Computing in chemical engineering for transport processes and polymer materials

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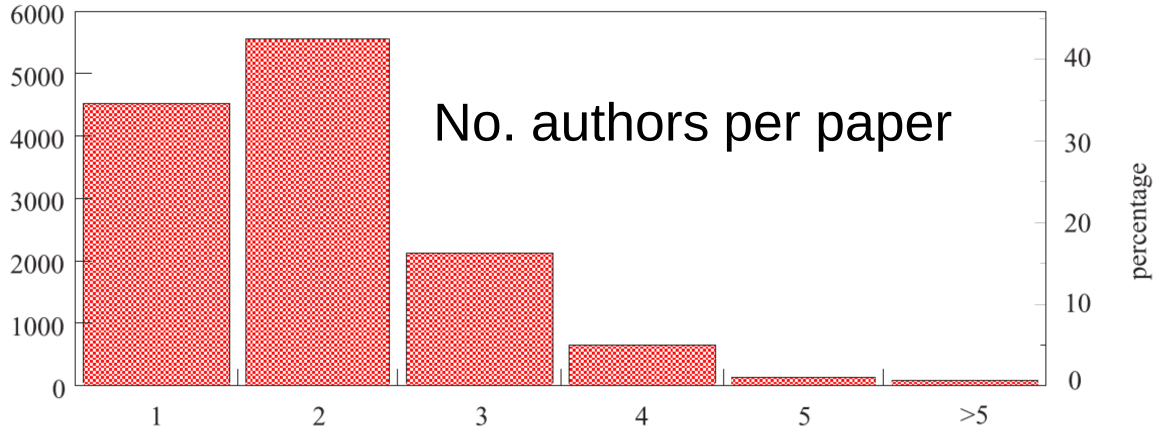
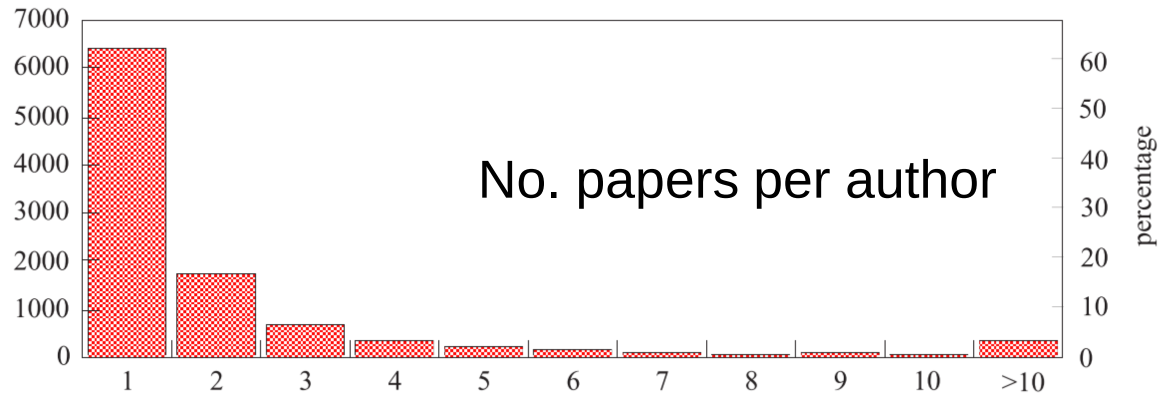
Who am I?

- fluid dynamicist?
  - probably...
- polymer physicist?
  - maybe...
- computationalist?
  - oh, yes!

Stats of papers published in *J. Fluid Mech.* between 1956-2006

-- H.E. Huppert, 50 years of impact of JFM, 2006





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Acknowledgment

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<u>Topic 1</u>

How do polymer additives reduce turbulent friction drag?

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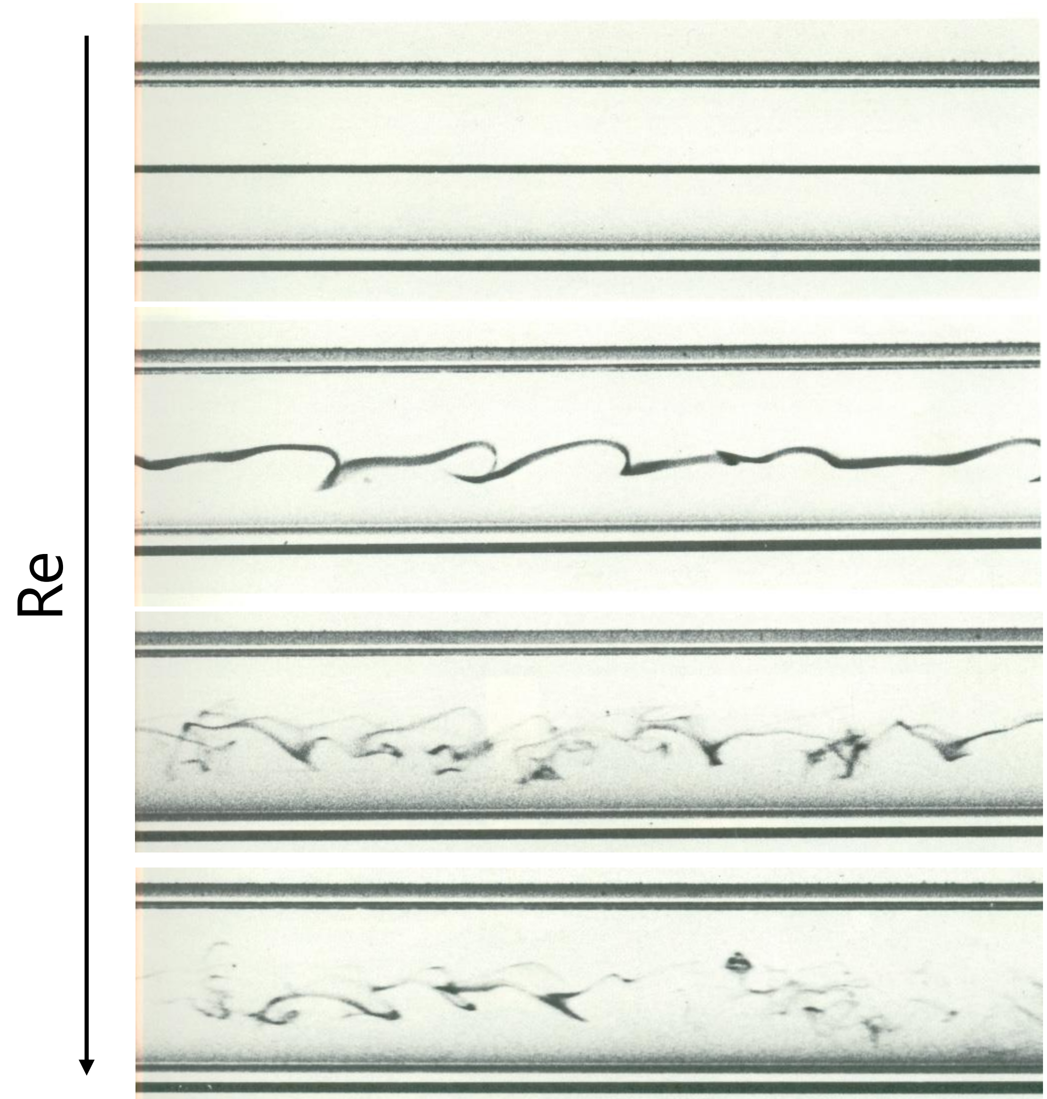
Background: Turbulence

$$\mathrm{Re} \equiv \frac{\rho U D}{\eta}$$



Reynolds O., *Philos. Trans.*, 1883
http://www.uic.edu/classes/me/me536/gallery.html

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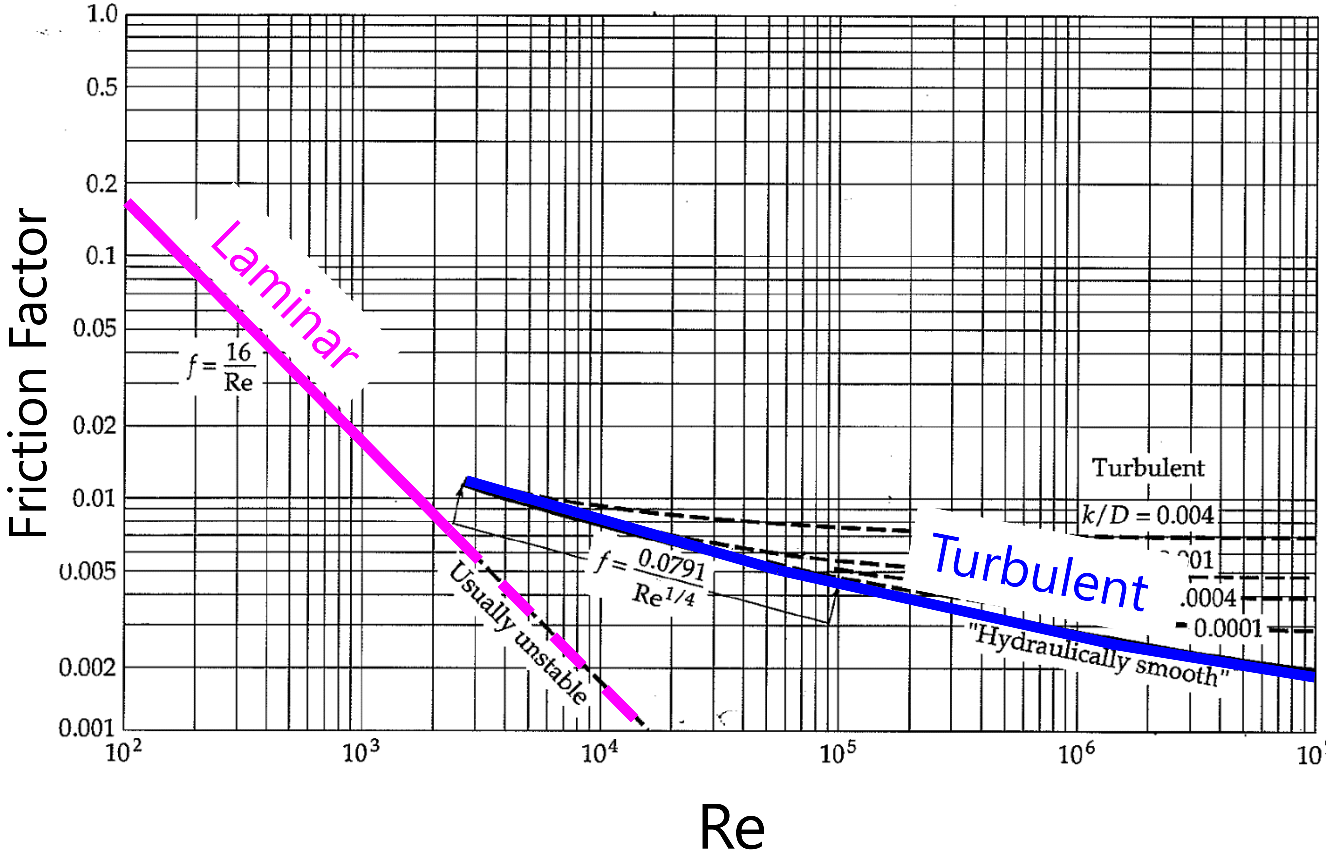
Fanning friction factor:

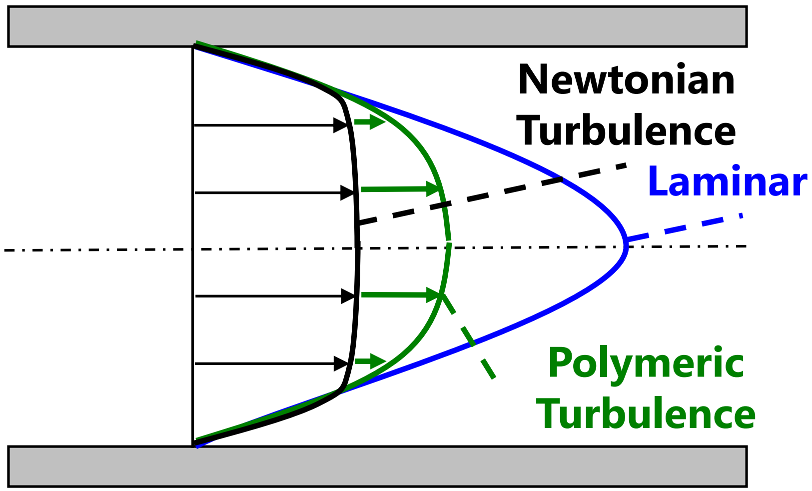
$$f \equiv \frac{1}{4}\left(\frac{D}{L}\right)\frac{\Delta P}{\frac{1}{2}\rho U^2}$$

Bird, Stewart and Lightfoot, *Transport Phenomena*, 2nd ed., 2002

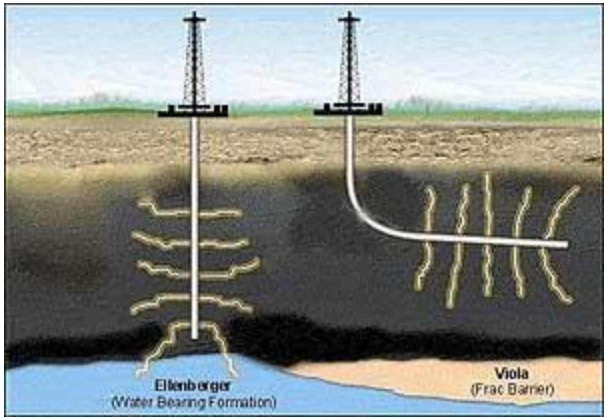


Introduction: Turbulent drag reduction

- Very low polymer concentration
  - O(10)-O(100) wppm
- DR% up to 80%.
- Applications:
  - energy saving in fluid transportation.
  - oil drilling & recovery.



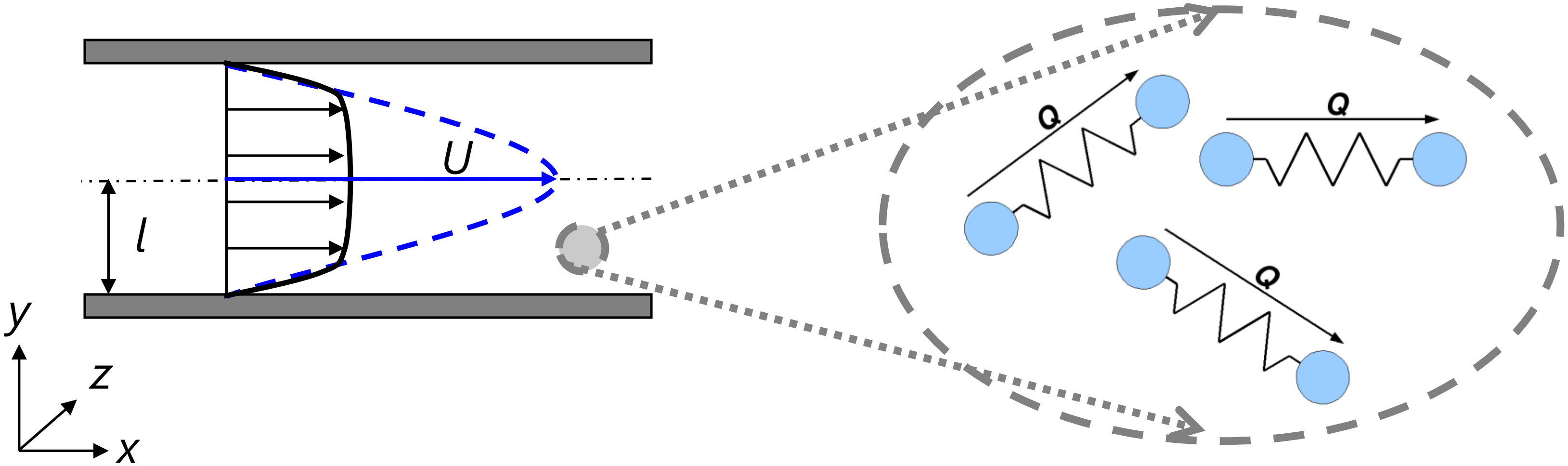
http://www.alyeska-pipe.com/



http://frack.mixplex.com/

Methodology: Direct numerical simulation (DNS)

Physical Systems



PDEs

Navier-Stokes Eq. ↔ **FENE-P Constitutive Eq.**

Fields

velocity ($\boldsymbol{v}$) & pressure (p)

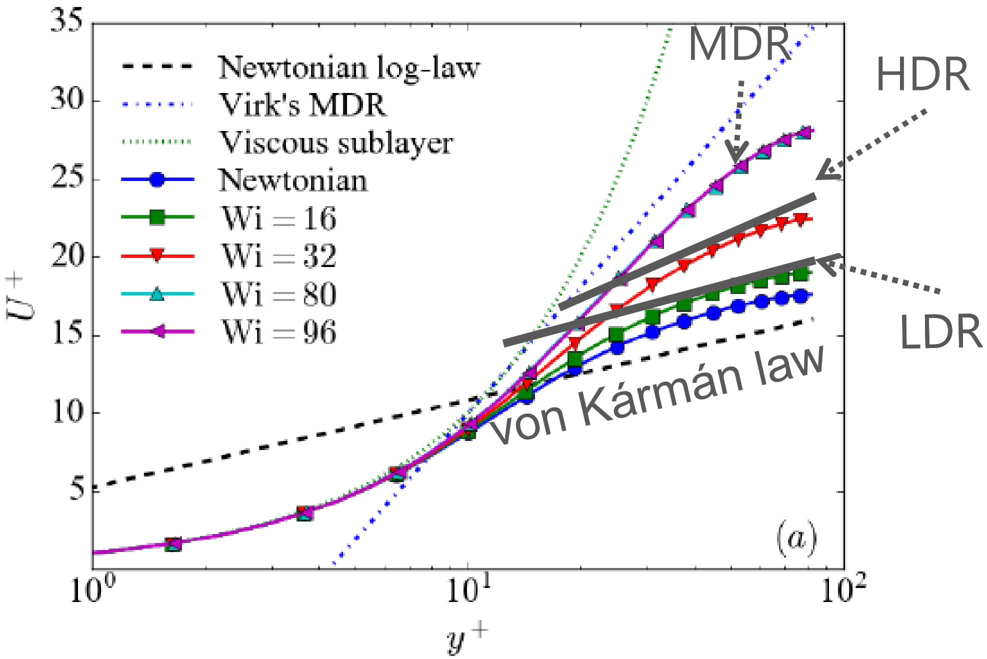
polymer conformation tensor: $\boldsymbol{\alpha} \equiv \frac{H\langle \boldsymbol{QQ} \rangle}{kT}$

Parameters

$$\mathrm{Re} \equiv \frac{\rho U l}{\eta_s + \eta_p} \qquad \beta \equiv \frac{\eta_s}{\eta_s + \eta_p} \qquad b \equiv \max(\mathrm{tr}(\boldsymbol{\alpha})) \qquad \mathrm{Wi} \equiv \lambda \frac{2U}{l}$$

