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Cracking the Whip in Driven Polymers

驱动高分子的“挥鞭”效应

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南京大学化学化工学院高分子系

Absolute versus relative motion

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Outside view

Absolute versus relative motion

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Inside view

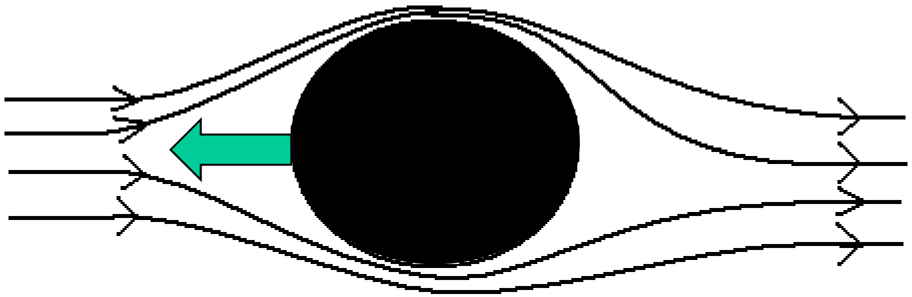
http://www.sohu.com/a/241065793_819453

Simple flow

The external force raises a relative velocity

$$f=\zeta v$$

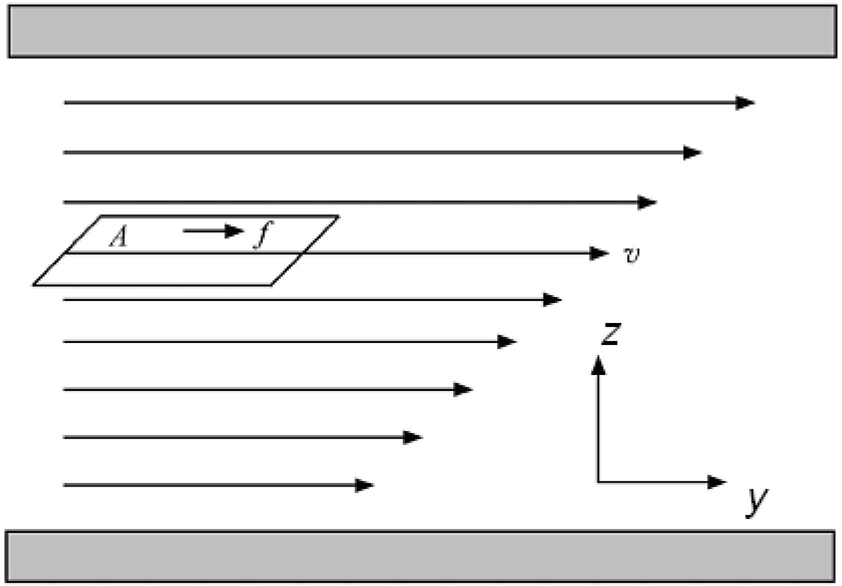
ζ is the friction coefficient of a particle



Similar to Newton's second law: f=ma

Polymer shear flow

Couette Flow



Shear stress $\sigma \equiv f/A$

Shear rate

$$\frac{dv}{dz} = \frac{d}{dz}\left(\frac{dy}{dt}\right) = \frac{d}{dt}\left(\frac{dy}{dz}\right) = \frac{d\gamma}{dt} = \gamma'$$

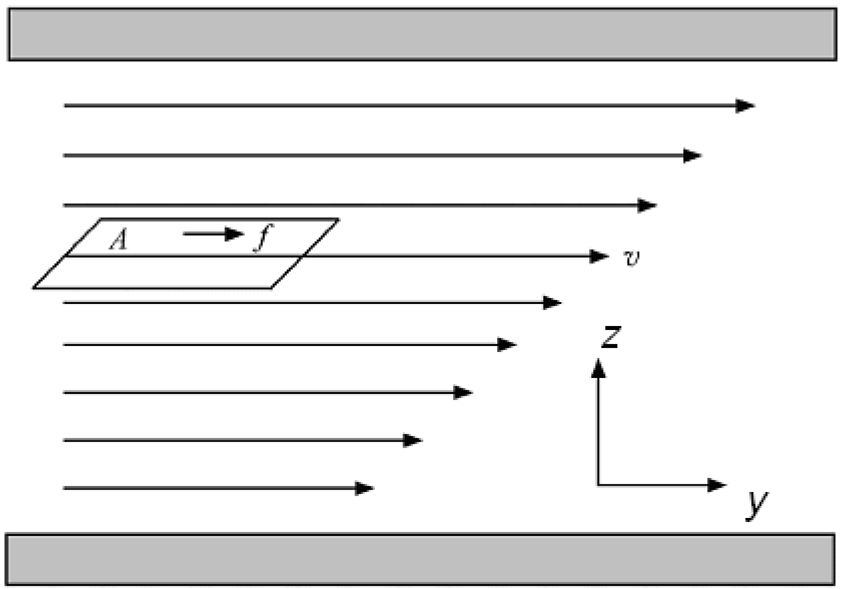
Newtonian fluid $\sigma = \eta\gamma'$

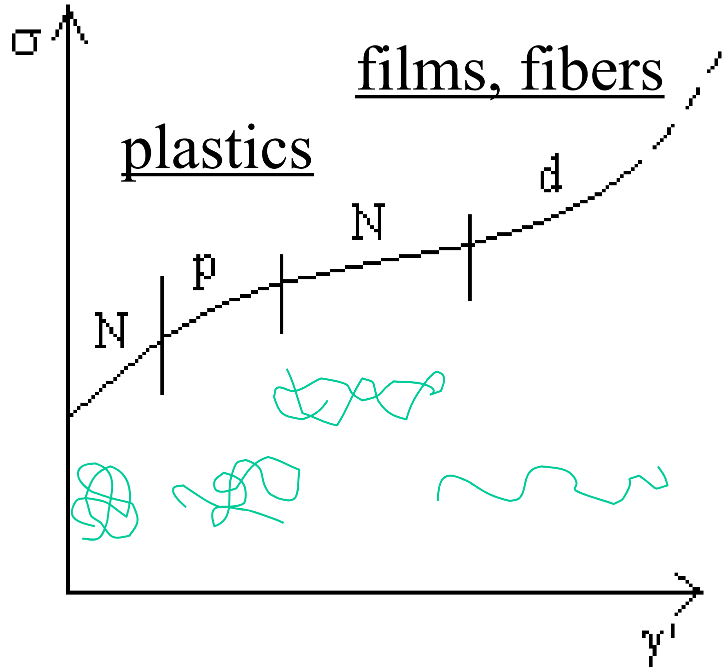
Newton's second law!

$f = \zeta v$

Polymer shear flow

Couette Flow

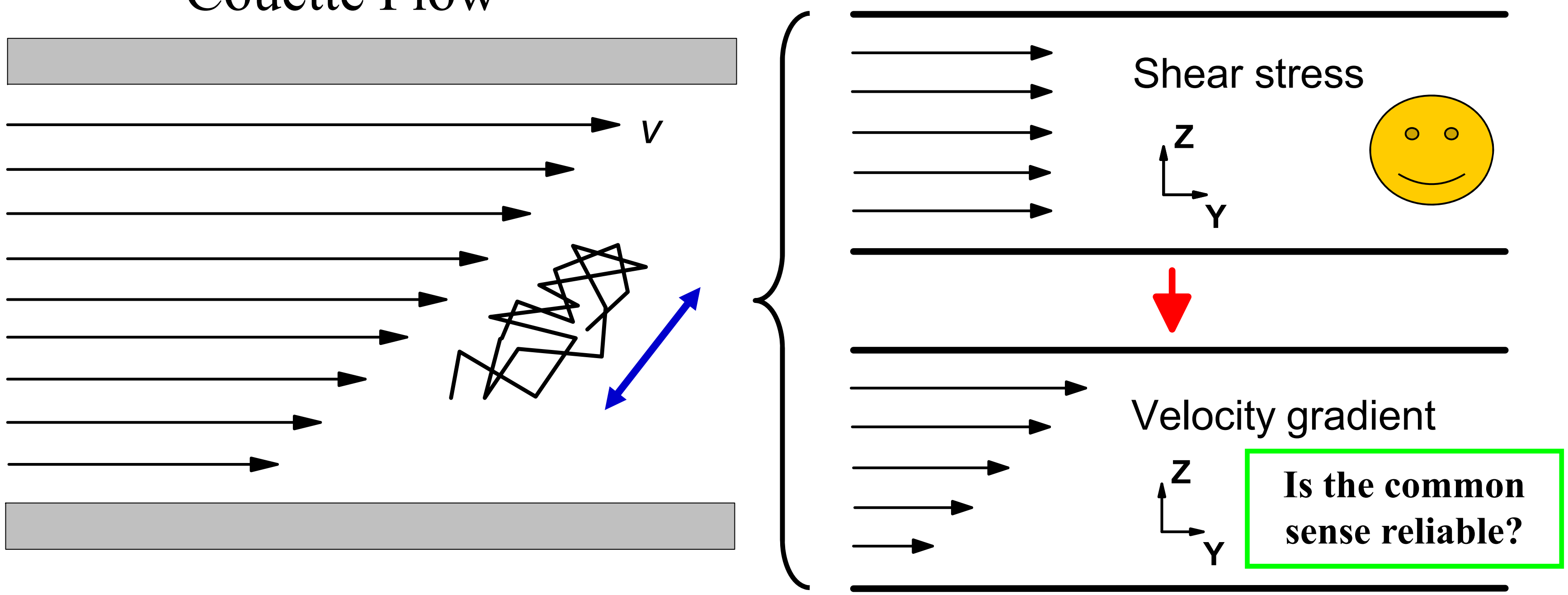




Why are polymer coils deformed?

