Constraint release and chain stretch in fast flows of linear polymer melts.

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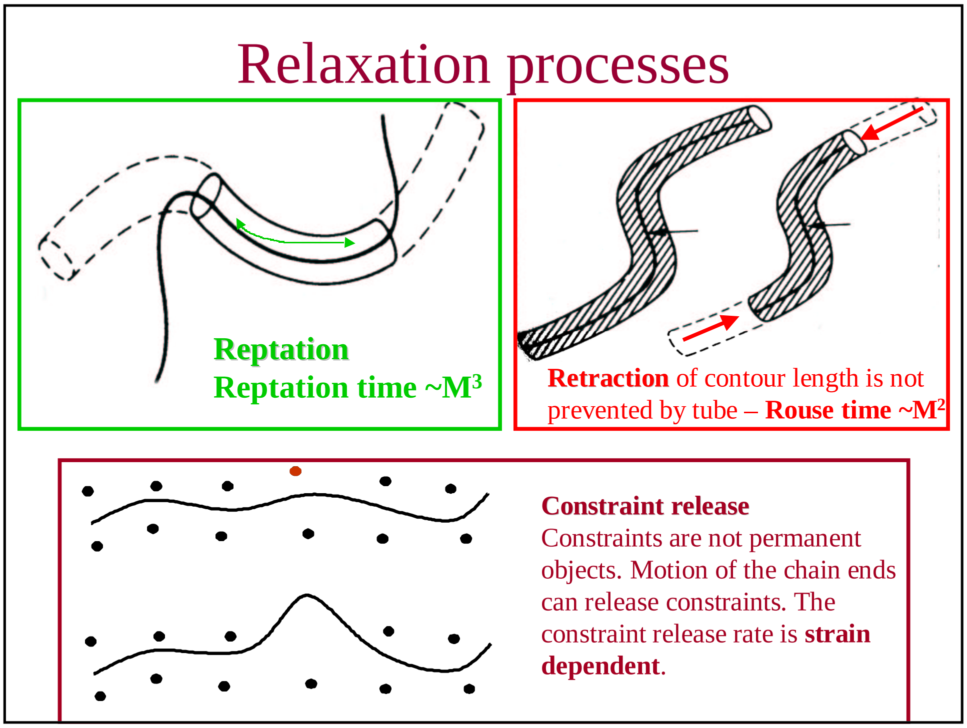
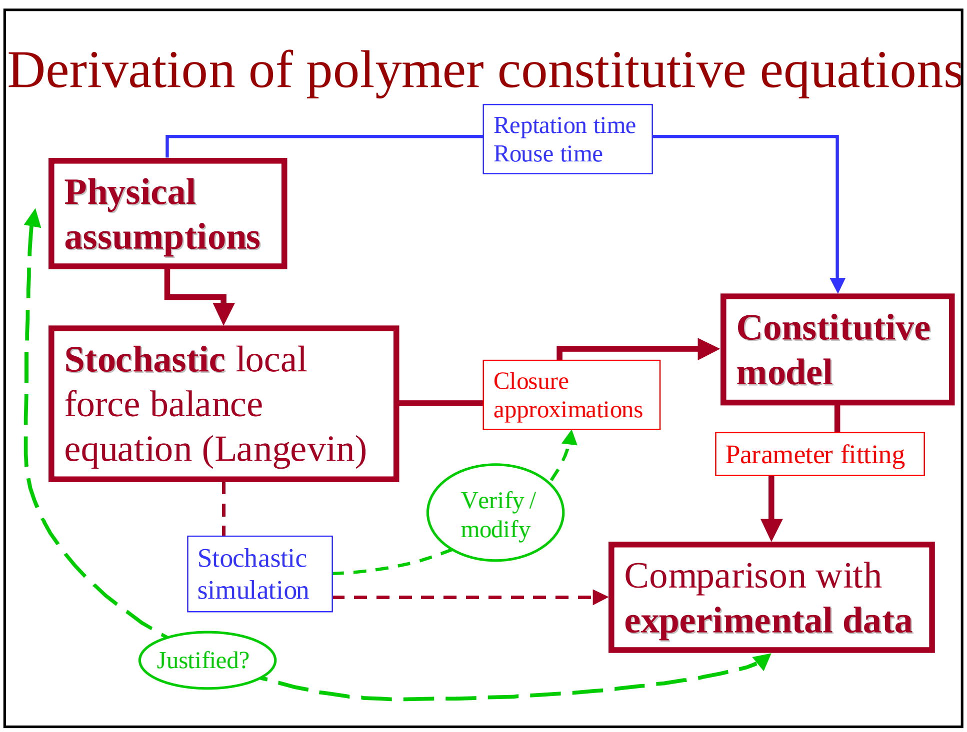
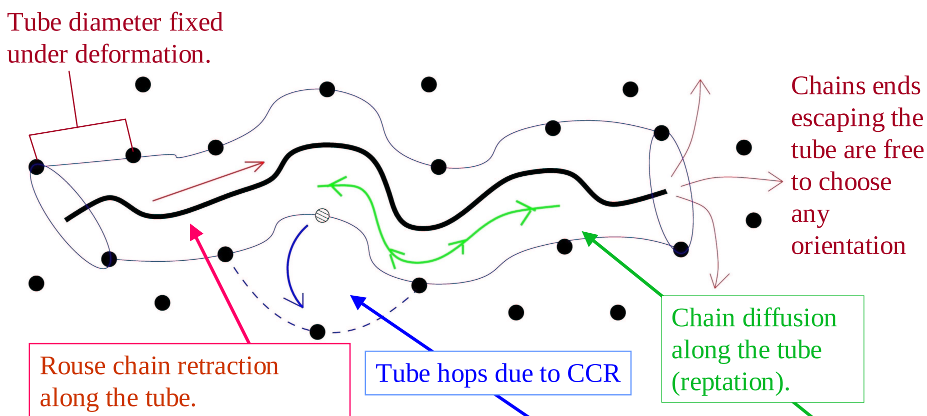
Outline