Wi↑ → higher elasticity

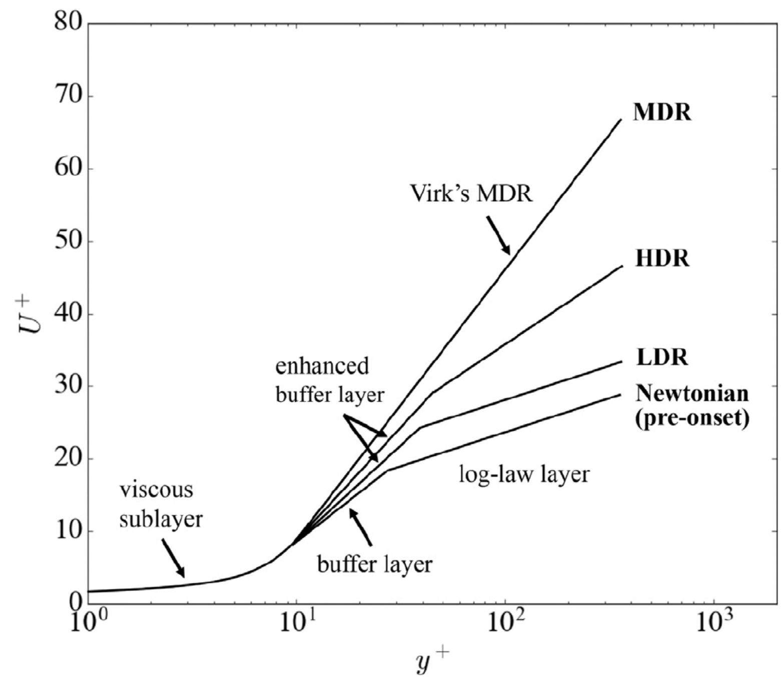
Transitions in drag-reduced turbulence



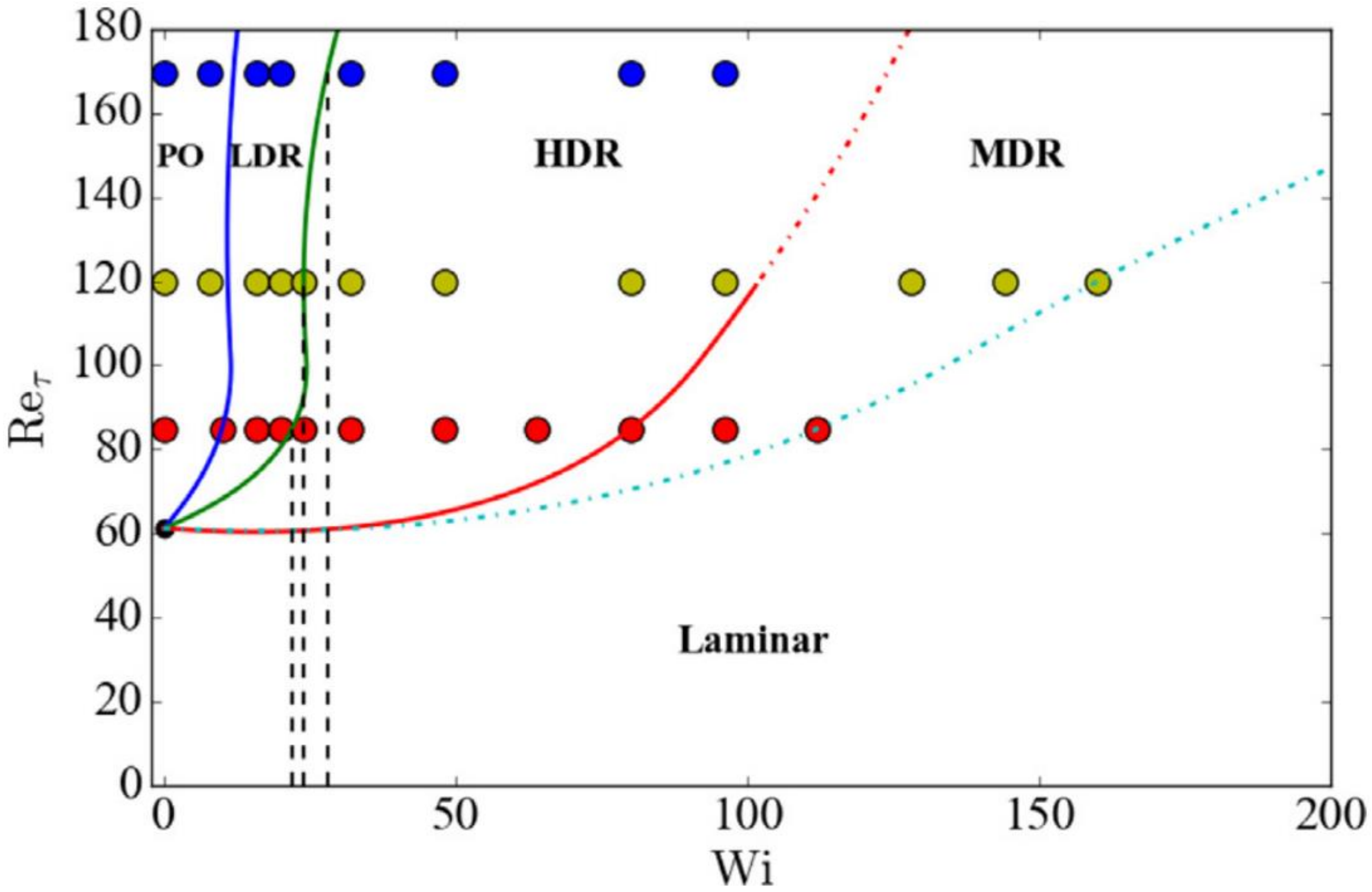
Zhu, Shrobsdorff, Schneider & Xi,
J. Non-Newt. Fluid Mech. (in press)

Transitions

- P.O.(Pre-Onset of DR)
- LDR (low-extent DR)
- HDR (high-extent DR)
- MDR (maximum DR)



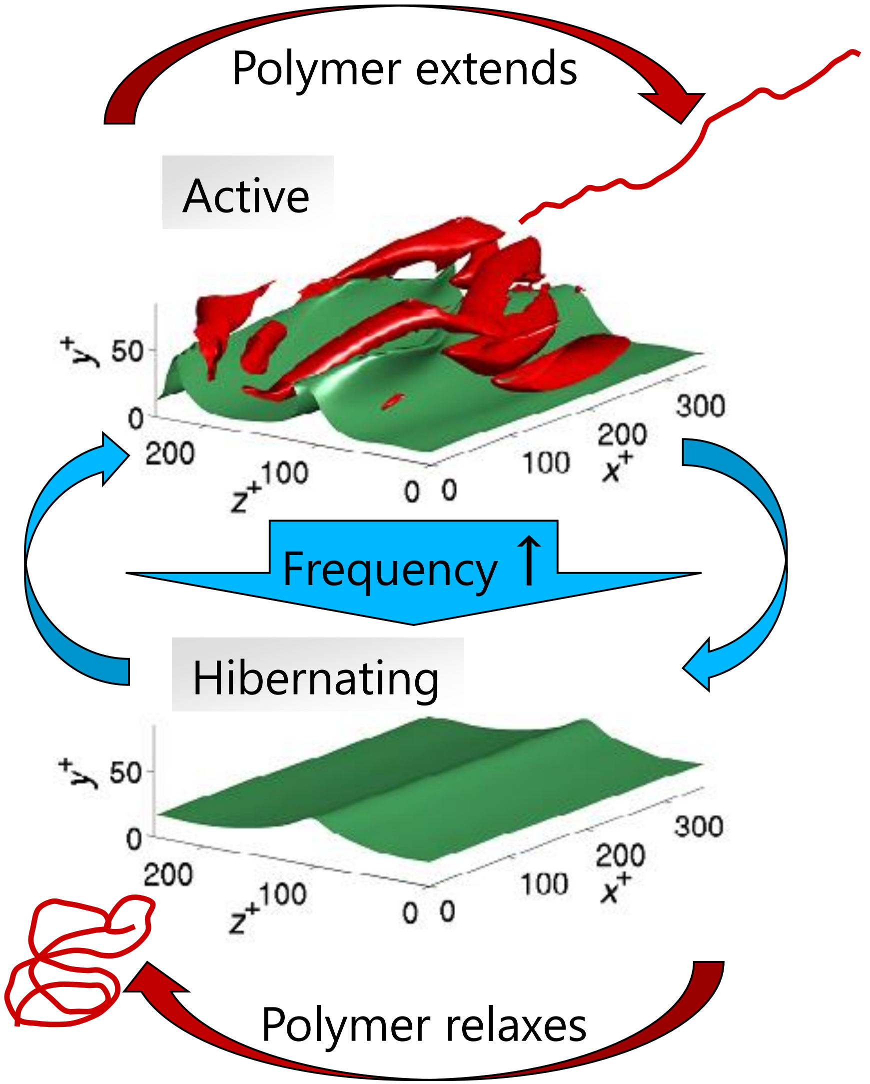
Transitions in drag-reduced turbulence



Zhu, Shrobsdorff, Schneider & Xi, *J. Non-Newt. Fluid Mech.* (in press)

MDR (maximum drag reduction)

- Asymptotic upper limit of DR at given Re.
- ***Universality***: the same mean flow rate regardless of polymer species, molecular weight, and concentration.



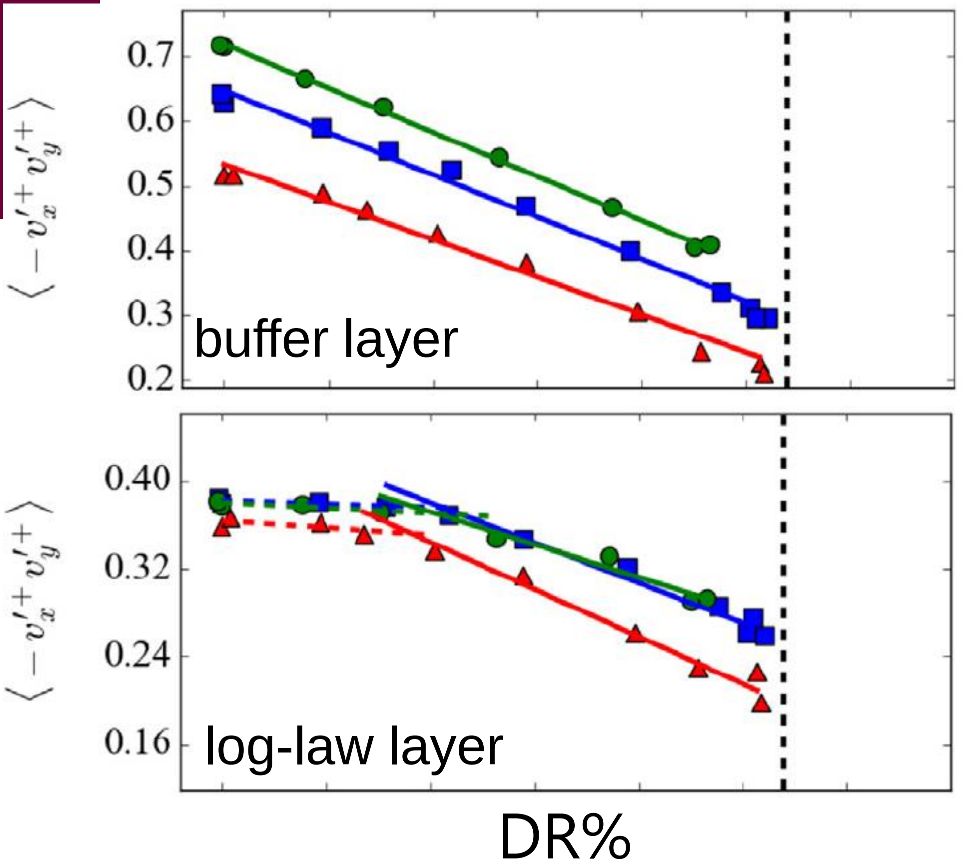
Xi & Graham, *Phys. Rev. Lett.* 2010
Xi & Graham, *J. Fluid Mech.* 2010
Xi & Graham, *Phys. Rev. Lett.* 2012
Xi & Graham, *J. Fluid Mech.* 2012

Current focus: HDR -- a new stage of DR?

Drag reduction is a two stage process with two distinct mechanisms

- Stage 1 (onset-LDR): across-the-board suppression of vortex motions
- Stage 2 (LDR-HDR): ???

