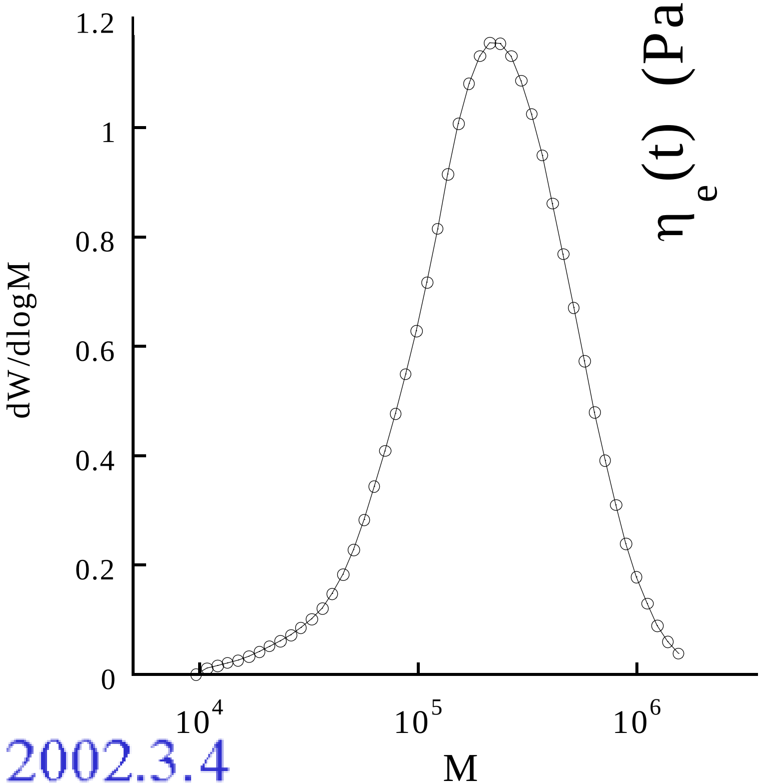
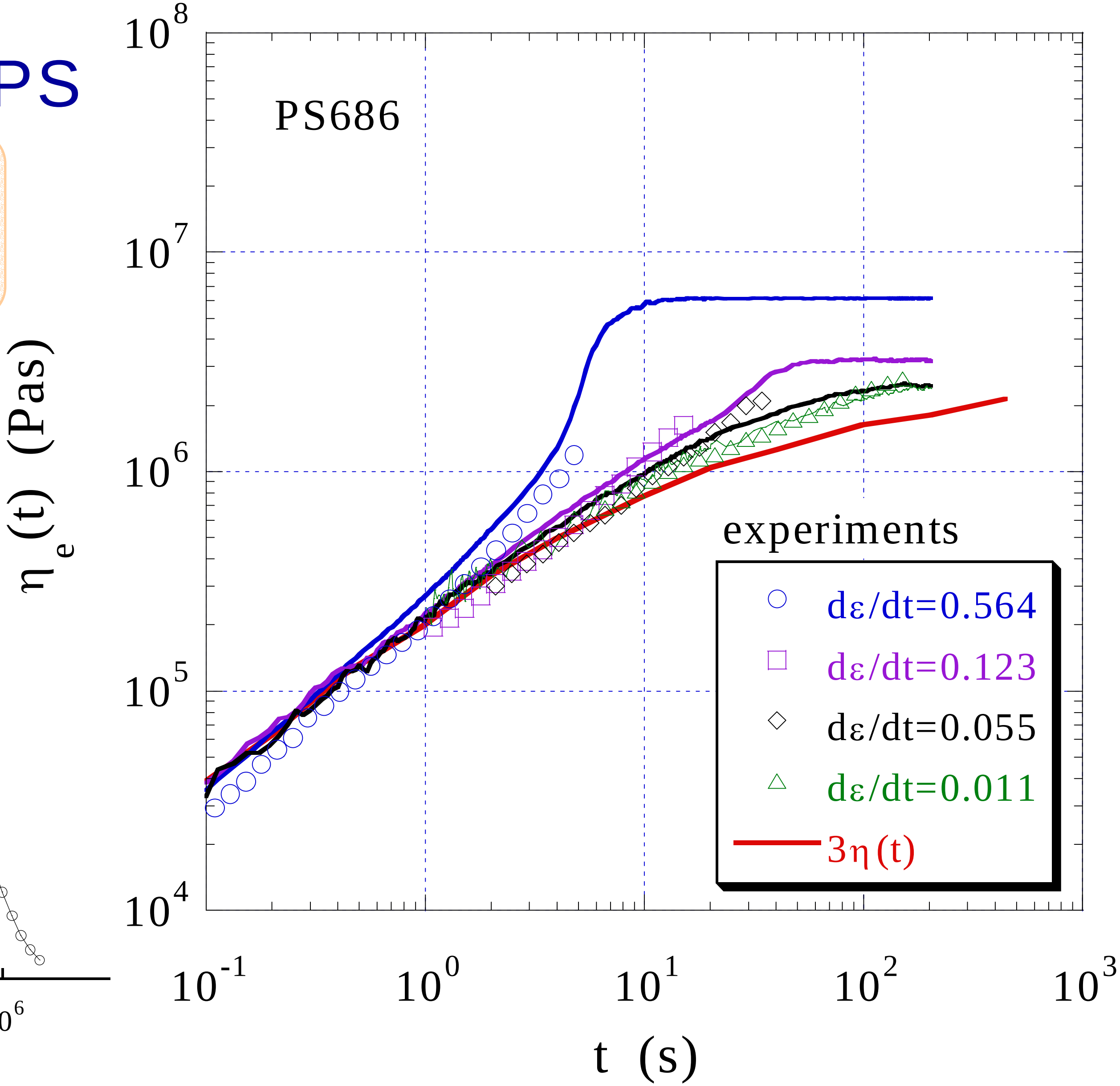
Elongational viscosity