- Overview of derivation methods
- Introduction to Leeds model
- Method of solution
- Model parameters
- Comparison with experimental data
  - Shear transients
  - Steady state in extension
- Summary
- Questions


Relaxation processes
Reptation
Reptation time ~M³
Retraction of contour length is not prevented by tube – Rouse time ~M²
Constraint release
Constraints are not permanent objects. Motion of the chain ends can release constraints. The constraint release rate is strain dependent.


Derivation of polymer constitutive equations
Reptation time
Rouse time
Physical assumptions
Stochastic local force balance equation (Langevin)
Closure approximations
Constitutive model
Parameter fitting
Verify / modify
Stochastic simulation
Comparison with experimental data
Justified?

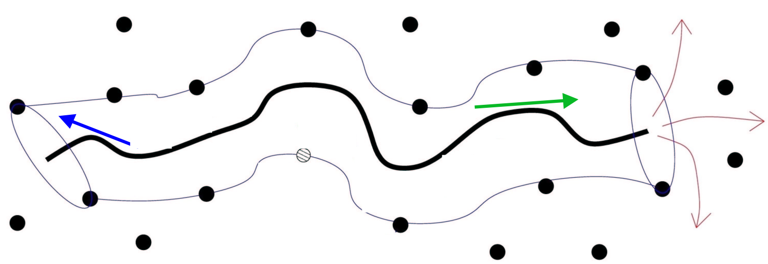
Stretching CCR model



$$\mathbf{R}(s,t+\Delta t)=\Delta t\left(D\frac{\mathbf{R}''.\mathbf{R}'}{\mathbf{R}'.\mathbf{R}'}\mathbf{R}'+\mathbf{k}.\mathbf{R}+\frac{3\nu}{2}\frac{1}{|\mathbf{R}'|}\frac{\partial^2\mathbf{R}}{\partial s^2}+\mathbf{g}(s,t)\right)+\mathbf{R}(s+\Delta\xi(t),t)$$

R(s,t)=Space curve equation of chain contour parameterised by s.

Tube tangent correlation function



$$\mathbf{f}(s,s',t)=\left\langle\frac{\partial\mathbf{R}(s)}{\partial s}\frac{\partial\mathbf{R}(s')}{\partial s'}\right\rangle \rightarrow$$

Stress tensor
Single chain structure factor

$$\mathbf{f}(s,s',t) = \left\langle \frac{\partial \mathbf{R}(s)}{\partial s} \frac{\partial \mathbf{R}(s')}{\partial s'} \right\rangle$$

$$\frac{\partial f_{\alpha\beta}}{\partial t}(s,s',t) = \frac{\partial^2}{\partial s \partial s'} \left(\left\langle \frac{\partial R_\alpha(s)}{\partial t} R_\beta(s') \right\rangle + \left\langle R_\alpha(s) \frac{\partial R_\beta(s')}{\partial t} \right\rangle \right)$$

Langevin equation

Just the CCR term in this example

$$\frac{\partial^2}{\partial s \partial s'} \left\langle \frac{\partial R_\alpha(s)}{\partial t} R_\beta(s') \right\rangle = \ldots + \frac{\partial^2}{\partial s \partial s'} \left(\left\langle \frac{3\nu}{2} R''_\alpha(s) R_\beta(s') \right\rangle \right)$$

$$= \frac{3\nu}{2} \frac{\partial^2}{\partial s^2} f_{\alpha\beta}(s,s')$$

…repeat for other terms

Langevin equation

Closure approximations

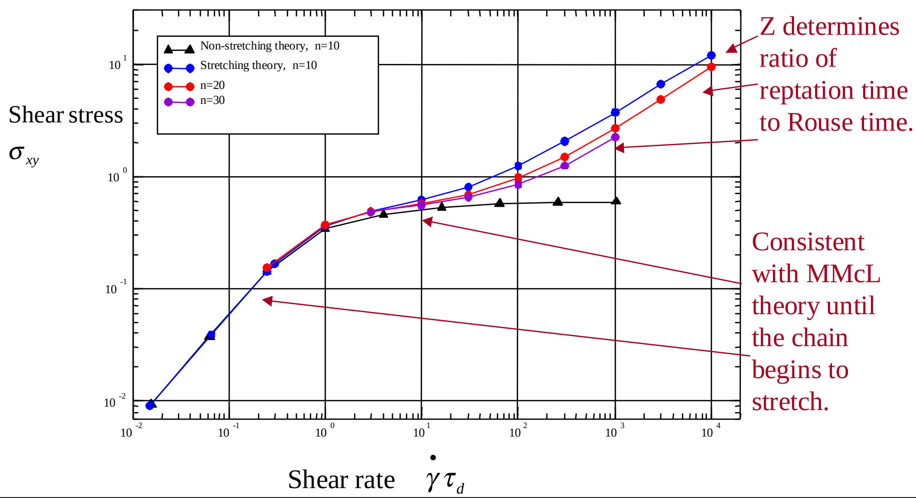
$$\left\langle \frac{\mathbf{R}'(s)\mathbf{R}'(s')}{|\mathbf{R}'(s)|} \right\rangle \approx \frac{\langle \mathbf{R}'(s)\mathbf{R}'(s') \rangle}{\sqrt{\langle \mathbf{R}'(s).\mathbf{R}'(s) \rangle}}$$

