The Coil-Stretch Transition after 30+ Years

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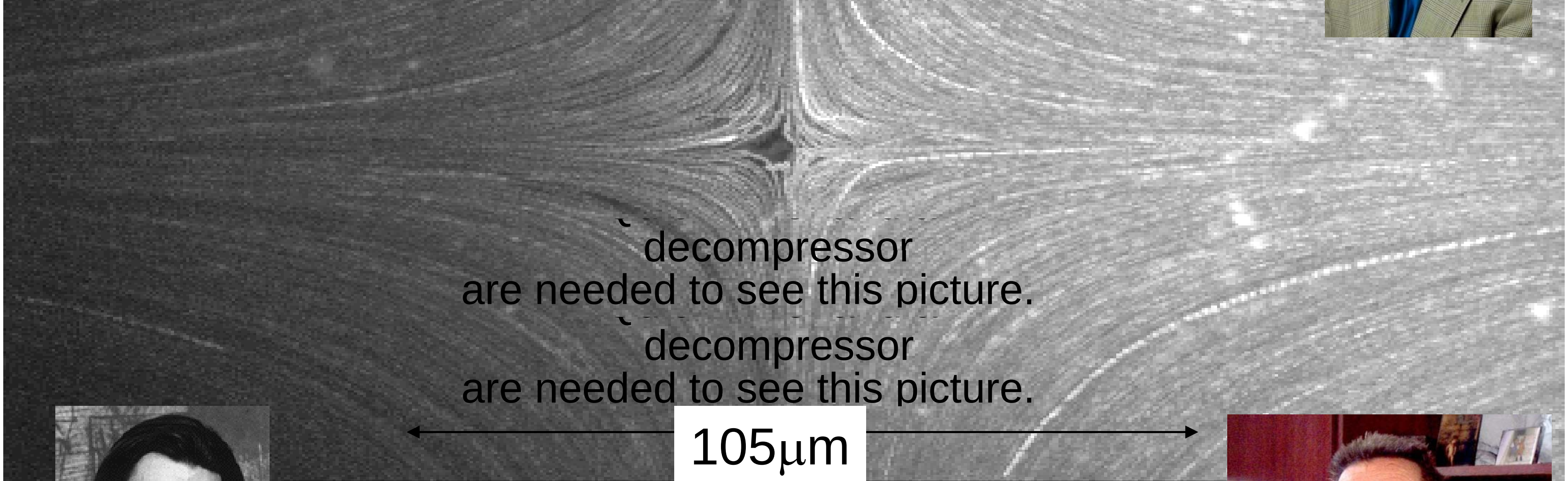
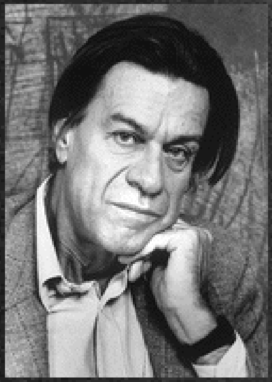
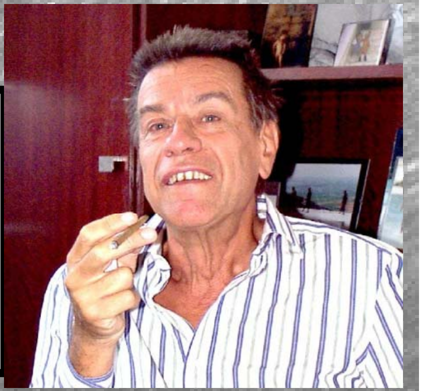


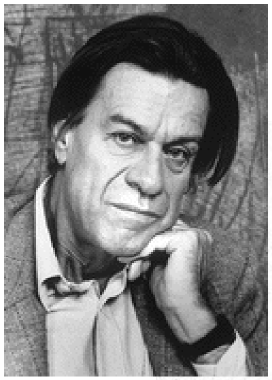


APS March 2008 Meeting
Symposium Honoring P.G. DeGennes
Murial Convention Center, New Orleans, LA
March 13, 2008

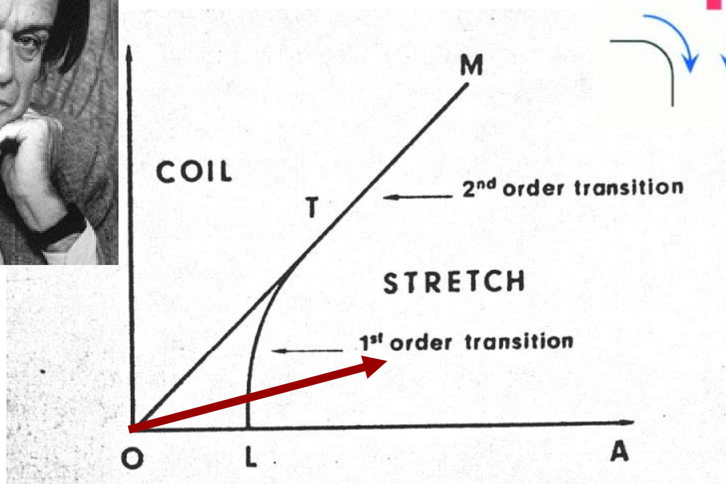


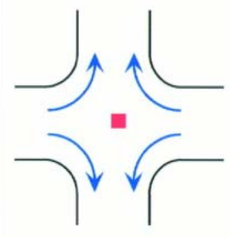
A Problem for More than Thirty Years: The “First Order” Coil-Stretch Transition in Extension

Coil-stretch transition of dilute flexible polymers under ultrahigh velocity gradients

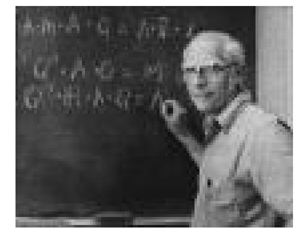


De Gennes, 1974

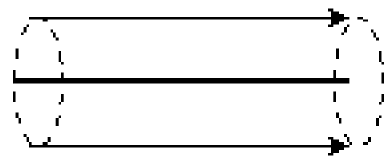




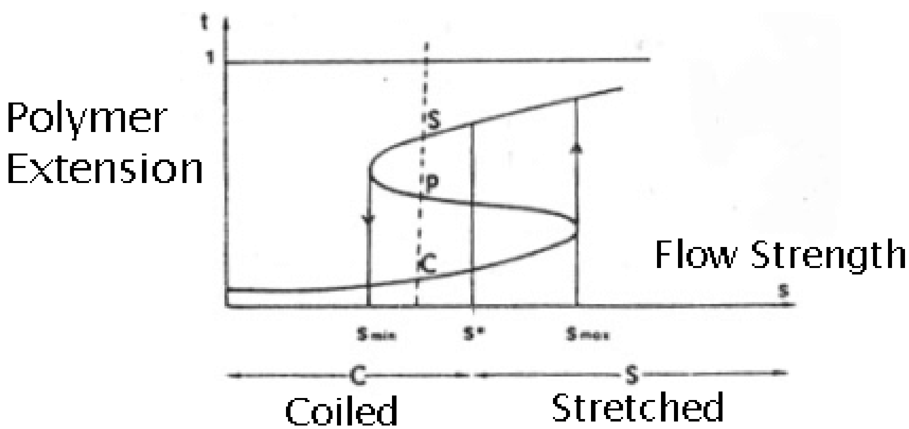
$$F^{Drag} \propto M^{0.6}$$



Bruno Zimm



$$F^{Drag} \propto M^{1}$$



$$\frac{F^{drag}_{extended}}{F^{drag}_{coiled}} \sim M^{0.4} \text{ or } N_k^{0.4}$$

$$\left(actually \quad \frac{N_k^{0.4}}{\ln N_k} \right)$$

Before DeGennes' work on the Coil-Stretch Transition…

It was well known that at a critical value of the flow strength for flows with "longitudinal gradients" (ie. extensional flows) that polymer dumbbell models exhibited a singularity in extension which could be relieved by including the nonlinearity of the effective spring force.

Peterlin, Pure Appl. Chemistry, 12, p. 273 (1966)

Takserman -Krozer J. Poly. Sci A 1 p. 2477 (1963)

This singularity had already been postulated as being at the root cause for turbulent drag reduction.

Lumley, Ann. Rev. of Fluid Mech. 1, 367 (1969)

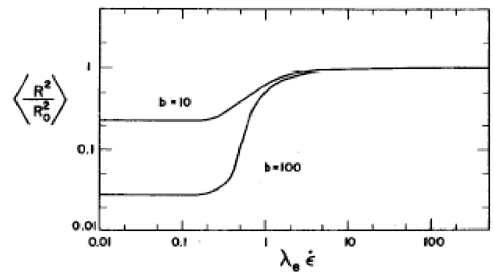


Fig. 4. Molecular elongation as a function of elongational rate $\dot{\epsilon}$ in steady elongational flow, as predicted by eqns. (7) and (41) for FENE-P dumbbells.

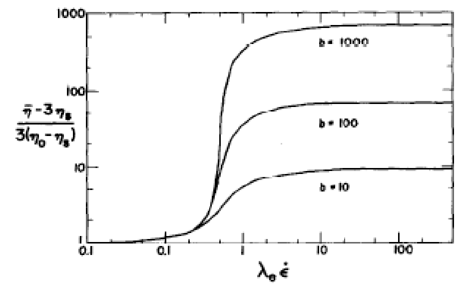


Fig. 3. Elongational viscosity of a dilute suspension of FENE-P dumbbells as a function of elongation rate $\dot{\epsilon}$, based on eqn. (35) (for the same molecular model used in Figs. 1 and 2).

$$F^{(c)} = HR/[1-(R^2/R_0^2)].$$

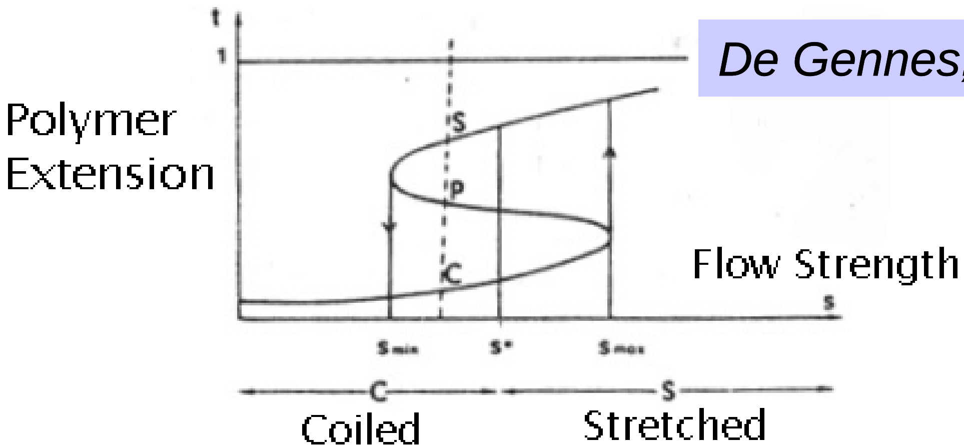
Indeed, DeGennes contribution was examining the known coil-stretch transition in light of Bruno Zimm's results for hydrodynamic interactions within a polymer chain.

B.H. Zimm, J. Chem. Phys. 24, 269 (1956)

The "S" shaped curve and the Double Well Potential….

Involves preaveraging

$F^{(c)} = HR/[1-(R^2/R_0^2)]$ ⟷ $F^{(c)} = HR/[1-\langle R^2/R_0^2\rangle]$



De Gennes, 1974

Supporters
- ***Fuller and Leal, 1980***
- ***Hinch, 1974***
- ***Tanner, 1975***

Critics…..
- ***Fan and Bird, 1985***
- ***Fan, Bird, and Renardy, 1985***
- ***Wiest, Wedgewood, and Bird, 1988***

Does not involve preaveraging, but other Boltzmann approximations…

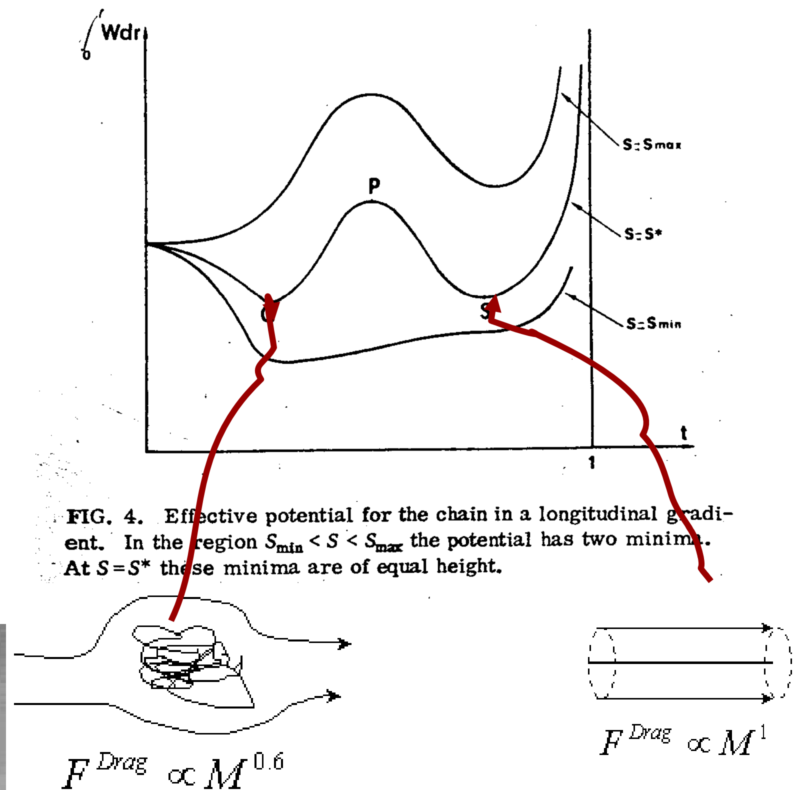


FIG. 4. Effective potential for the chain in a longitudinal gradient. In the region $S_{min} < S < S_{max}$ the potential has two minima. At $S = S^*$ these minima are of equal height.

Words from John Hinch 1974, 1977, 1992….

Hinch, E.J. 1974 Mechanical models of dilute polymer solutions for strong flows with large polymer deformations in Polymeres et Lubrification Colloques Internl. du C.N.R.S. 233, 241-247.

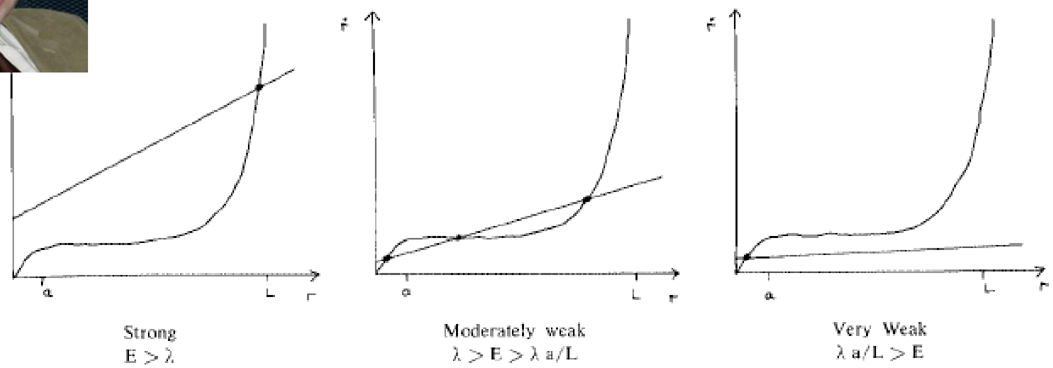
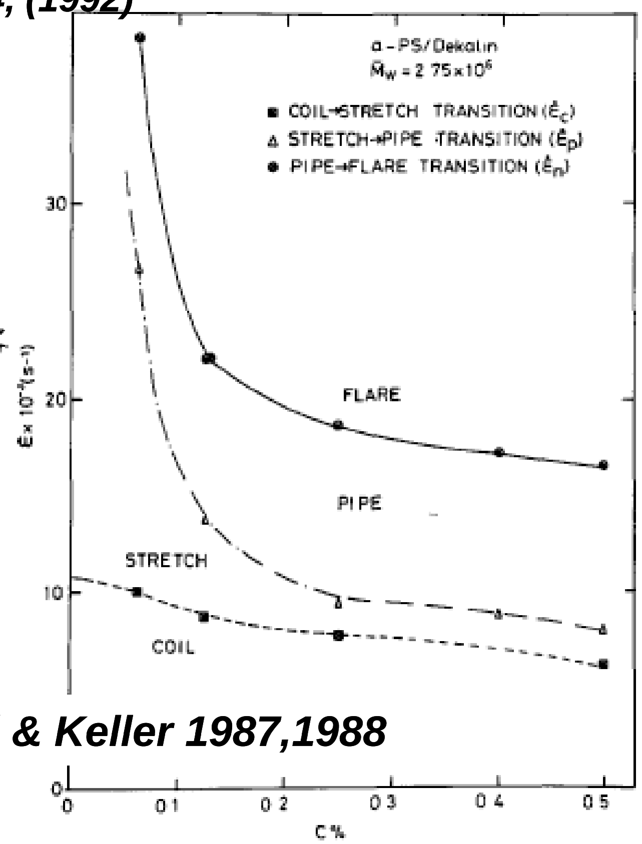


FIG. 3. — Classes of flow strengths for the nonlinear dumb-bell.

Birefringent Pipes (w/ Harlen, Rallison), JNNFM 44, (1992)



Odell & Keller 1987,1988

Mechanical Models of Dilute Polymer Solutions in Strong Flows, Phys. Of Fluids, 20, (1977)

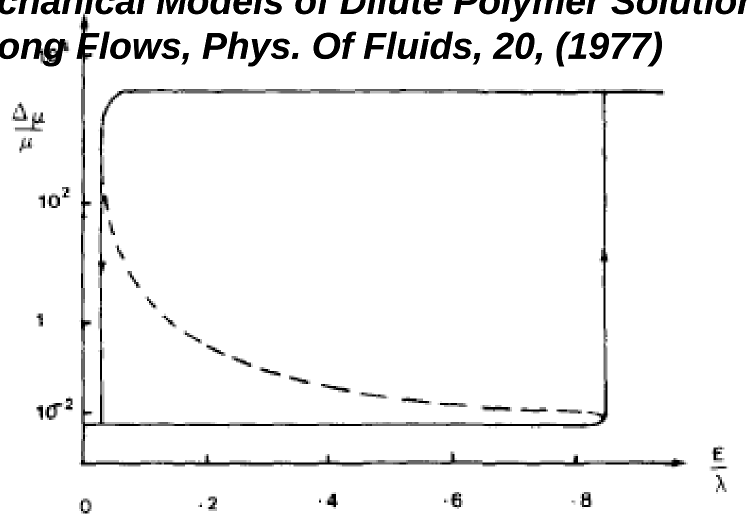
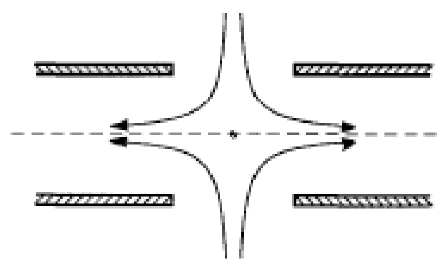


FIG. 3. The polymer contribution to the viscosity as a func of the axisymmetric strain rate.



QuickTime?and a
decompressor
are needed to see this picture.

Words from Roger Tanner….

Stresses in dilute solutions of Bead-Nonlinear-Spring Macromolecules. III. Friction Coefficient Varying with Dumbbell Extension, *Transactions of the Society of Rheology*, 19:4 557-582 (1975)

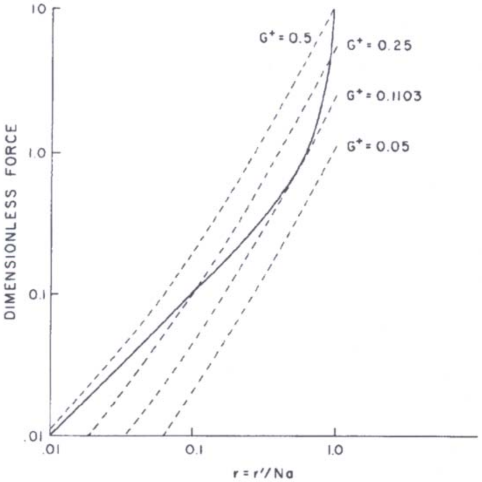


Fig. 3. Spring force (F^s) for Warner spring as a function of extension (r) shown by (—) curve. The (---) curves show the hydrodynamic forces (no Brownian motion) for various dimensionless elongation rates G^* for the case $\beta = 10$, $N = 100$.

"Corresponding to the two stable equilibrium positions we expect two humps in the distribution function (really two potential wells)… where the bead has to 'leak' from one well to another to achieve permanent equilibrium, these processes may take a very long time."

Words from Bob Bird….

Configuration-Dependent Friction Coefficients and Elastic Dumbbell Rheology, JNNFM, 18 pp. 255-272 (1985) (w/ Fan and Renardy)

Comment #1

end-to-end distance. Previous investigators did report S-shaped curves and related "hysteresis" effects. However, their results were based on using mathematical approximations that now appear to be inappropriate.

Comment #2

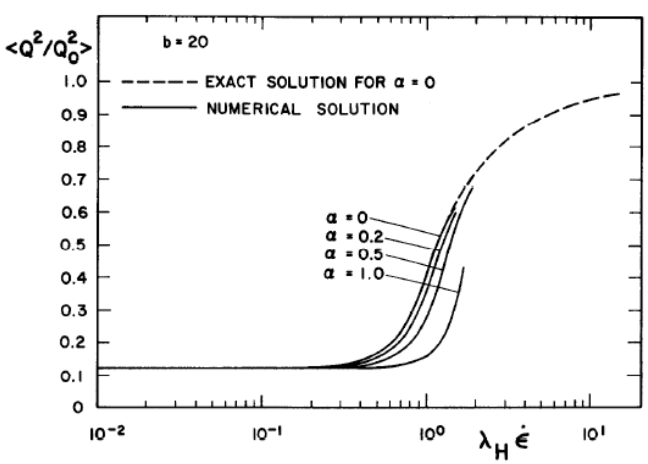
As a remark on the side, even if the steady state distribution function were not unique, this would not lead to S-shaped curves, because a linear equation can never have two solutions (or three solutions). If a linear equation has two solutions, it has an infinite number.

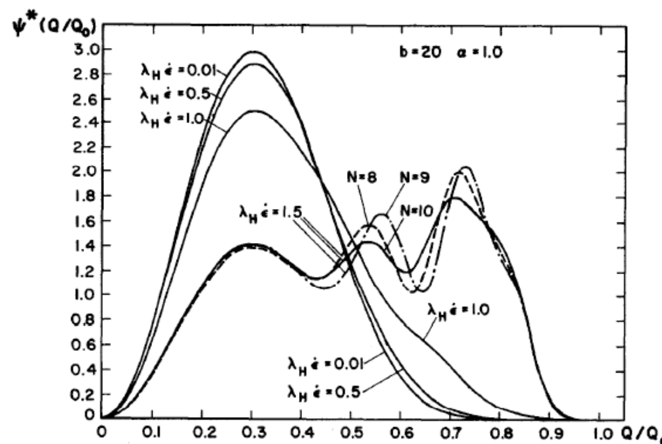
Comment #3

It has been pointed out to us by several others who have worked with variable-ζ dumbbells that it may not be sufficient to study just the steady-state situation discussed here, and that the question of the time required to attain steady state may be an interesting and challenging problem [29].

SEE →

J.M.L. Wiest, L.E. Wedgewood, R.B. Bird, On coil-stretch transitions in dilute polymer solutions, J. Chem. Phys. 90 (1988) 587–594.