Polydisperse PS

Mw =2.85 × 10^5
Mw/Mn =2.0





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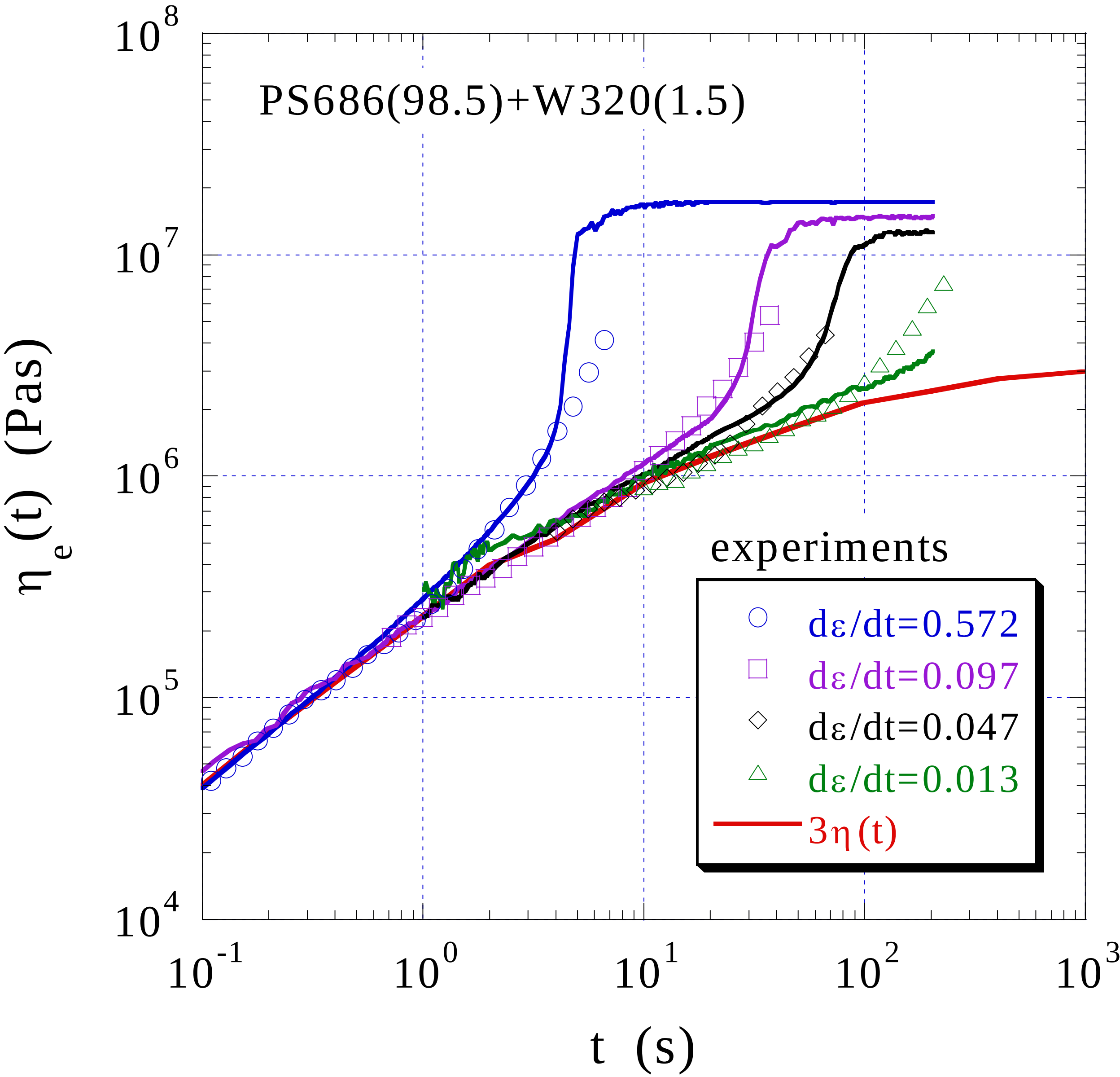
Elongational viscosity