$$\langle \ln(\mathbf{R}'(s).\mathbf{R}'(s))\mathbf{R}'(s)\mathbf{R}'(s') \rangle \approx \ln(\langle \mathbf{R}'(s).\mathbf{R}'(s) \rangle)\langle \mathbf{R}'(s)\mathbf{R}'(s') \rangle$$

$$\frac{\partial \mathbf{G}}{\partial t} = \boldsymbol{\kappa}.\mathbf{G} + \mathbf{G}.\boldsymbol{\kappa}^T + \frac{1}{3}(\boldsymbol{\kappa} + \boldsymbol{\kappa}^T)\delta(s-s') + \frac{D}{Z}\left(\frac{Z}{Z^*(t)}\right)^2 \left(\frac{\partial}{\partial s} + \frac{\partial}{\partial s'}\right)^2 \mathbf{G}$$
$$+ \frac{3\nu}{2}\left(\frac{\partial}{\partial s}\left[\frac{1}{\sqrt{\mathrm{Tr}\,\mathbf{G}(s,s)+1}}\frac{\partial}{\partial s}\right] + \frac{\partial}{\partial s'}\left[\frac{1}{\sqrt{\mathrm{Tr}\,\mathbf{G}(s',s')+1}}\frac{\partial}{\partial s'}\right]\right)\mathbf{G}$$
$$+ \frac{3D}{2}\left(\frac{\partial}{\partial s}\left(\frac{\partial}{\partial s}\left[\ln(\mathrm{Tr}\,\mathbf{G}(s,s)+1)\right]\right) + \frac{\partial}{\partial s'}\left(\frac{\partial}{\partial s'}\left[\ln(\mathrm{Tr}\,\mathbf{G}(s',s')+1)\right]\right)\right)(\mathbf{G} + \delta(s-s')\mathbf{I}/3)$$

$$\mathbf{G}(s,s') = \left\langle \frac{\partial \mathbf{R}(s)}{\partial s} \frac{\partial \mathbf{R}(s')}{\partial s'} \right\rangle - \frac{1}{3}\mathbf{I}\partial(s-s')$$

Steady state in simple shear



Contour length fluctuations

•Easy to add to Langevin equation, in principle.

•Solution to system becomes very difficult!

•Modify reptation term to obtain an approximate treatment which agrees with the linear theory at low rates.

Derived reptation term

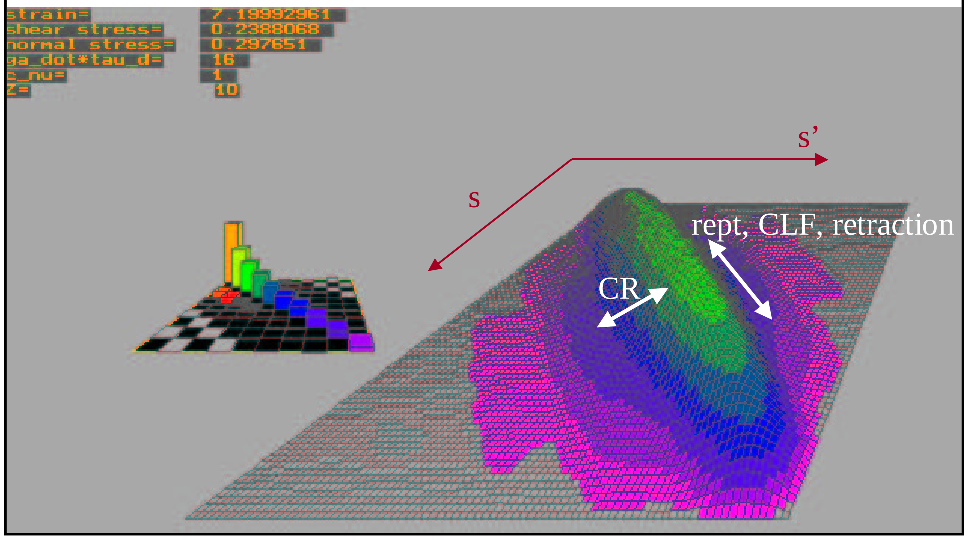
Approximate CLF term

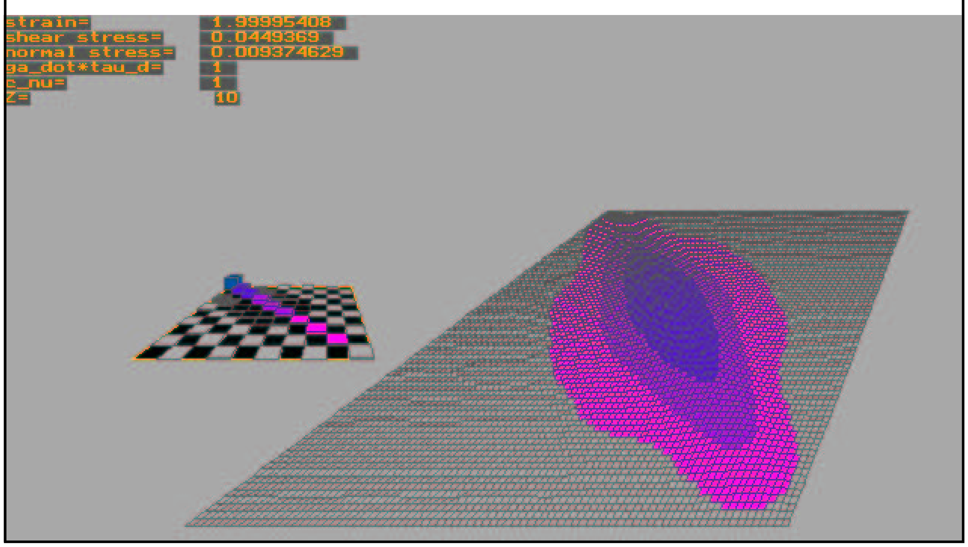
$$D\left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right)^2\left(\mathbf{f}-\mathbf{f}_{eq}\right) \mapsto \left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right)D_{CLF}(s,s')\left(\frac{\partial}{\partial s}+\frac{\partial}{\partial s'}\right)\left(\mathbf{f}-\mathbf{f}_{eq}\right)$$