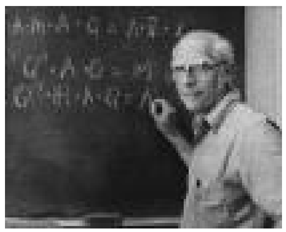


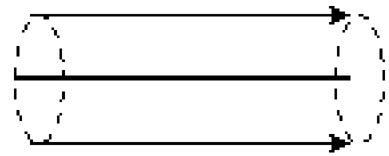
[29] E.J. Hinch, Private Communication

A Further Complication: High Molecular Weights Needed for Large Drag Ratios

$$F^{Drag} \propto M^{0.6}$$

Bruno Zimm





$$F^{Drag} \propto \frac{M}{\ln(M)}$$

E J Hinch

$$\frac{F^{drag}_{extended}}{F^{drag}_{coiled}} \sim \frac{N_k^{0.4}}{\ln N_k}$$

(Slender body theory, Batchelor 1971)

$$\zeta^{rod} / \zeta^{coil} =$$

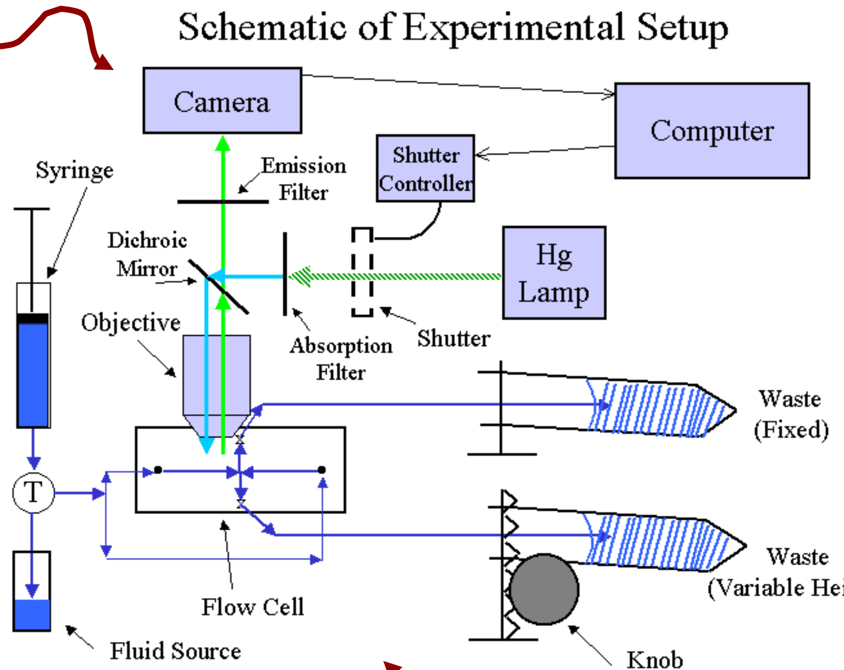
- 1.6 - 1-lambda DNA (N_k=150, 48.5 Kb, 21 μm)
- 2.7 - 8-lambda DNA (N_k=1200, 388 Kb, 168 μm)
- 3.3 - 15-lambda DNA (N_k=2250, 728 Kb, 315 μm)
- 4.7 - 1 mm DNA (N_k=7140, 2.3 MB → 5.3E6 g/mol PS)
- 6 - 2.1 mm DNA (N_k=14280, 4.8 MB)
- 18 - 20 million g/mol polystyrene, θ-solvent (N_k=26,939 → 3.8 mm DNA)

<u>Comment by Hatfield & Quake after simulating polymers of 20 Kuhn steps</u> *"Dynamic Properties of an Extended Polymer in Solution" PRL,* ***82*** *(1999)*

"Thus the notion that extended polymers have longer relaxation times is inconsistent with our calculations… We conclude that hysteresis exists only in the highly idealized case of an infinite length polymer"

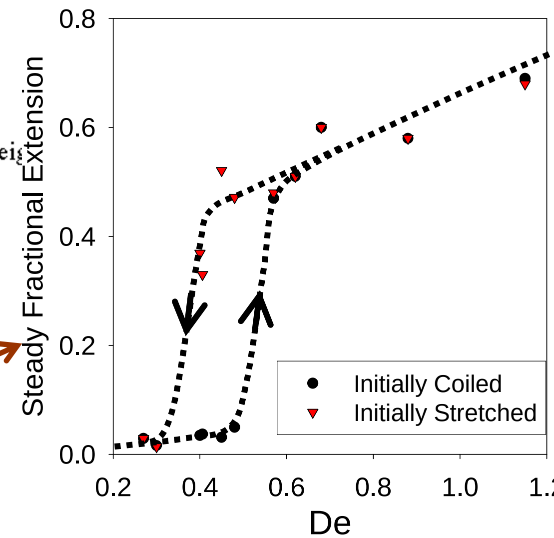
Hysteresis Experimentally Demonstrated in 2003

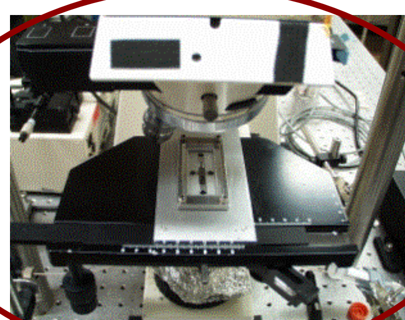
C.M.Schroeder, H. Babcock, E.S.G. Shaqfeh, S. Chu <u>Observations of Polymer Conformation Hysteresis in Extensional Flow</u>, Science, 301, 1515-1519 (2003)



DNA Fractional Extension

E. Coli DNA 10000 N_k



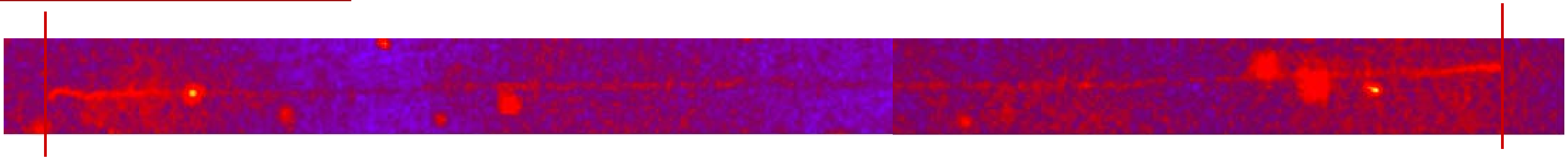


U.S. Patent No. 7,013,739

Hysteresis: Extended and Coiled States at De=0.45 for SAME MOLECULE 1300 μm DNA

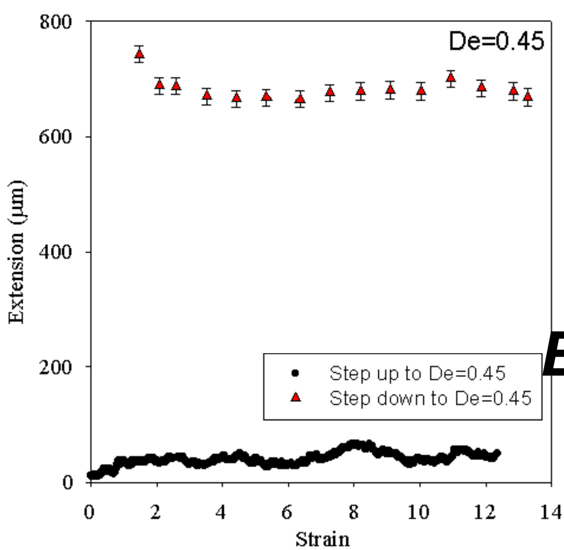
Step down

After 13 strain units



Step up

QuickTime?and a
Microsoft Video 1 decompressor
are needed to see this picture.

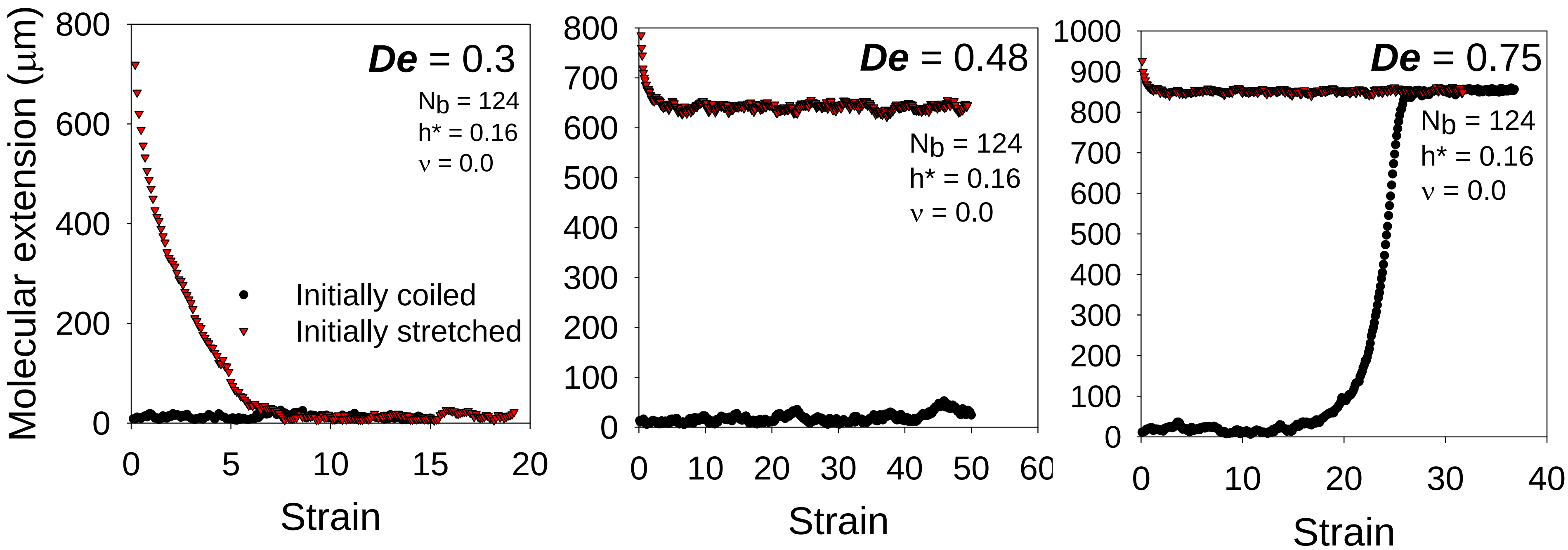


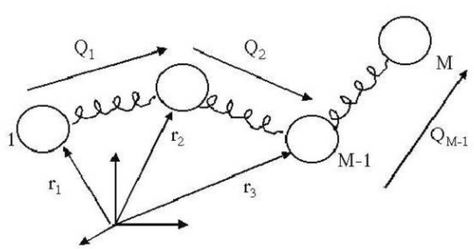
100 μm

Strain over course of movie = 12.5

Experimental time approx. 1 hour

Transient Fractional Extension for bead-spring chains with 124 beads, $N_{k,s}$ = 80, and h = 0.16 with Rotne Prager Yamakawa HI (L=1.3 mm, Nk=9840)*





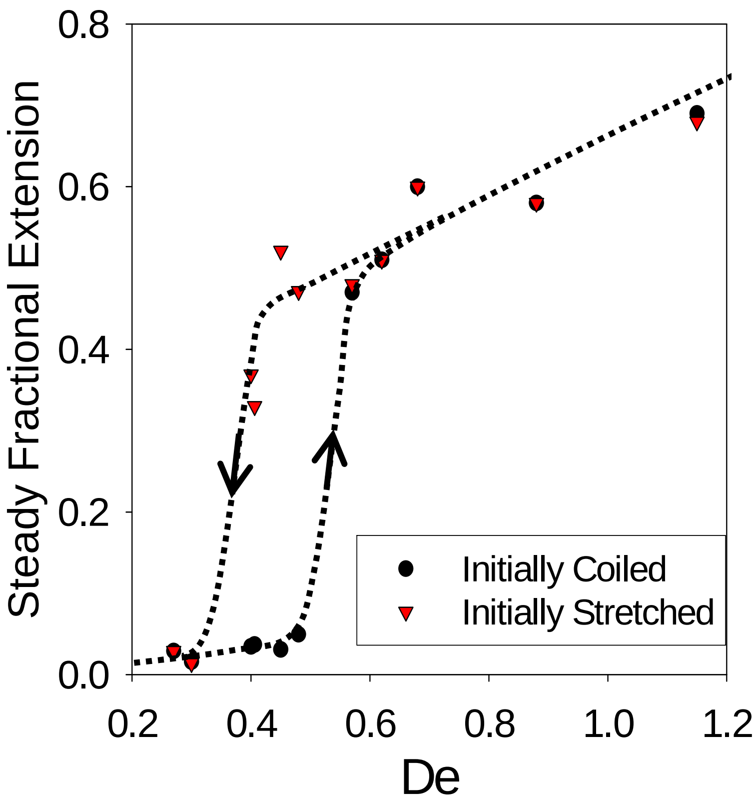
FOKKER-PLANCK EQUATION FOR BEAD SPRING CHAIN (WITH HI):

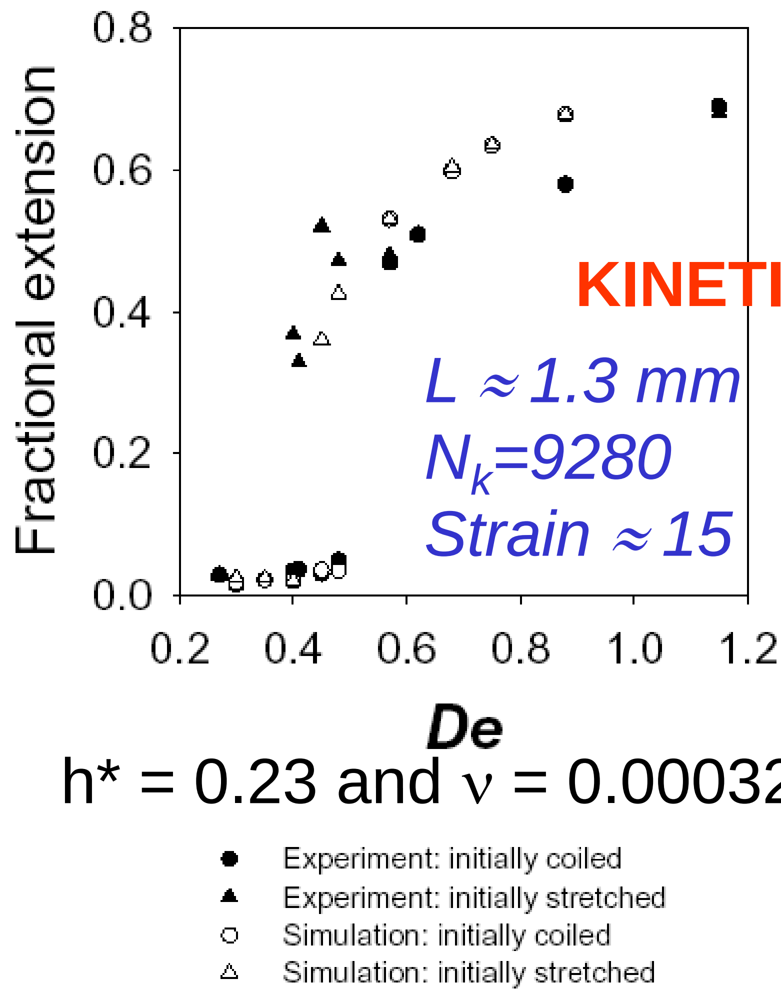
$$\frac{\partial \Psi}{\partial t} = -\sum_{i=1}^{M} \frac{\partial}{\partial \mathbf{r}_i} \cdot \left\{ \left[\boldsymbol{\kappa} \cdot \mathbf{r}_i + \sum_{j=1}^{M} \mathbf{D}_{ij} \cdot \mathbf{F}_j \right] \Psi \right\} + \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{D}_{ij} \cdot \frac{\partial}{\partial \mathbf{r}_j} \Psi$$

Schroeder, C., E.S.G. Shaqfeh, and S.Chu, The Effect of Hydrodynamic Interactions on the Dynamics of DNA in Extensional Flow: Simulation and Single Molecule Experiment, Macromolecules, 37, pp. 9242-9256 (2004)

Simulating the Hysteresis with Brownian Dynamics and Comparison to Experiment

Schroeder, C., E.S.G. Shaqfeh, and S.Chu, The Effect of Hydrodynamic Interactions on the Dynamics of DNA in Extensional Flow: Simulation and Single Molecule Experiment, Macromolecules, 37, pp. 9242-9256 (2004)





KINETICS??

L ≈ 1.3 mm

N_k=9280

Strain ≈ 15

h* = 0.23 and ν = 0.00032 mm^3

Simulating Hysteresis with Brownian Dynamics for Polystyrene

C. C. Hsieh and R. G. Larson, J. Rheol. **49**, 1081 (2005)

Not "Extra-terrestrial Molecular Weights !

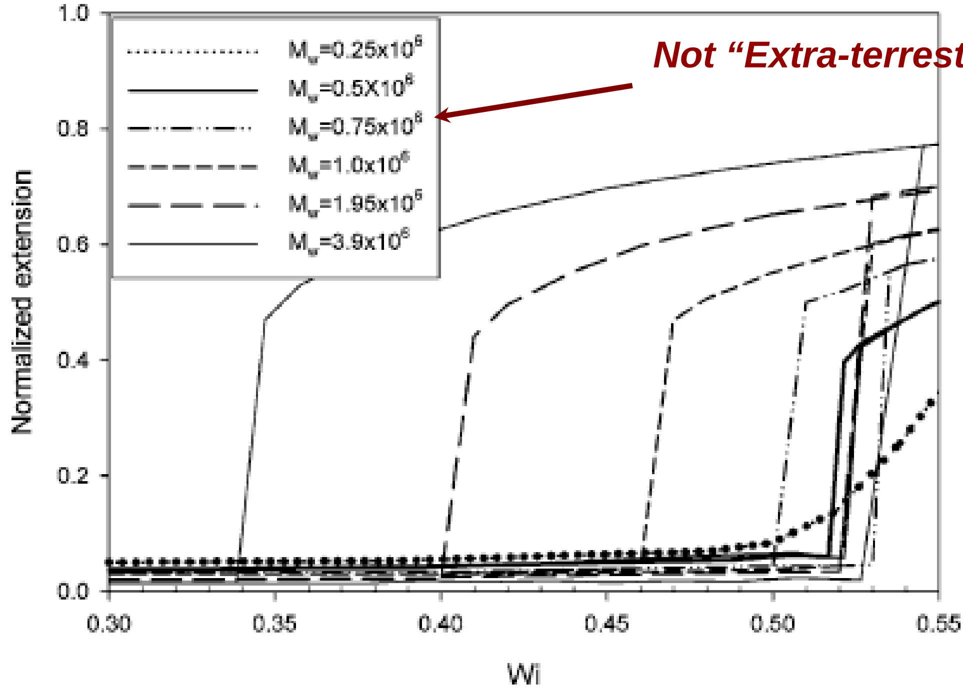
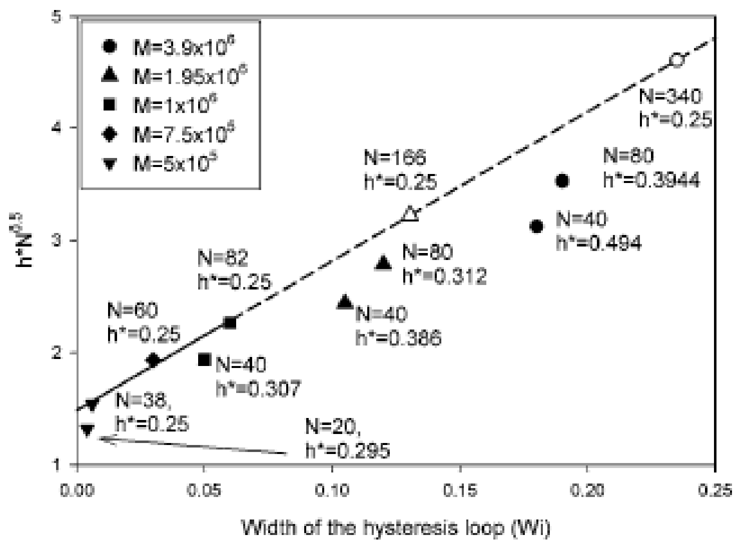
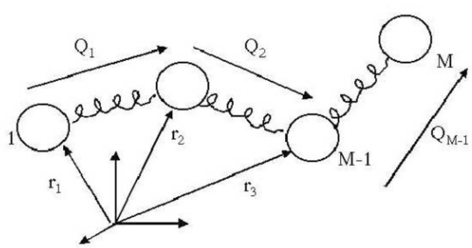


FIG. 1. Steady-state chain extension vs Weissenberg number (Wi) for polystyrene with different molecular weights in dilute solutions predicted for bead-spring chains with N=16–82 beads; see Table I.