Polydisperse PS

Mw =2.85 × 10^5
Mw/Mn =2.0

+

HMW-PS
Mw =3.2 × 10^6
1.5 %



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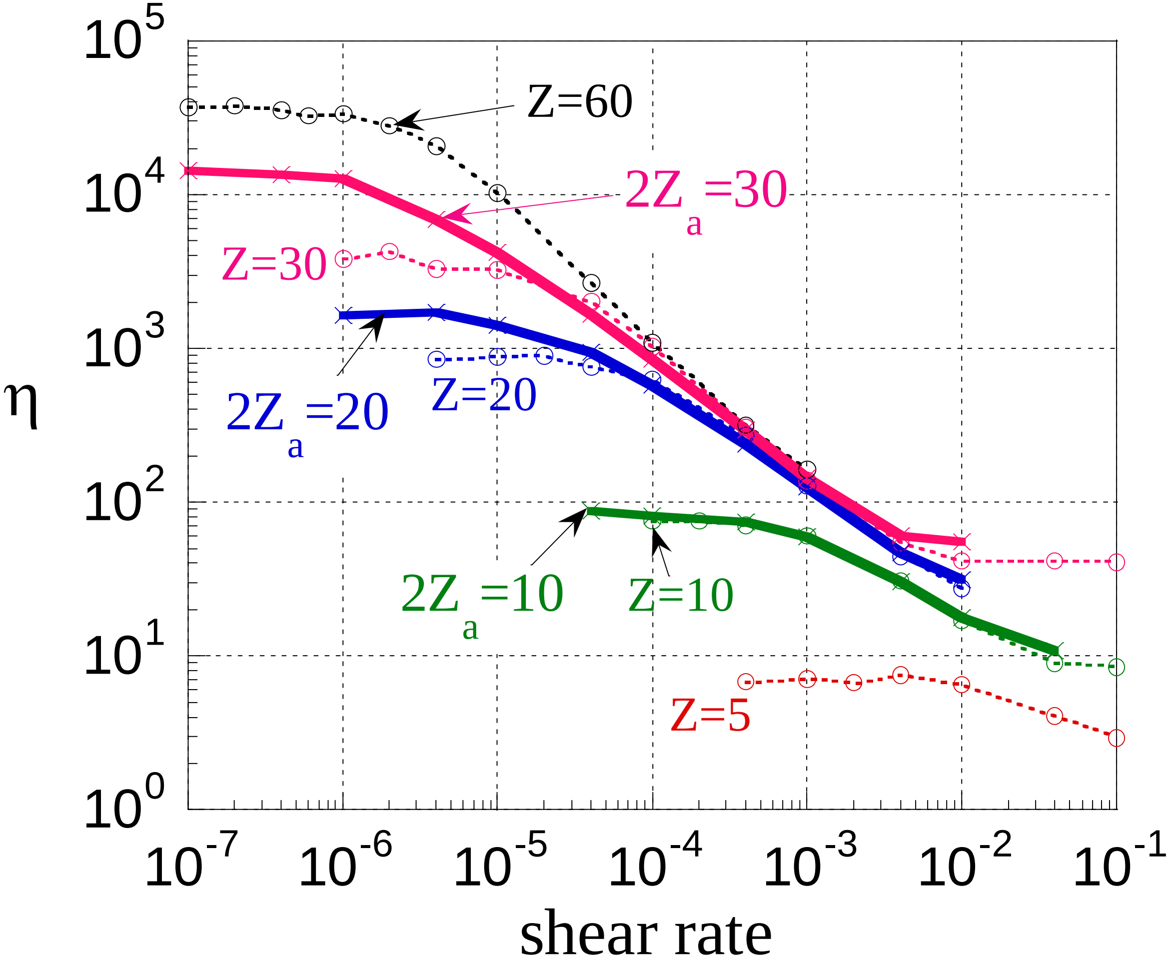
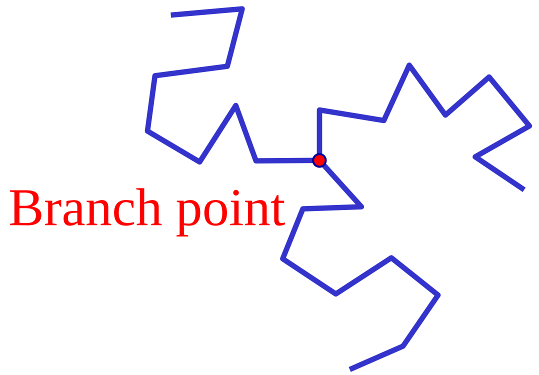
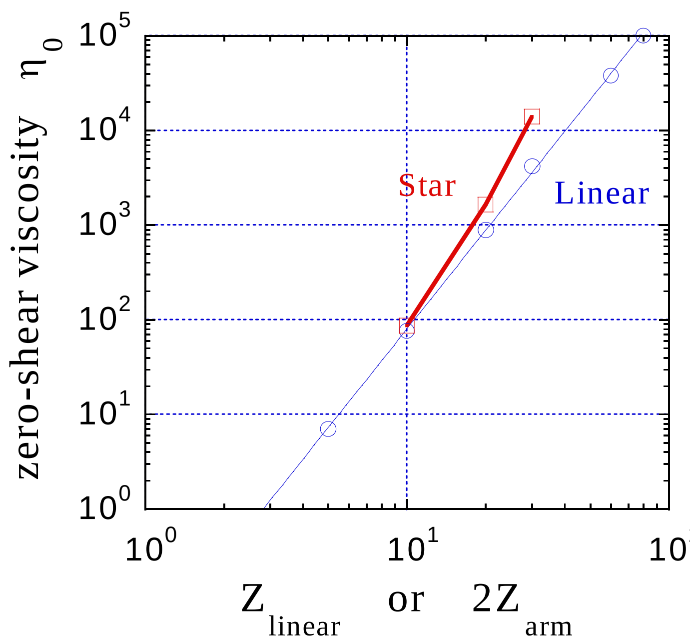
Shear viscosity of star polymer