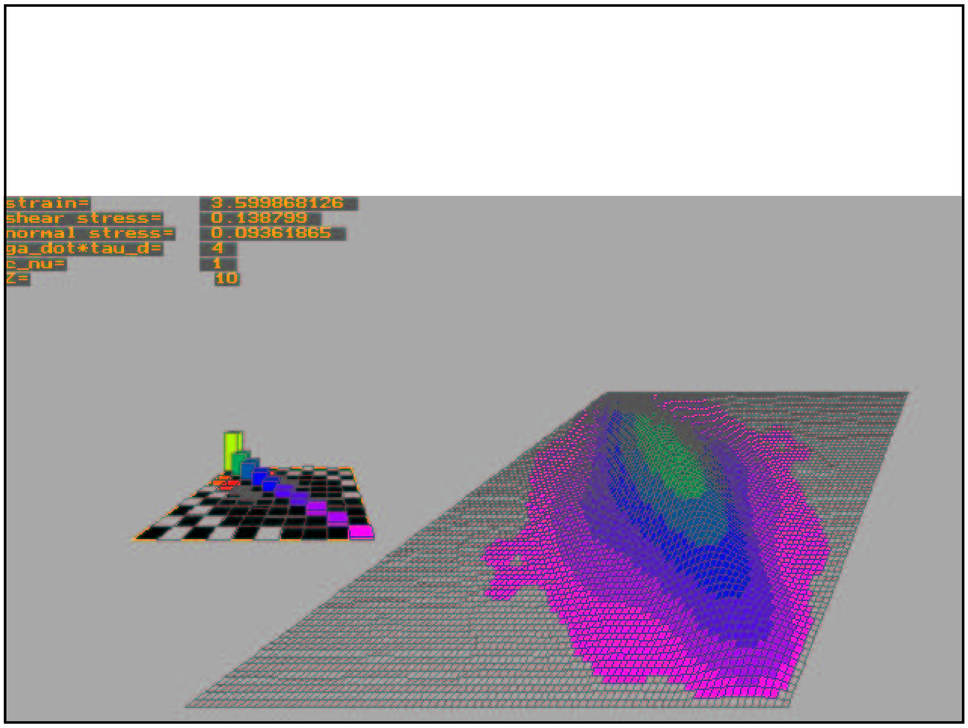
•Choose a form for D_{CLF}(s,s') which agrees with the linear theory for a wide range of values of Z.

Tangent correlation function

$$f_{\alpha\beta}(s,s') = \left\langle \frac{\partial R_\alpha}{\partial s} \frac{\partial R_\beta}{\partial s'} \right\rangle$$