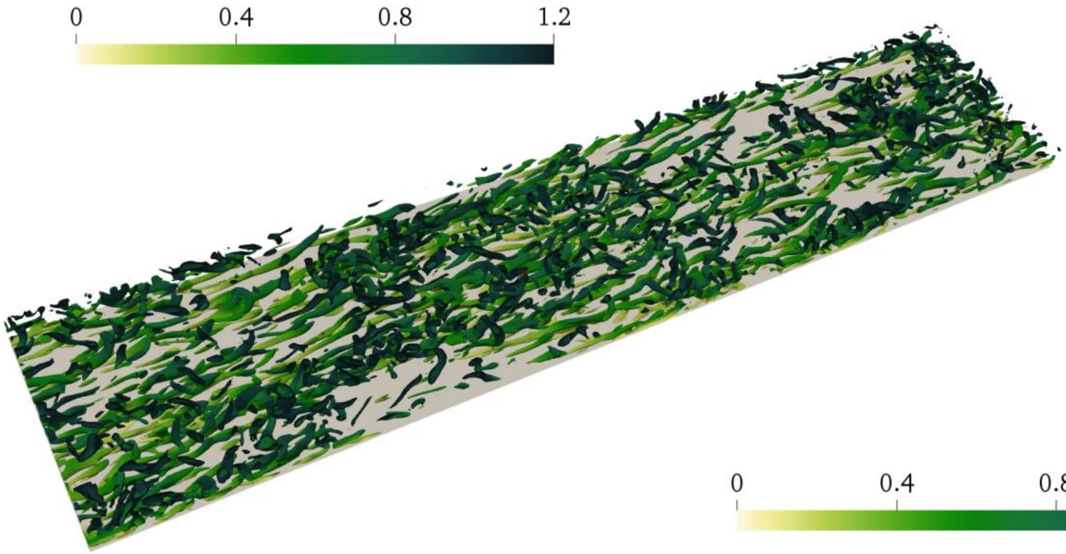
Reynolds Shear Stress

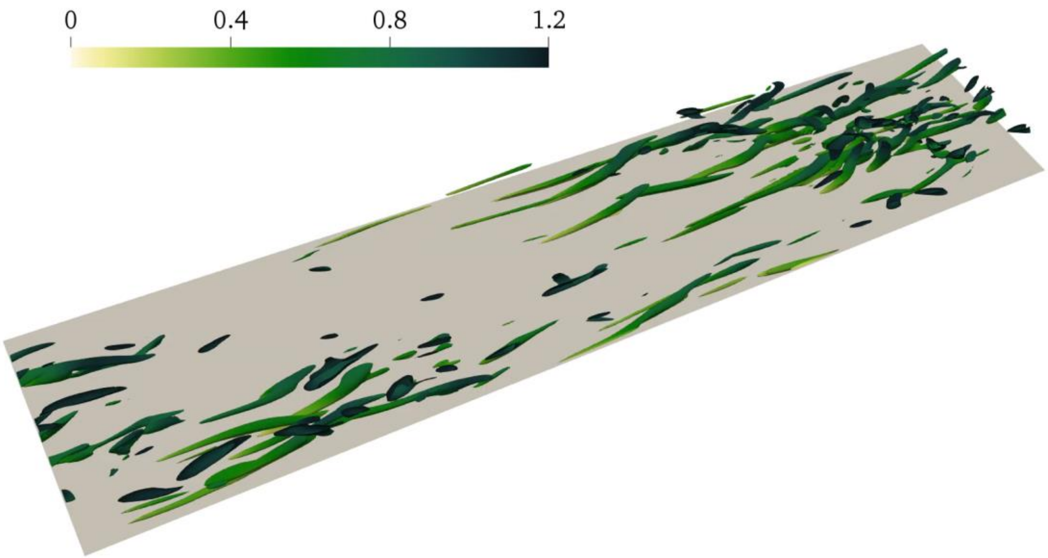


Zhu, Shrobsdorff, Schneider & Xi,
J. Non-Newt. Fluid Mech. (in press)

Vortex configuration and dynamics

Newt. & LDR





HDR & MDR

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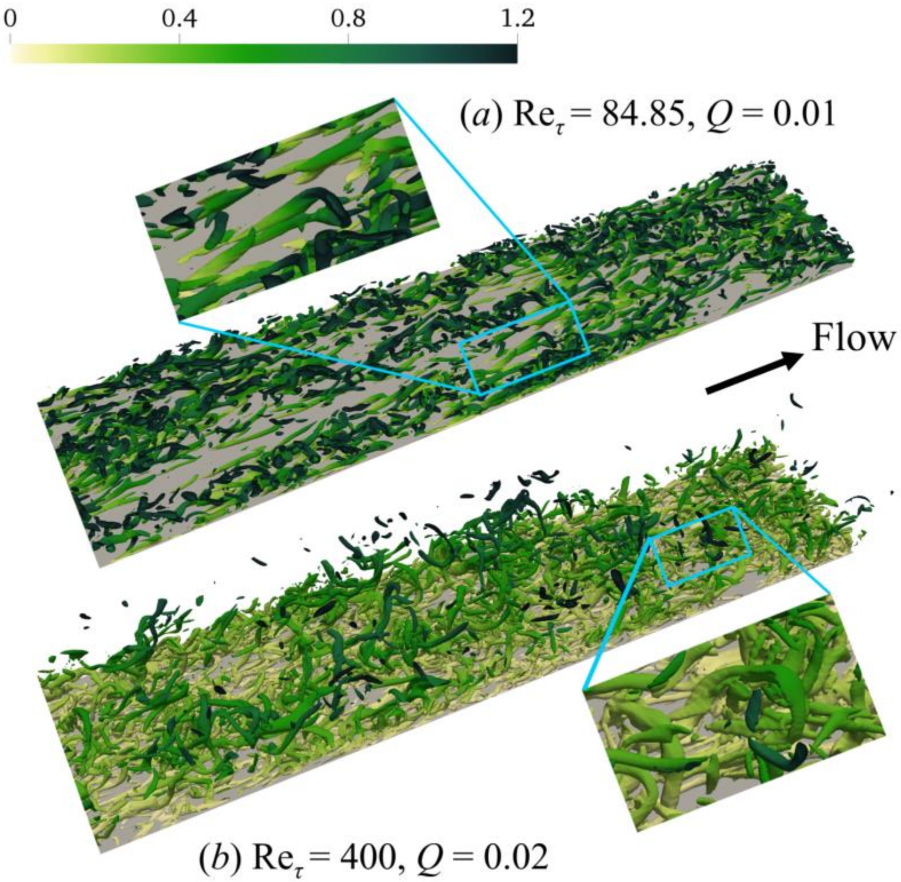
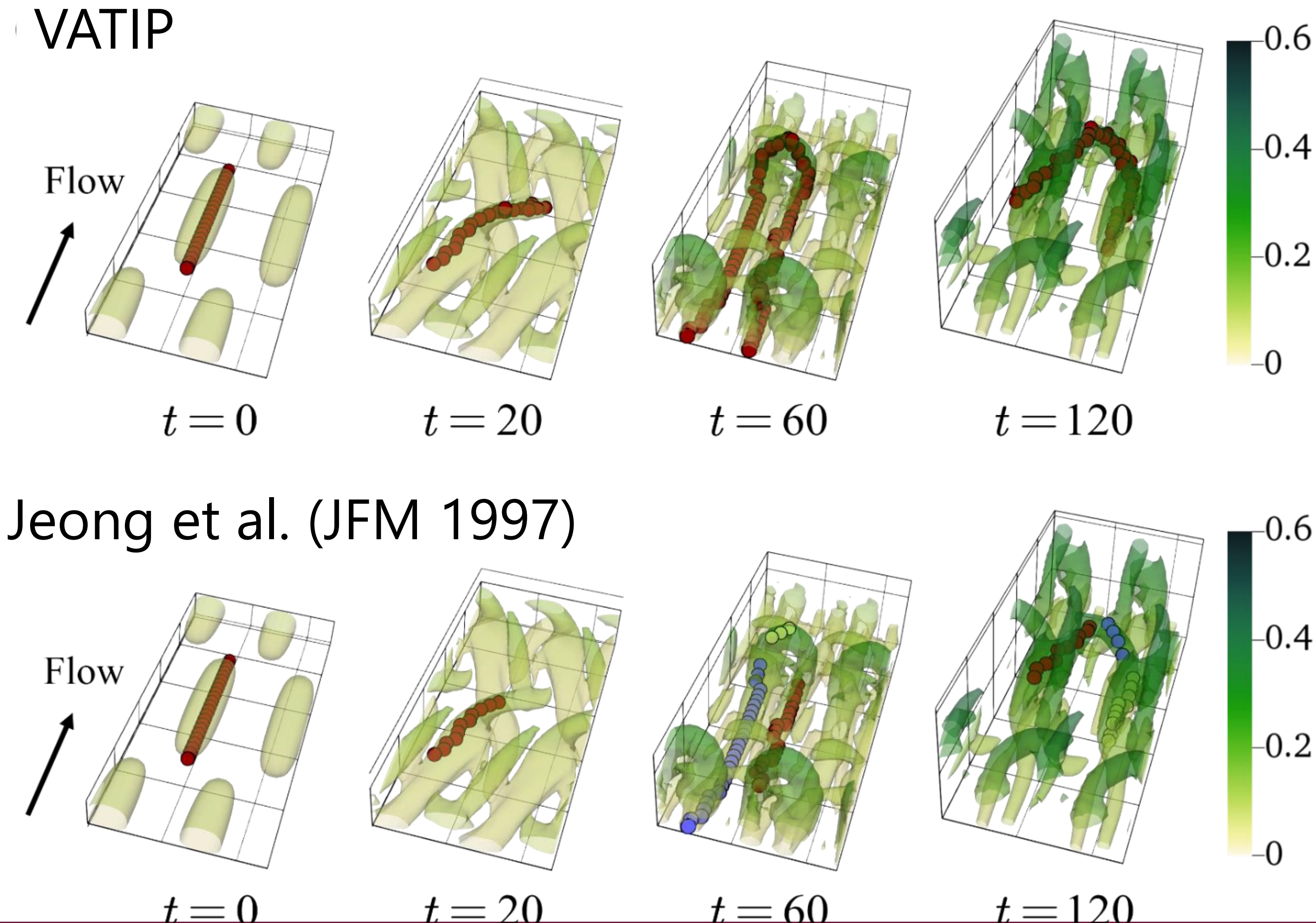
Vortex tracking and analysis

How to tell a computer program to automatically detect, count, and analyze vortices of different types?