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PASTA on GOURMET

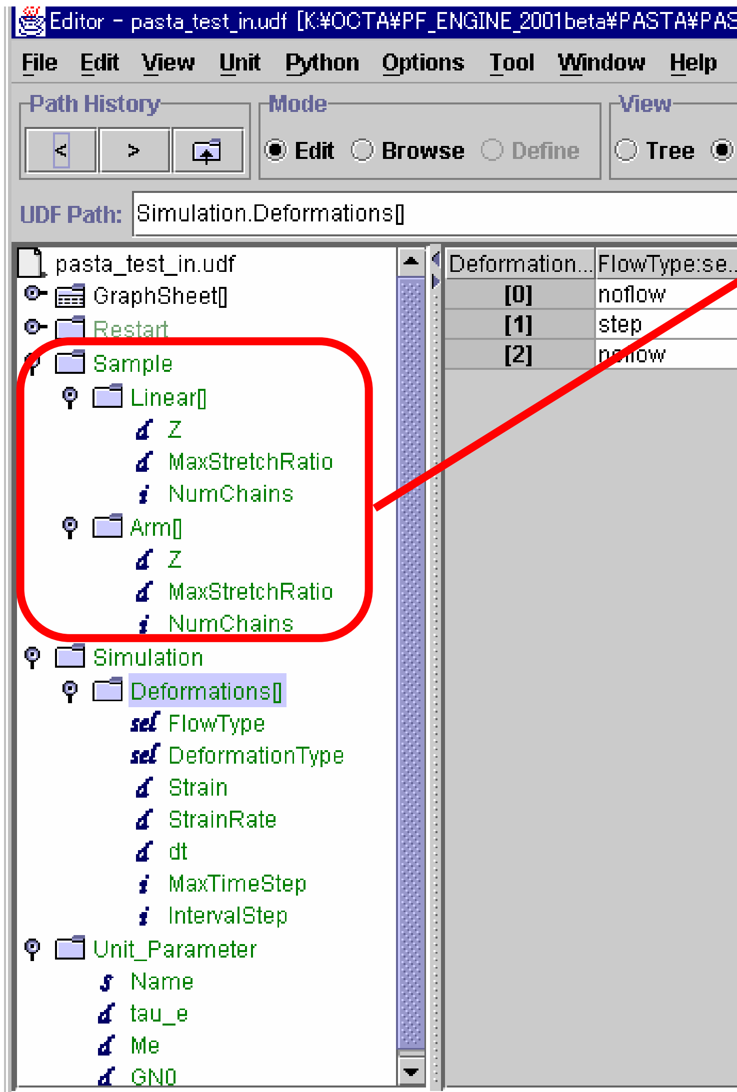
Usage

Step1. Creating inputUDF of PASTA

Step2. Running PASTA

Step3. Analysis of outputUDF

Editing InputUDF of PASTA on GOURMET



Sample:

Chain type: Linear or Arm

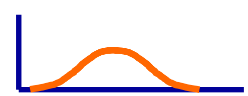