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shear stress= 0.138799
normal stress= 0.09361865
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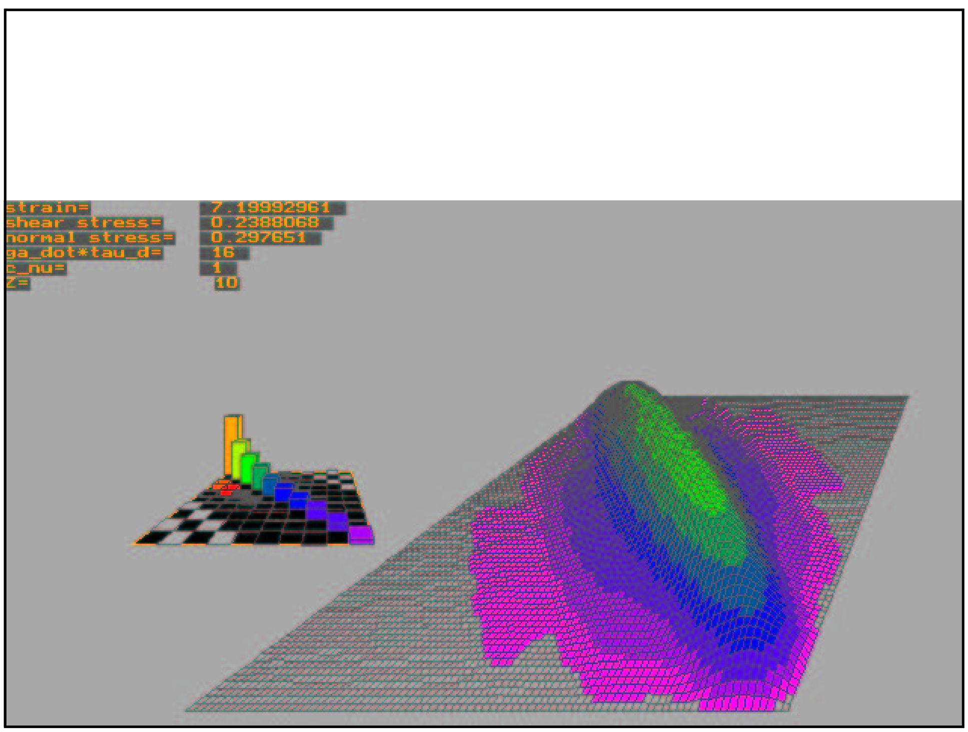
c_nu= 1
Z= 10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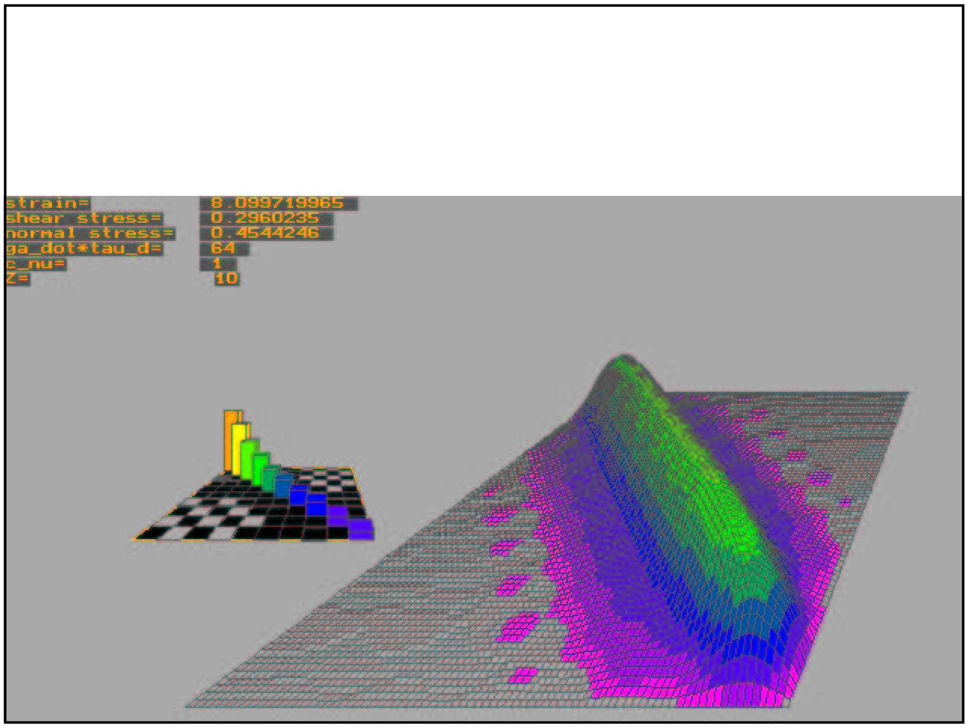
shear stress= 0.2388068
normal stress= 0.297651
ga_dot*tau_d= 16
c_nu= 1
Z= 10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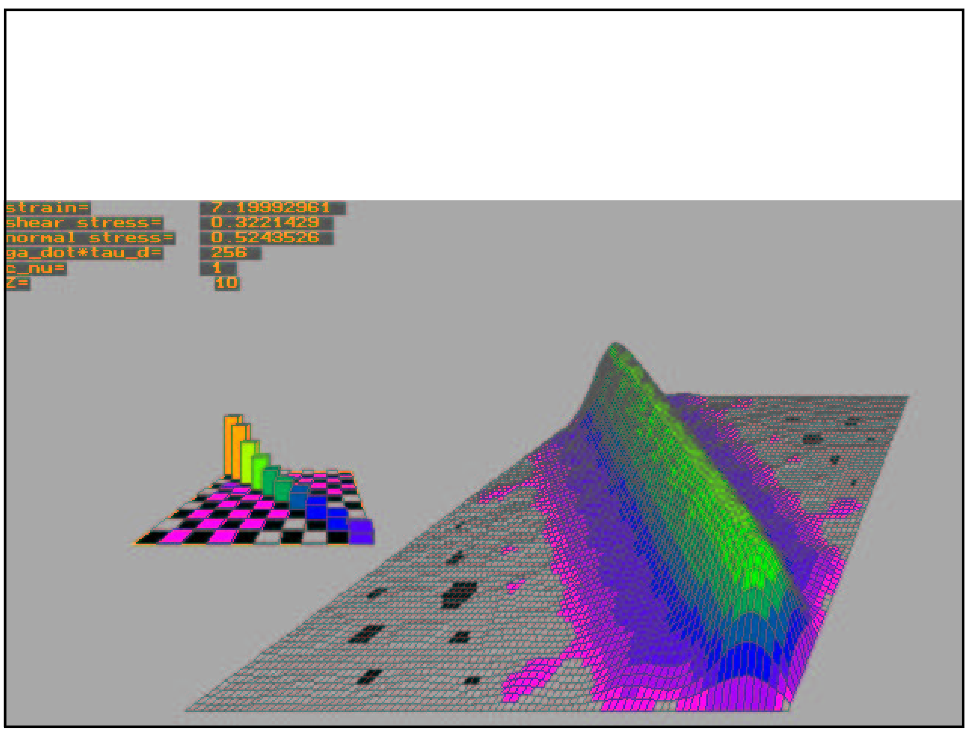
8.099719965
shear stress=
0.2960235
normal stress=
0.4544246
ga_dot*tau_d=
64
c_nu=
1
Z=
10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7.19992961
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0.3221429
normal stress=
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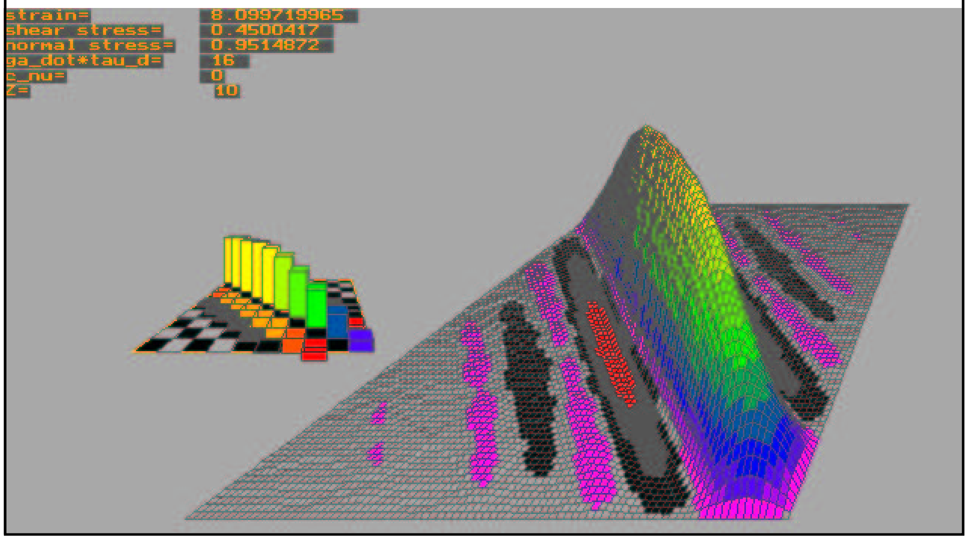
ga_dot*tau_d=
256
c_nu=
1
Z=
10