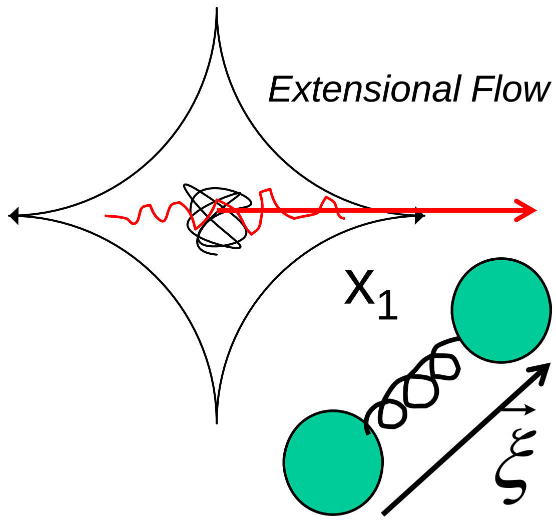




FOKKER-PLANCK EQUATION FOR BEAD SPRING CHAIN (WITH HI):

$$\frac{\partial \Psi}{\partial t} = -\sum_{i=1}^{M} \frac{\partial}{\partial \mathbf{r}_i} \cdot \left\{ \left[\boldsymbol{\kappa} \cdot \mathbf{r}_i + \sum_{j=1}^{M} \mathbf{D}_{ij} \cdot \mathbf{F}_j \right] \Psi \right\} + \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{D}_{ij} \cdot \frac{\partial}{\partial \mathbf{r}_j} \Psi$$

DeGenne's Framerwork : Variable Drag Dumbbell



$$2\,De\frac{\partial}{\partial \xi_1}(\xi_1\psi)-\frac{\partial}{\partial \xi_1}\left(\frac{f(\xi_1)}{g(\xi_1)}\xi_1\psi\right)=\frac{\partial}{\partial \xi_1}\frac{1}{g(\xi_1)}\frac{\partial \psi}{\partial \xi_1}$$

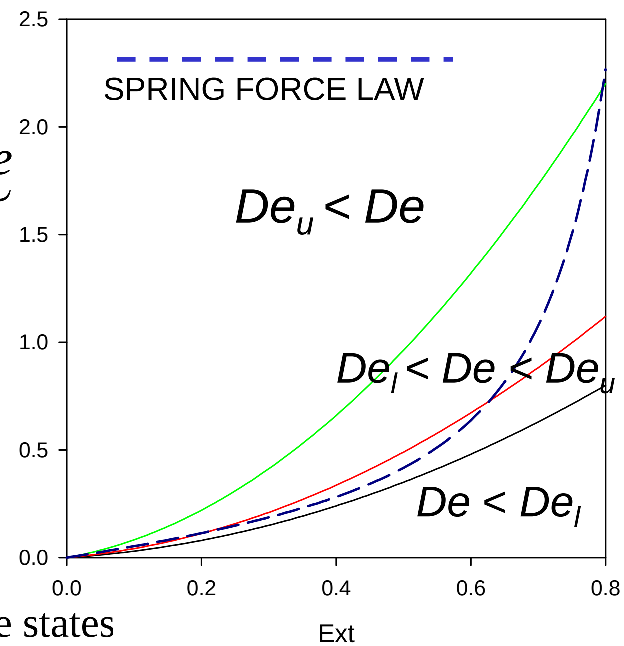
$$\psi = K\,\exp\left\{-\int_0^{\xi_1}(\sigma f(\sigma)-2\,De\sigma g(\sigma))\,d\sigma\right\}$$

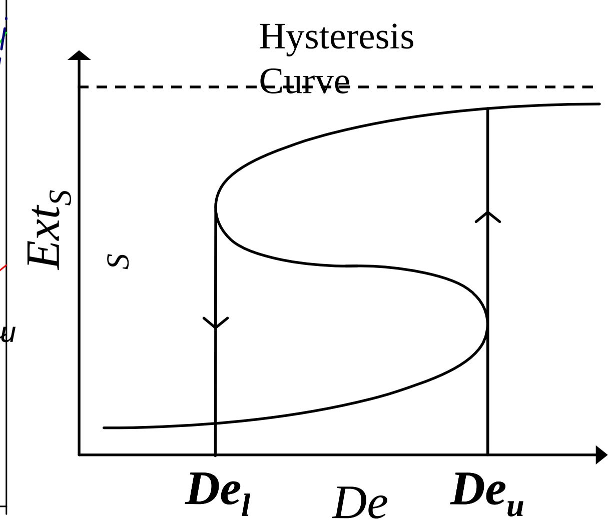
$$\boxed{\frac{E}{kT}=\int_0^{\xi_1}(\sigma f(\sigma)-2\,De\,\sigma g(\sigma))\,d\sigma}$$

$$\frac{d\xi_1}{dt}=-\underbrace{Spring\,Force}_{\text{Term 1}}+\underbrace{Drag\,Force}_{\text{Term 2}}$$

$$=\xi_1 f(\xi_1)-2De\xi_1 g(\xi_1)$$

$$=\frac{d(E/kT)}{d\xi_1}$$

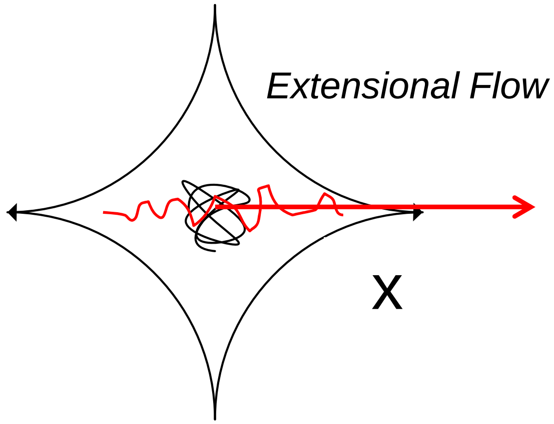


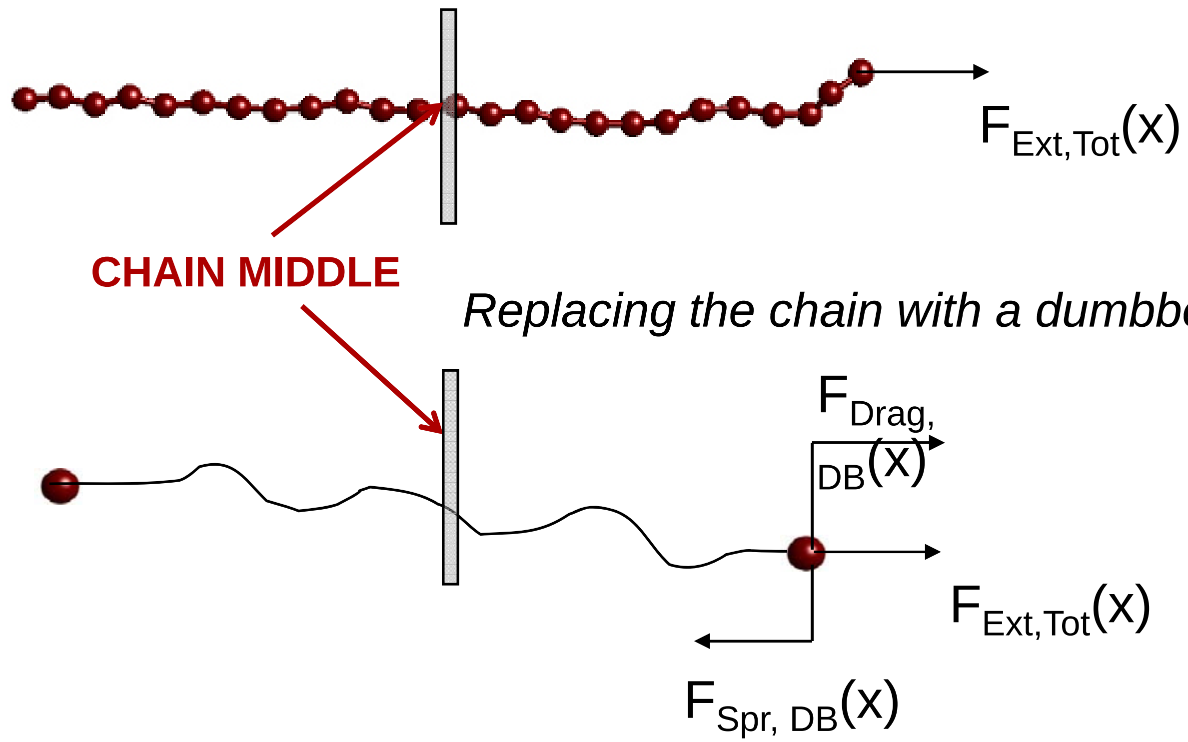


$\frac{d(E/kT)}{d\xi_1}=0$ define stable and unstable states

Developing the Model using Computer Simulation

Beck, V.A. and E.S.G. Shaqfeh, ``Ergodicity-Breaking and the Unravelling Dynamics of a Polymer in Linear and NonLinear Extensional Flows", J. Rheol. 51(3), pp. 561-574 May/June (2007)





$F_{Drag,\ DB}(x) \equiv F_{Spr,\ DB}(x) + F_{Ext,Tot}(x)$

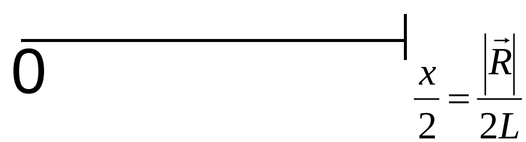
or

$$F_{Drag,DB} = \dot{\varepsilon}\varsigma(x)x \Rightarrow$$

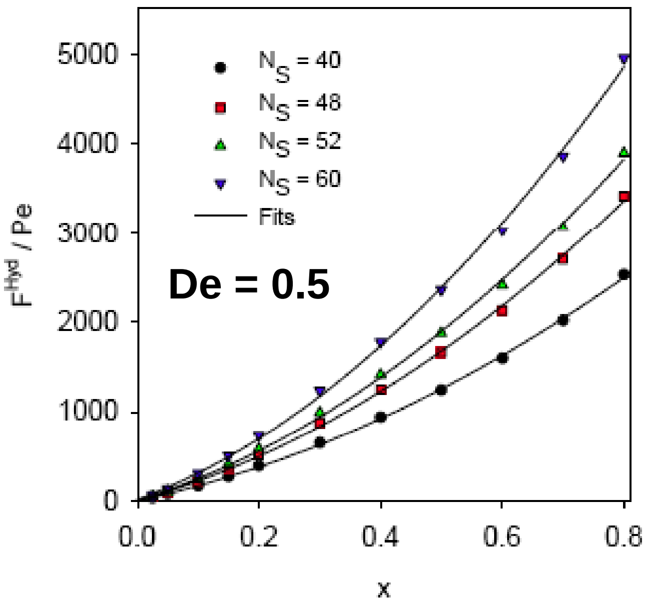
$$\varsigma(x) \equiv \frac{F_{Spr,DB} + F_{Ext,Tot}}{\dot{\varepsilon}x}$$

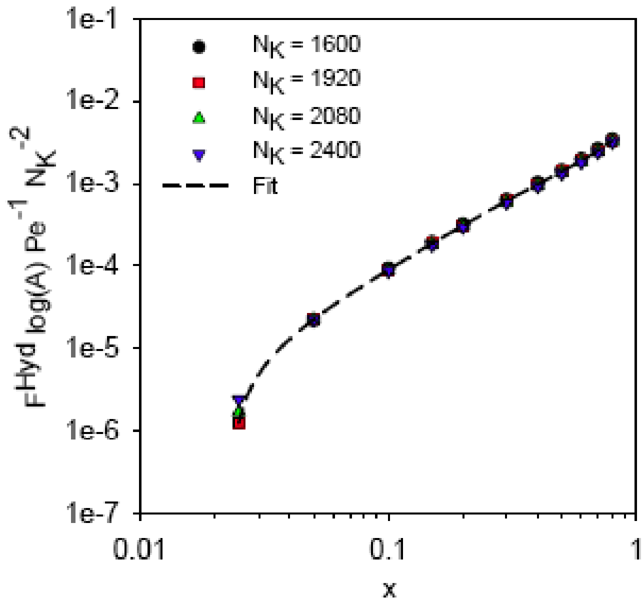
Drag Law

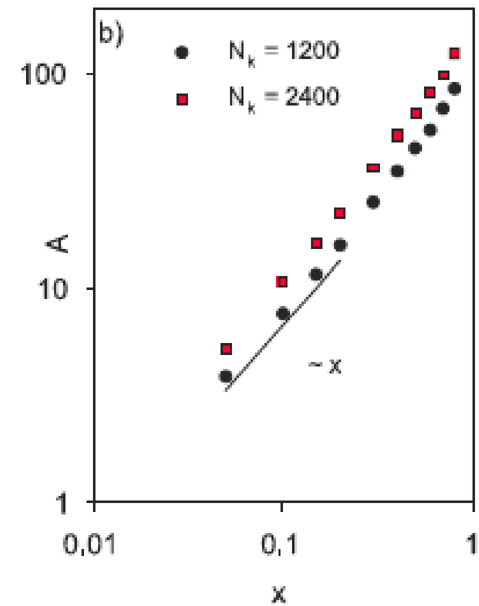
$$\varsigma = \varsigma_0\, g(ext)$$



Parameterizing the Model: Drag Force (ILC Chains)







$$F_{SBT}^{Drag} = \frac{K\mu\dot{\varepsilon}}{\log(A)} N_k^2 b_k^2 x^2 \quad \Leftrightarrow \text{SLBT}$$

$$A \equiv \sqrt{\frac{R_x^2}{R_y^2}} \approx x N_k^{0.5}$$

Kenward & Slater
MD Simulations

QuickTime?and a
decompressor
are needed to see this picture.

QuickTime?and a
decompressor
are needed to see this picture.

$$F^{Drag} \log(A) / N_k^2 \propto x^2$$

QuickTime?and a
decompressor
are needed to see this picture.

$$F^{Drag} / \dot{\varepsilon} x \equiv \varsigma \propto \frac{x}{\log(A)}$$

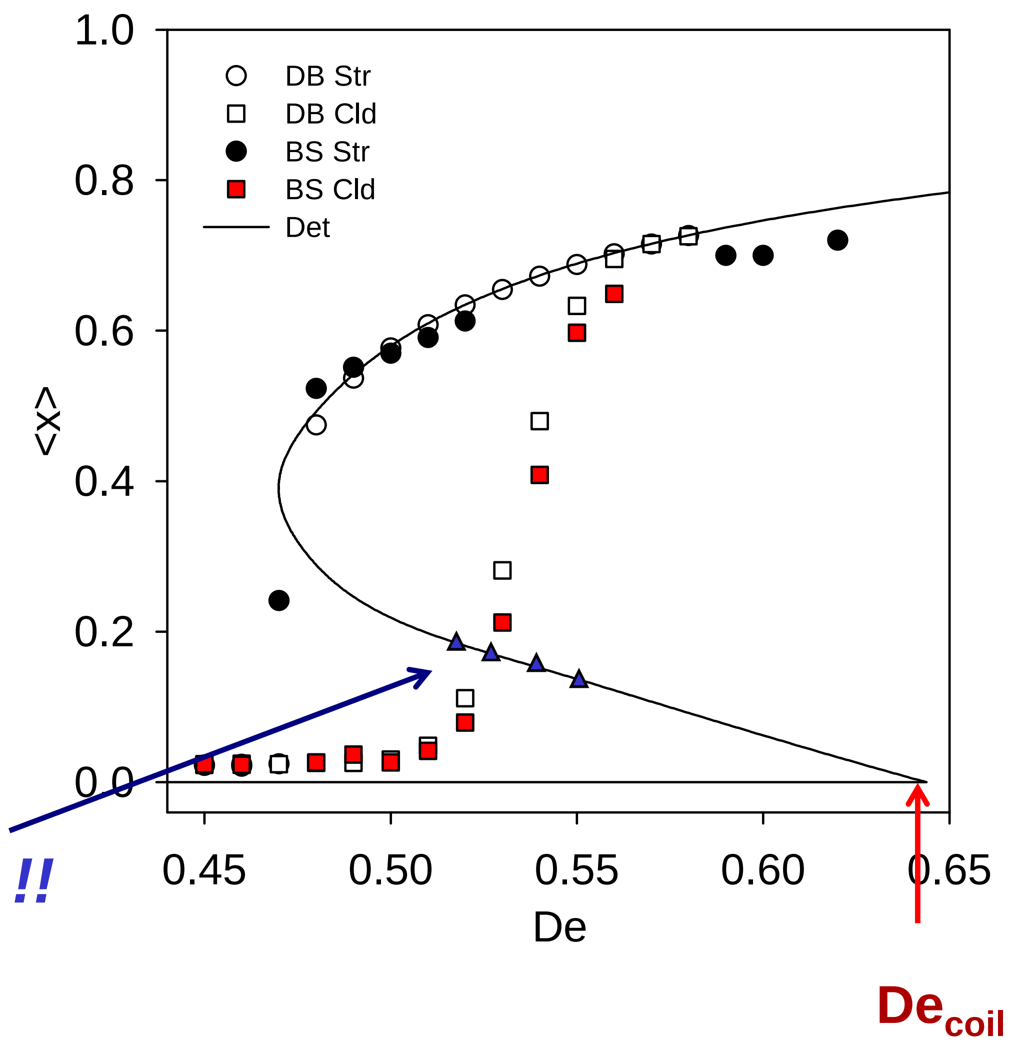
STANFORD
UNIVERSITY

Model is Quantitative (ILC Chains)

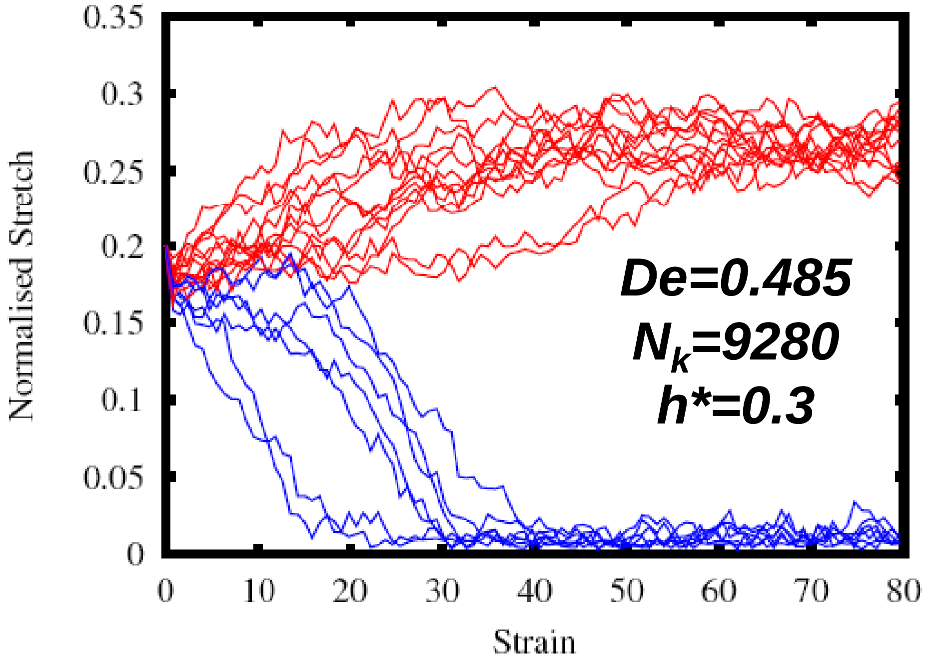
Average Extension after 1100 Relaxation Times
Inverse Langevin Chain N_k = 1600; h*=0.5

- BS = Bead-Spring Multimode
- TS = Transition State Multimode
- DB = Deterministic Dumbbell Theory
- Str = Start Stretched
- Cld = Start Coiled

Relaxation time based on Fit to last 30%. Scales as $N_k^{3/2}$



Brownian Dynamics Does Show Transition States

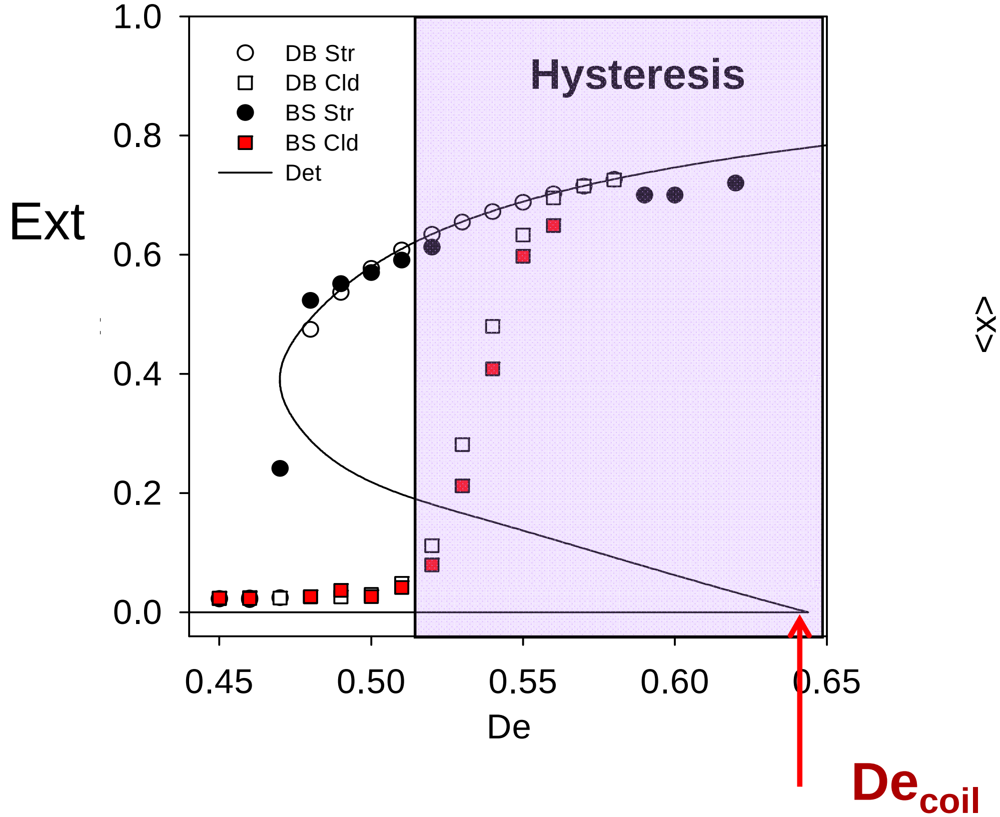


QuickTime?and a
decompressor
are needed to see this picture.

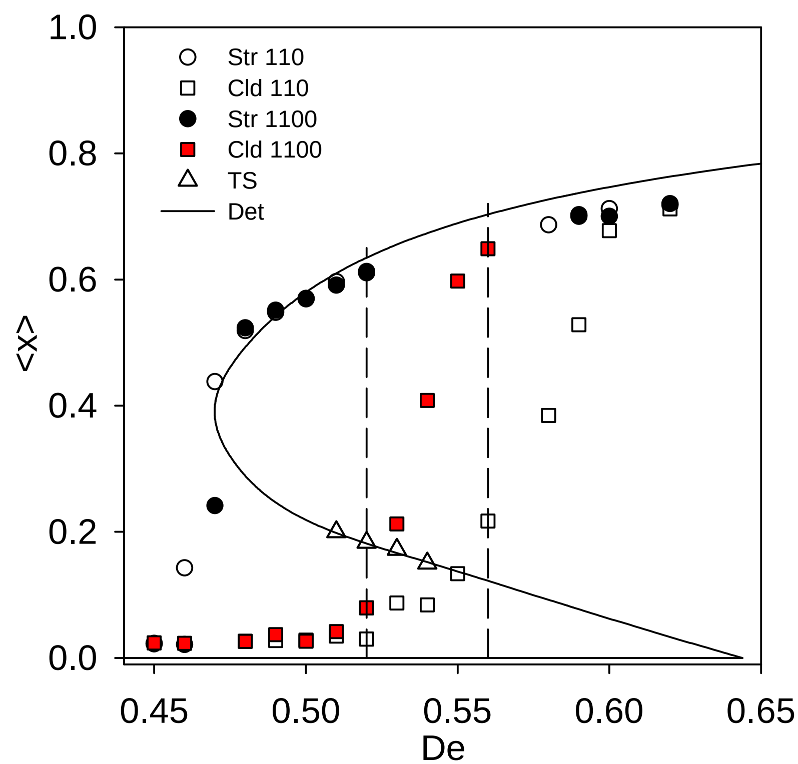
Model Demonstrates C-S Depends on the Time you wait….