❖ **Common sense: velocity gradients**

Couette Flow



Dynamic Monte Carlo simulations

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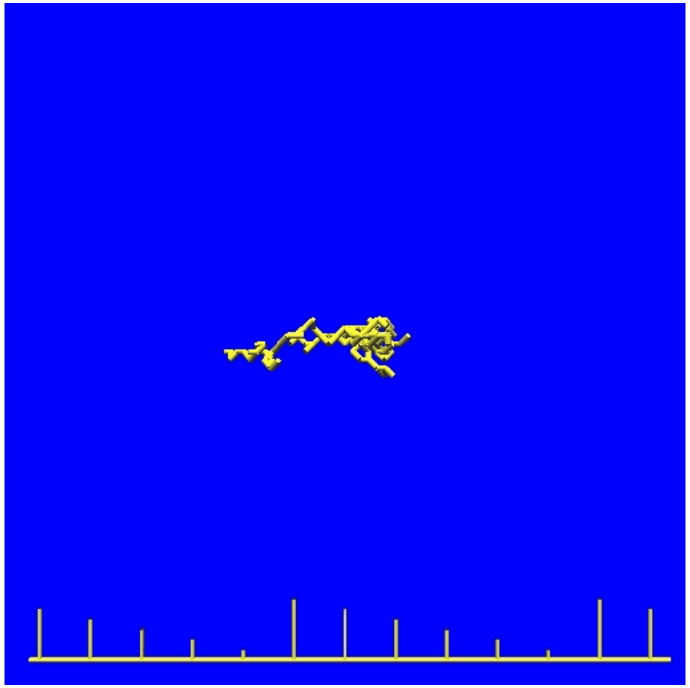
Metropolis sampling on Brownian motions:

n **net** monomers **moving forward decided by**

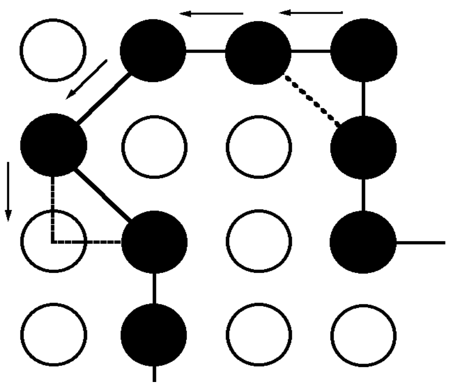
$$P_{(o\to n)} = \begin{cases} 1, & if \quad n \geq 0 \\ \exp(nF), & if \quad n < 0 \end{cases}$$

F=1



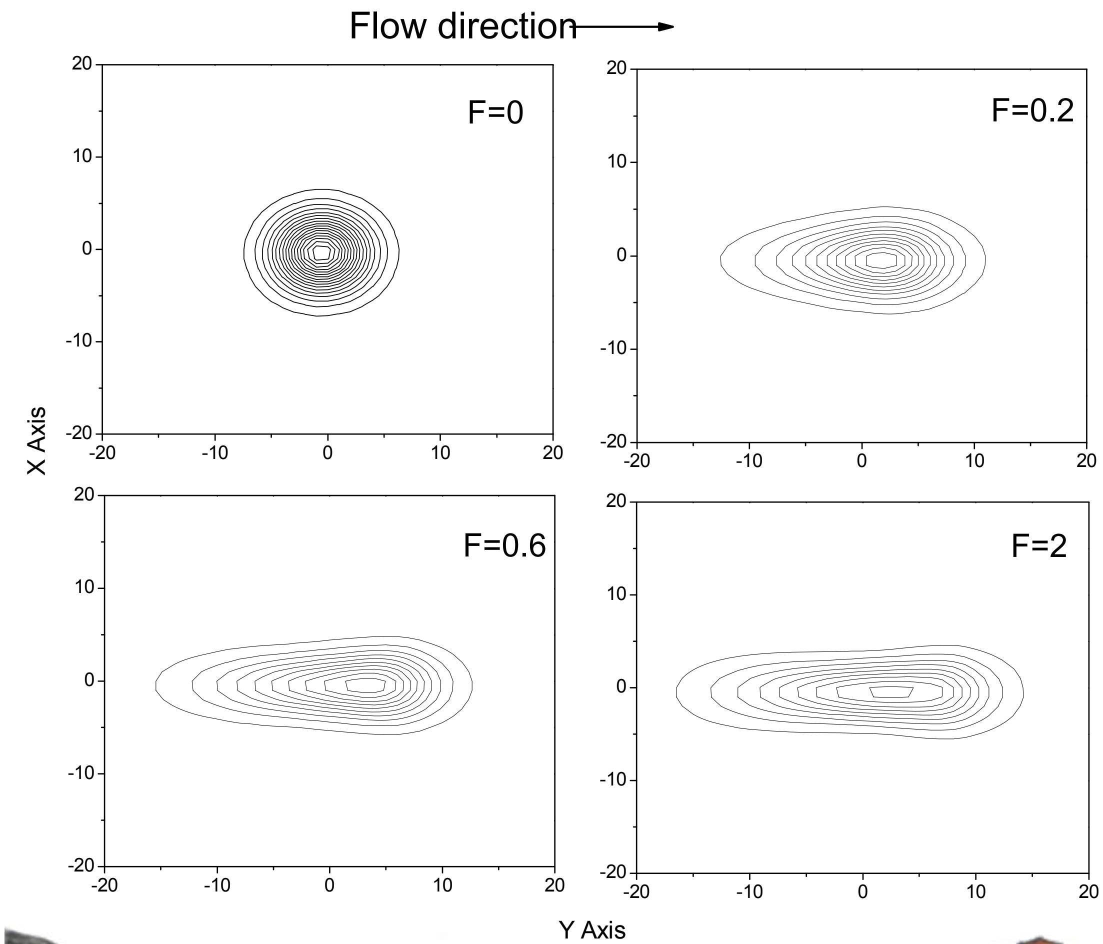
Damping motion

Random updating

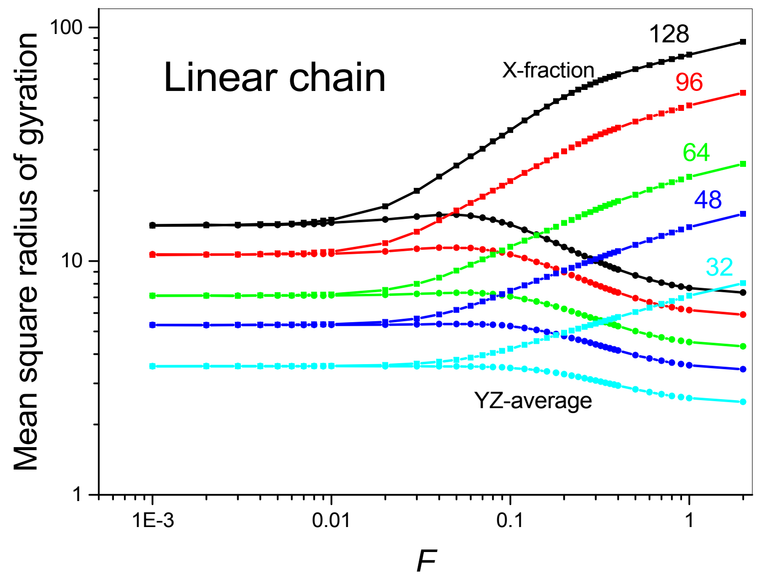


Driving a single phantom chain

❖ **128-mer under uniform driving forces**



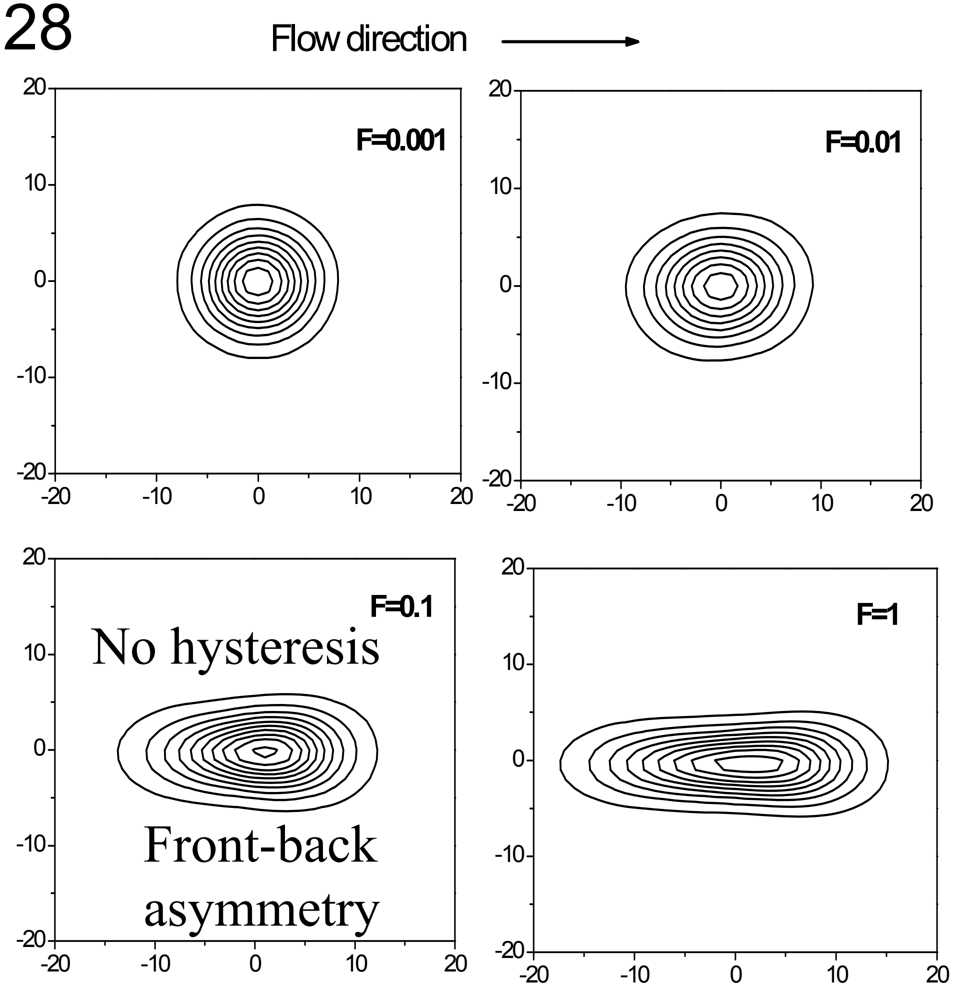
Coil size asymmetry



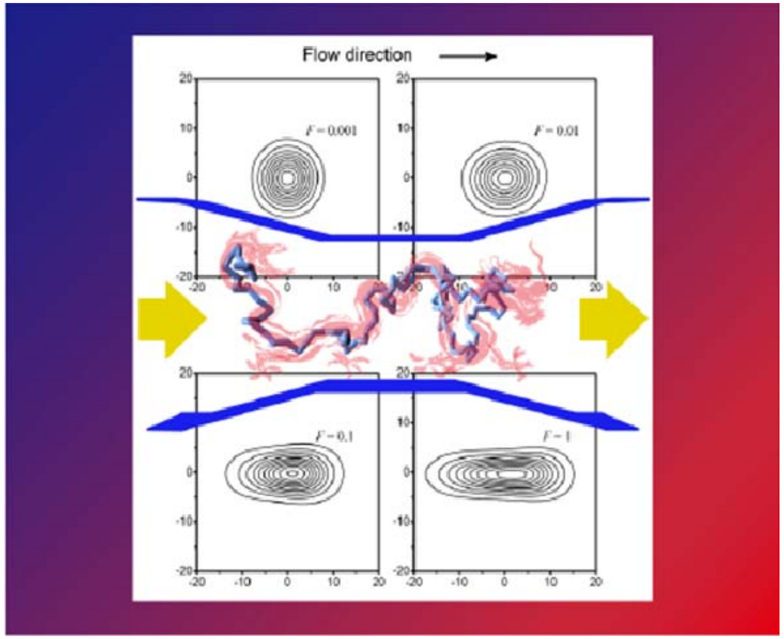
J. Li, Y. Ma, W.-B. Hu
Molecular Simulation
2016, 42(4), 321–327