NO CCR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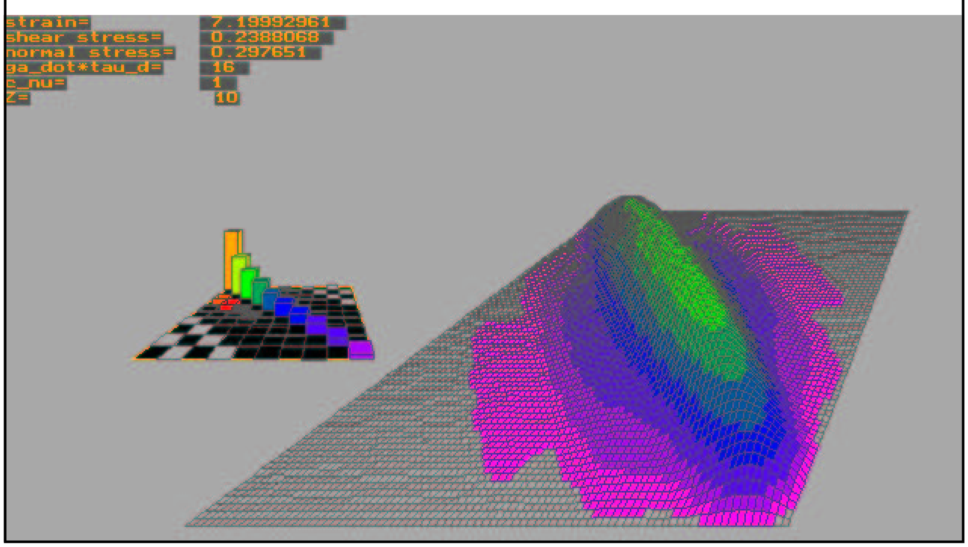
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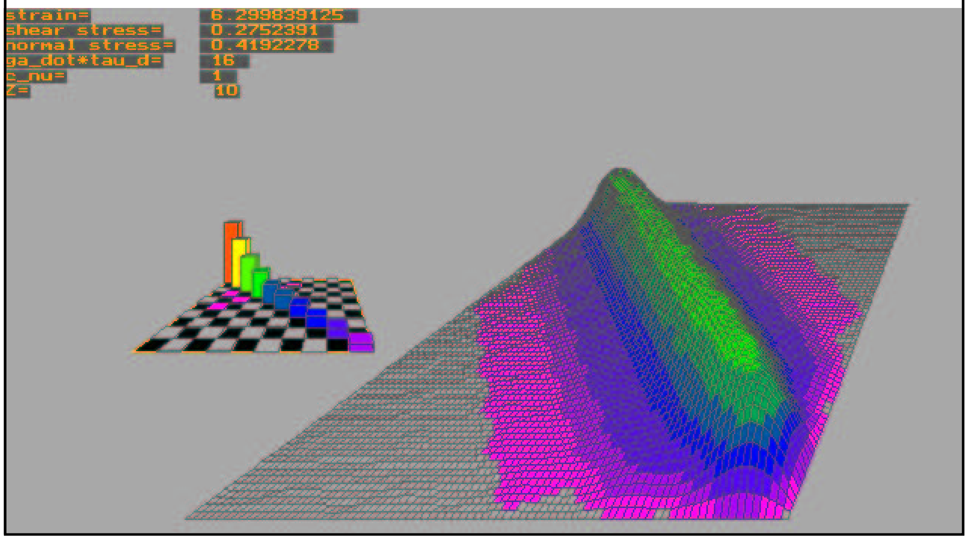
shear stress= 0.2388068
normal stress= 0.297651
ga_dot*tau_d= 16
c_nu= 1
Z= 10