Inverse Langevin Chain N_k = 1600; h*=0.5

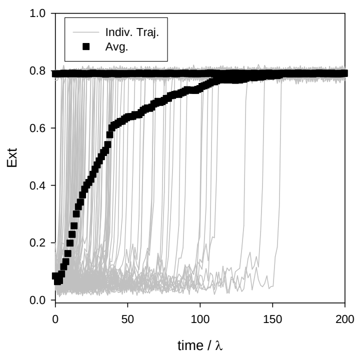
1100 relaxation times



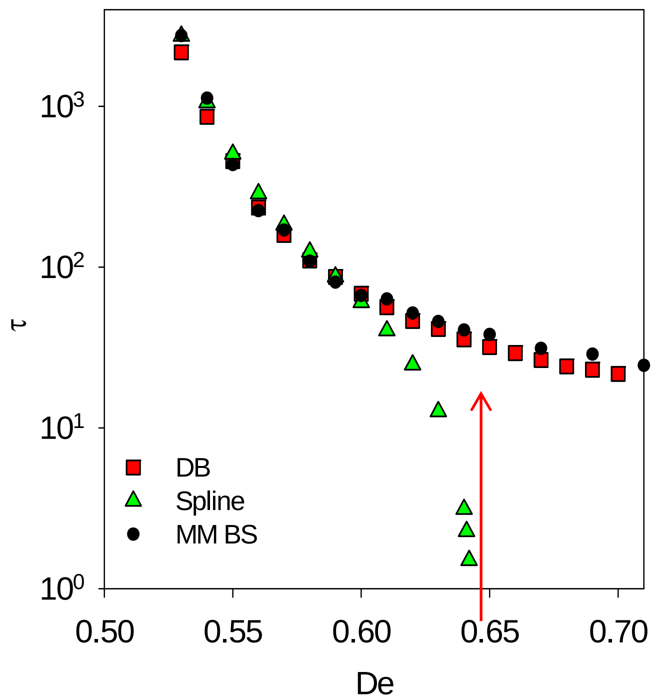
1100 & 110 relaxation times

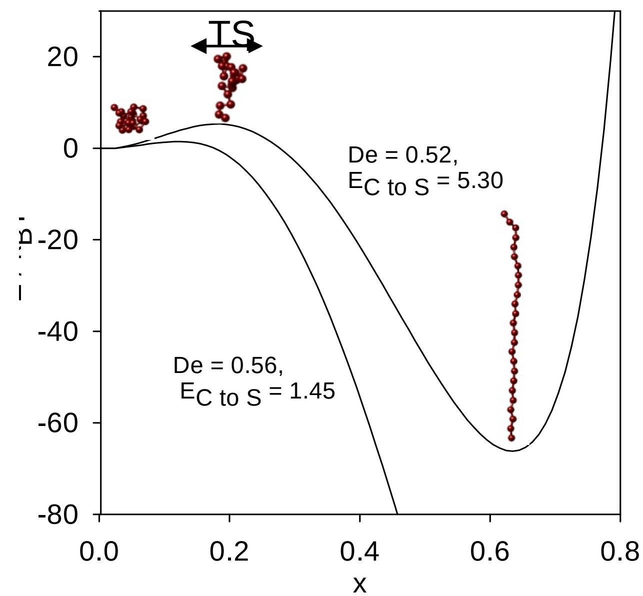


… Because the chains "hop" over an energy barrier



Inverse Langevin Chain N_k = 1600; h*=0.5





Transition time

t_{MFPT} = 1/r

$$\Phi(x) = \frac{E(x)}{k_B T} = 6N_k \int_0^x s(\sigma)\, d\sigma$$

$$s(x) = \frac{x f(x)}{2} - De_{Coil} \frac{\zeta(x; N_K)}{\zeta_{Coil}}$$

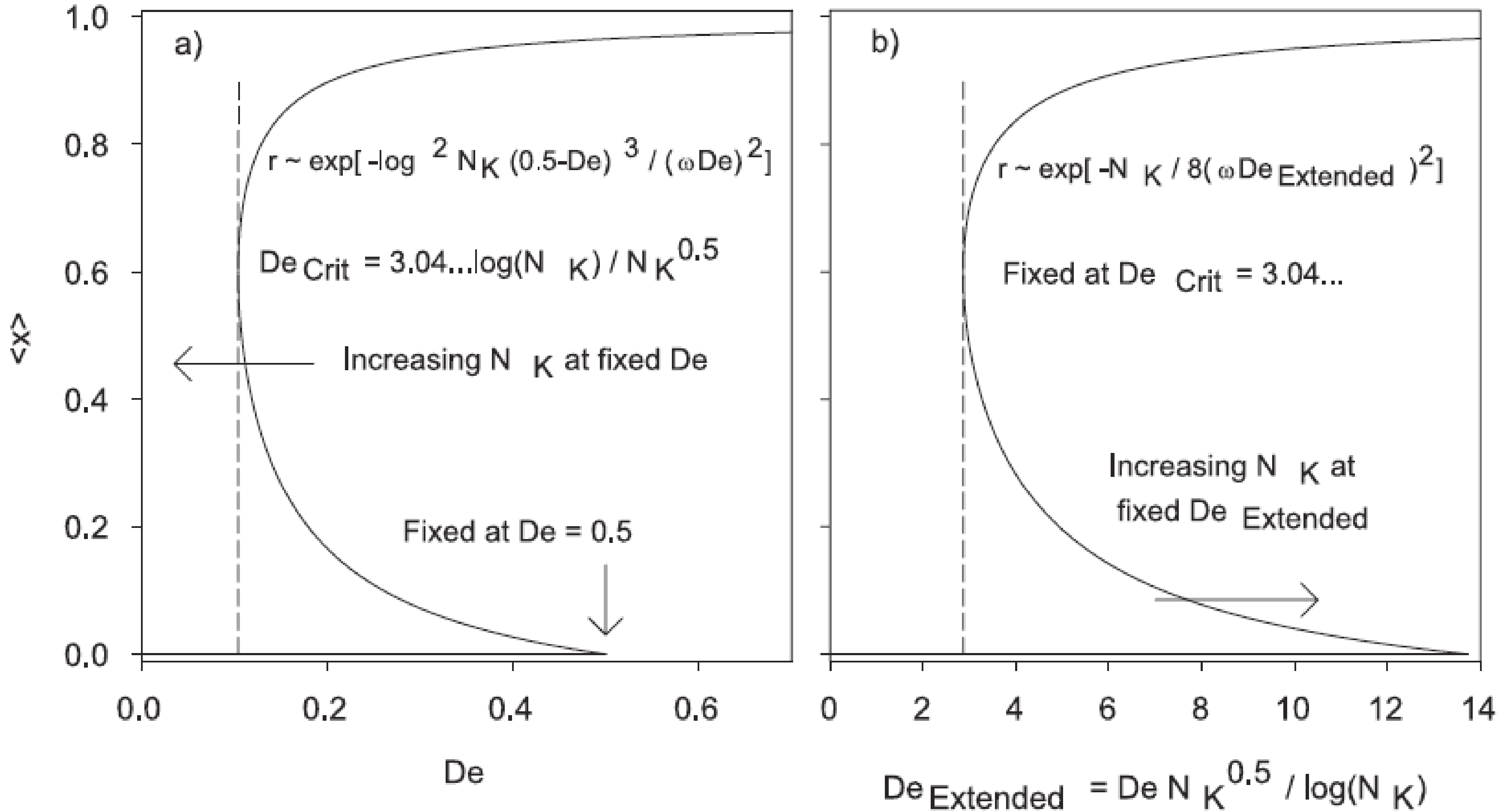
Theory of Markov Processes

$$r = \left[6N_K \int_{x_0}^{x_f} \frac{\zeta(x; N_K)}{\zeta_{Coil}} e^{\Phi(x)} \int_{x_0}^{x} e^{-\Phi(\eta)} d\eta\, dx \right]^{-1}$$

$$r = B(De_{Coil}) \exp\left[-\log^2 N_K \frac{\left(\frac{1}{2} - De_{Coil}\right)^3}{(\omega De_{Coil})^2} \right]$$

N_k>>1

Hysteresis Loop Depends on Chosen De



Ergodicity Breaks at a Fixed Deborah Number !

Rheological Consequences

PRL **98,** 167801 (2007)

PHYSICAL REVIEW LETTERS

week ending
20 APRIL 2007

Rheological Observation of Glassy Dynamics of Dilute Polymer Solutions near the Coil-Stretch Transition in Elongational Flows

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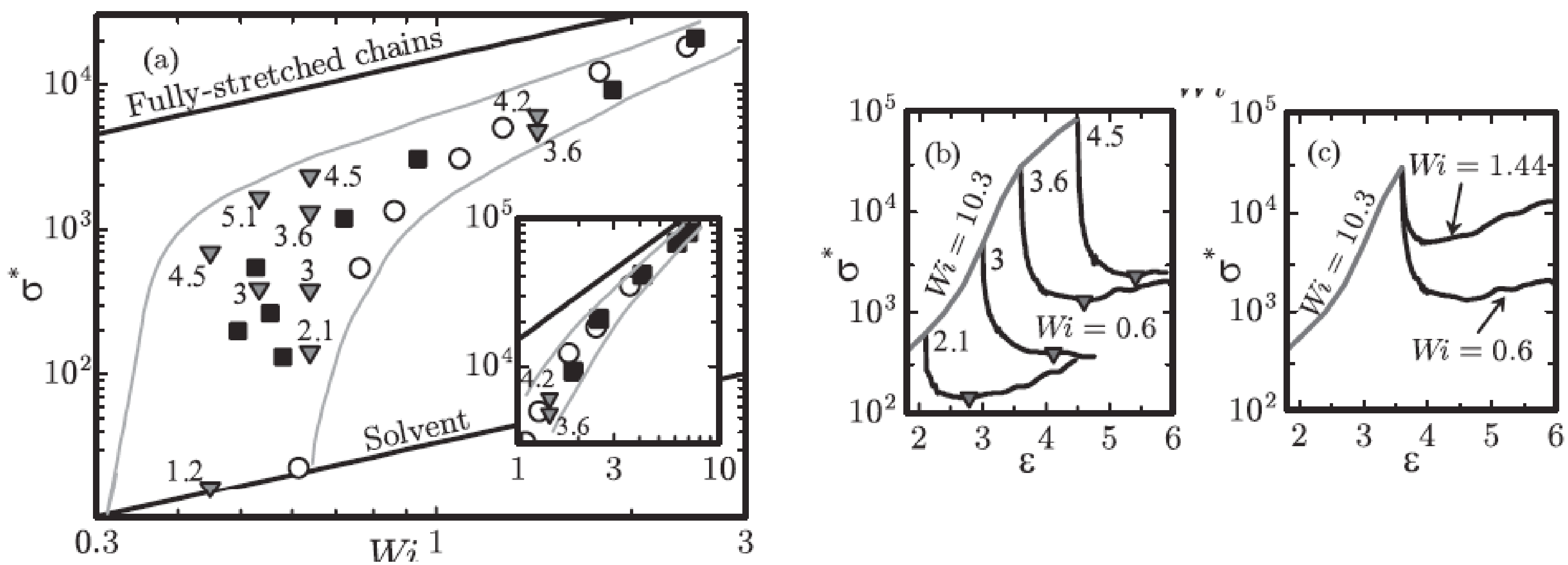
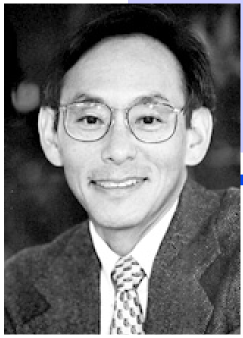
[2]*Research School of Chemistry, Australian National University, Canberra, ACT-0200, Australia*

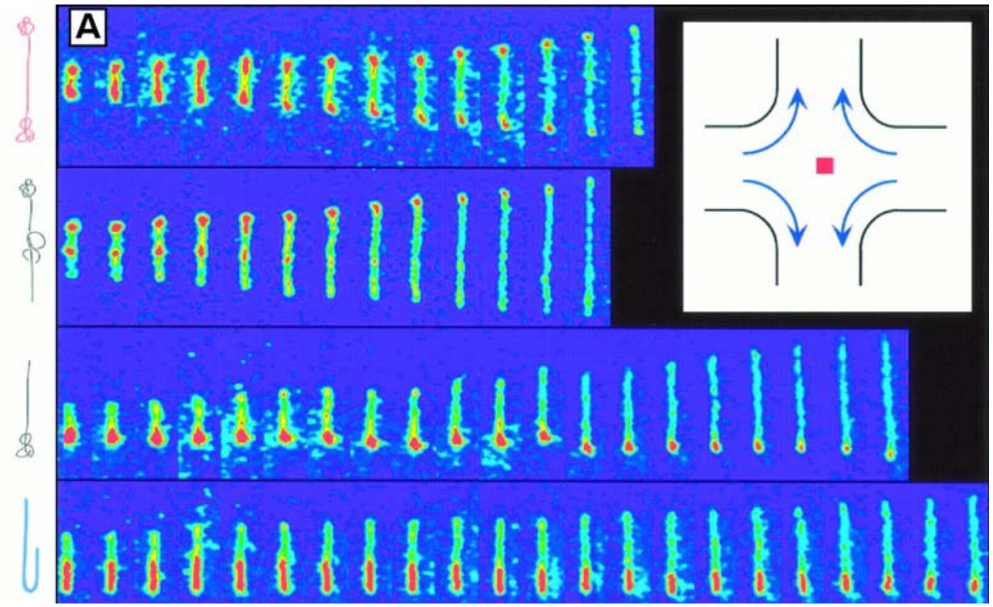
(Received 23 November 2006; published 20 April 2007)

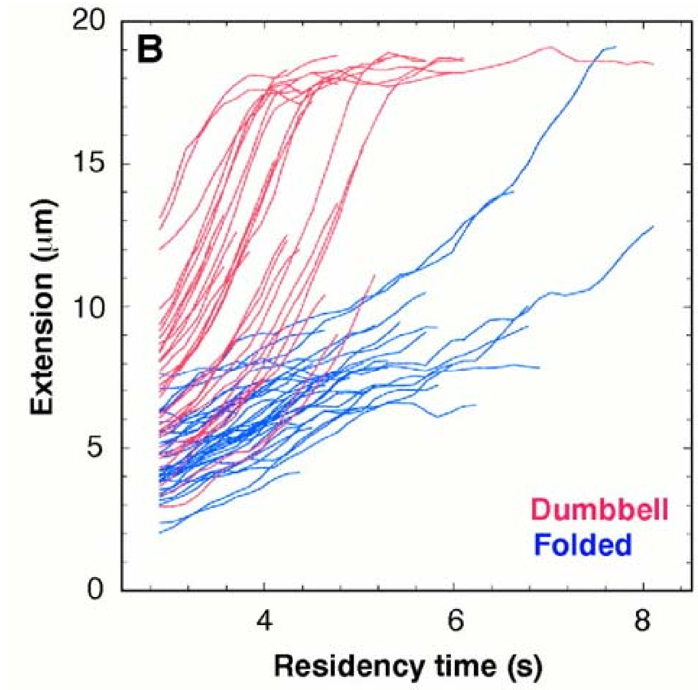


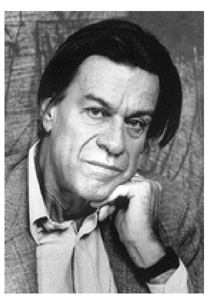
The Coil-Stretch Transition: Molecular Individualism



Perkins et al., Smith et al. , Science(*1995,1997), Larson et al. (1999)*





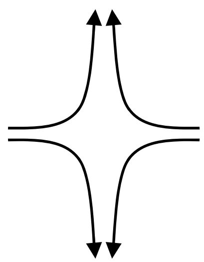


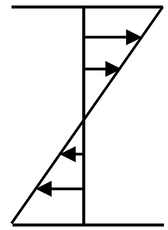
De Gennes, “Molecular Individualism”, 1997

Mixed Flows

Pure Extensional

100%Extensional
0%Rotational



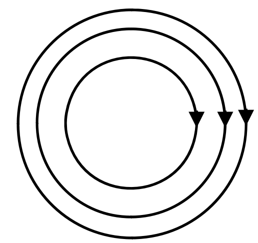


Simple Shear

50%Extensional
50%Rotational

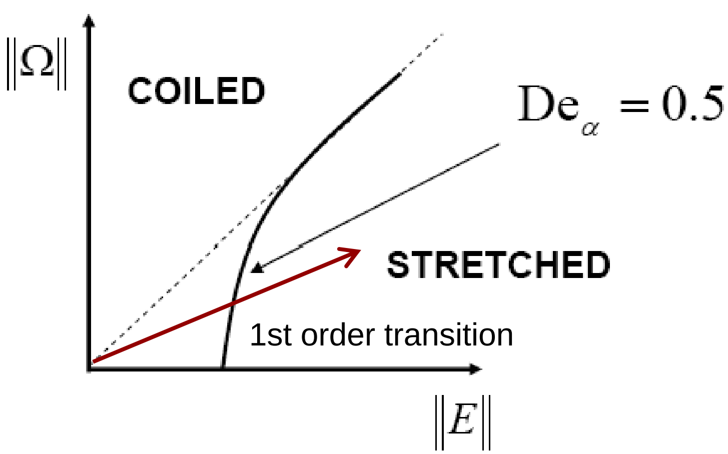
Pure Rotational

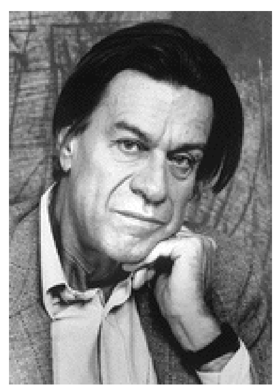
0%Extensional
100%Rotational



$$\underline{\underline{\dot{\gamma}}} = \dot{\gamma}\begin{bmatrix} 0 & 1 \\ \alpha & 0 \end{bmatrix} = E + W \qquad E = \frac{\dot{\gamma}}{2}\begin{bmatrix} 0 & 1+\alpha \\ 1+\alpha & 0 \end{bmatrix} \qquad W = \frac{\dot{\gamma}}{2}\begin{bmatrix} 0 & 1-\alpha \\ -1+\alpha & 0 \end{bmatrix}$$

$$\%E = 50(1+\alpha) \qquad \%W = 50(1-\alpha)$$





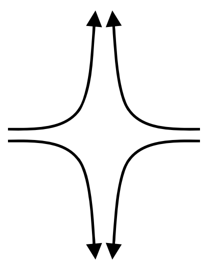
$$\textit{Eigenvalues of } \underline{\underline{\dot{\gamma}}} = \pm\dot{\gamma}\sqrt{\alpha}$$

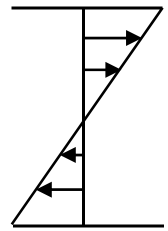
$$De_\alpha = \dot{\gamma}\tau\sqrt{\alpha}$$

Mixed Flows

Pure Extensional

100%Extensional
0%Rotational



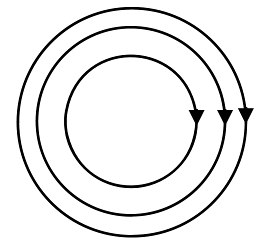


Simple Shear

50%Extensional
50%Rotational

Pure Rotational

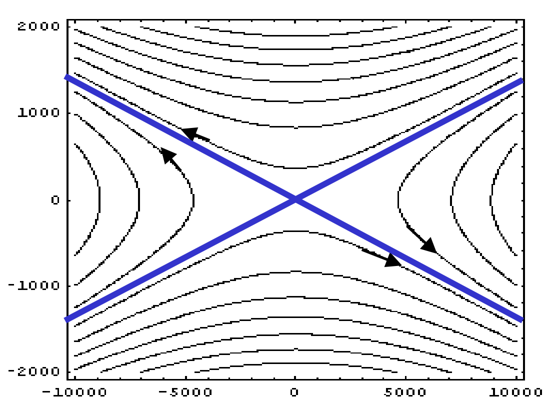
0%Extensional
100%Rotational



$$\%E = 50(1+\alpha)$$

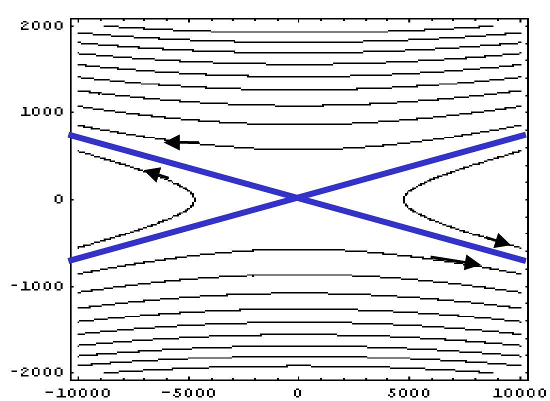
$$\%W = 50(1-\alpha)$$

51%E



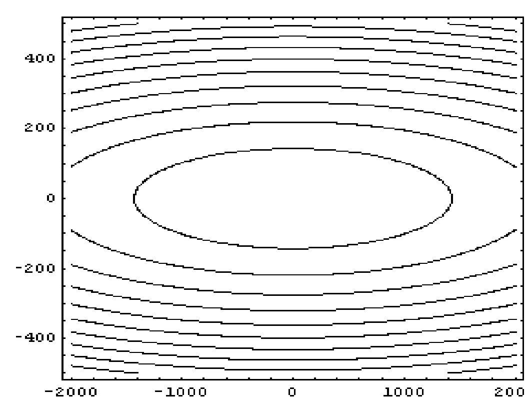
16.1°

50.2%E



7.24°

49.5%E

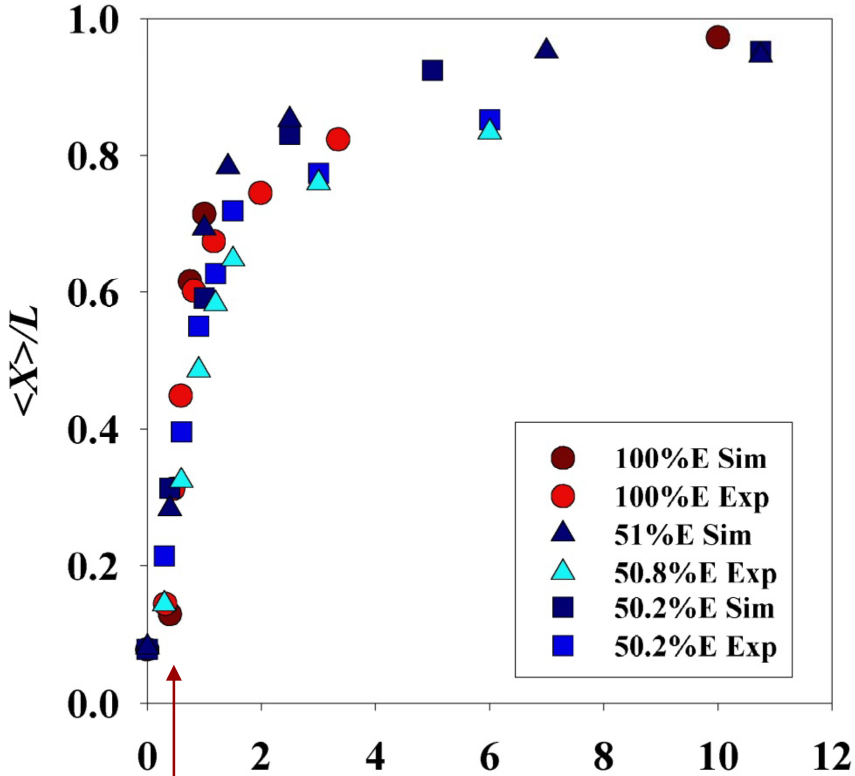


Eigenvalues of $\underline{\underline{\nabla v}} = \pm\dot{\gamma}\sqrt{\alpha}$

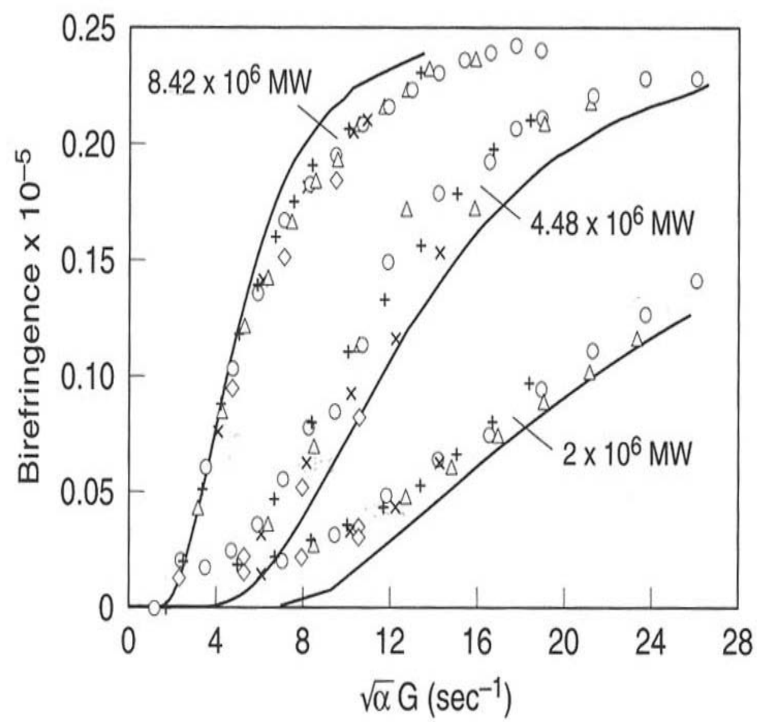
$$De_\alpha = \dot{\gamma}\tau\sqrt{\alpha}$$

Dynamics of a DNA Molecule in Mixed flows : Steady Average Extension(rescaled)

Simulations and Experiments seem to agree, so what's the rub ??