Zhu & Xi, submitted to *J. Fluid Mech.*

VATIP - ***V**ortex **A**xis **T**racking by **I**terative **P**ropagation*



Zhu & Xi, submitted to *J. Fluid Mech.*

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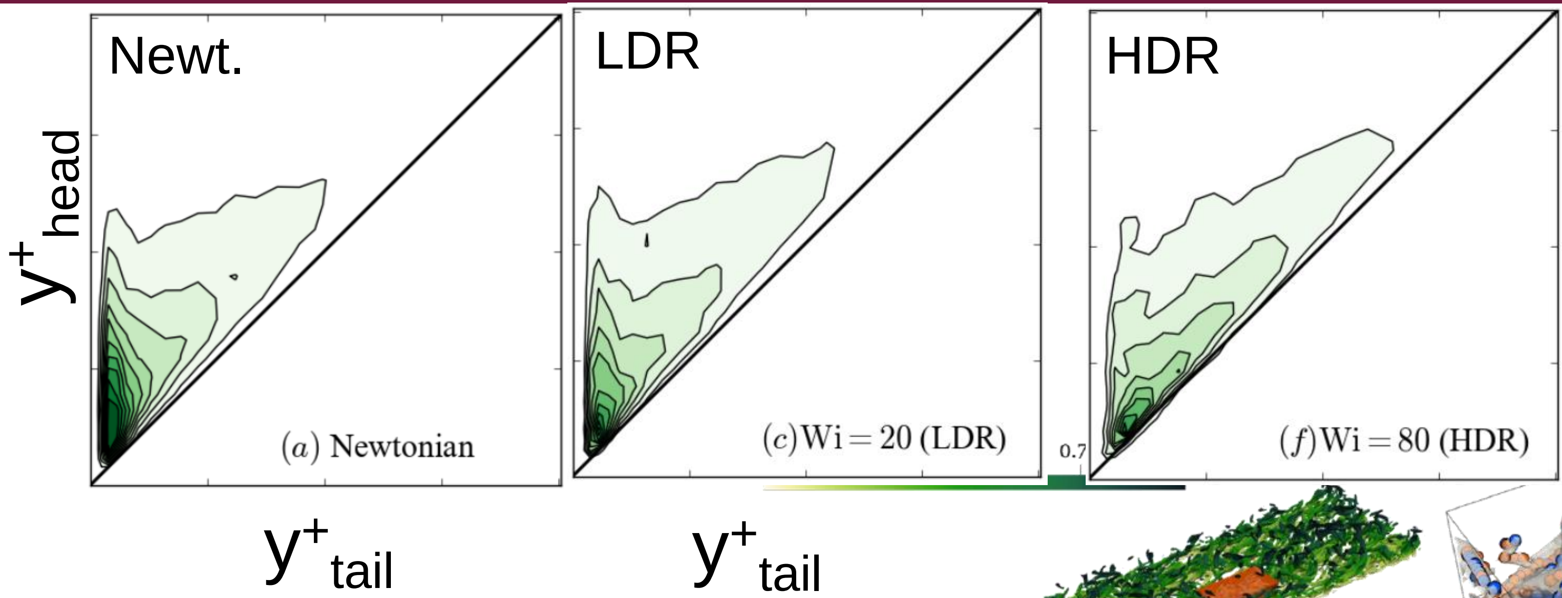
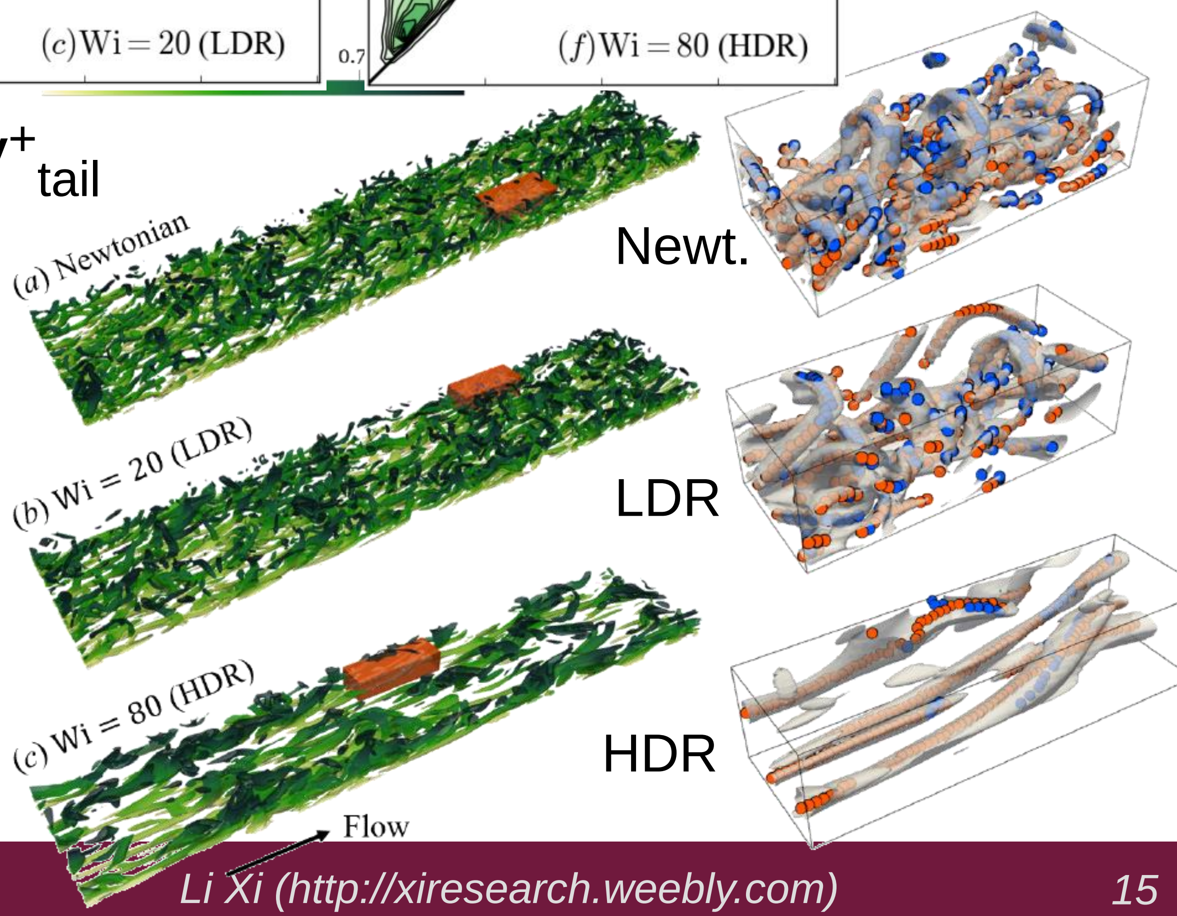
Transitions in vortex configuration between LDR and HDR





Zhu & Xi, submitted to *Phys. Fluids*

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Acknowledgment

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CGT
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Topic 2

Can molecular modeling help us design better plasticizers for PVC?

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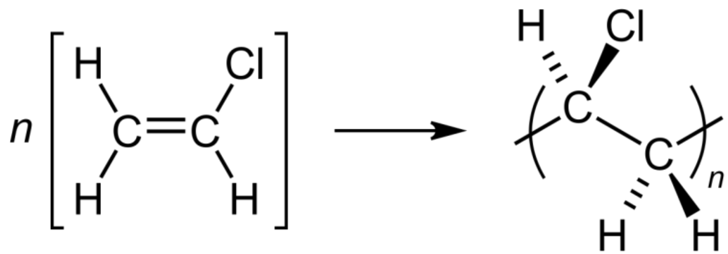
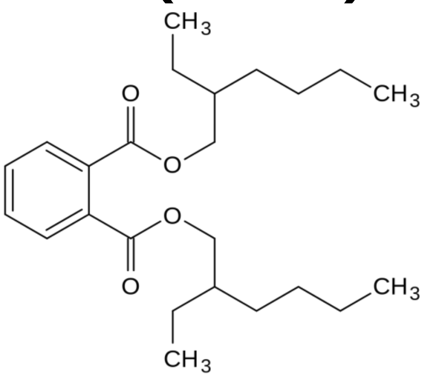
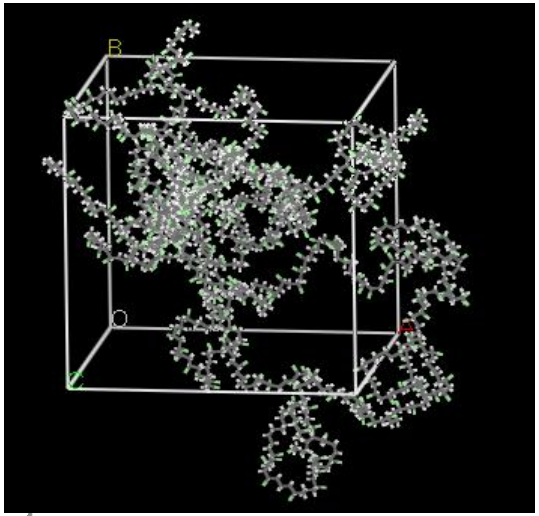
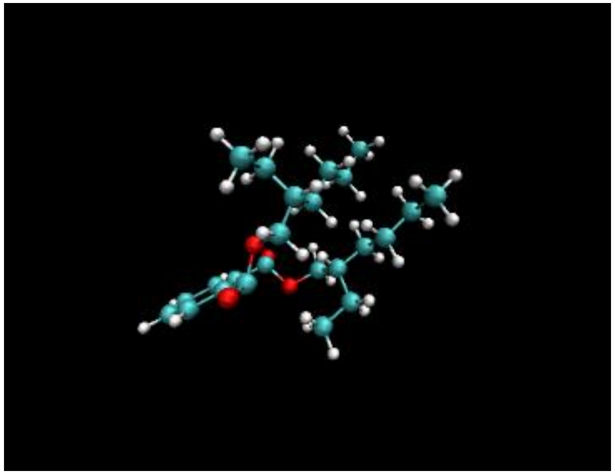
Polyvinyl chloride (PVC)

Bis(2-ethylhexyl) phthalate (DEHP)









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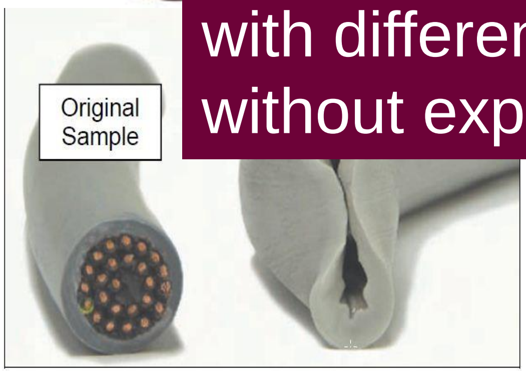


Can we predict the properties of PVC with different plasticizers *a priori*: i.e., without experimental input?