Driving melt polymers

N=128



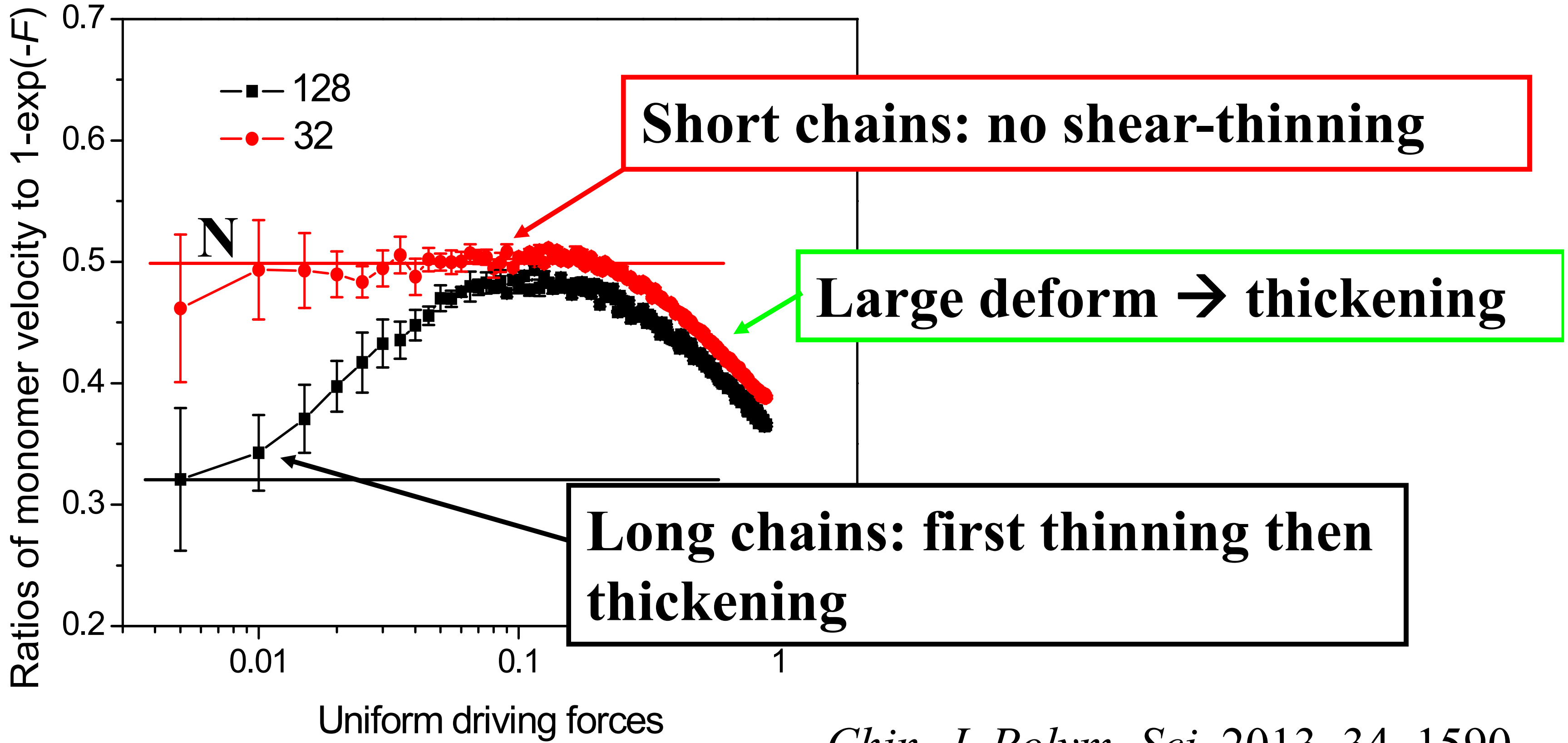
<u>Cover art</u>



J. Li, Y. Nie, Y. Ma, W.-B. Hu, *Chin. J. Polym. Sci.* 2013, 34, 1590-1598

Driving melt polymers

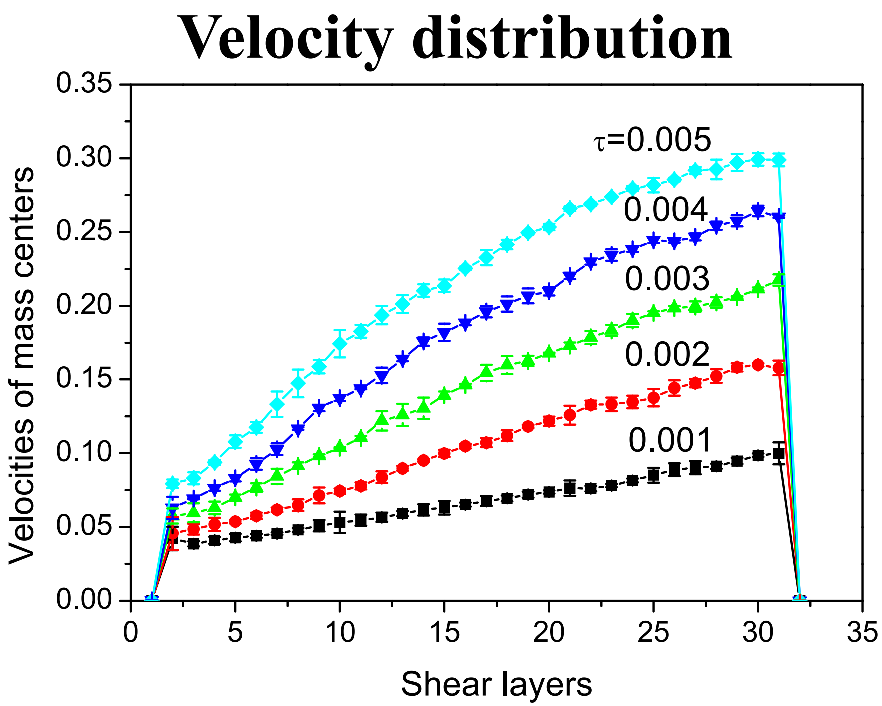
- Uniform driving forces

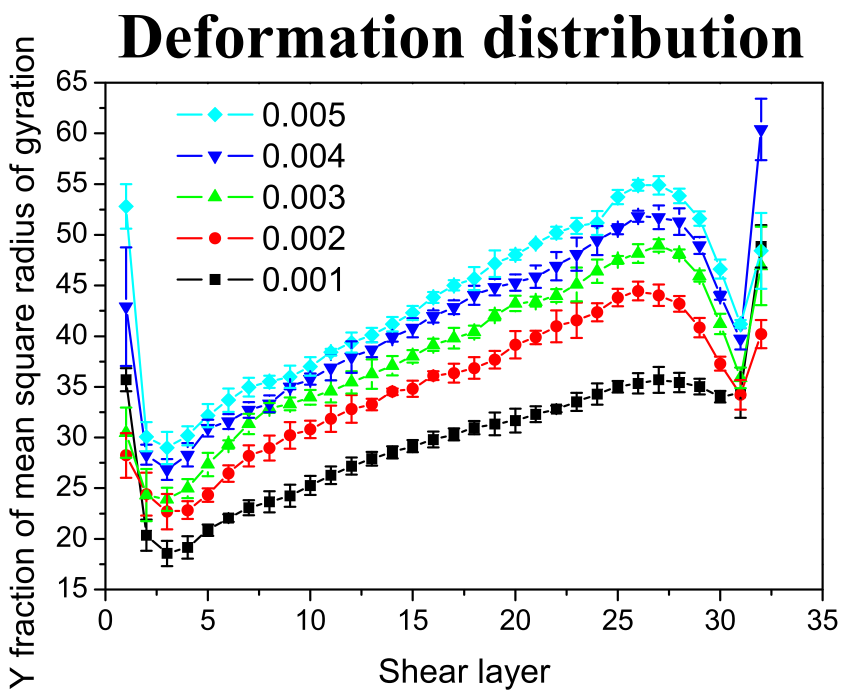


Chin. J. Polym. Sci. 2013, 34, 1590

Stress versus velocity gradient

- Gradient driving forces (N=128)





Chin. J. Polym. Sci. 2013, 34, 1590

Stress versus velocity gradient

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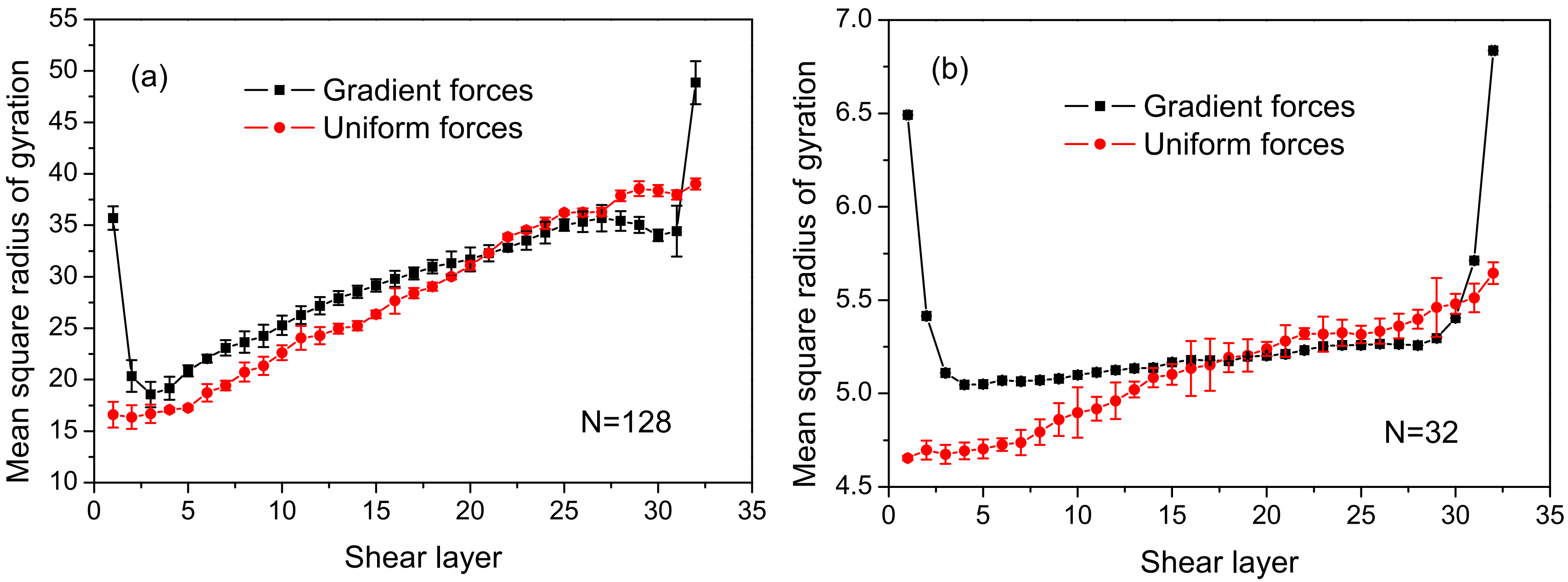
- Compare deformations from uniform and gradient fields



Velocity gradient dominates deformation at weak forces
Shear stress dominates deformation at strong forces

Chin. J. Polym. Sci. 2013, 34, 1590

What is the mechanism of coil deformation in Monte Carlo simulations of driven polymers?

Time: the sequence of Markovian events

When the time scale >> particle collision,
and the space scale >> particle size,
Monte Carlo dynamics is convergent to Brownian dynamics

Sanz E, Marenduzzo D. Dynamic Monte-Carlo versus Brownian dynamics: a comparison for self-diffusion and crystallization in colloidal fluids. *J. Chem. Phys.* 2010;132:194102.