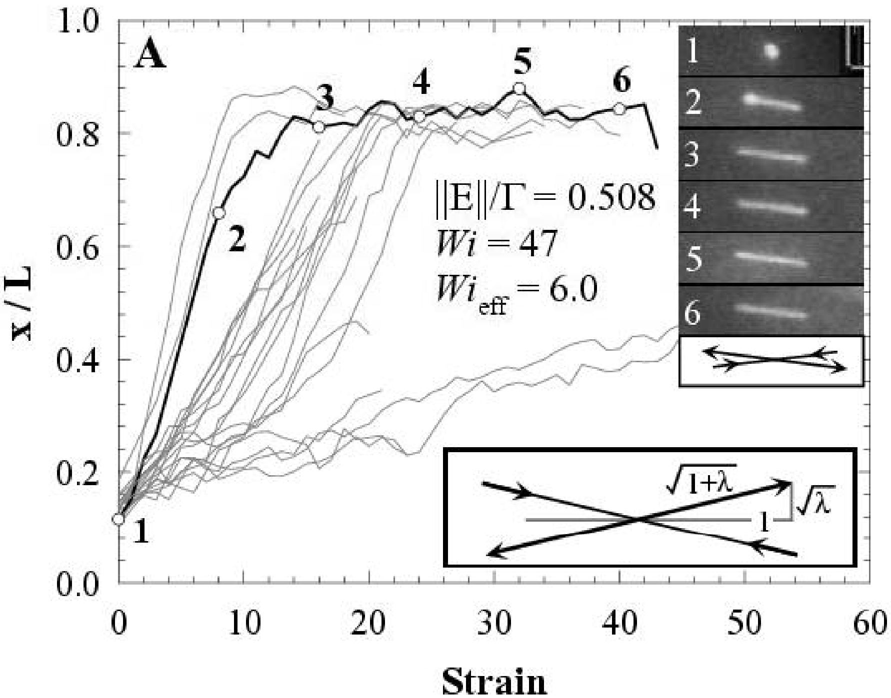
$$De_\alpha = \dot{\gamma}\tau\sqrt{\alpha}$$

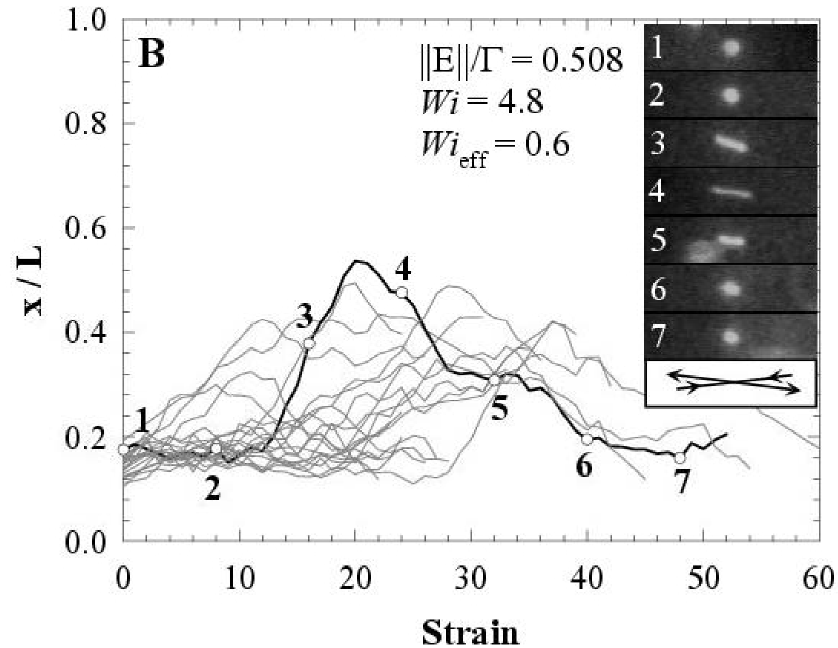


Babcock, H., R. Teixeira, J. Hur, E.S.G. Shaqfeh, and S. Chu, ``Visualization of molecular fluctuations near the critical point of the coil-stretch transition in polymer elongation'', Macromolecules **12** pp. 4544-4548 (2003)

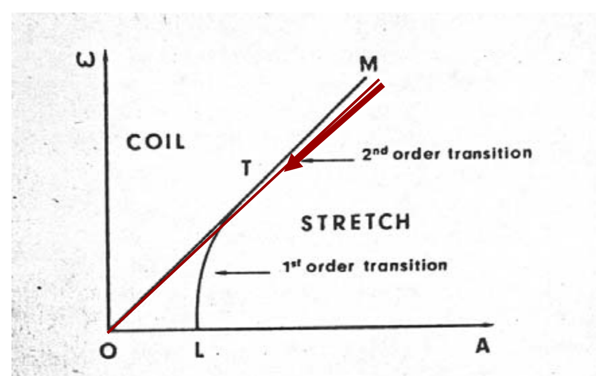
Fuller et al. (1980)

Dynamics of a DNA Molecule in *Mixed flows :*
Experimental Chain Trajectories and Configurational Fluctuations





Experimentally one sees stretch and collapse near the critical point if the Weissenberg number is small enough !

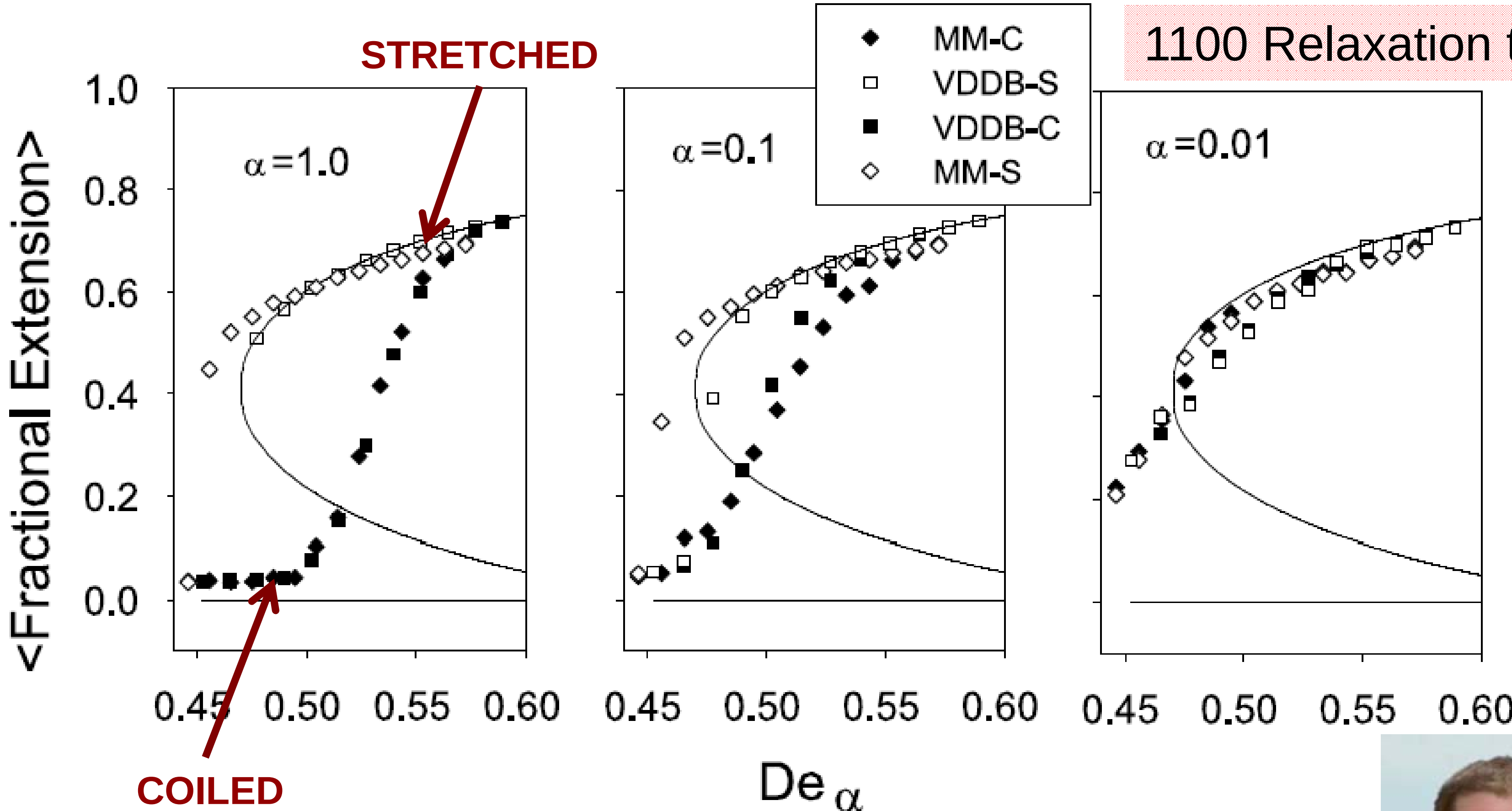


Babcock, H., R. Teixeira, J. Hur, E.S.G. Shaqfeh, and S. Chu, ``Visualization of molecular fluctuations near the critical point of the coil-stretch transition in polymer elongation'', Macromolecules **12** pp. 4544-4548 (2003)

Hysteresis in Mixed Flows: Not Just De_{α}

Hoffman, B., E.S.G. Shaqfeh, *`The Dynamics of the Coil-Stretch Transition for Long, Flexible Polymers in Planar Mixed Flows'*, J. Rheol. 51(5), pp. 947-969 (2007)

1100 Relaxation times



Inverse Langevin Chain N_k = 1600; h*=0.5

$$De_{\alpha} = ?\tau\sqrt{\alpha}$$

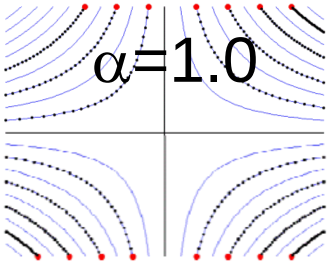
Nk= 1600

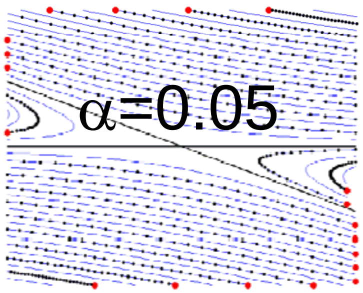
MM = Multimode, Ns=40, Nks=40, ILC

VDDB = Variable drag dumbbell, drag law by Beck

Fluctuations Created by Convective Dispersion

De=0.6 N_k=800





QuickTime?and a
mpeg4 decompressor
are needed to see this picture.

Correct "Projected Model" Includes Drift and Taylor-Dispersion

FLUCTUATION INDUCED !

The reduced model PDF is

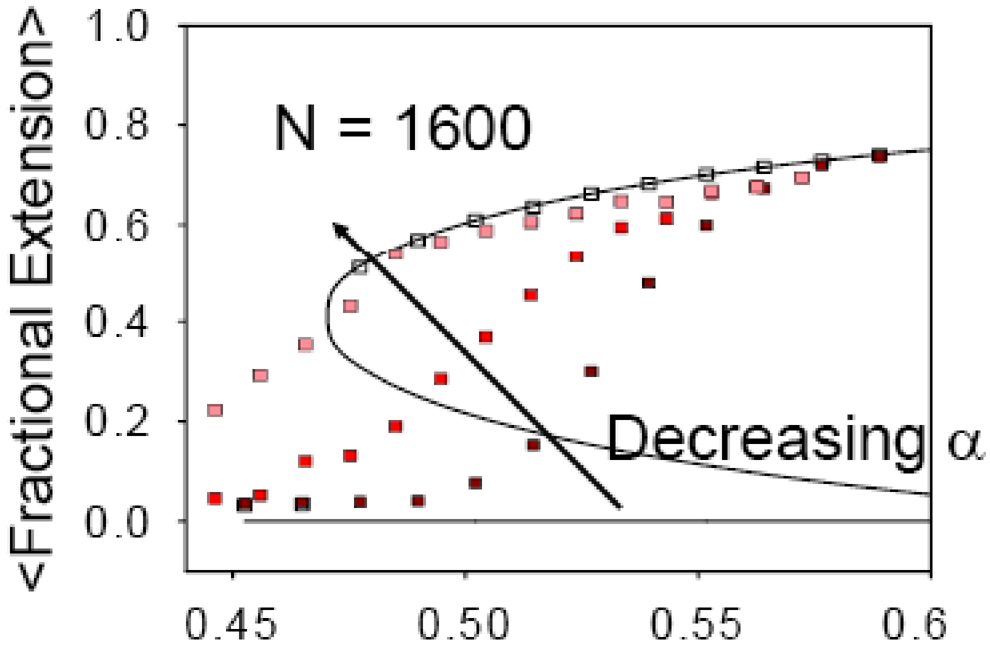
$$\frac{\partial \Phi}{\partial t} = -\frac{\partial}{\partial x}\left[\left(\dot{\gamma}\sqrt{\alpha}x - \frac{2fx}{\zeta(x)} + \frac{kT\beta^2}{2\zeta(x)}\frac{\partial f/\partial x}{f}\right)\Phi - \frac{2kT}{\zeta(x)}\left[1+\frac{\beta^2}{4}\right]\frac{\partial \Phi}{\partial x}\right]$$

Drift velocity

Diffusivity enhancement

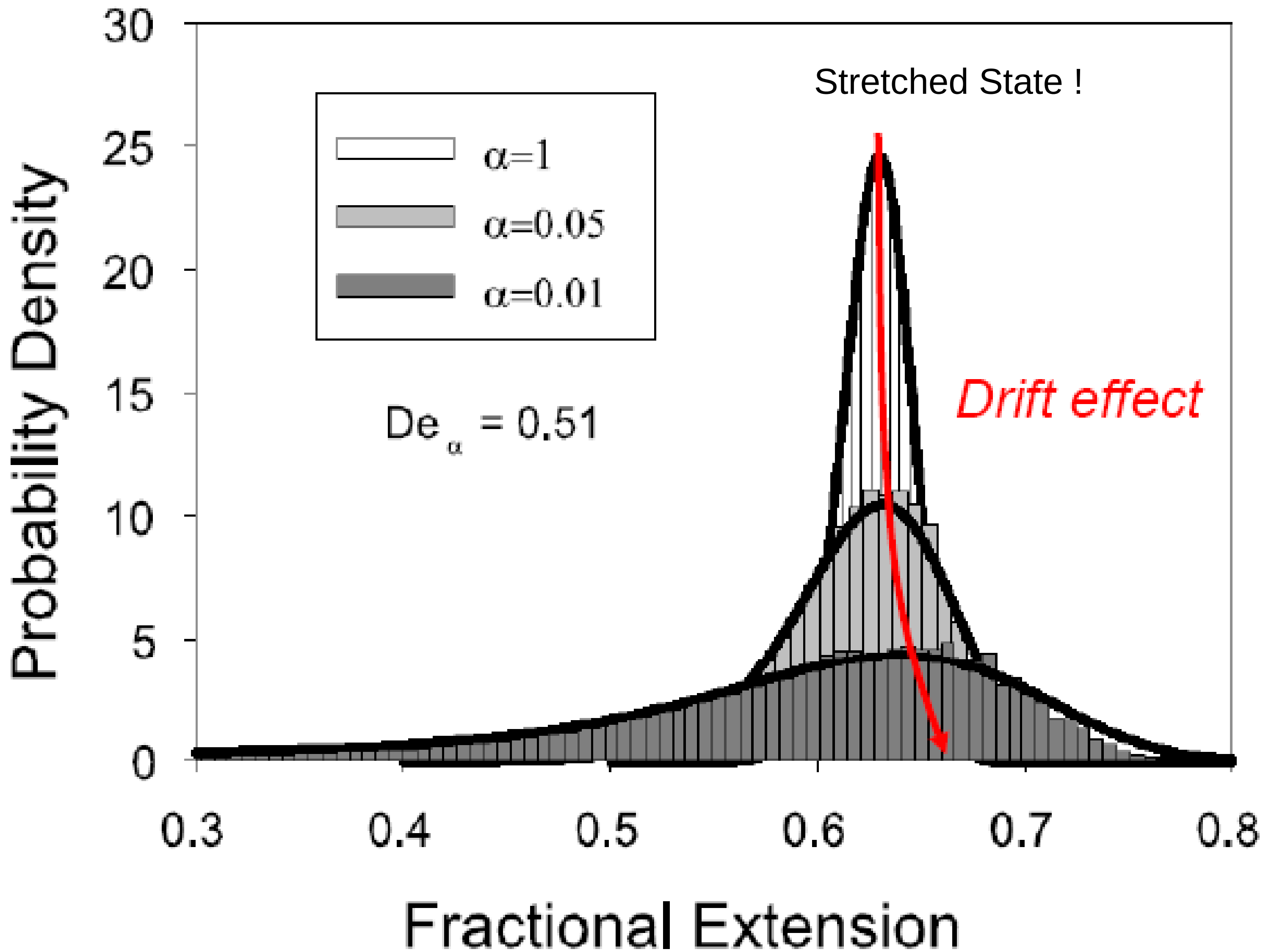
Drift velocity enhances convection for finitely extensible springs

$$f'(x) > 0$$



$$\beta = \frac{1-\alpha}{\sqrt{\alpha}}$$

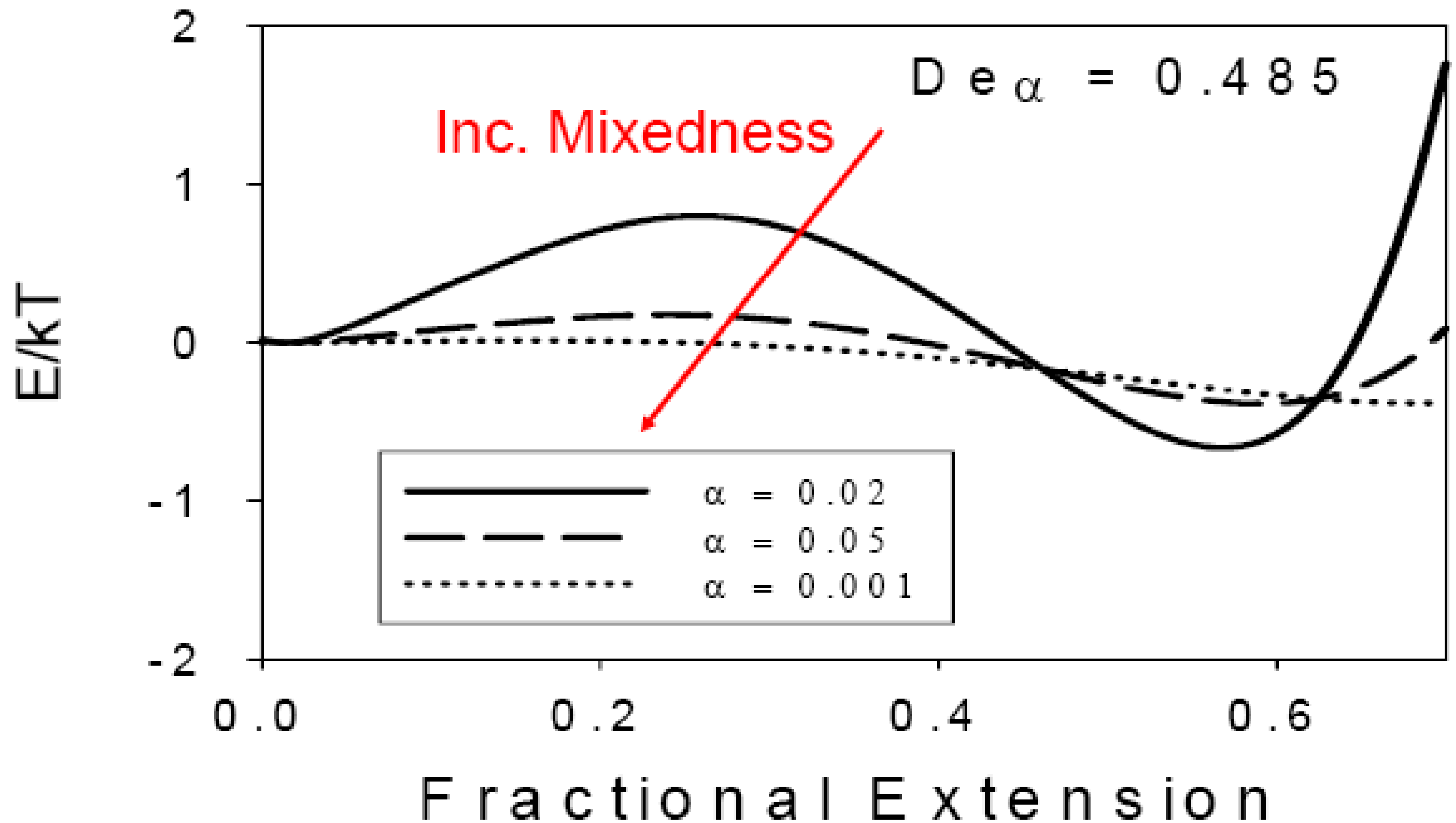
Comparison of BD to Projected Model (1-D Boltzmann Distribution)



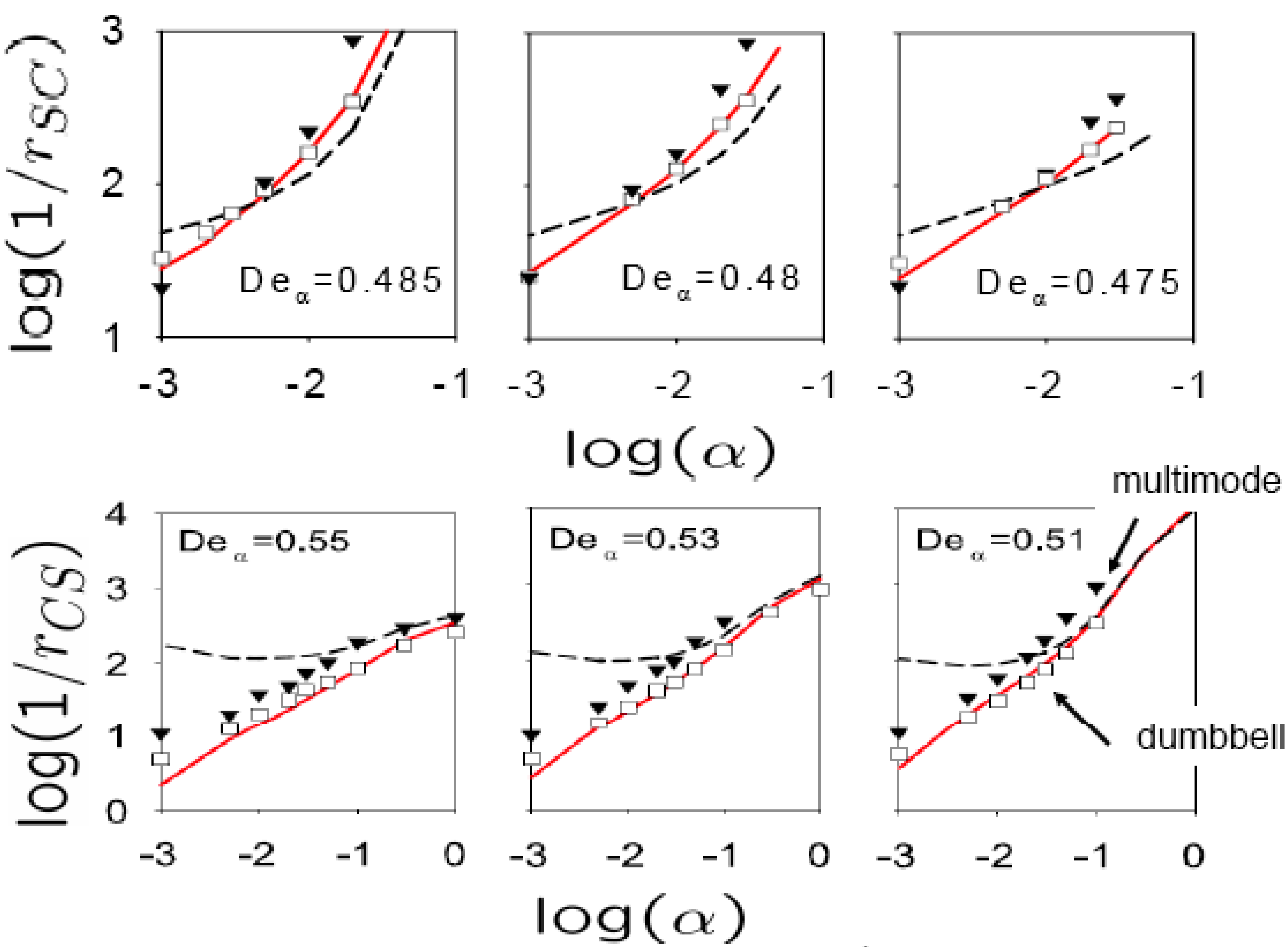
Transition Kinetics: Still first order but….