Commonly used plasticizers would be prohibited at levels greater than 0.1% by weight in most products

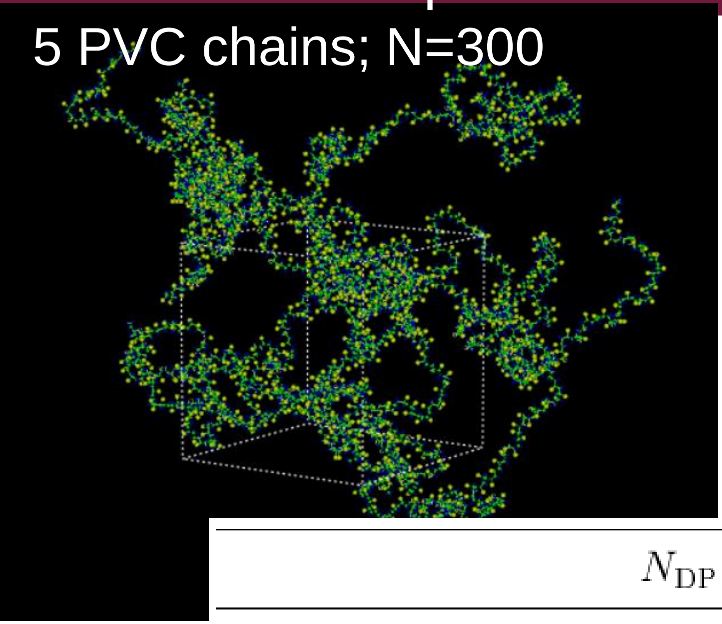
By ***Britt E. Erickson***

The European Union is a step closer to prohibiting the use of four phthalates in consumer products. The Socio-Economic Analysis Committee of the European Chemicals Agency voted on June 20 in favor of restricting most uses of the chemicals under the EU's Registration, Evaluation, Authorisation & Restriction of Chemicals (REACH) law.

The four phthalates are butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and diisobutyl phthalate (DIBP).

Picture credit:
www.lappusa.com

Predictions of pure PVC



		N_{DP}	N_{chains}	δ $(J/cm^3)^{\frac{1}{2}}$	T_g (K)	ρ (g/cm^3)
Our Results		100	15	17.3 ± 0.026	354 ± 3.53	1.35 ± 0.021
		300	5	17.1 ± 0.172	359 ± 2.67	1.35 ± 0.011
		500	3	16.6 ± 0.108	361 ± 1.58	1.35 ± 0.012
		1500	1	14.6 ± 0.016	354 ± 3.16	1.35 ± 0.014
Reference	Expt.	-	-	19.35 [65]	355.5 [66]	$1.35 \sim 1.45$ [67]
	MD [41]	100	2	17.61 ± 0.45	350	1.39

[a]Density and solubility parameters are reported for 25 °C for experiments and 300 K for MD.

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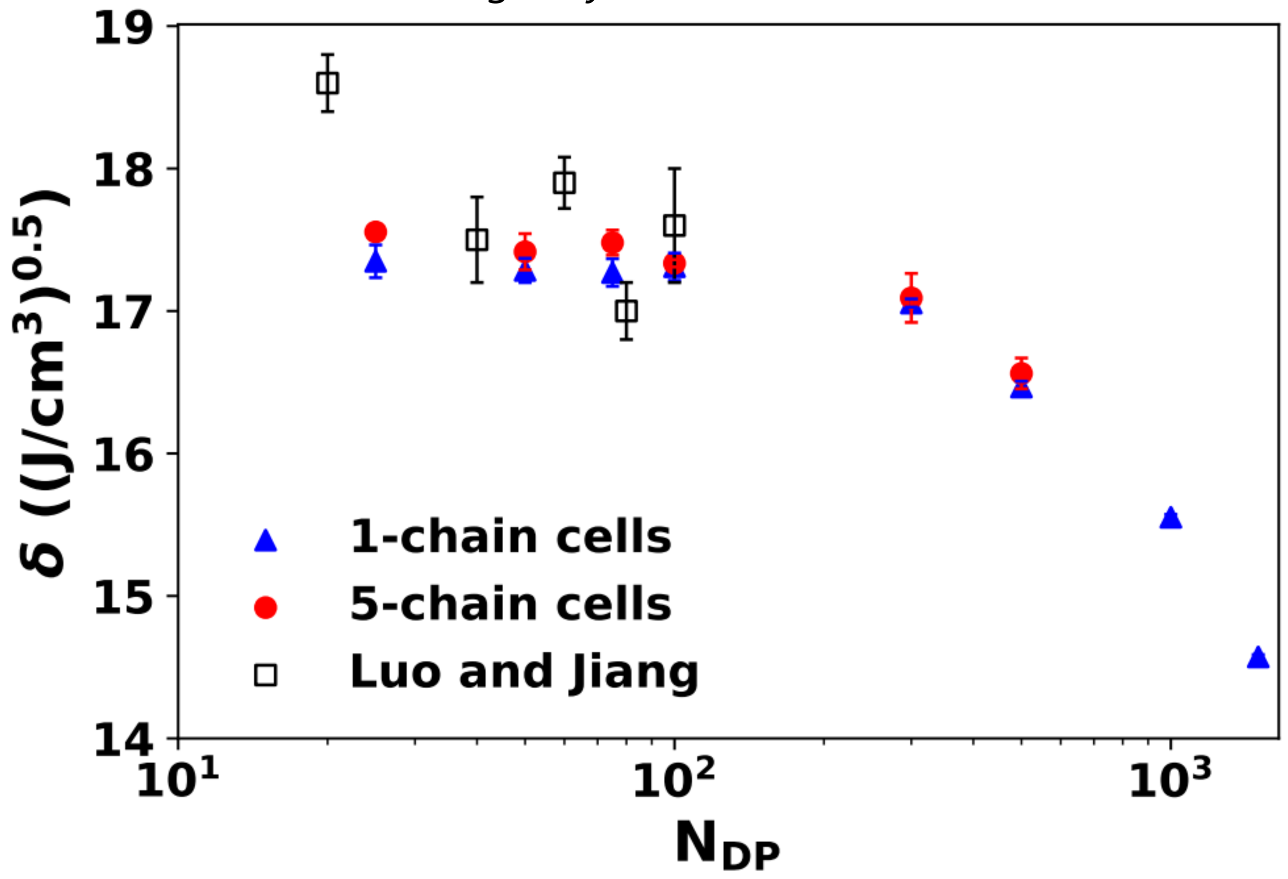
Li, Panchal, Mafi, & Xi, *Macromolecules*, 2018

Solubility parameter of polymers -- an ill-defined property

$$\delta^2 \equiv \frac{E_{\mathrm{coh}}}{V} = \rho E_{\mathrm{coh}} \equiv \mathrm{CED}$$

Li, Panchal, Mafi & Xi, *Macromolecules*, 2018
Luo & Jiang, *Polymer*, 2010



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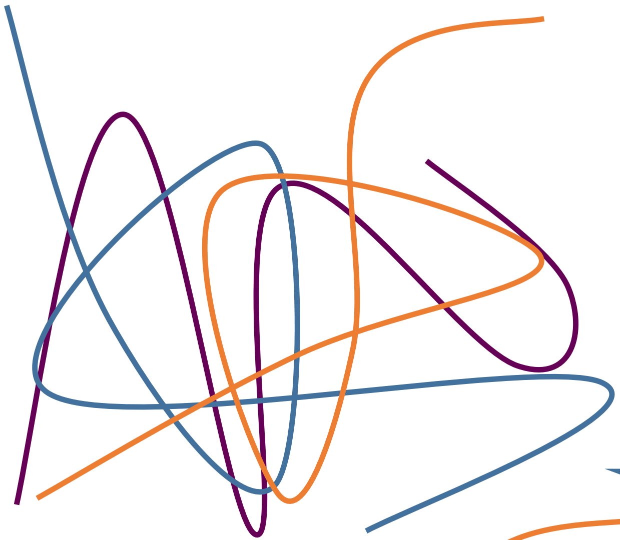
Solubility parameter of polymers -- an ill-defined property

The cohesive energy $\mathbf{E}_{coh}$ of a substance in a condensed state is defined as the increase in internal energy U per mole of substance if all the intermolecular forces are eliminated: The cohesive energy $\equiv \mathbf{E}_{coh} = \Delta U$ (dimension: J/mol).