Zi (=Mi/Me :Average number of slip links)

Ni (Number of the i-th Chain)

λ_{max} (Max Stretch Ratio)

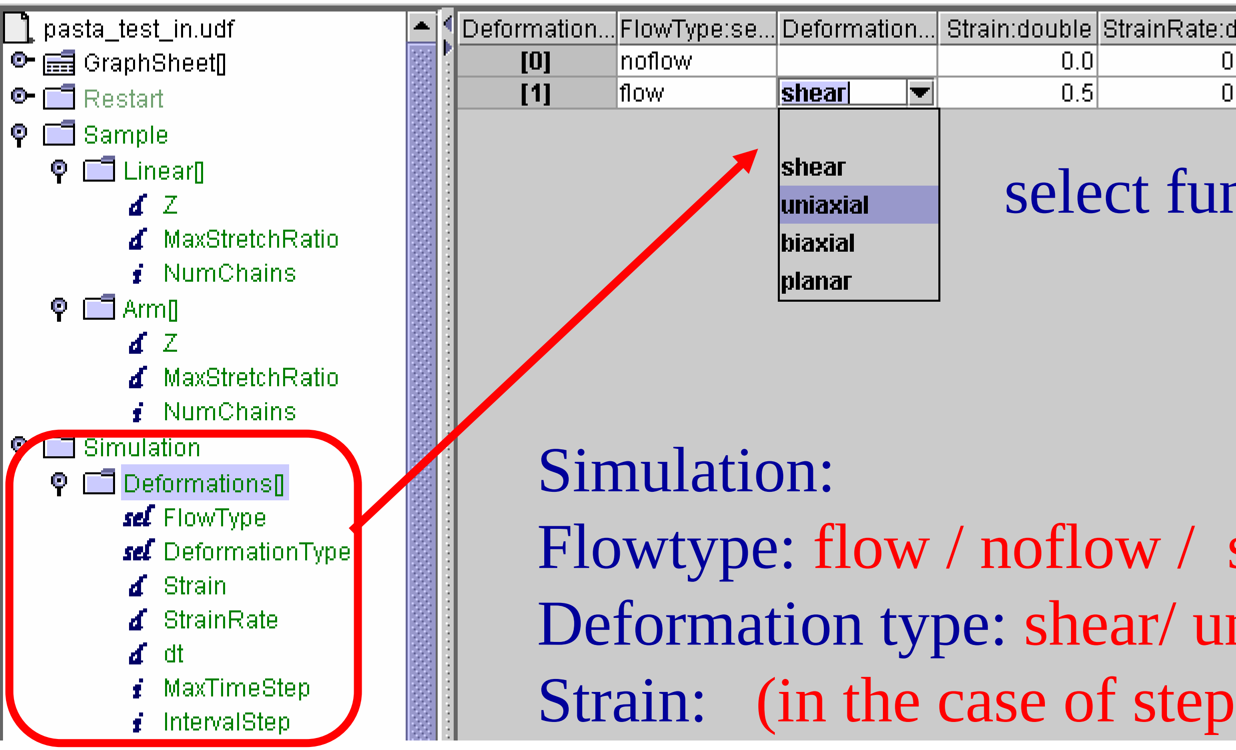
Z	λ_{max}	Ni
10	4.4	1000

- Monodisperse
- Polydisperse



Z	λ_{max}	Ni
1.5	4.4	10
2.8	4.4	45
4.9	4.4	135
6.8	4.4	256
8.9	4.4	168
.....	...	....
.....	...	....