Brownian Dynamic simulations

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Bead-spring model: N=20

$$F_{drag\ i} + F_{spring\ i} + F_{Brownian\ i} + F_{driving\ i} = 0$$

Langevin Eq.

$$F_{drag\ i} = -\xi(r_i' - v)$$

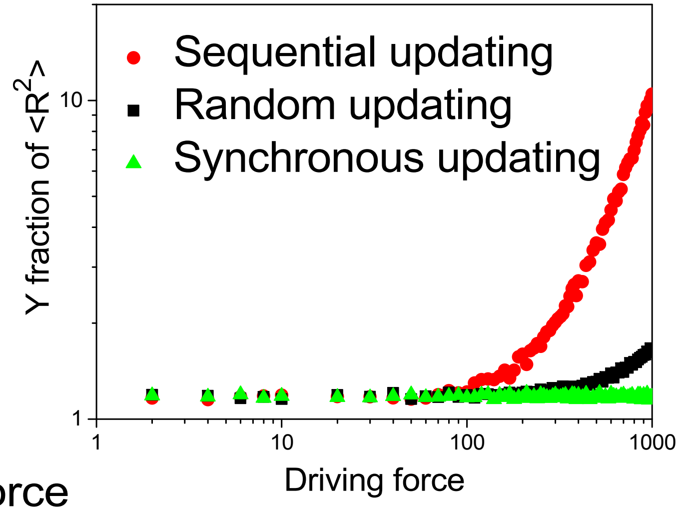
$$F_{spring\ i} = f_{spring\ i} - f_{spring\ i-1}$$ FENE model: $f_{sping\ i} = \frac{3k_BT}{b^2} \cdot \frac{R_i}{1-\lambda_i^2}$

$$F_{Brownian\ i} = g_i\sqrt{\frac{6\xi k_BT}{\Delta t}}$$

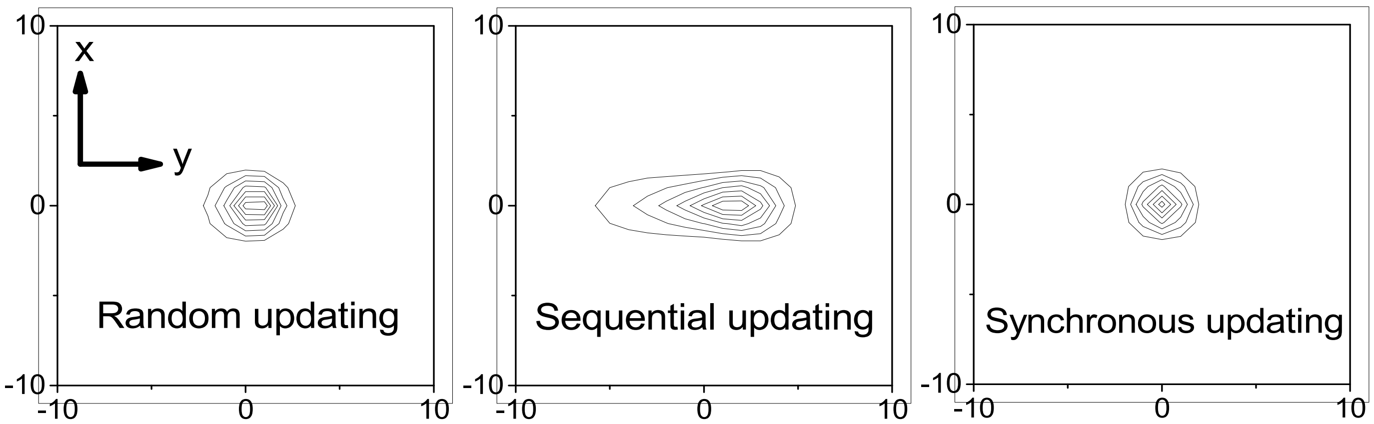
J. Li, W.-B. Hu,
Polymer International
2015, 64, 49–53

Non-synchronous motion: Dynamic heterogeneity

"Non-synchronous motion"
raises coil-deformation



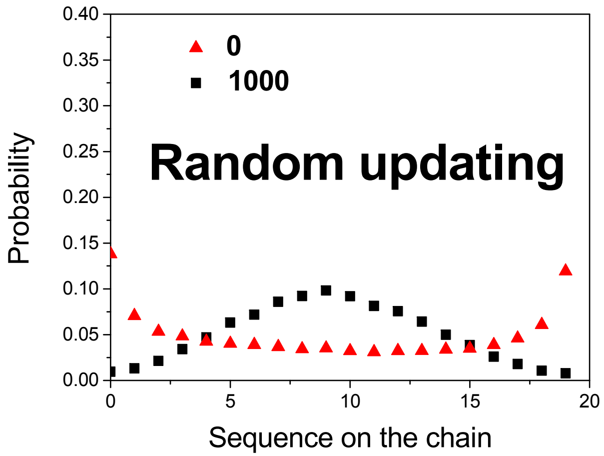
Driving force

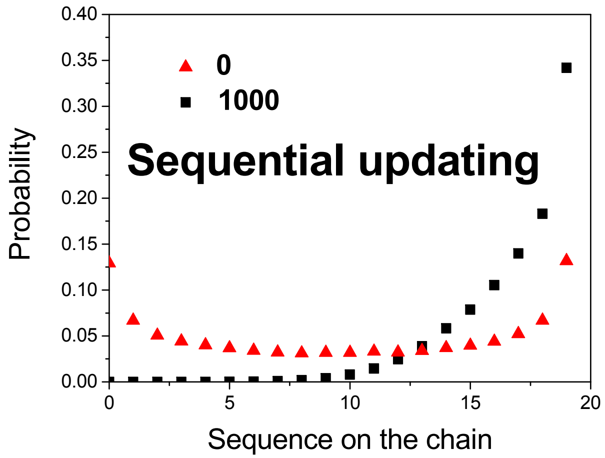


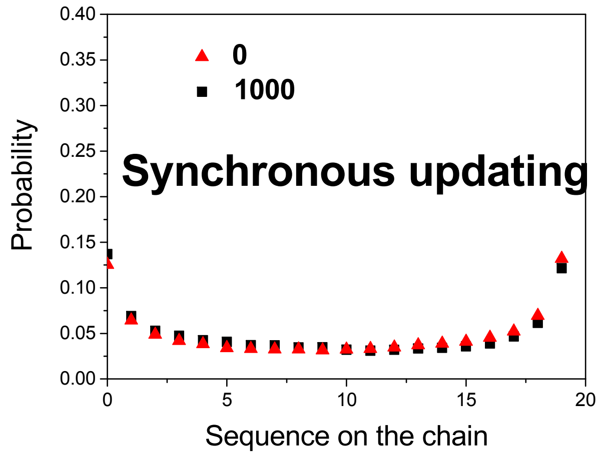
Which monomer at the coil front?

Random: chain end-and-middle asymmetry!

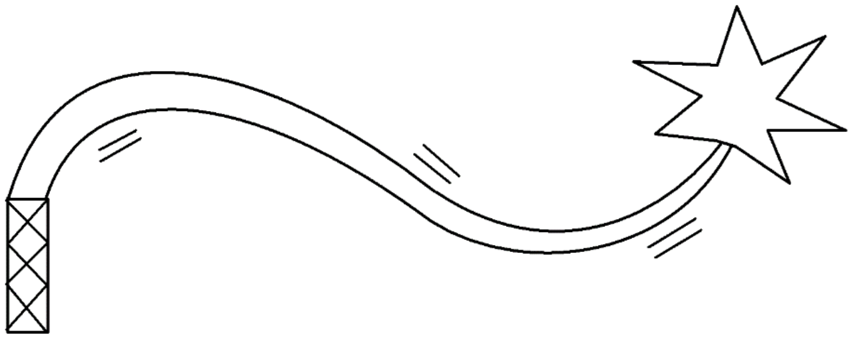
Sequential: Cracking the whip





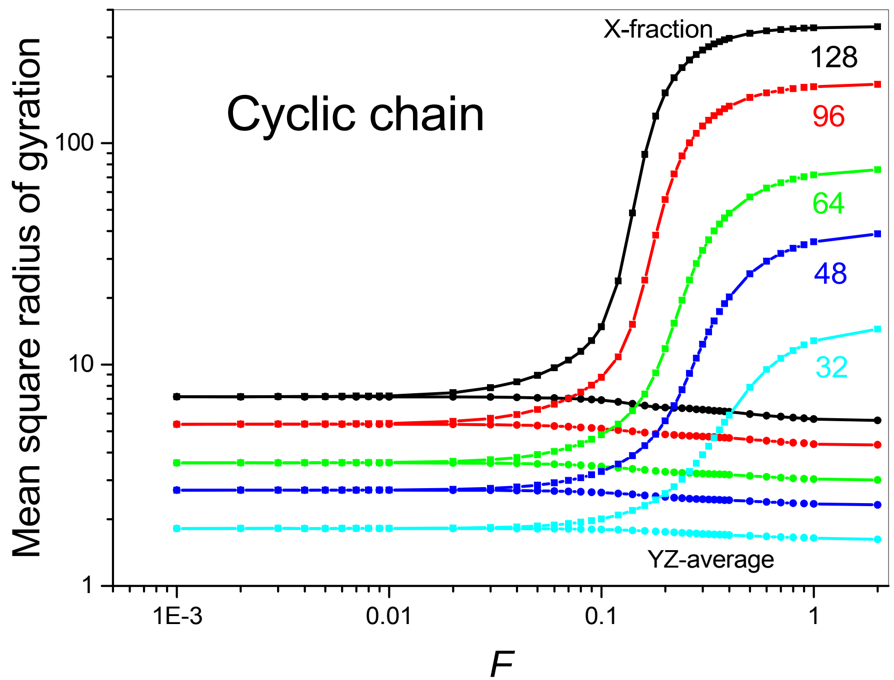


挥鞭效应 “cracking the whip”

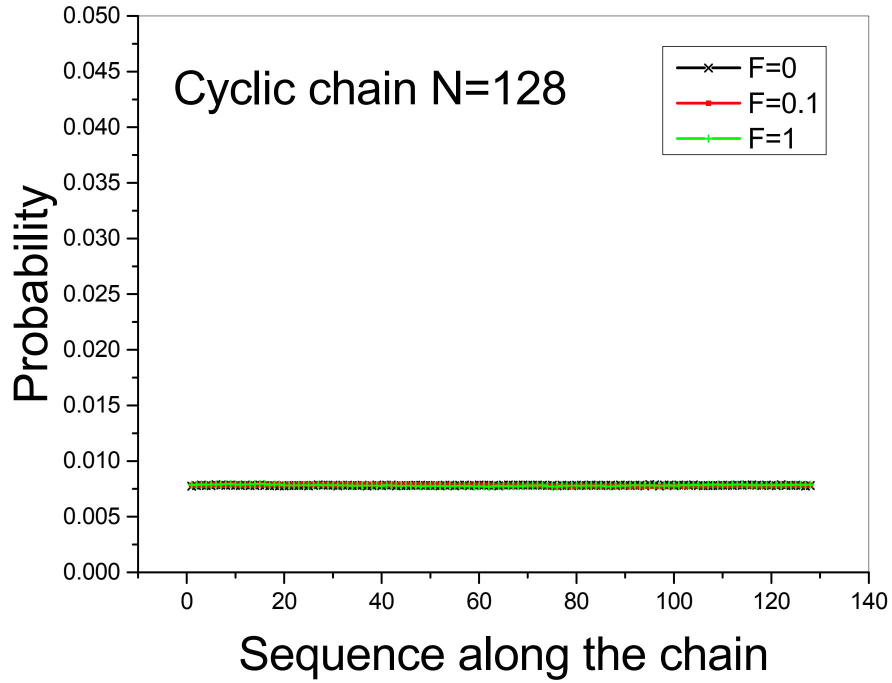


Cyclic polymer *New!*

Cyclic chains are still deformed!