van Krevelen and te Nijenhuis, *Properties of Polymers*, 4th edn., 2009

$$E_{\mathrm{coh}} \equiv E_{\mathrm{sep}} - E_{\mathrm{bulk}}$$

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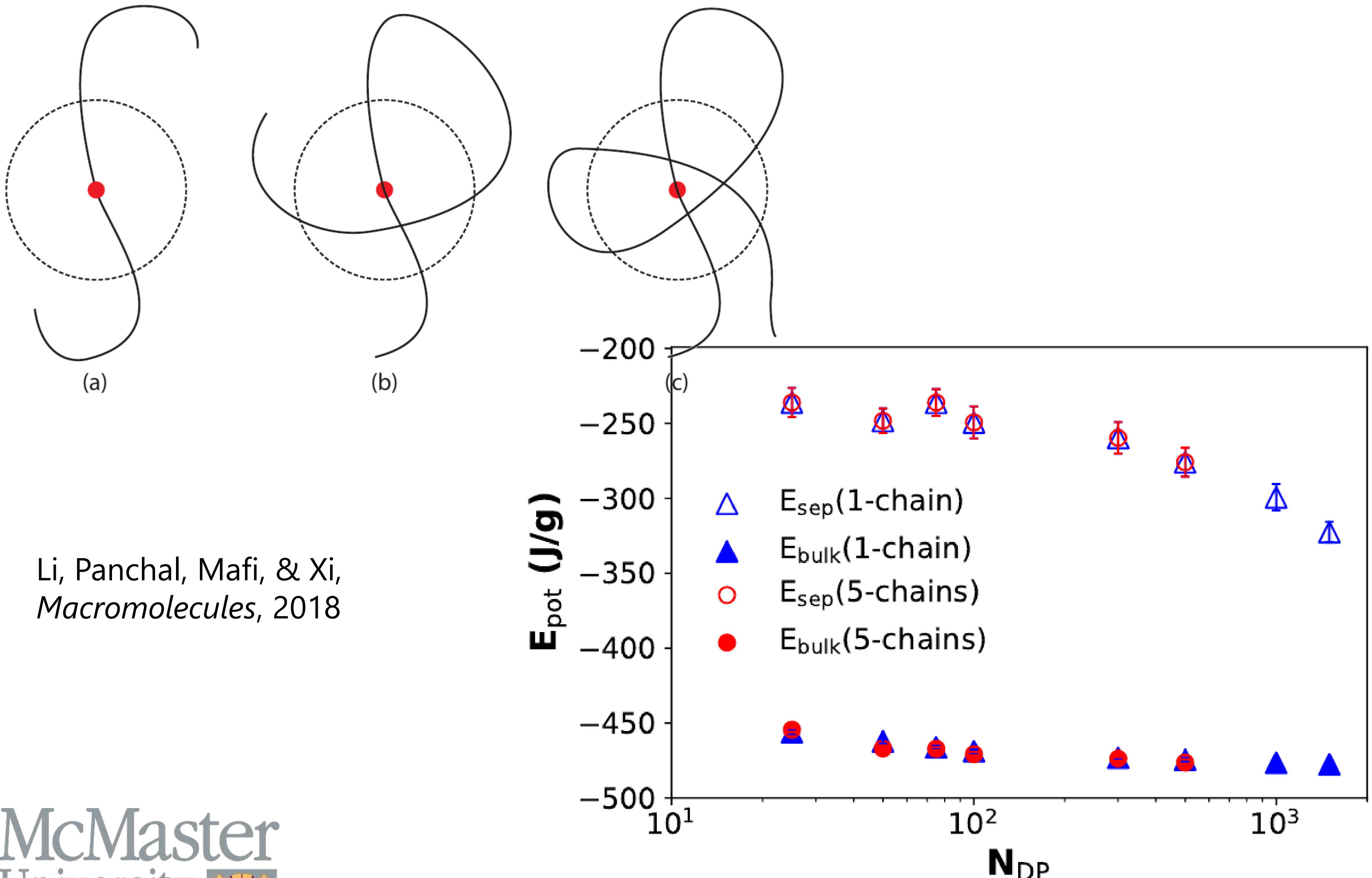
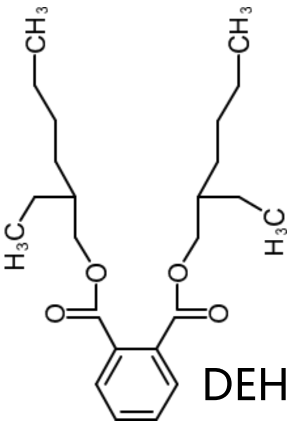
Solubility parameter of polymers -- an ill-defined property

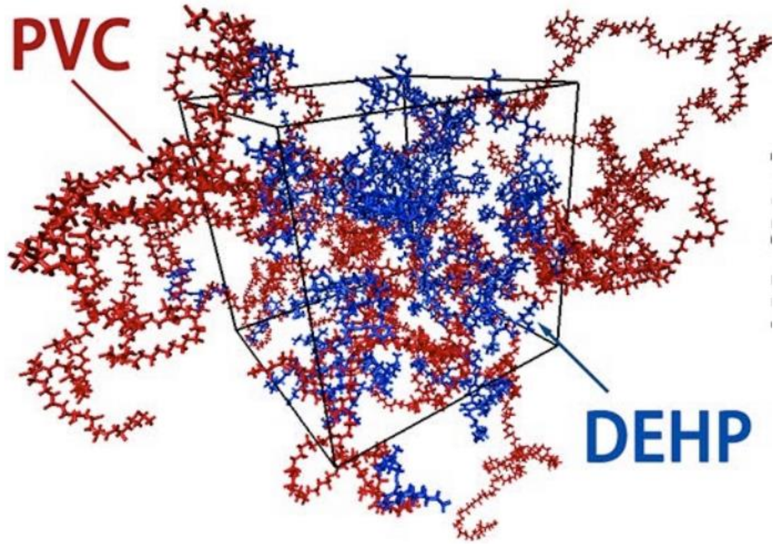


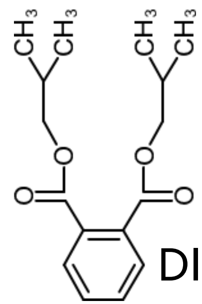
Li, Panchal, Mafi, & Xi, *Macromolecules*, 2018

Model systems: common phthalates

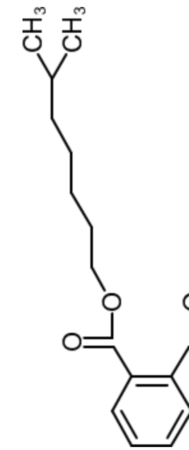


DEHP(8)

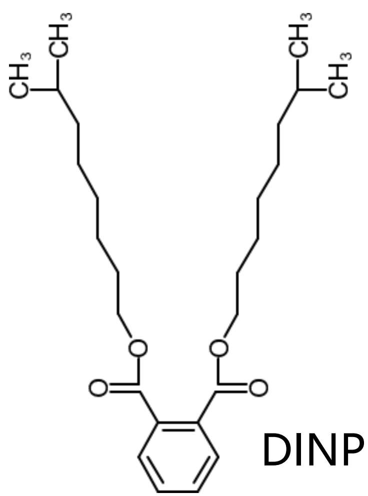




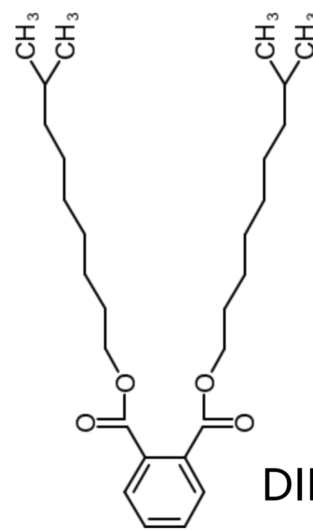
DIBP(4)



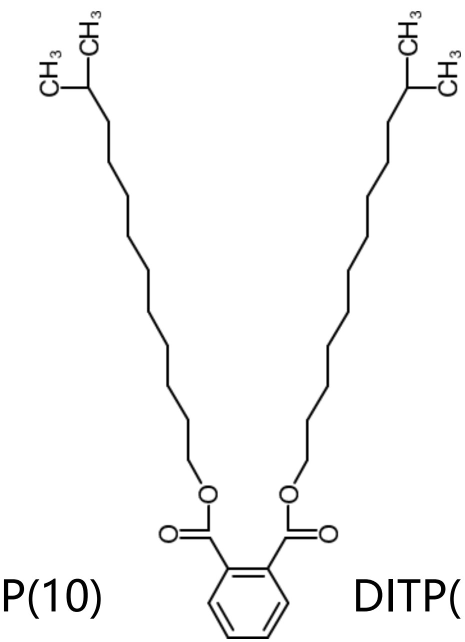
DIOP(8)



DINP(9)



DIDP(10)



DITP(13)

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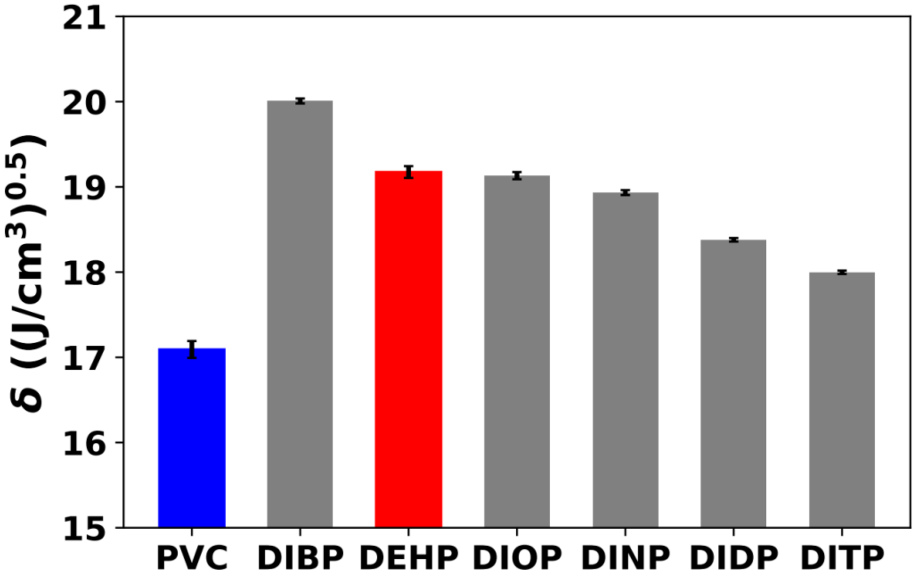
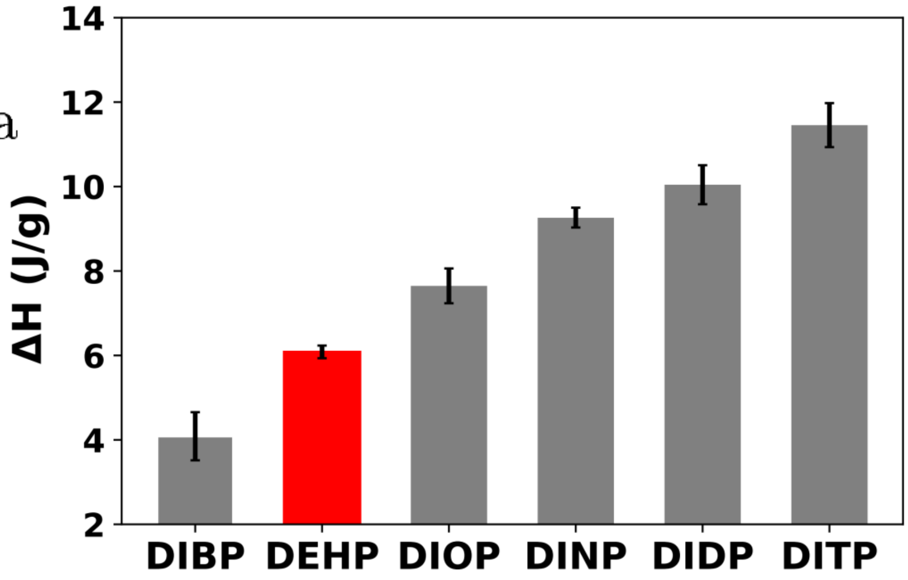
Results: Thermodynamic compatibility