Editing InputUDF of PASTA on GOURMET



select function

Simulation:

Flowtype: flow / noflow / step

Deformation type: shear/ uniaxial/ biaxial/ planar

Strain: (in the case of step)

Strain rate:

dt: time step per 1 τ_e

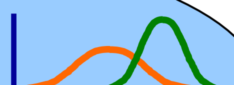
MaxTimeStep: Number of iteration

IntervalStep: output every IntarvalStep steps

FORK (a support tools for PASTA)

FORK is a tool to generate inputUDF for PASTA.

properties of polymer
Me, M0, GN0, τe...etc

MWD
Mw, Mw/Mn,

distribution function,
GPC data

simulation condition
deformation type

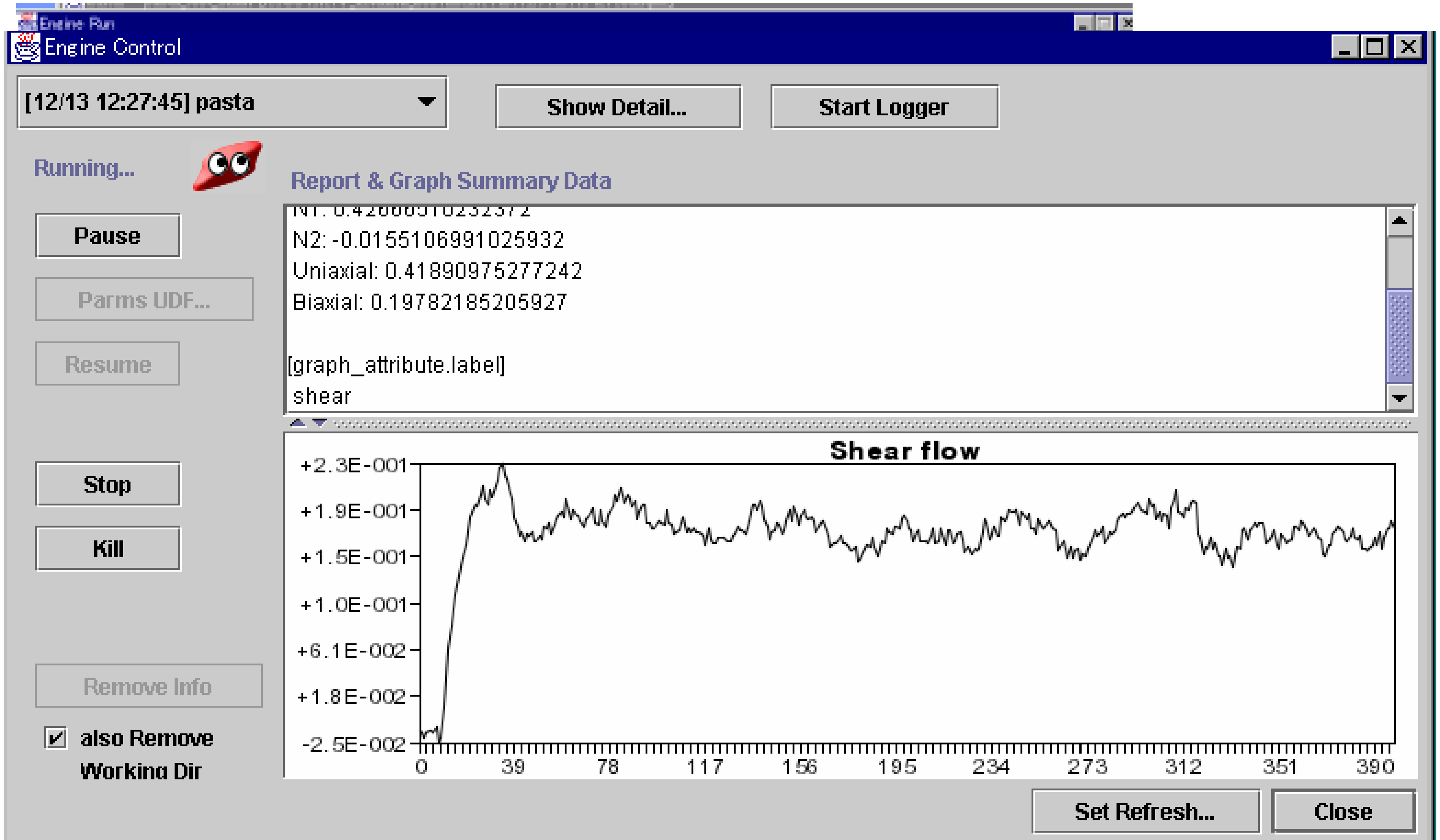
shear, ε =0.01, 10000step

FORK

inputUDF
for PASTA

i	Zi	Ni
1	2.5	3
2	3.7	10
3	4.8	47
4	6.2	28
5	8.1	9
...	....	....

Running PASTA on GOURMET



Monitor
Engine Run Window

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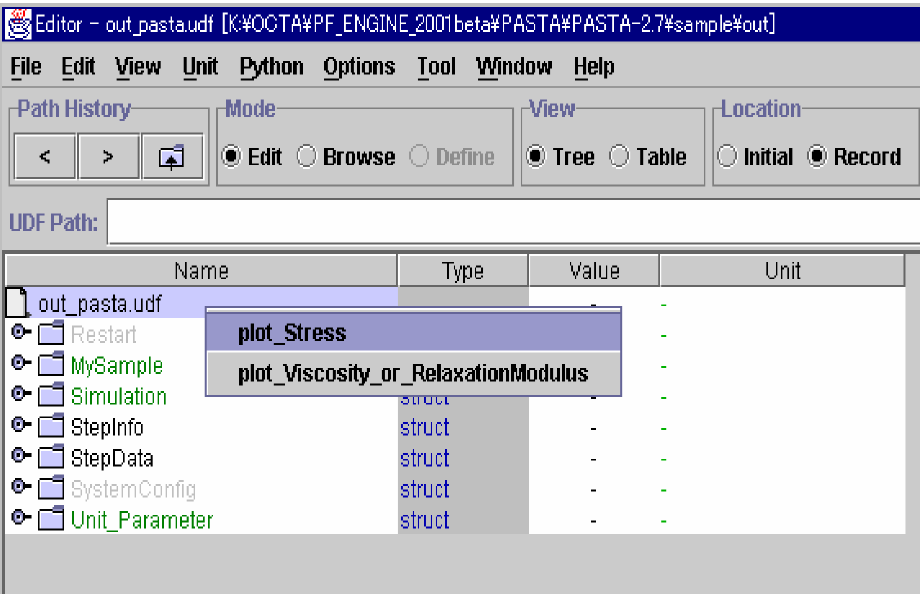
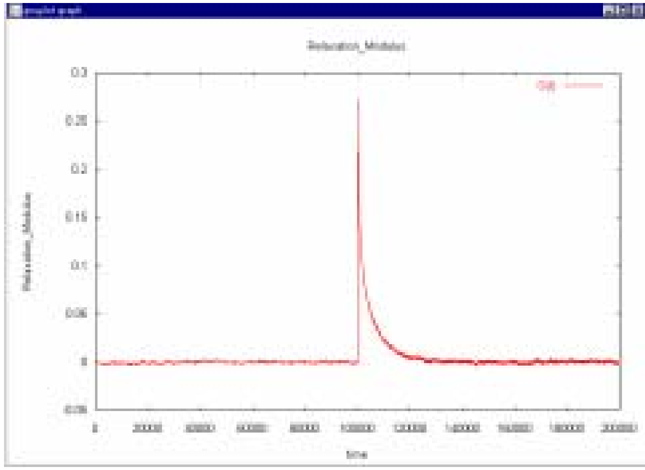
Analyze output by GOURMET

- By "Action", Python script and the other tools
  - shear viscosity, elongational viscosity, relaxation modulus G'(ω), G"(ω), etc....