Frontier monomer distribution

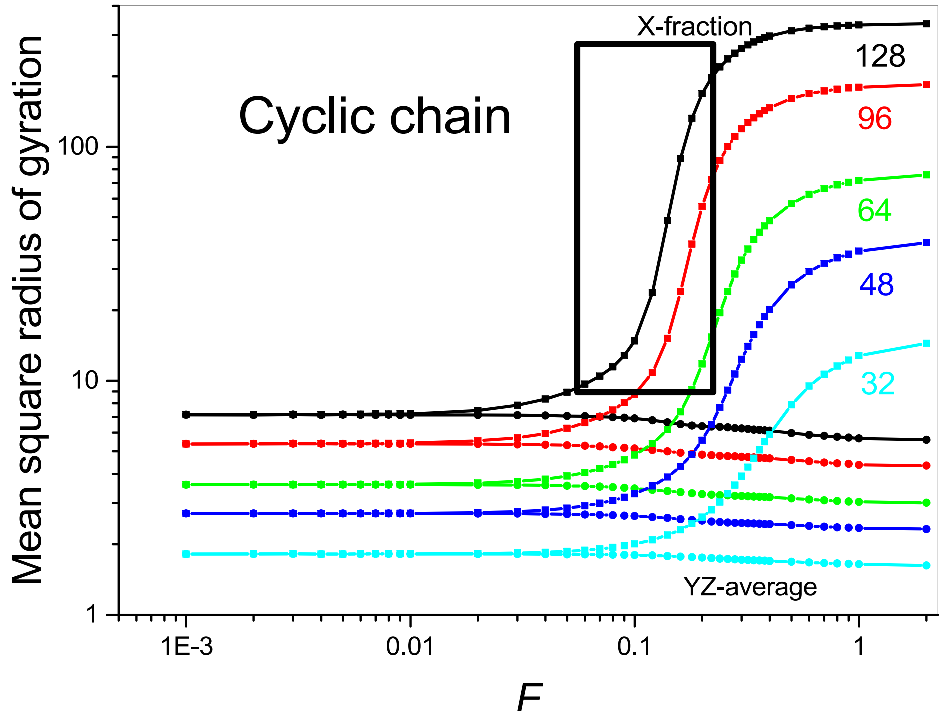


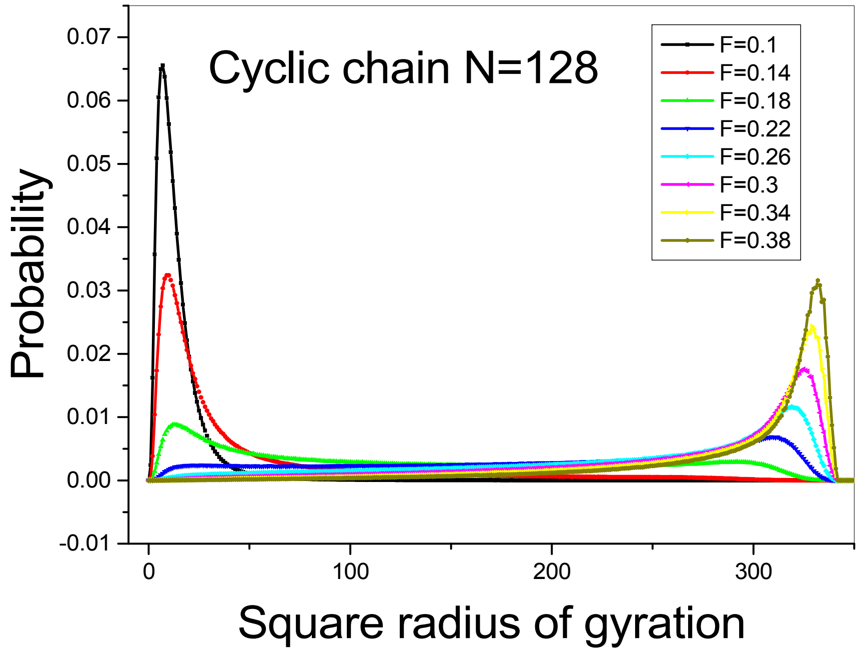
Chain end not matter!

Tao HC, Gao HH, Hu WB. *Mat. Chem. Front.* 2017, 1, 1349-1353.

How does the coil deform?

All or none in sizes

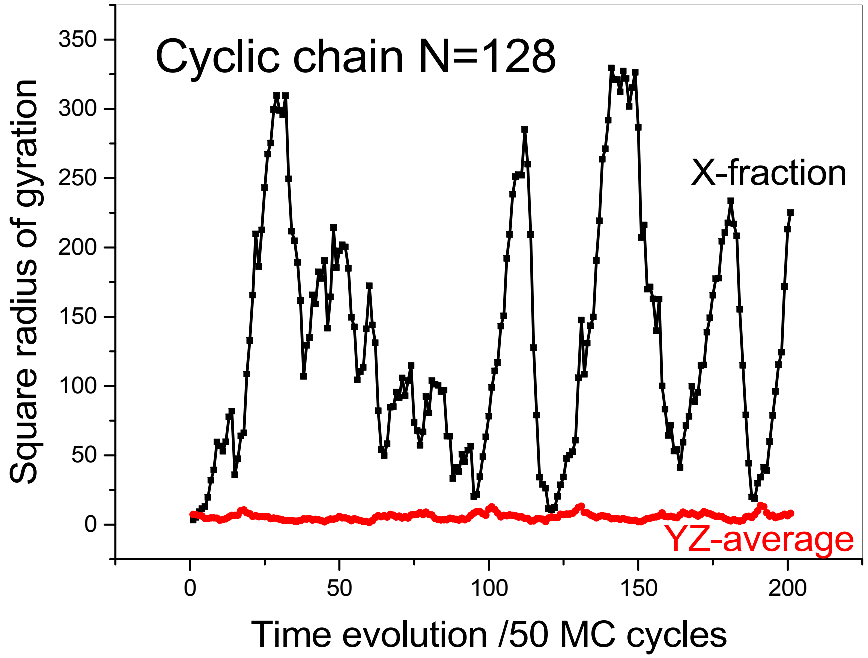


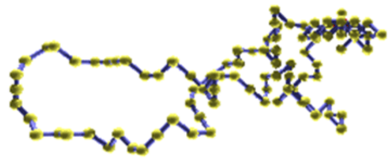


Tao HC, Gao HH, Hu WB. *Mat. Chem. Front.* 2017, 1, 1349-1353.

Cyclic polymer chain

No hysteresis



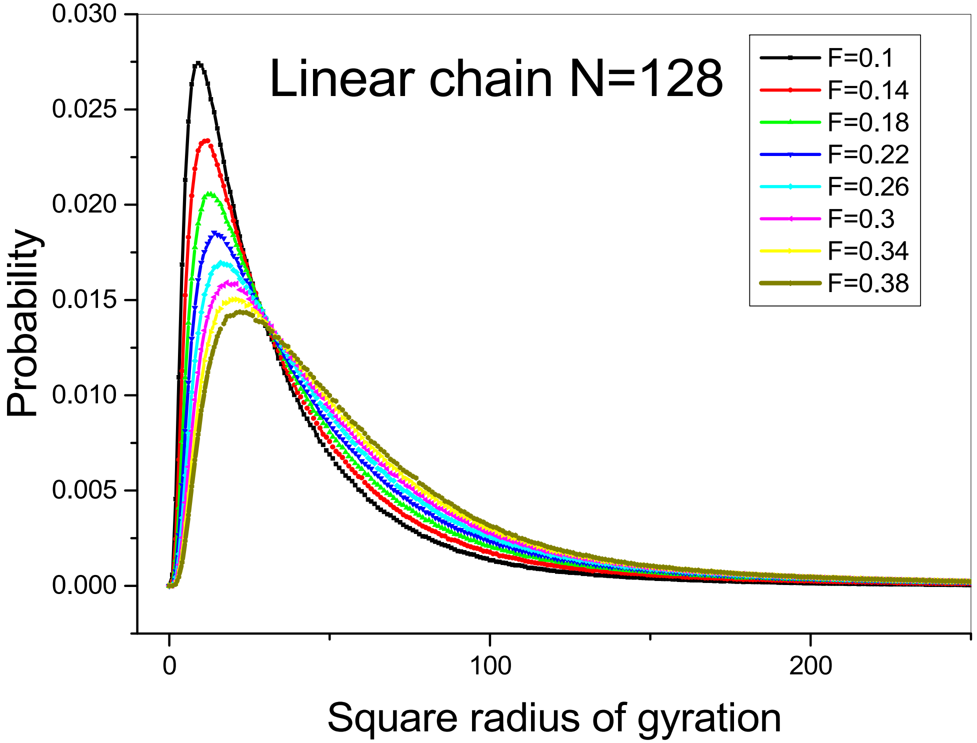


1

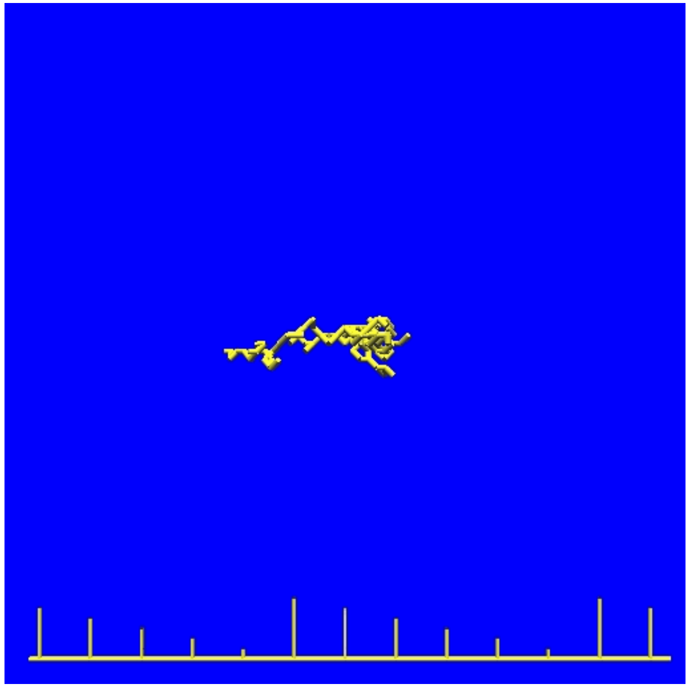
Tao HC, Gao HH, Hu WB. *Mat. Chem. Front.* 2017, 1, 1349-1353.

Linear polymer chain

Free chain ends smear out the coil-stretch transition!