NO CLF - pure rertation



Procedure for obtaining model parameters

Require:

-Entanglement mass, M_e

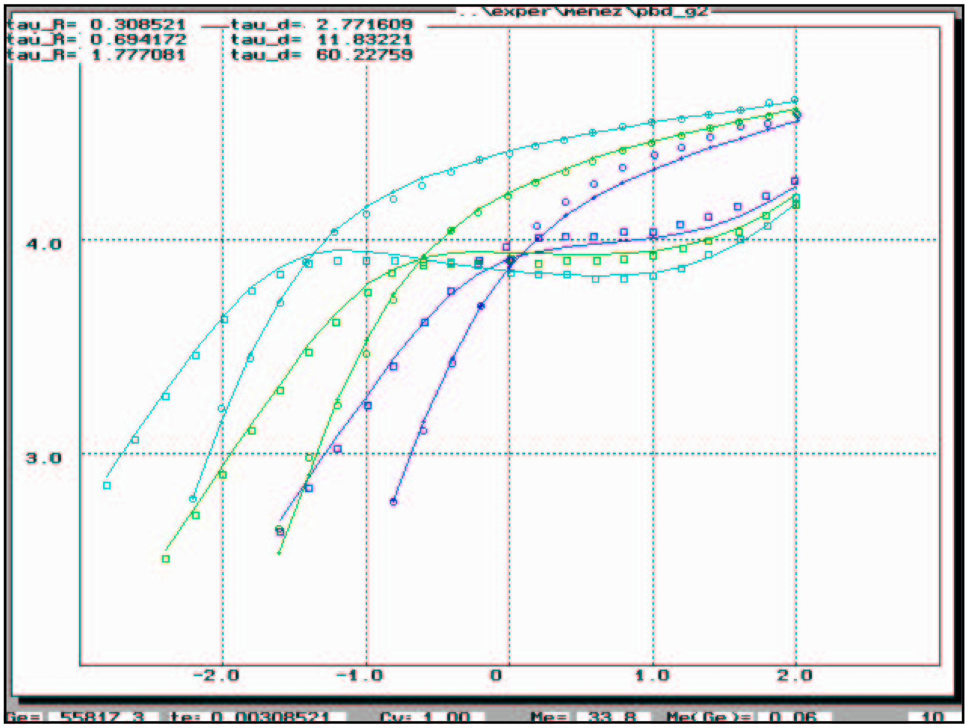
-Entanglement modulus, G_e

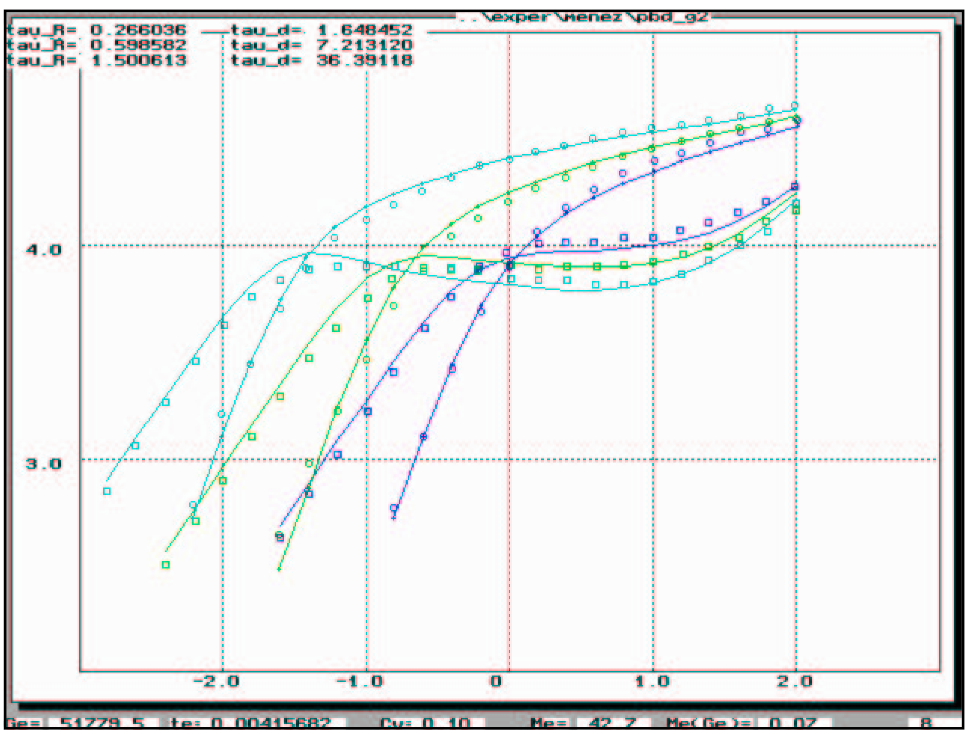
-Rouse time of an entanglement segment, τ_e

Obtained from fitting linear theory of Likhtman and McLeish to G' and G''

-Constraint release parameter, Cν

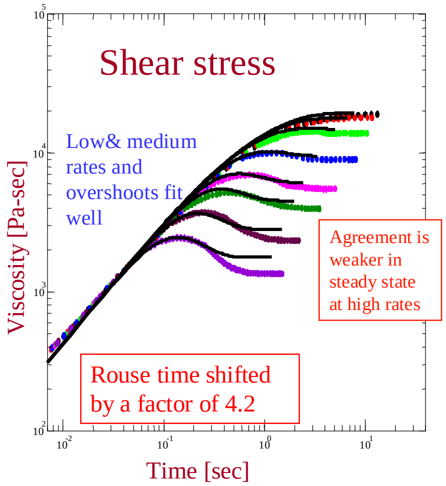
Linear rheology of solutions suggests Cν~2-5. Non-linear steady shear predictions improved when Cν=0.1