Example of Action (plot_stress)



instant plot by Gnuplot

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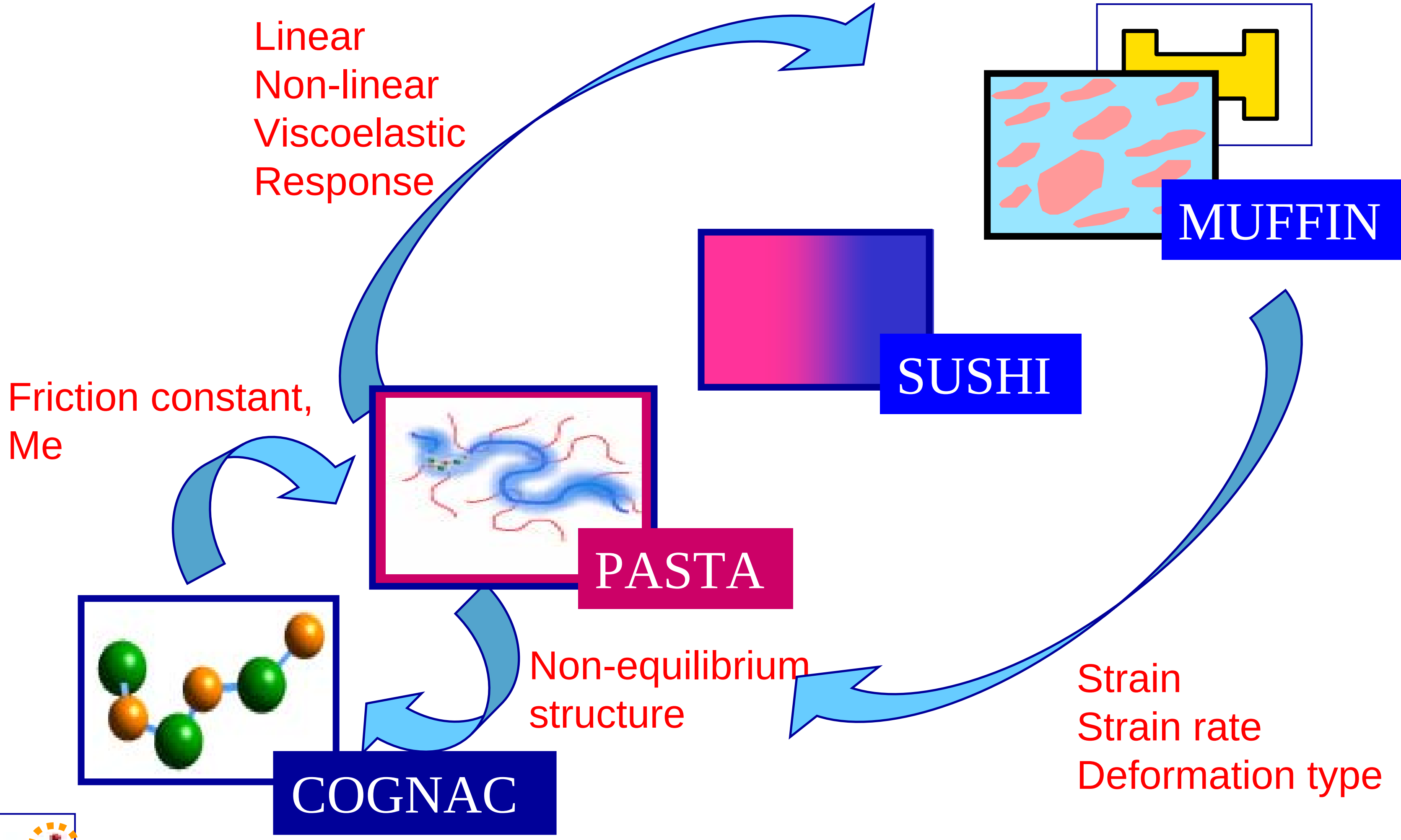
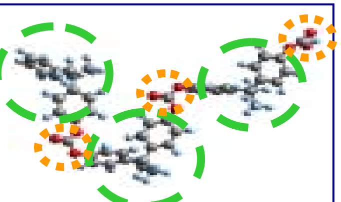
PASTA: Linking to other layers





Summary

PASTA

- New stochastic simulation method
  tube model
  + contour length fluctuation
  + constraint renewal
- Successfully calculates most of the
  linear/nonlinear rheology of
  monodisperse/polydisperse linear/star
  polymer

- Easy and convenient manipulation on GOURMET

Developer of PASTA

- Theory & Program — Prof. Jun-ichi Takimoto (Nagoya Univ.)
- Verification — Hiroyasu Tasaki (JCII, Doi Project)
- Connection with GOURMET & FORK — Tatsuya Shoji (JCII, Doi Project)

Acknowledgements

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