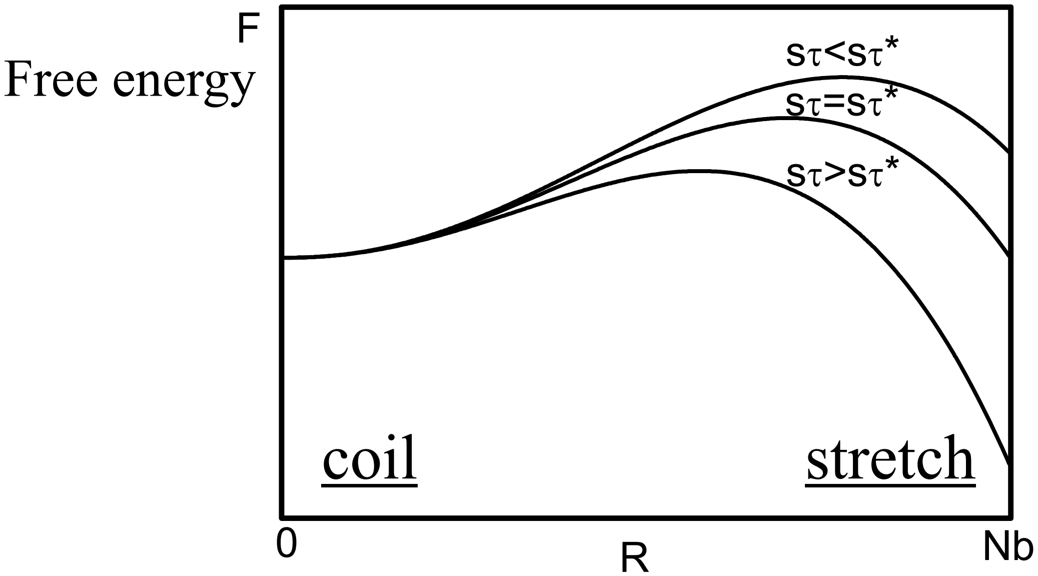


F=1



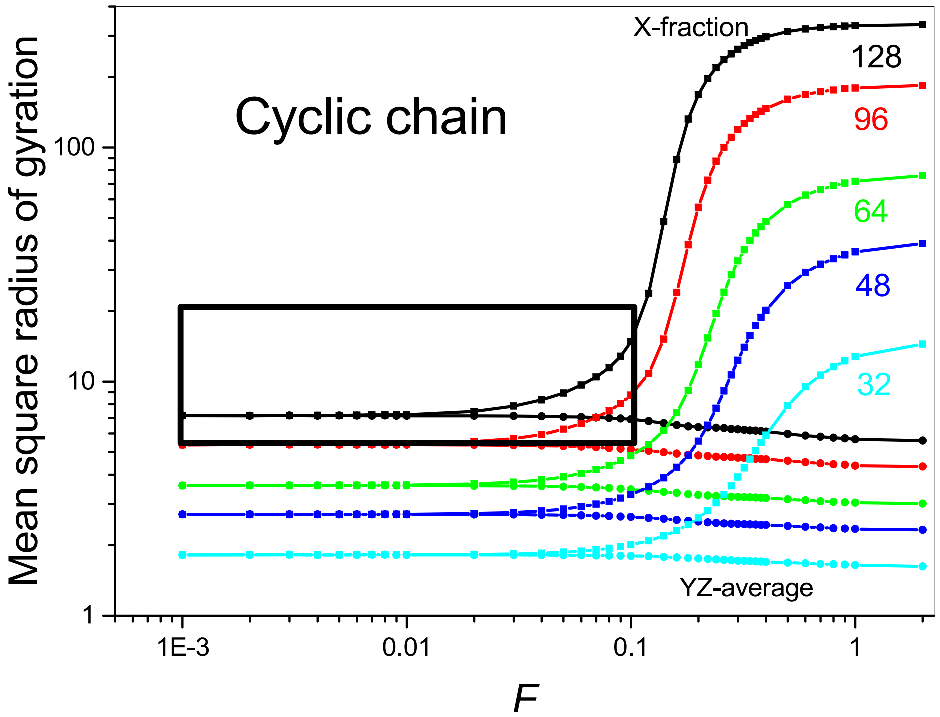
Coil-stretch transition

$$F = F_e + F_f \sim R^{5/2} - s\tau R^3$$



P. G. de Gennes. *Scaling Concepts in Polymer Physics*, Ithaca: Cornell University Press, 1979, p189

How does the coil deform?



Tao HC, Gao HH, Hu WB. *Mat. Chem. Front.* 2017, 1, 1349-1353.

Early-stage deformation

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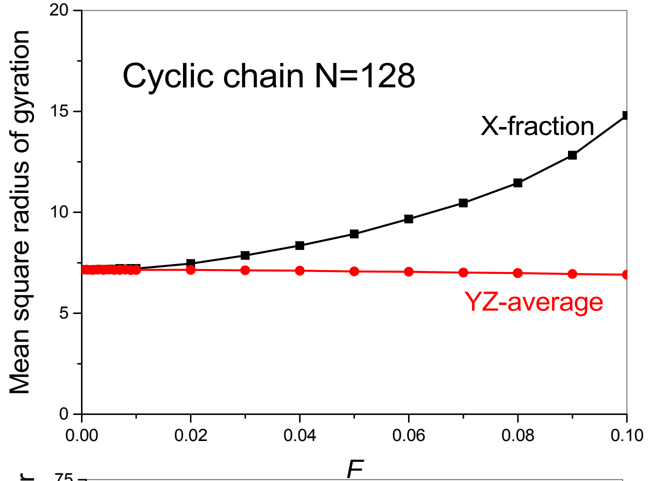
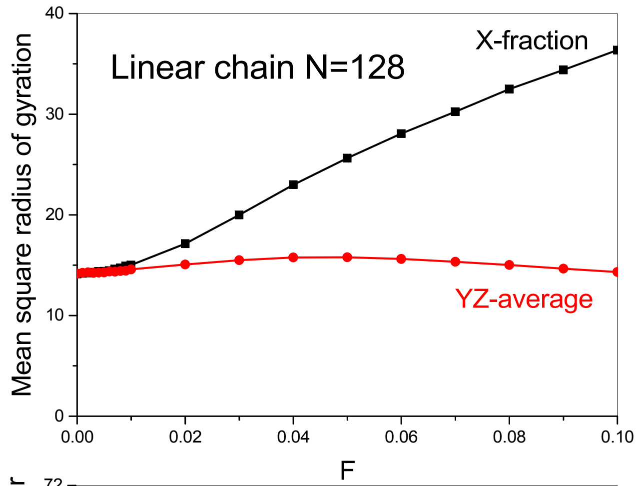
Cyclic chain

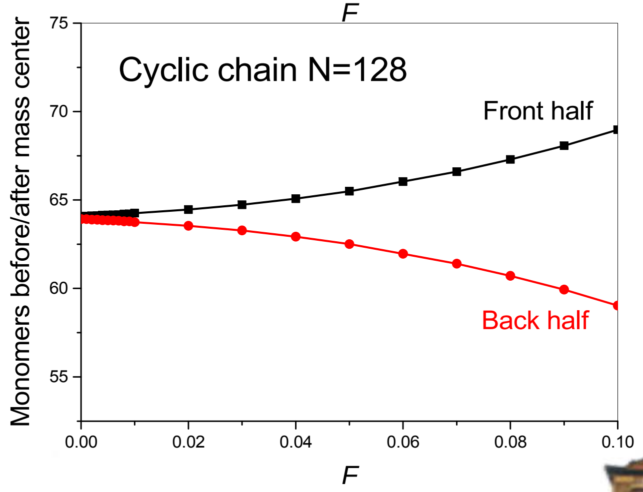
Linear chain

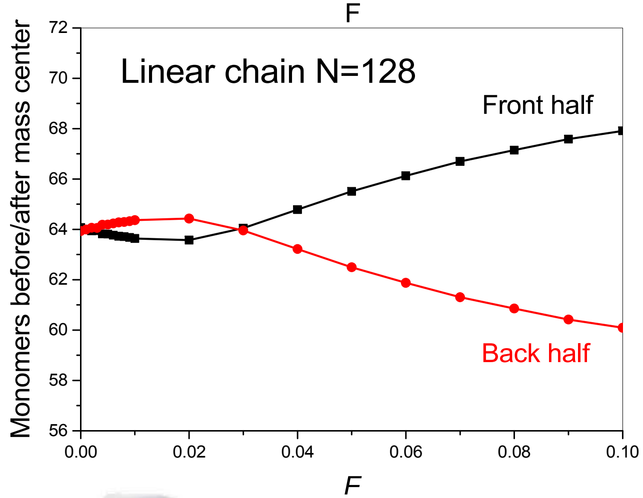
Coil size





Mass symmetry





Correlation length of forward motion: “cracking the whip”

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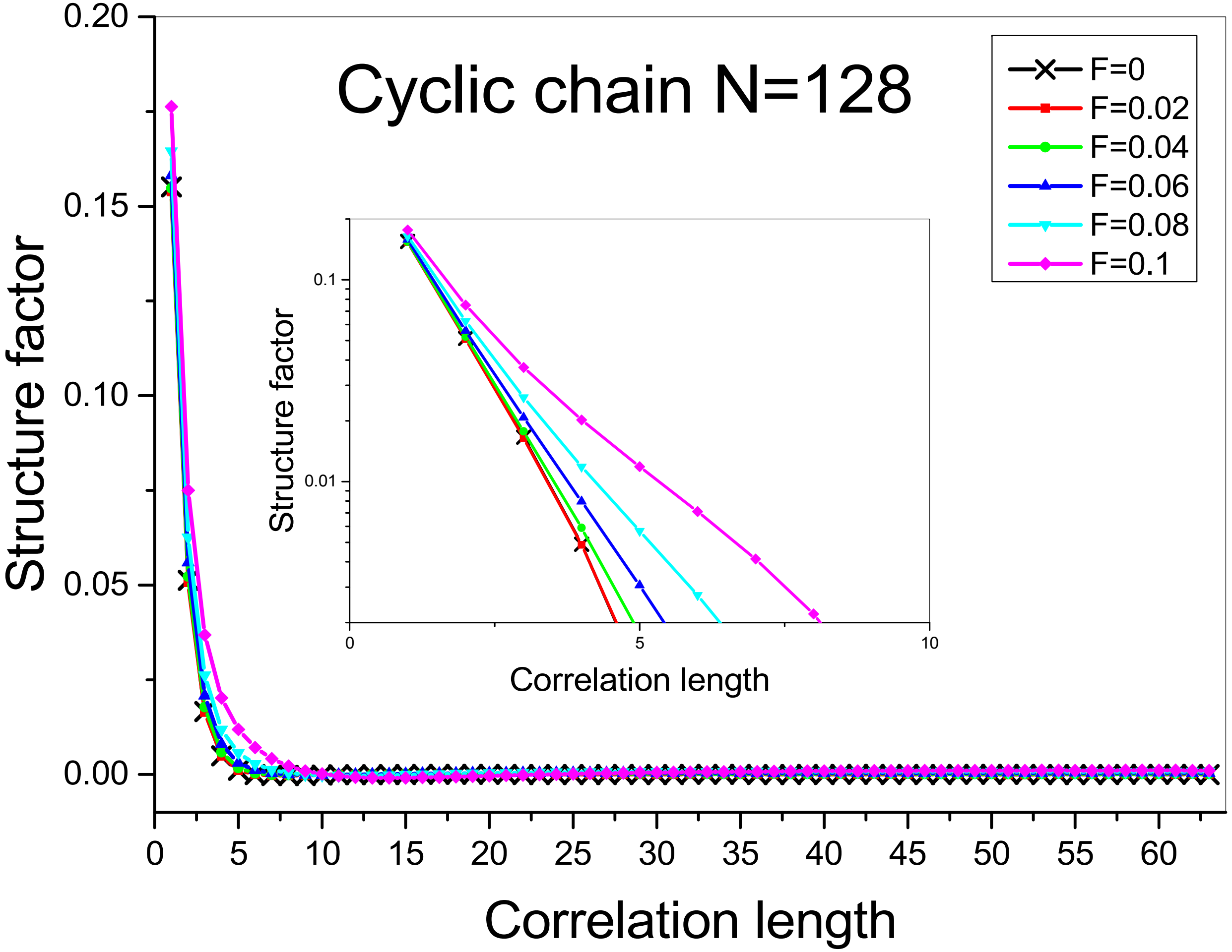

Summary for driven polymers

① Dynamic heterogeneity raises "cracking-the-whip" effect

② Stress(besides velocity gradient)-induced deformation

③ This deformation brings non-Newtownian fluid behaviors similar to the feature of polymer shear flow

Learn from anomalous!