The solution to the 1-D problem is Boltzman

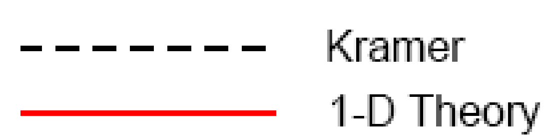
$$\frac{E}{kT} = -6N \int_0^x \frac{1}{D^{\mathrm{eff}}(z)} \left(\mathrm{De}_\alpha z - \frac{f^{sp}}{6g} + u_d \right) dz$$



Transition Rates from Markov Theory



$$r_{CS} = \left[6N \int_0^{x_s} \frac{1}{D_{\text{eff}}} e^{E/kT} dx \int_0^{x_M} e^{-E/kT} dx \right]^{-1}$$



Conclusion: The Coil to Stretch Transition after 30+ Years…

➢ ***DeGennes (… Hinch, Tanner….) was right about the qualitative aspects of the coil-stretch transition for purely extensional flows and extension dominated mixed flows. Remarkable. BRAVO!***

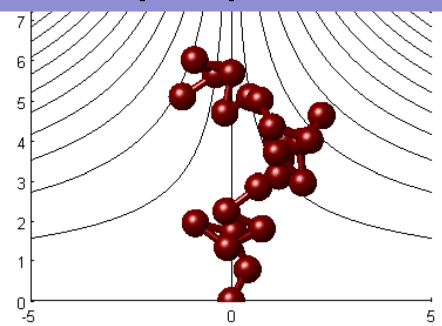
Elements that are perhaps new and unforeseen by these researchers:

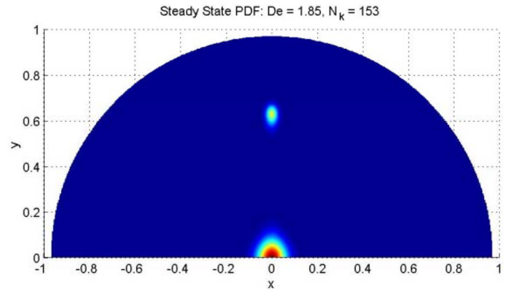
- ❖ ***Ergodicity Breaking***
- ❖ ***Role of Conformational (Critical) NonEquilibrium Fluctuations***
- ❖ ***NonLinear Flows***

Beck, V.A. and E.S.G. Shaqfeh, ``Ergodicity-Breaking and Conformational Hysteresis in Polymer Dynamics Near a Surface Stagnation Point'', *J. Chem Phys*. 124, 094902 (2006)

More to do in the areas of:

- ❖ ***Rheological consequences***
- ❖ ***Connecting Molecular Individualism & Hysteresis***
- ❖ ***3-D Mixed Flows***

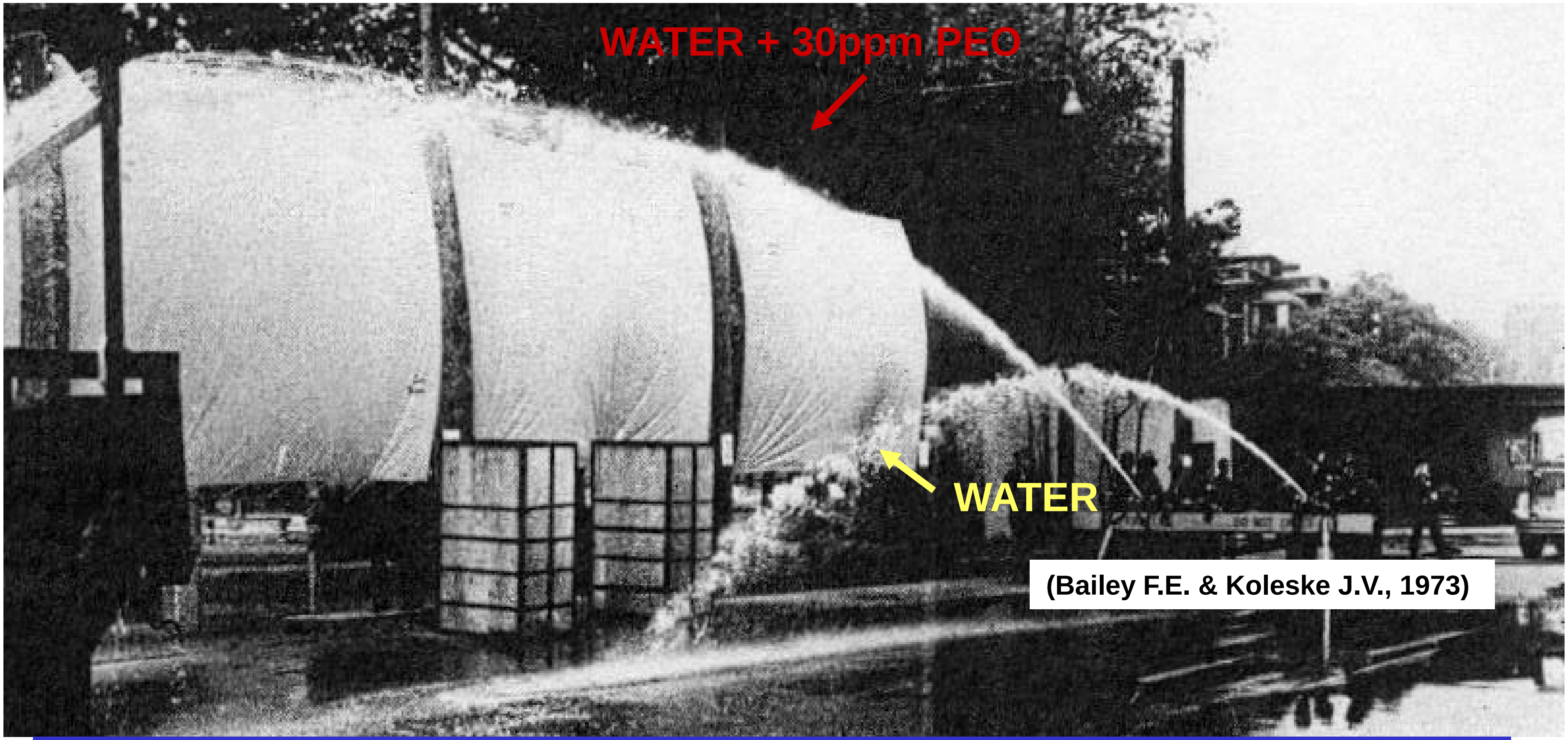




Drag Reduction Basics: Skin Friction Reduction by Polymer Additives

Skin friction drag in turbulent flows is up to 10 times larger than in laminar flows

Addition of few *ppm* of a high molecular weight polymer to a turbulent flow can result in large (up to 80%) reduction of skin friction drag (Toms effect, 1949)



Applications are generally “internal” flows - new applicatons for “external” flows

Drag Reducing Materials *(Structure, Size, Concentration)*

Re_m ~O(10^4 - 10^5) : Channel Flows

Polymers

flexibility ↑

Polymers	M_w	C (ppm)	Model	%DR
• PEO *(water)*	$6 \cdot 10^4$ - $5 \cdot 10^6$	2 ~ 500	# Kuhn steps 400 ~ 80,000	7 ~ 85
• PAAm *(water)*	$4 \cdot 10^5$ - $1.5 \cdot 10^7$	3 ~ 250		
• (PAA) *(water)*	$8 \cdot 10^6$	35		
• PS *(toluene)*	$7 \cdot 10^5$ - $2 \cdot 10^7$	1 ~ 2,000		
• Xanthan gum *(water)*	$2 \cdot 10^6$	10 ~ 2,400	Semiflexible 6 Kuhn steps	

Fibers

Fibers	d	aspect ratio	C (ppm)	Model
• asbestos	30-40nm	40,000	100 ~ 300	*Brownian Rod*
• nylon	20μm	100 ~ 350	100 ~ 10,000	*Non-Brownian Rod*

%DR : 10 ~ 60

Comments

- increasing M_w = increase in %DR
- For high M_w less conc. is needed to achieve the same %DR
- semi-flexible polymers are more stable to degradation by flow

… and even DNA…

EUROPHYSICS LETTERS 15 December 2003

Europhys. Lett., **64** (6), pp. 823–829 (2003)

Turbulent-drag reduction of polyelectrolyte solutions: Relation with the elongational viscosity

C. Wagner[1], Y. Amarouchene[1,2], P. Doyle[3] and D. Bonn[1](*)

[1] *Laboratoire de Physique Statistique, UMR CNRS 8550, Ecole Normale Supérieure 24 rue Lhomond, 75231 Paris Cedex 05, France*

[2] *Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux 1 (UMR 5798) - 351 Cours de la Liberation, 33405 Talence, France*

[3] *Department of Chemical Engineering, Massachusetts Institute of Technology Cambridge, MA 02139, USA*

(received 16 July 2003; accepted in final form 6 October 2003)

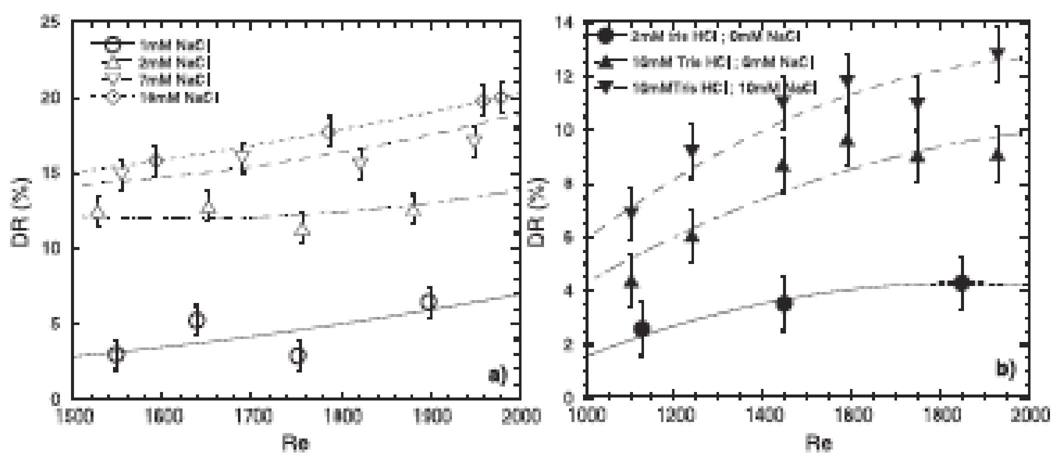
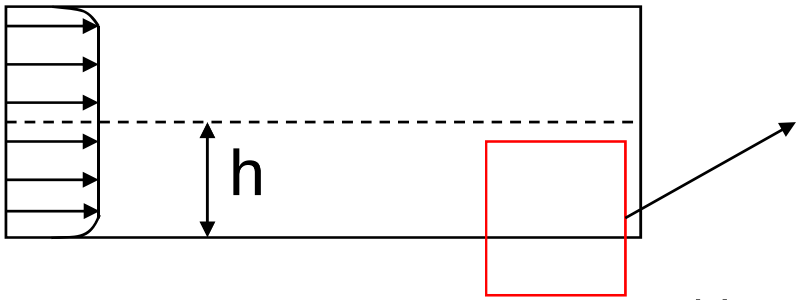
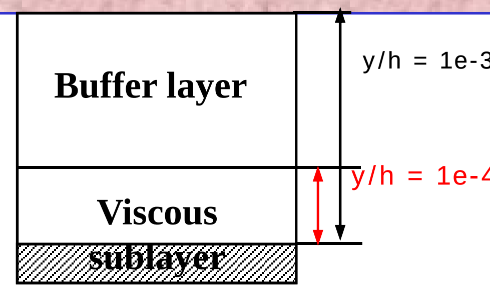


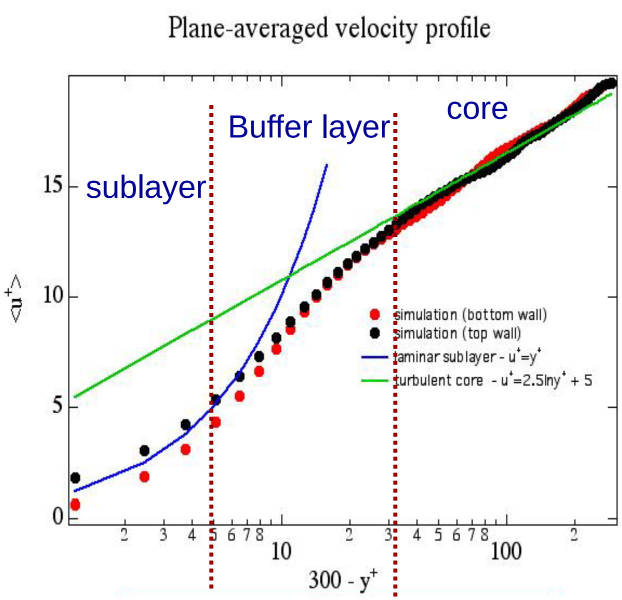
Fig. 3 – The turbulent-drag reduction DR as a function of the Reynolds number *Re* for 40 μg/ml HPAA (a) and 40 μg/ml DNA (b) solution.

Turbulent Drag Reduction: Flow Field Basics in Channels

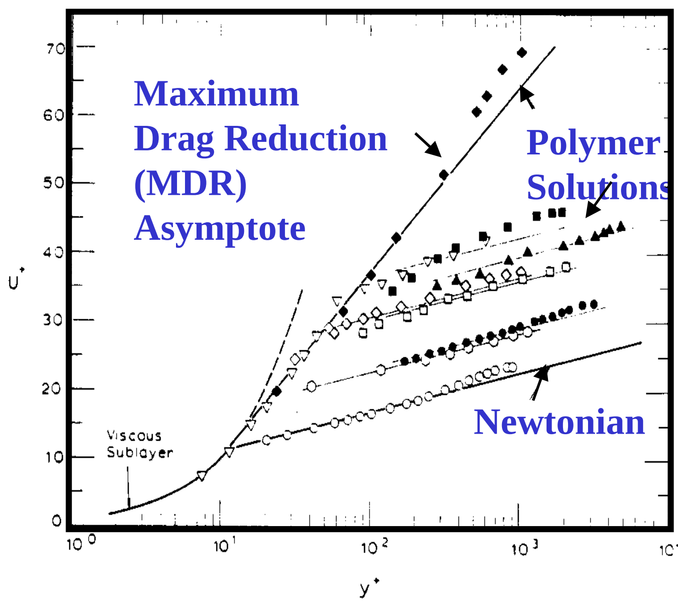




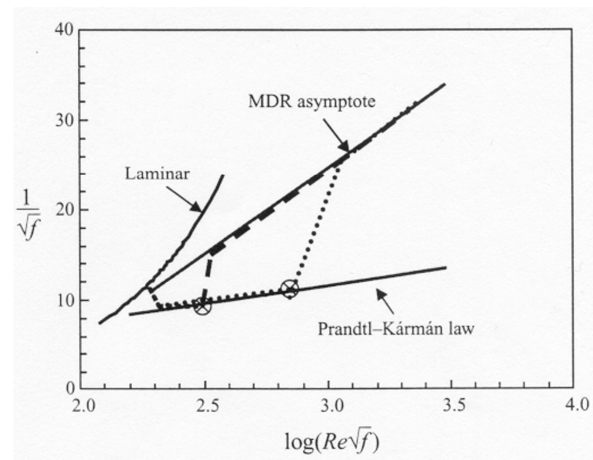
$$\mathrm{Re} = \frac{U_{mean} h}{\nu}$$



Virk, 1975



(Sreenivisan&White, JFM, 2000)

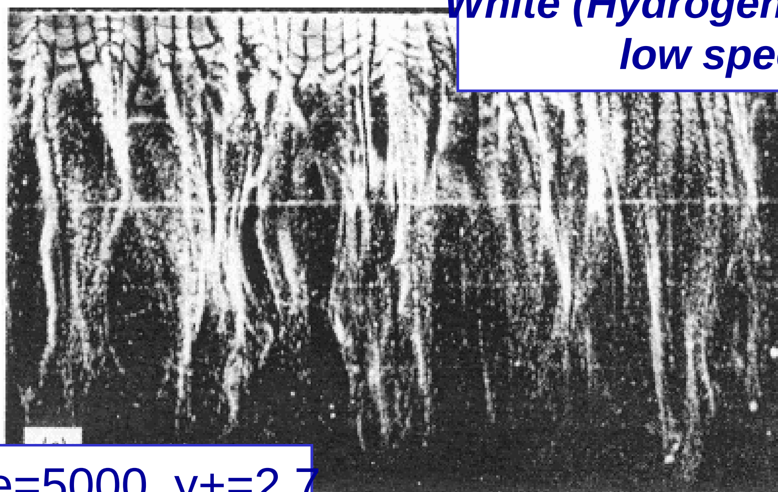


<u>Turbulent scalings</u>

$$u_\tau = \sqrt{\tau_w / \rho} \qquad u^+ = u / u_\tau \qquad y^+ = y\left(u_\tau / \nu\right) = y / \delta_v \qquad t^+ = \frac{u_\tau t}{\delta_v} = \frac{t\tau_w}{\mu} = t\left\langle \frac{\partial u}{\partial y} \right\rangle_{wall}$$

Turbulent Drag Reduction Fundamentals

White (Hydrogen bubbles): low speed



Re=5000, y+=2.7

<u>Coherent structures in turbulent flow</u>

Streaks

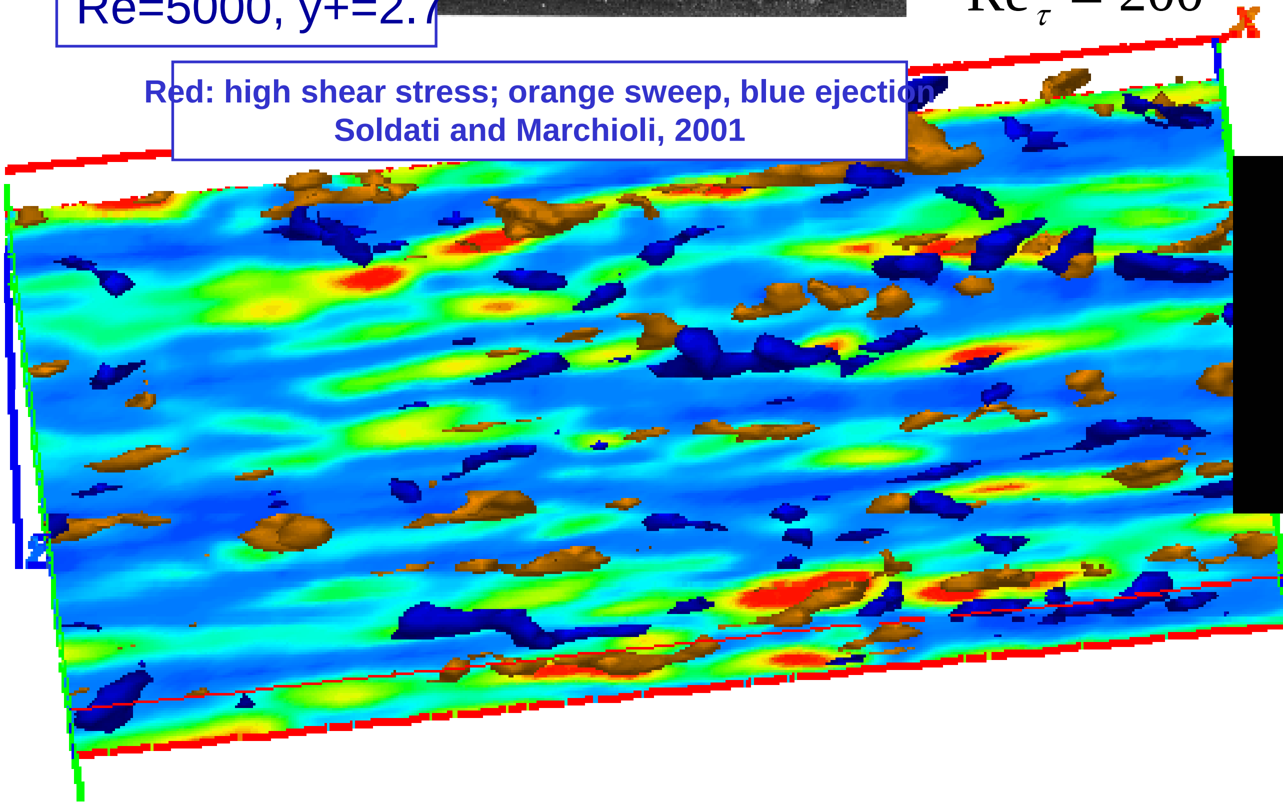
Bursts

Quasi-streamwise vortices

“Sweeps” and “ejections”

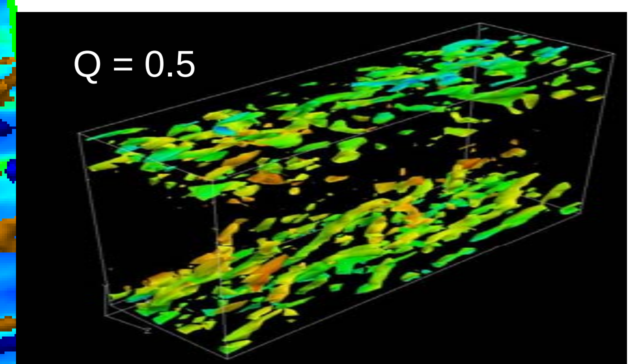
Relation to skin friction

$$\mathrm{Re}_\tau = 200$$



Red: high shear stress; orange sweep, blue ejection
Soldati and Marchioli, 2001

Hunt, Wray, and Moin, 1988



$$Q = -1/2\mathrm{tr}\left((\nabla u)^2\right),$$

A BRIEF Overview Prior Research

Polymers

Experiments

- **Virk (1975): Descriptive statistics**

Scaling Arguments

- ***Lumley: Timescales and Coil-Stretch***
- ***deGennes (and Tabor): Energy***

Uncoupled simulations

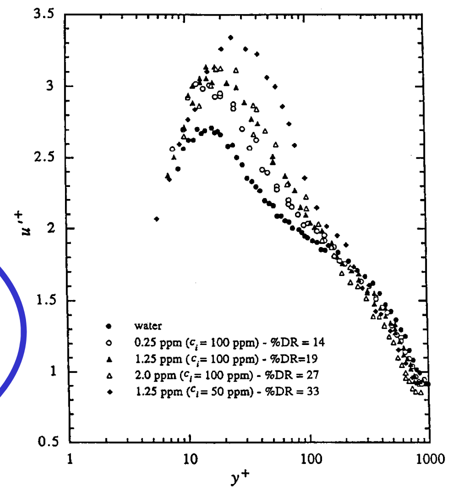
- **Massah, Kontomaris, Schowalter, Hanratty ('92)**
- **Massah and Hanratty (1993,1997)**
  - **FENE-PM**

Coupled simulations

- **Beris et al (1997)**
  - **FENE-P**
  - **Re=1890, small extensibility, hi conc.**
  - **Flow statistics, onset Wi, streaks**

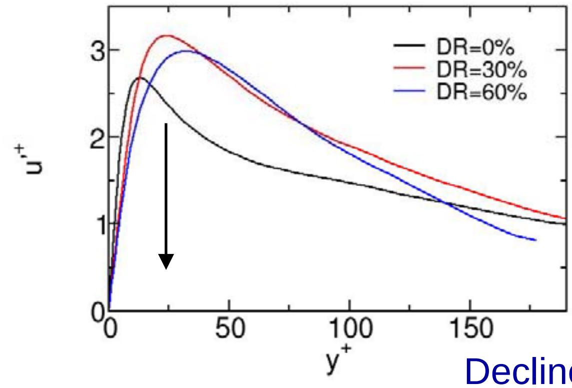
Present…

Warholic,Massah, Hanratty '97



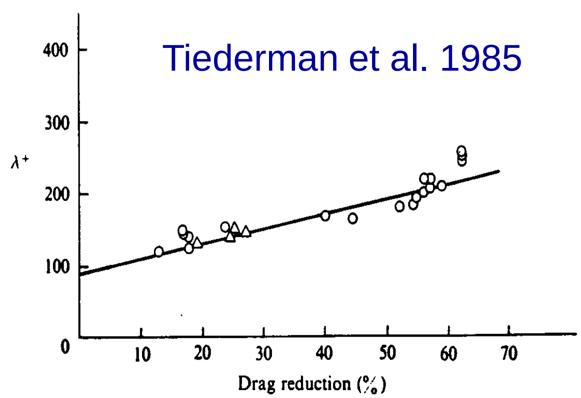
Increasing drag reduction

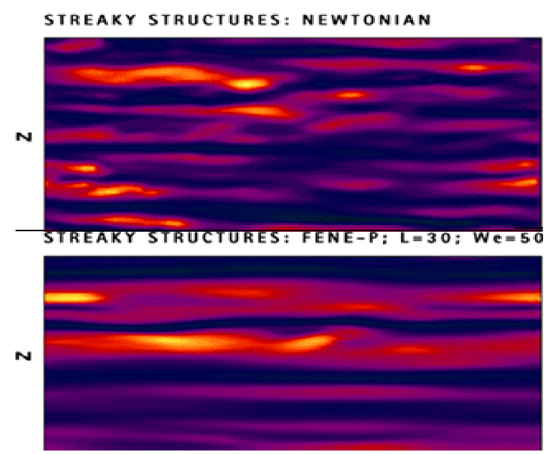
DuBief et. al. 2003



Declines in HDR

Tiederman et al. 1985





Sureshkumar, Beris, Handler '97

Three General Classes of Theory Regarding Turbulent Drag Reduction

Lumley 1969:
The coil to stretch transition of the polymers by the turbulent flow gives rise to and increased extensional viscosity and a thickening of the buffer layer near the channel/pipe wall.

decompressor
are needed to see this picture

DeGennes (and Tabor) 1986
Strain is in general not enough to create a coil-stretch transition. Elasticity of the polymers modifies the Kolmogorov scales and small-scale turbulent kinetic energy is absorbed by the polymers and radiated away in the form of shear waves.

decompressor
are needed to see this picture.