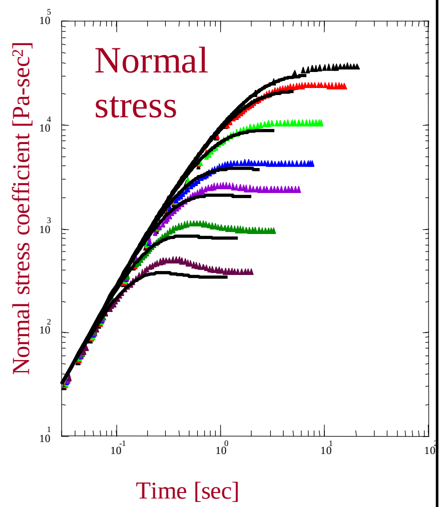

..\exper\menez\pbd_g2
tau_R= 0.308521
tau_R= 0.694172
tau_R= 1.777081
tau_d= 2.771609
tau_d= 11.83221
tau_d= 60.22759
4.0
3.0
-2.0
-1.0
0
1.0
2.0
Ge= 55817.3
te= 0.00308521
Cv: 1.00
Me= 33.8
Me(Ge)= 0.06
10


..\exper\menez\pbd_g2
tau_R= 0.266036
tau_R= 0.598582
tau_R= 1.500613
tau_d= 1.648452
tau_d= 7.213120
tau_d= 36.39118
4.0
3.0
-2.0
-1.0
0
1.0
2.0
Ge= 51779.5
te= 0.00415682
Cv: 0.10
Me= 42.7
Me(Ge)= 0.07
8

Comparison with data

Shear of monodisperse linear entangled PB solution. (Menezes & Graessley)

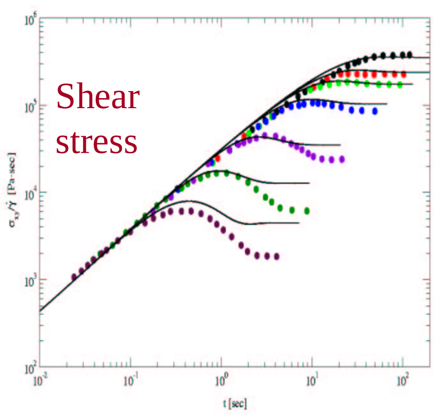


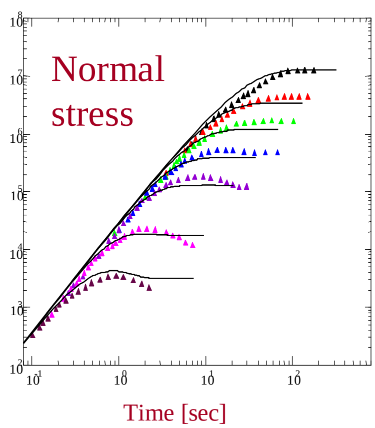


Mw=350K, 7% solution

Extension to a higher molecular weight

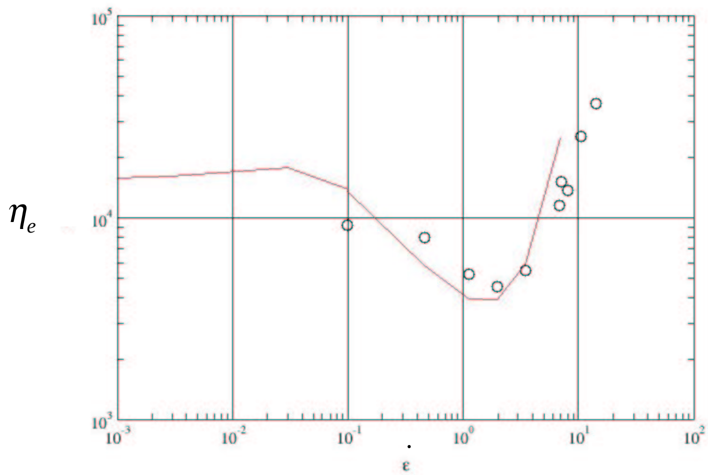
Mw=813K, 7% solution





No further parameter fitting

Steady state extension data



Summary

- We have derived a molecularly based non-linear constitutive model starting from a Langevin equation for the local dynamics of a chain in a tube.
- The model has no shear stress maximum for any separation of τ_{rept} and τ_{Rouse}.
- Taking most of the model parameters from linear rheology gives agreement with experimental data subject to a shift in Rouse time.
- The required Rouse shift is the same when the molecular weight, the polymer species and the non-linear flow geometry are changed!!!!!! (For the data modeled so far.)
- For solutions G’’ suggests a larger value for Cn than expected whereas lowering Cn improves the agreement with high rates at large strains.

Current questions

Other measurements

•What about damping function and other shear histories (double step etc)?

•Will the model capture behaviour of other molecular probes (SANS, dielectric, NMR)?

Issues with current comparisons

•What is the reason for the need to shift the Rouse time and why do the data suggest a consistent change?

•Under which circumstances are the closure approximations valid? - can we improve them?

•Why does the model over-predict steady state shear stress? - can this be rectified?

•Why does G’’ for solutions suggest such a large value for Cv?