Chain connection of polymer units

What’s consequence if one of them misses his/her step? → “Dynamic heterogeneity”

“Snap the whip” 1872 by Winslow Homer

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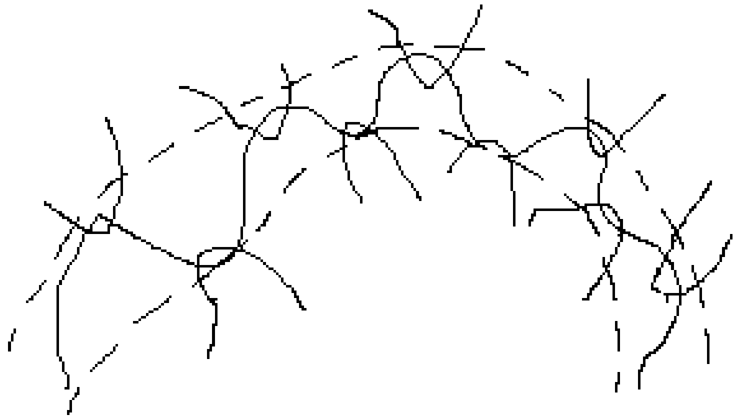
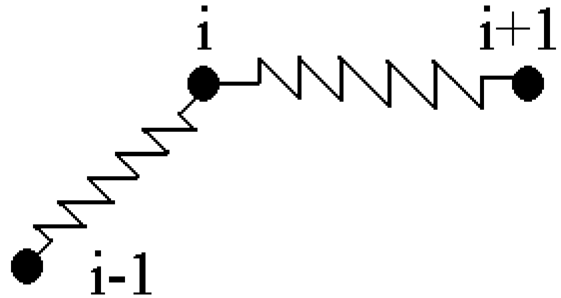
Hawk catches chicken

Origins of non-linear dynamics

Intermolecular plus Intramolecular





Entanglement confinement

Linear integration: tube model

Non-linear: Disentanglement

Entropic elasticity

Linear integration: Rouse model

Non-linear: Dynamic heterogeneity

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Acknowledgement

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  Yu Ma马禹

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  Huachen Tao陶华宸

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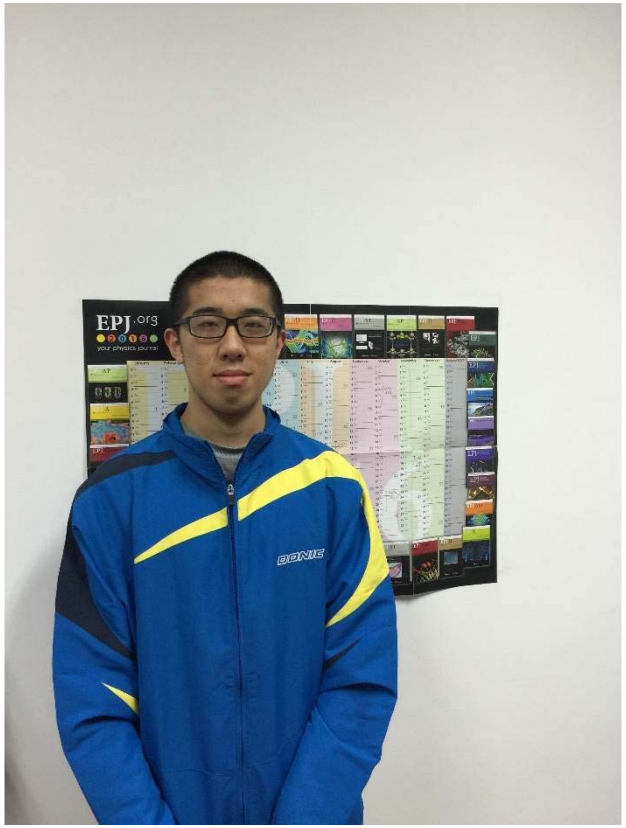
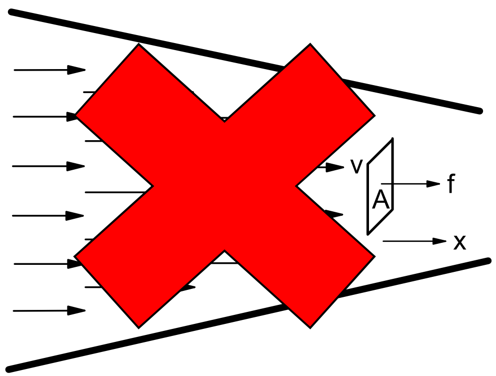
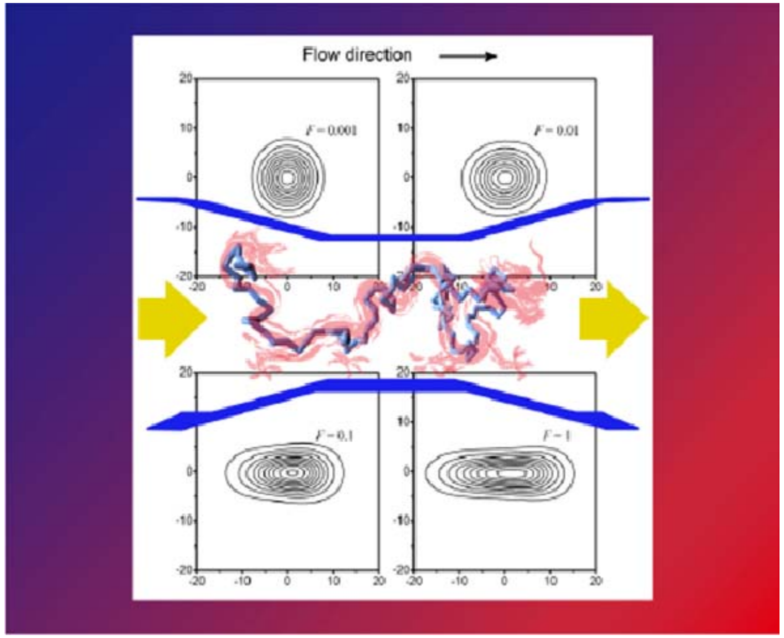


Simulation of extensional flow

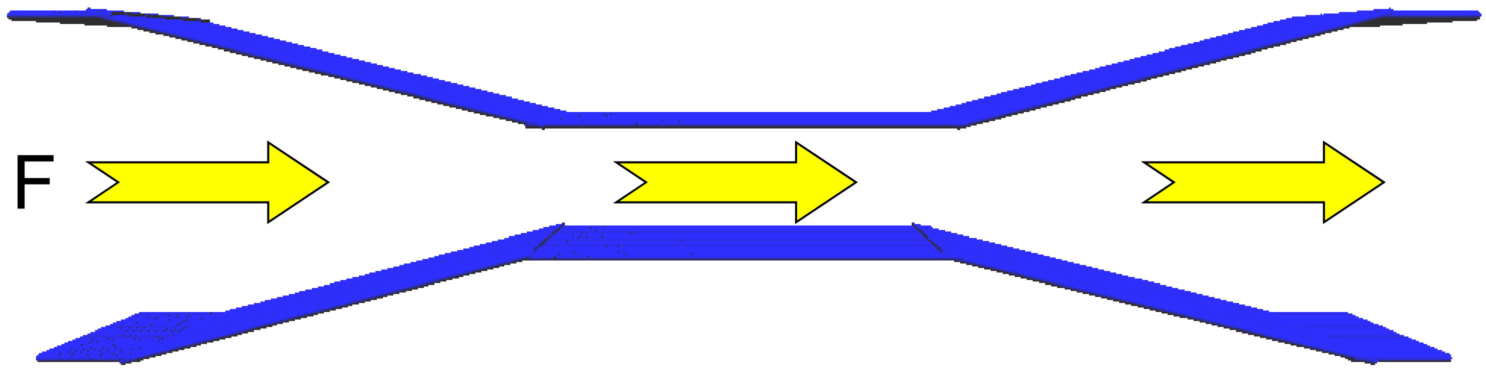


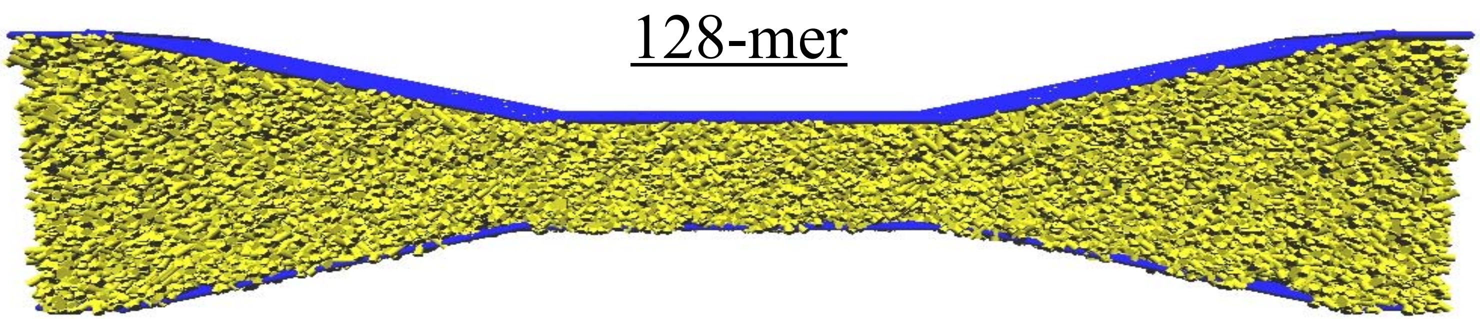
Cover art



Ma Y, Zhang XH, Hu WB. *Chinese J. Polym. Sci.* 2013, 31(11), 1463-1469.