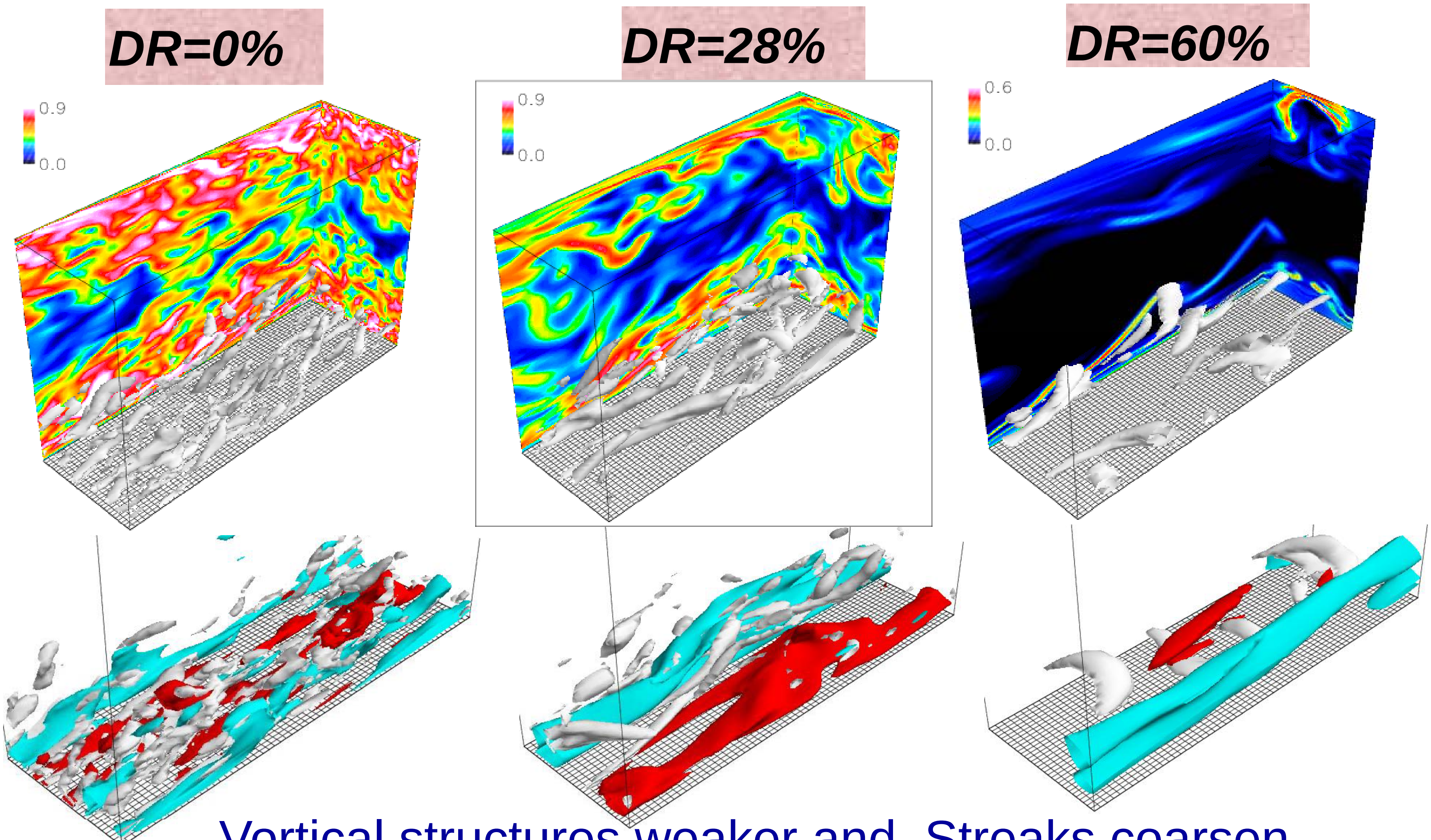
Ryskin (1987), Orlandi (1995), Procaccia et al. (2001+), Iaccarino & Shaqfeh (2007)
The polymer stretch in the near wall region creates an added shear viscosity which scales with distance from the wall, reducing the local Reynolds number and broadening the buffer layer

decompressor
are needed to see this picture

Ryskin, G. 1987 Turbulent drag reduction by polymers: A Quantitative Theory, PRL 59(18)

Note: Hinch’s 1974 & 1977 papers were nearly entirely directed at how to use Lumley’s ideas to describe turbulent drag reduction

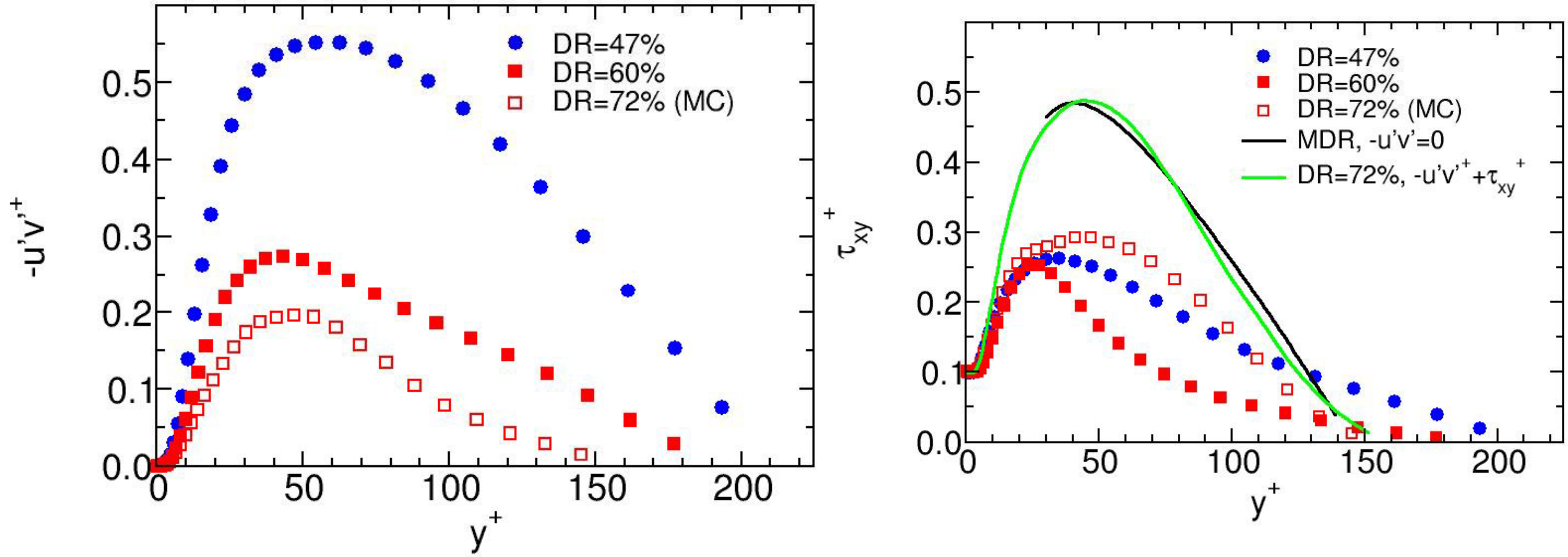
Large Scale Simulaton



Vortical structures weaker and Streaks coarsen

Similar results now available by Khomami, Akhavan, Hunt, Beris, etc. Predictions can be qualitative and even quantitative agreement with expt…w/ one big caveat…

Reynolds shear stress and Polymer stress



Evolution of the stresses with increasing drag reduction

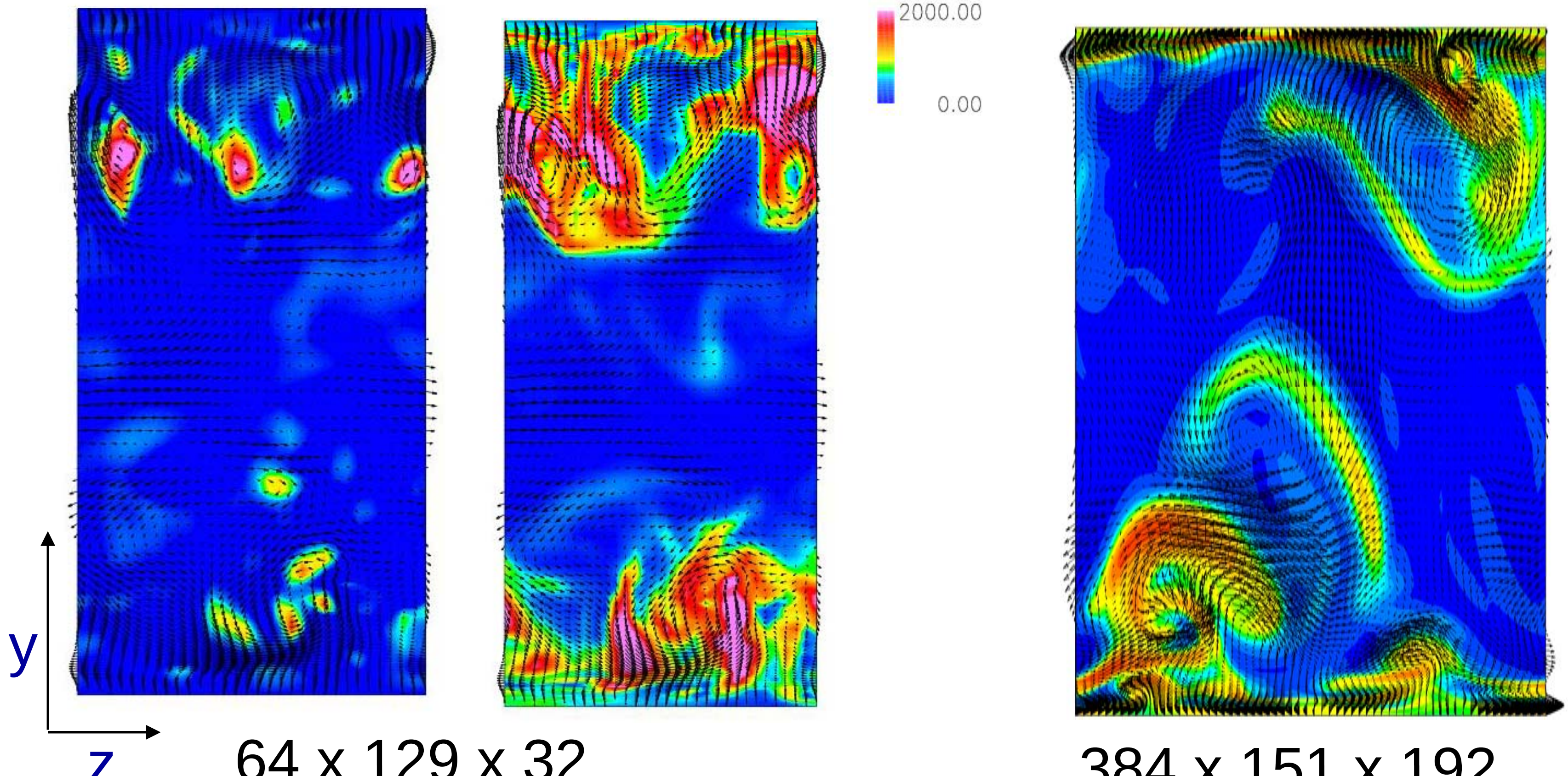
Warholic, Hanratty, et al. (1999)'s observation of zero-Reynolds shear stress means that polymer need to produce more shear stress than Reynolds stress

Similar results now available by Khomami, Akhavan, Hunt, Beris, etc. Predictions can be qualitative and even quantitative agreement with expt…w/ one big caveat…

Stretch in Upwashes and Downwashes: LDR and HDR

DR=28%; We = 70; L=30 MC ***DR=60%; We = 120; L=100 LC***

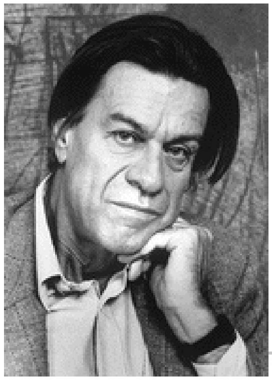
Vorticity Polymer stretch Polymer stretch



64 x 129 x 32 384 x 151 x 192

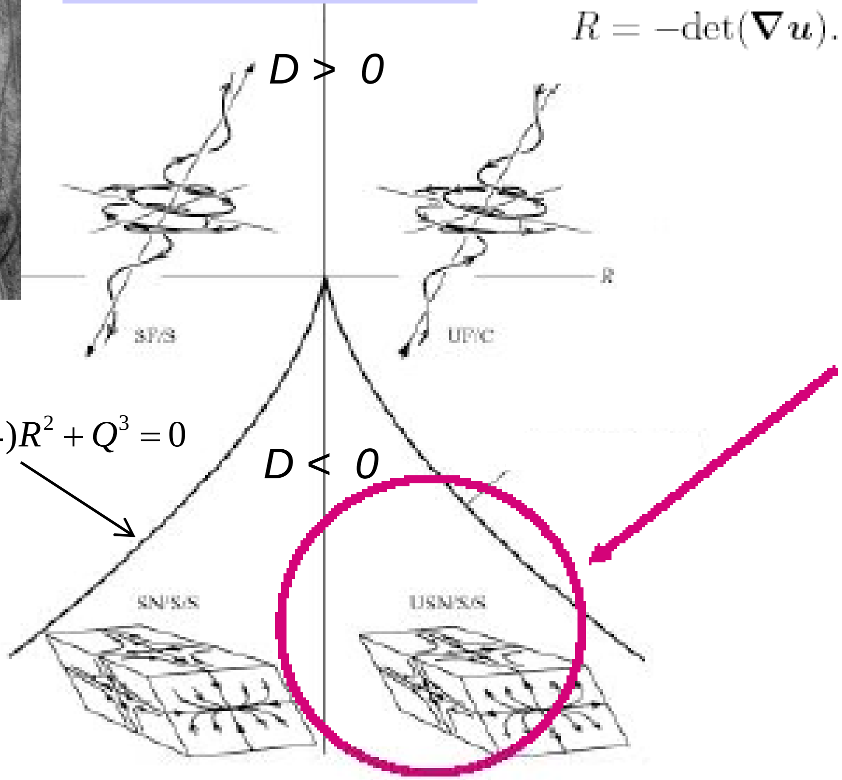
Dubief, Y.,C.M. White, V.E. Terrapon, E.S.G. Shaqfeh, P. Moin, and S. K. Lele, ``On the coherent drag reducing and turbulence enhancing behavior of polymers in wall flows", J. Fluid Mech 514, pp. 271-280 (2004)

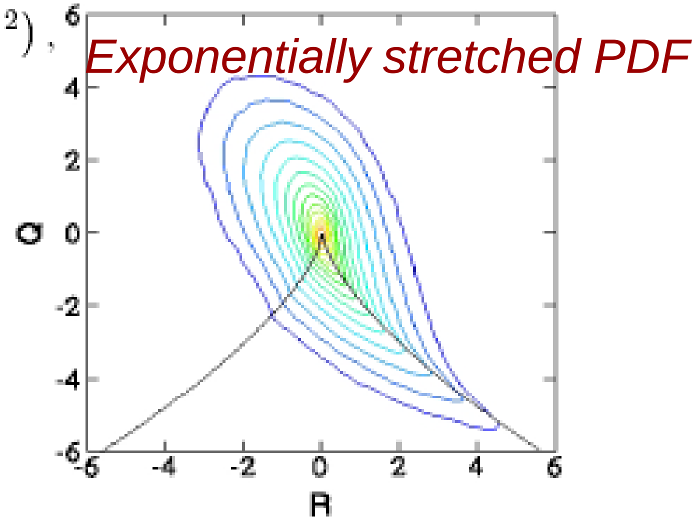
Characterization of the Velocity Gradients in Newtonian Turbulent Channel Flow



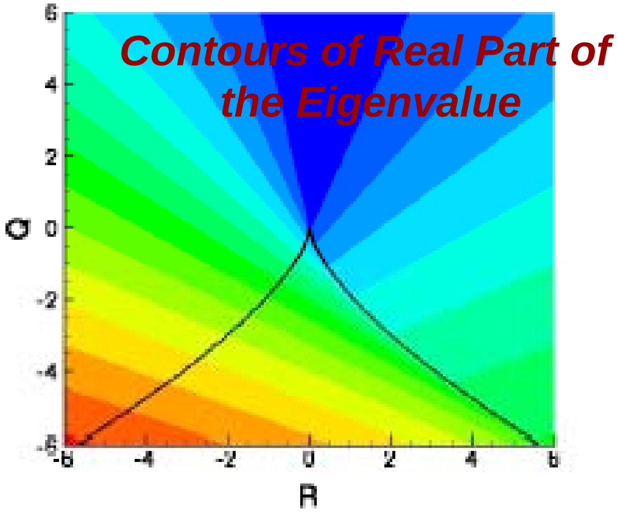
De Gennes, 1974

$$Q = -1/2\mathrm{tr}\left((\nabla \boldsymbol{u})^2\right),$$
$$R = -\det(\nabla \boldsymbol{u}).$$





but



Straining flows for Q < 0 & R > 0 !

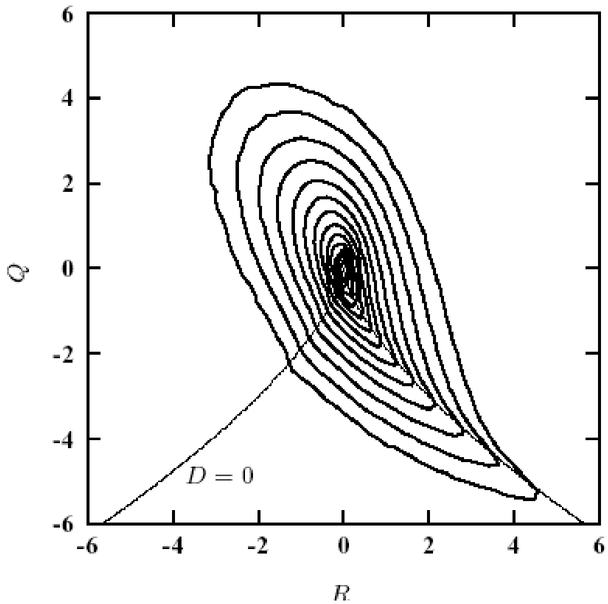
BLACKBURN, H., MANSOUR, N. & CANTWELL, B. 1996 Topology of fine-scale motions in turbulent channel flow. *J. Fluid Mech.* **310**, pp. 269–292.