Simulation of extensional flow





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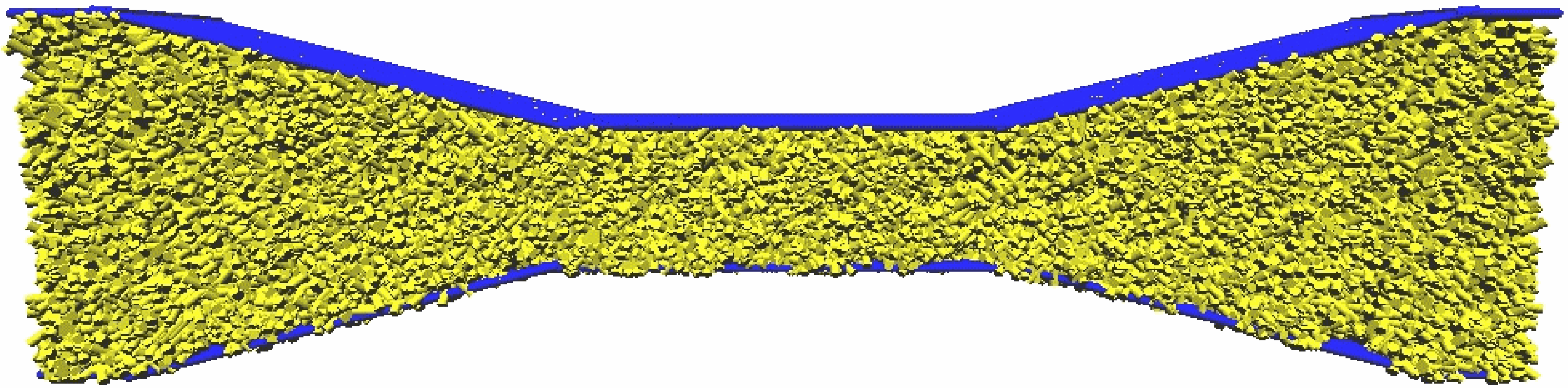
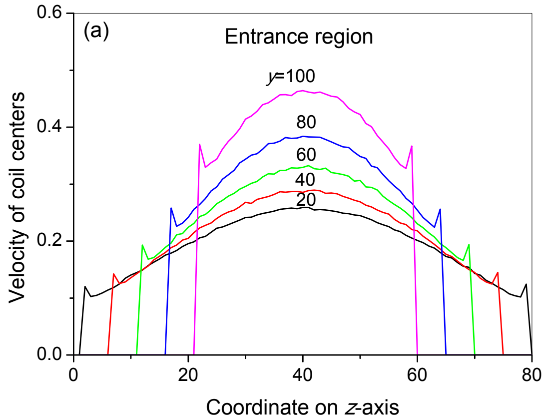
Simulation of extensional flow

F=1.0

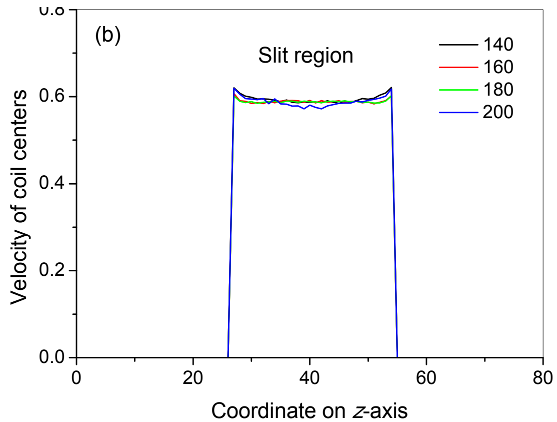


Velocity

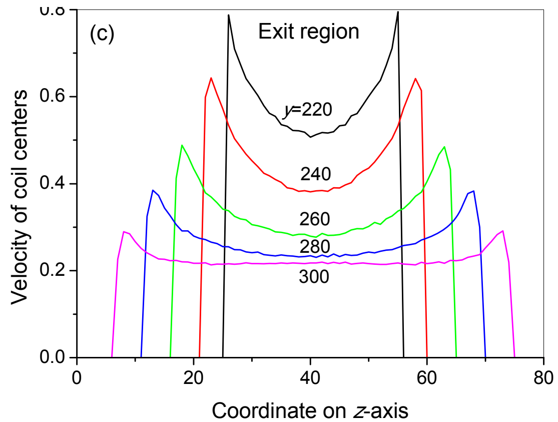
Acceleration



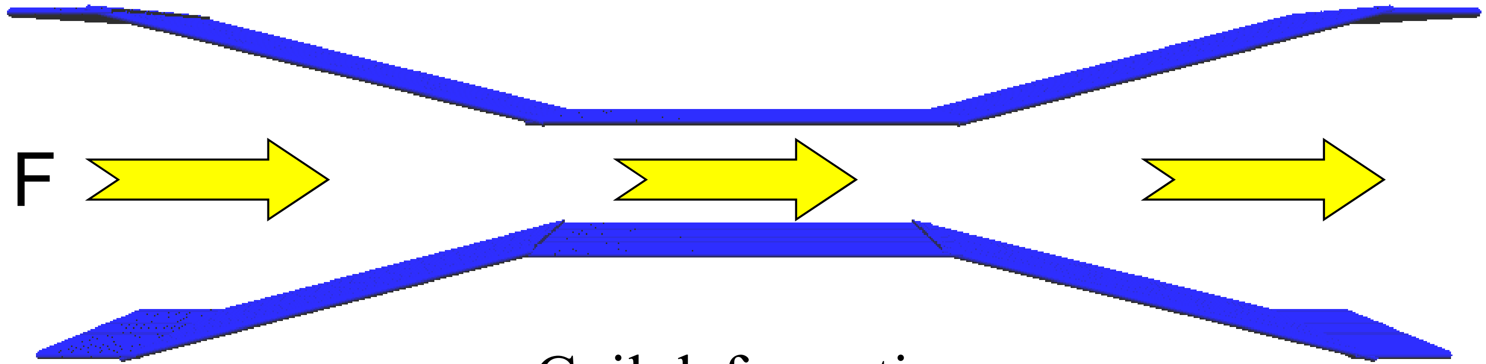
High speed

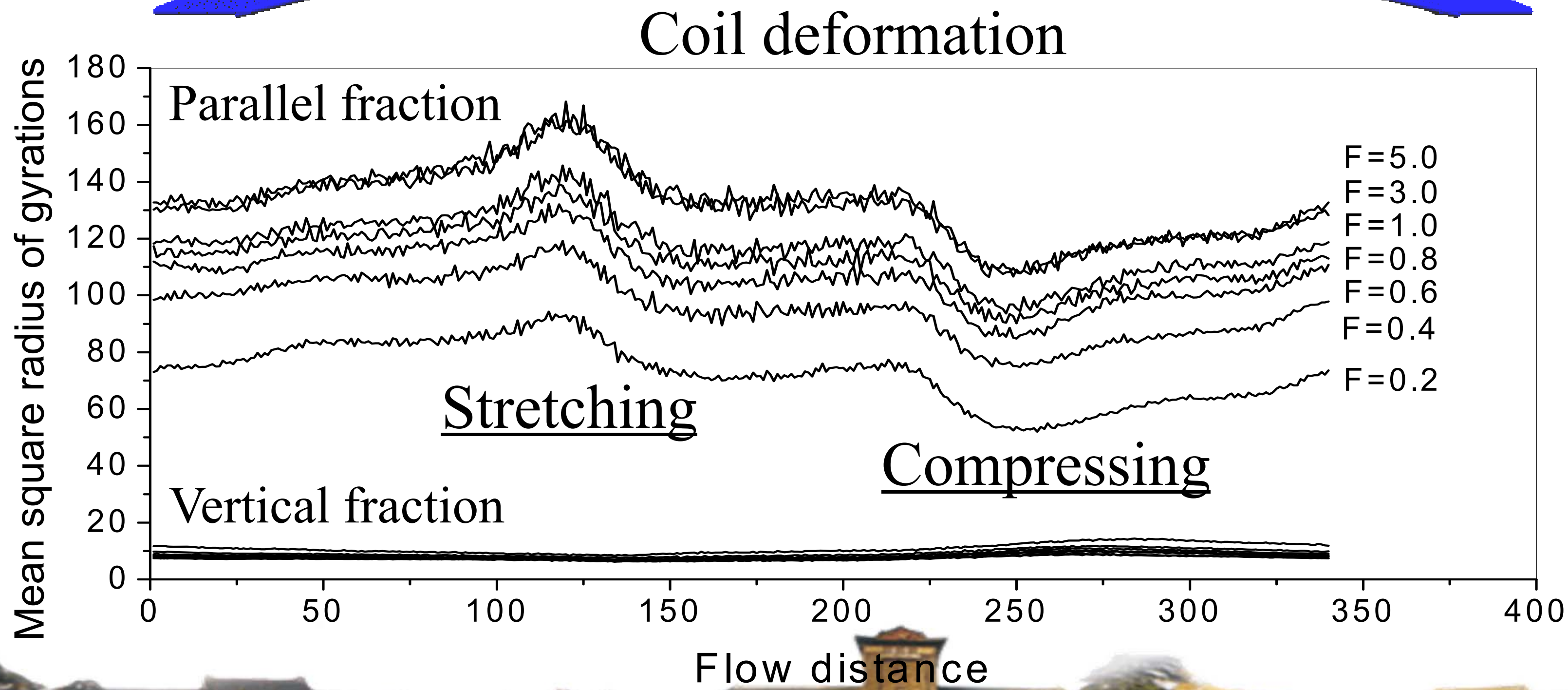


Slow-down



Simulation of extensional flow





Simulation of extensional flow

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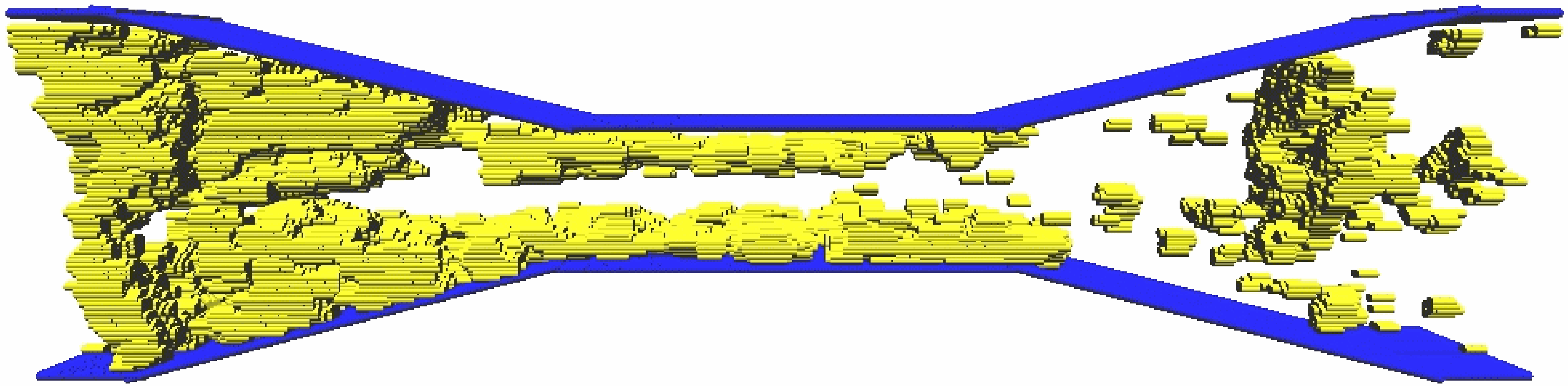
F=1.0



Thanks for your attention !

Welcome discussion!