Now in the drag reduced flow….. First a look at the statistics

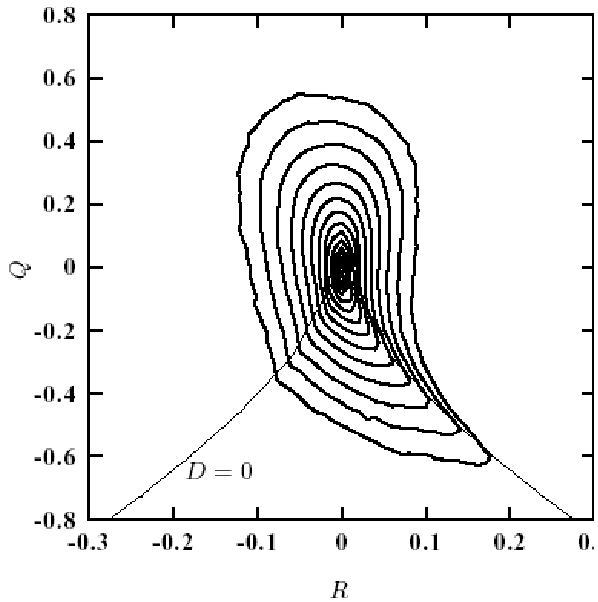
Terrapon, V.E., Y. DuBief, P. Moin, E.S.G. Shaqfeh, and S.K. Lele, J. Fluid Mech. 504, pp. 61-71 (2004)

L = 100, Wi = 120,
Re = 5000, β = 0.99

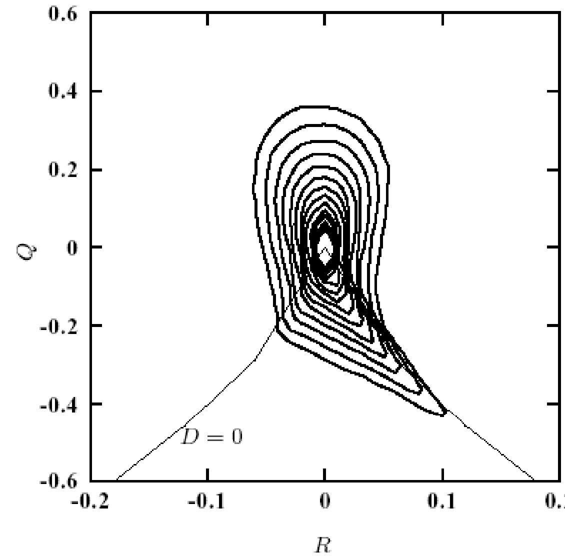
Newtonian

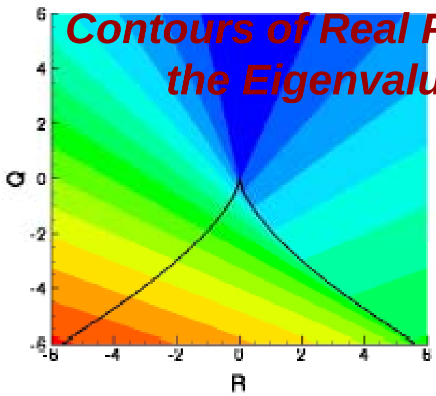


Polymer (30%DR)



Polymer (57%DR)

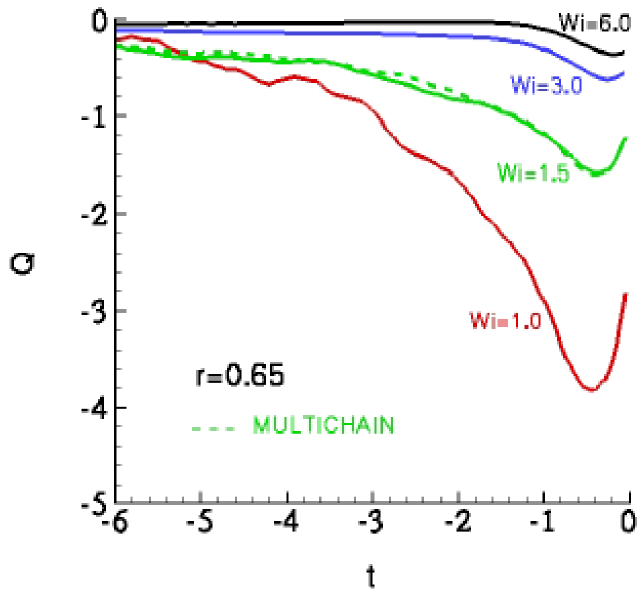


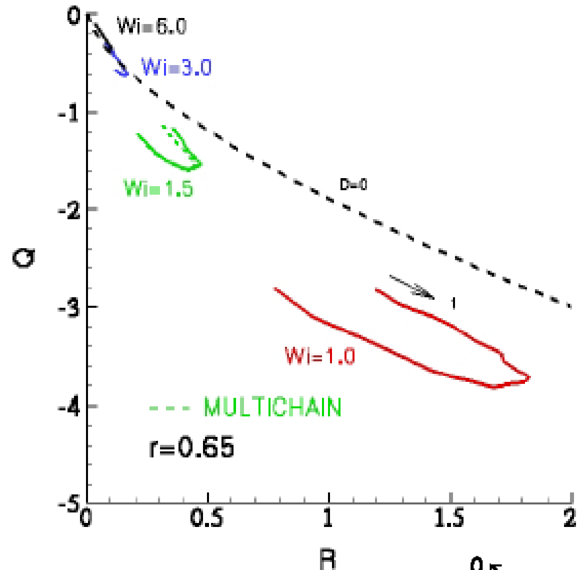


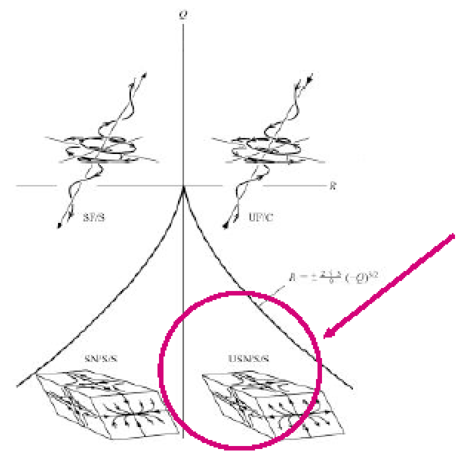
Contours of Real Part of the Eigenvalue

<u>Flow characteristics are qualitatively similar</u> :
Dominant flow that with largest real part of the eigenvalue is BIAXIAL straining flow (Q<0, R>0)

Conditionally Averaged Lagrangian Time Histories of Polymer Stretch



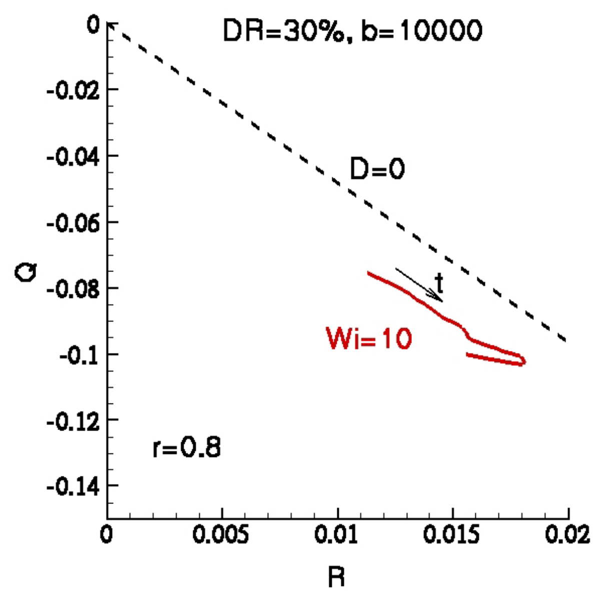




$$\mathrm{Re}_{mean} = 5000, \quad Wi_{mean} = 1, 1.5, 3.0, 6$$

$$\mathrm{Wi}^{+} = 11, 16, 34, 68$$

Total strain in
Leadup behavior 1-2



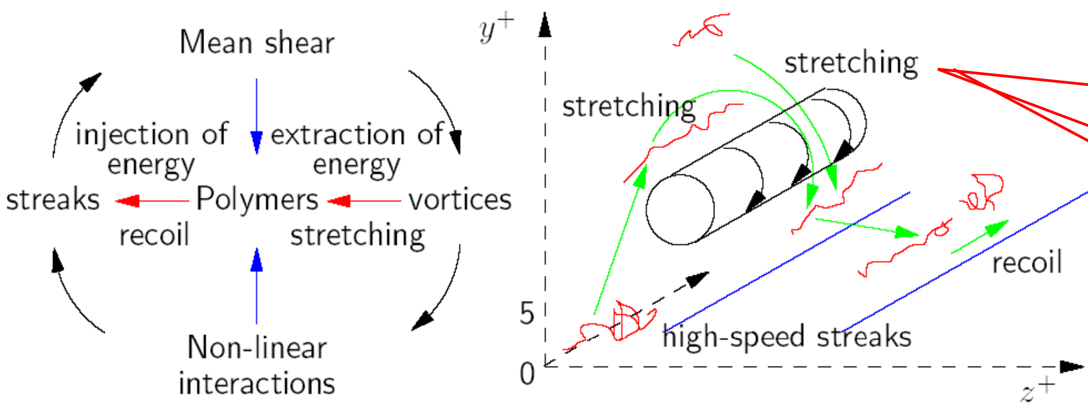
Terrapon, V.E., Y. DuBief, P. Moin, E.S.G. Shaqfeh, and S.K. Lele, ``Simulated polymer stretch in a turbulent flow using Brownian dynamics'', J. Fluid Mech. 504, pp. 61-71 (2004)

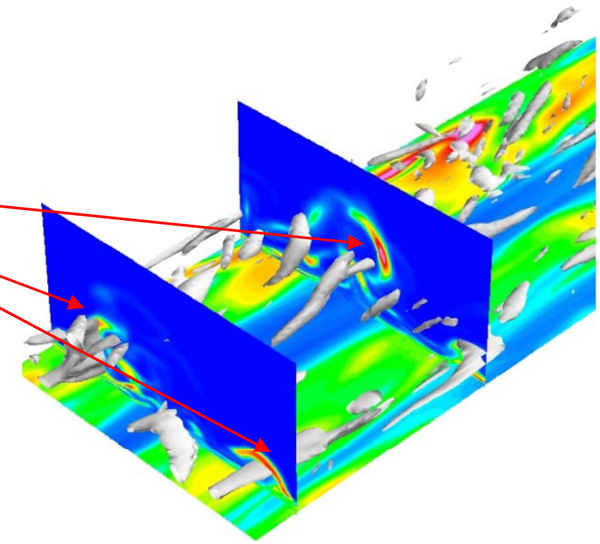
Original uncoupled results by Massah & Hanratty but different interpretation…

Simulated Mechanism of Drag Reduction with Flexible Polymers

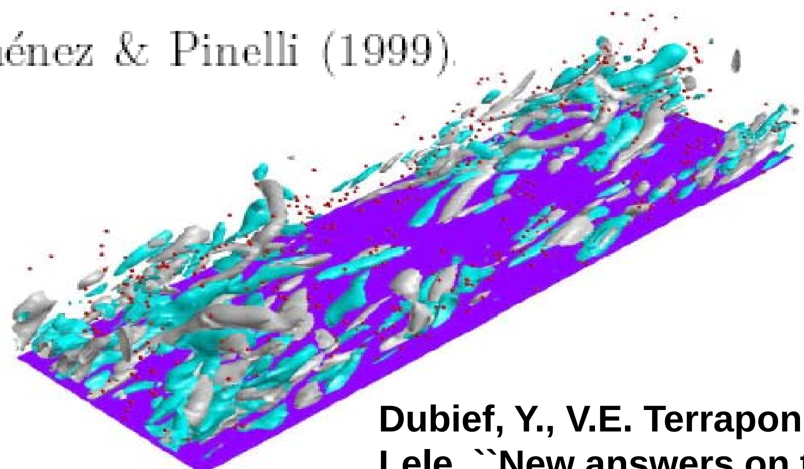
Extraction of energy around vortices by associated biaxial extensional regions

Modified near-wall regeneration cycle





Jiménez & Pinelli (1999)



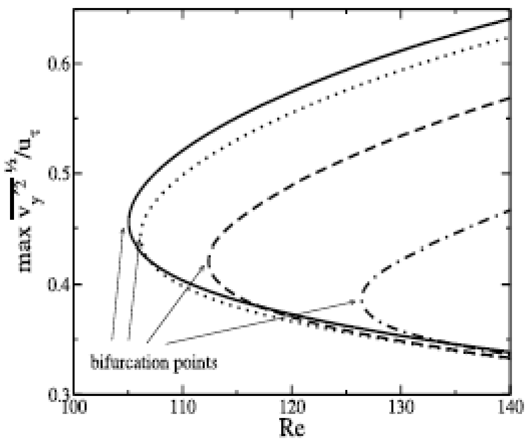
Biaxial straining flows shown in turquoise -- Q = -2.3

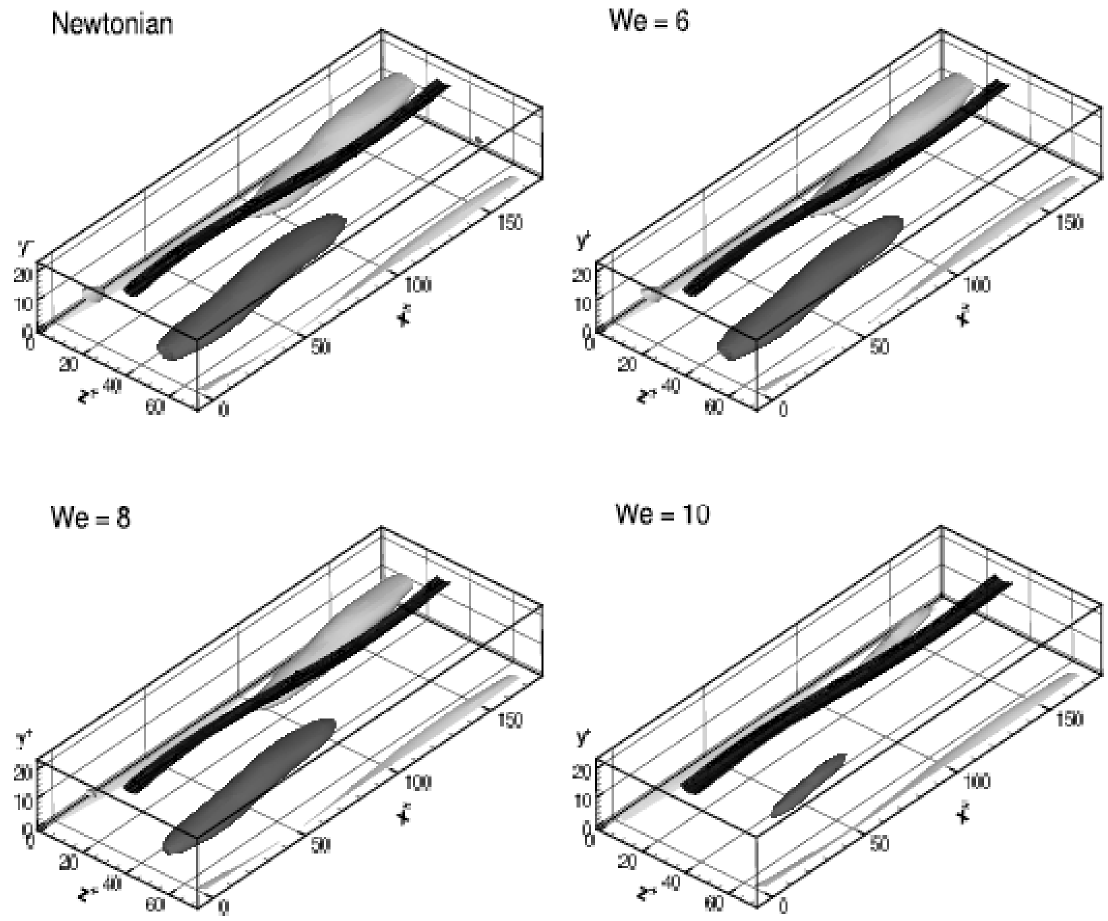
Vortices shown in gray -- Q = 1.9

Dubief, Y., V.E. Terrapon, C.M. White, E.S.G. Shaqfeh, P. Moin, and S. K. Lele, ``New answers on the interaction between polymers and vortices in turbulent flows'', Flow, Turbulence and Combustion, 74 pp. 311-329 (2005)

Mechanism consistent with the “Waleffe” Model

Stone, Roy, Larson, Waleffe, Graham, Phys. Of Fluids, 2004



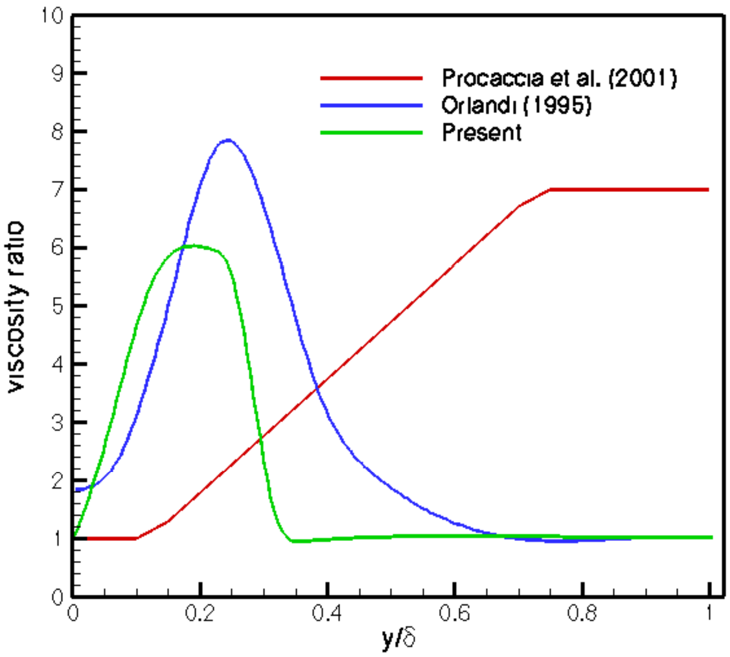


…again the “culprit” is the biaxial extensional flows between vortices

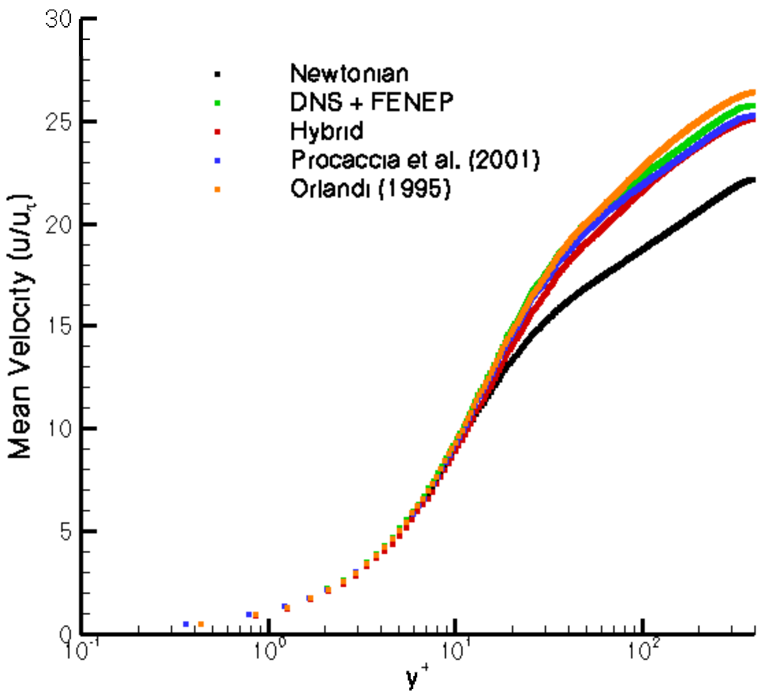
"Simple" Models for Turbulent Polymer Flows (Based on the microstructural mechanism)

Models based on the concept of "viscosification" via turbulent fluctuations

- *Ryskin (1987) introduced the Yo-Yo model*
- *Orlandi (1995) introduced incr. viscosity based on the Q criterion*
- *Procaccia & coworkers (2001+) introduced a simple linear viscosity model.*
- *Our model correlates the viscosity with the turbulent kinetic energy*

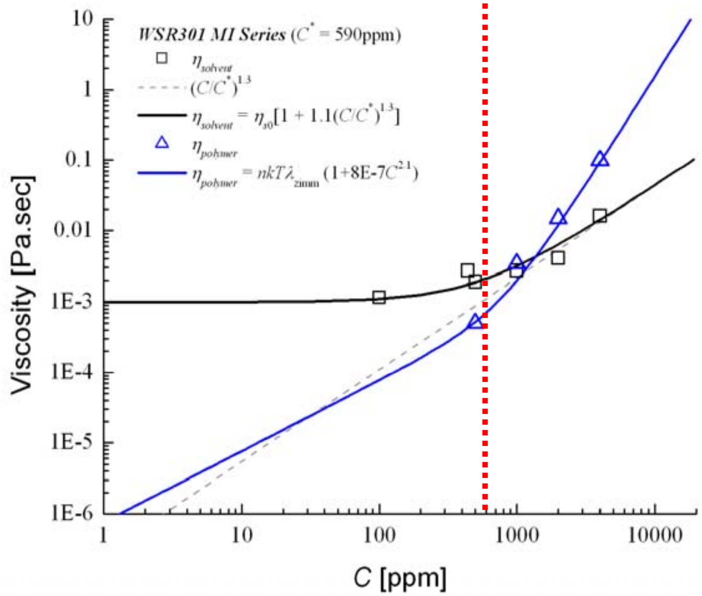


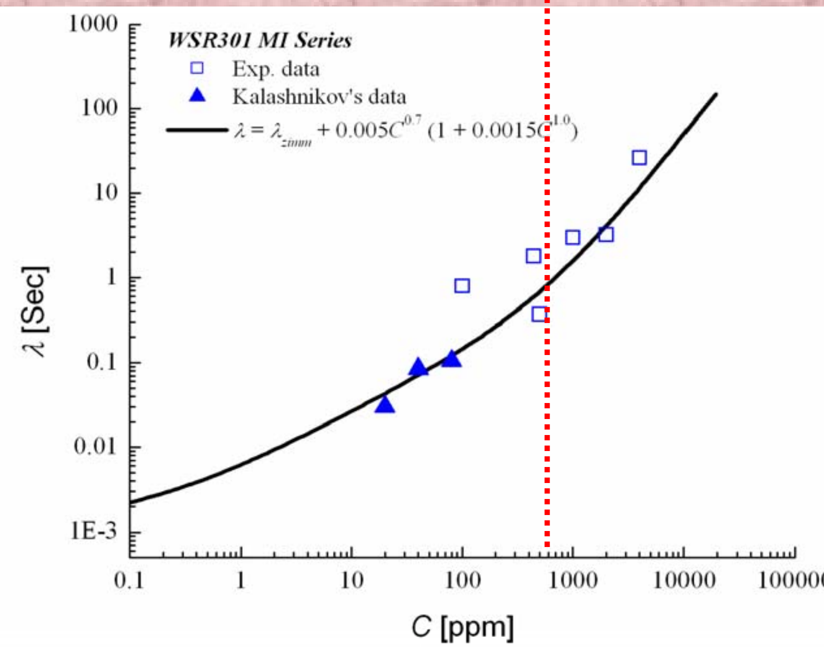
Polymer to Newtonian viscosity ratio in DNS of a channel flow at Re_τ=395 We_τ~40



Comparison of the various model with a fully coupled DNS/FENEP calculation

The caveat… direct comparisons of numerical simulations to data are still “phenomenological”





Curve Fit to the“best” available data. (Summary of work by Kalashnikov, Solomon, Larson, McKinley, etc. for PEO)

But we can work with well characterized solutions and then connect to well vetted numerical models…

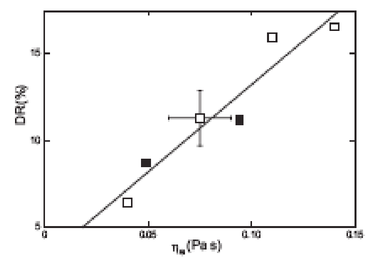


Fig. 6 – The drag reduction DR at a Reynolds number $Re_{poly} = 1400$ as a function of the elongational viscosities of the aqueous polymer solutions, for different salinities at a Hencky strain of $\dot{\epsilon}t = 1$. To allow for a comparison between samples with a different shear viscosities, the Reynolds number Re_{poly} is calculated using the laminar shear viscosities of the polymer solutions at a shear rate $\dot{\gamma} = 2000$. Filled squares: DNA solutions, open squares: HPAA solutions (the drawn line is a guide to the eye).

Turbulent-drag reduction of polyelectrolyte solutions: Relation with the elongational viscosity

C. Wagner[1], Y. Amarouchene[1,2], P. Doyle[3] and D. Bonn[1](*)

Conclusion II: The Coil to Stretch Transition after 30+ Years…

➢ ***DeGennes 1974 paper had a bigger impact on TDR research than Tabor & DeGennes 1986, however, the latter did identify the fact that a full coil-stretch transition is not the main workhorse in TDR.***

Elements that are perhaps a meld of the ideas of DeGennes & Lumley

❖ ***Biaxial extensional flows (preferentially the "upwashes") viscosify or "dissipate" turbulent energy in the buffer layer (Lumley-like)***
❖ ***Events are 1-2 strain which cause viscosification (Tabor & DeGennes)***

More to do in the areas of:

❖ ***Quantitative connection between rheology and microstructural dynamics (e.g. Yo-Yo model not needed?)***
❖ ***Polymer viscosity or Reynolds Stress models are promising***
❖ ***MDR (Polymer sustained turbulence?)***