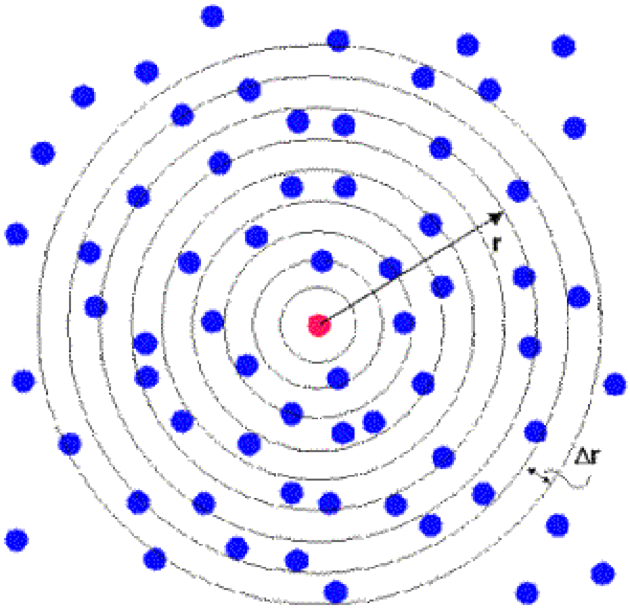
χ parameter	Experiments [1]	Predicted from (UNIFAC-FV) [2]
PVC/DIBP	-0.13	~
PVC/DEHP	-0.10	-0.14
PVC/DINP	-0.03	-0.02
PVC/DIDP	-0.01	0.04
PVC/DITP	0.22	0.59

$$\Delta H \equiv H_{\mathrm{p+a}} - w_{\mathrm{p}} H_{\mathrm{p}} - w_{\mathrm{a}} H_{\mathrm{a}}$$

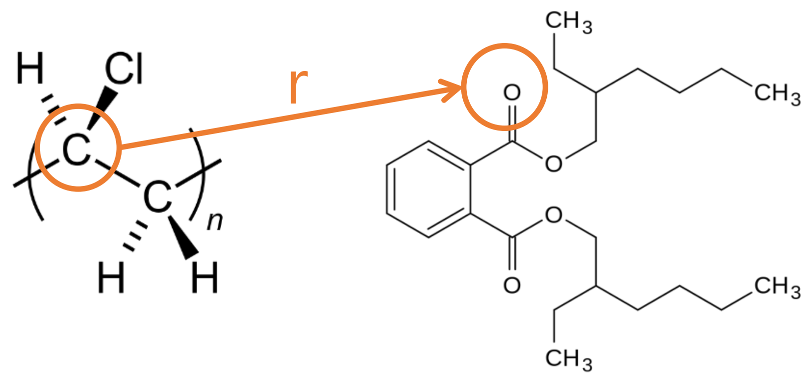


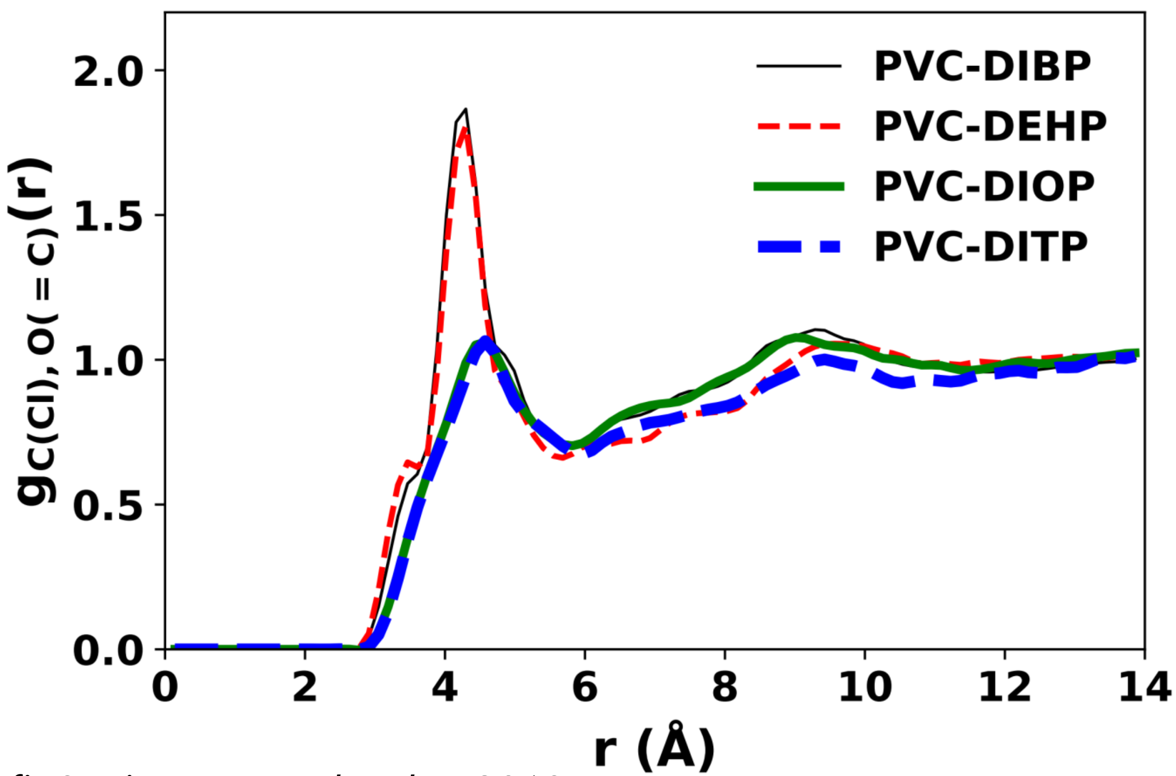
Li, Panchal, Mafi, & Xi, *Macromolecules*, 2018

Results: PVC-phthalate interactions



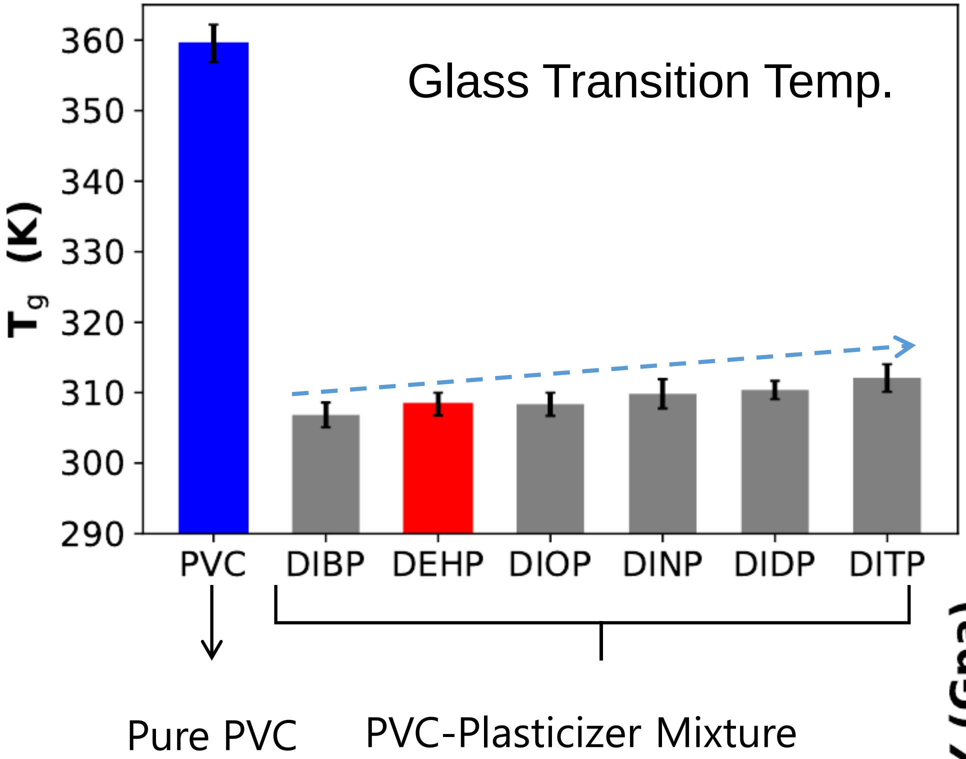
http://www.compsoc.man.ac.uk/~lucky/Democritus/Theory/rdf.html

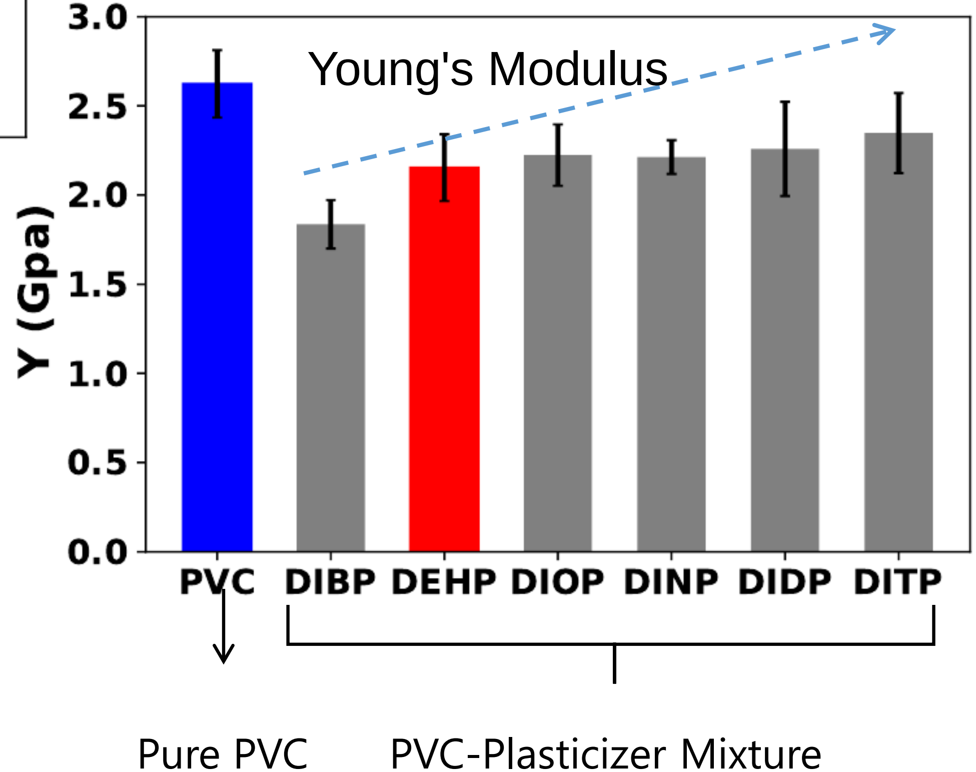




Li, Panchal, Mafi, & Xi, *Macromolecules*, 2018

Results: Plasticization efficiency





Li, Panchal, Mafi, & Xi, *Macromolecules*, 2018

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Summary

Turbulent drag reduction

- Multistage transition: pre onset->LDR->HDR->MDR.
- Framework for explaining MDR.
- Mechanism proposed for LDR-HDR transition.
- VATIP: algorithm for detecting and tracking vortices.

Molecular modeling for plasticizers

- Reliable molecular model for amorphous polymer materials.
- Non-trivial chain-length dependence of the solubility parameter.
- Predicted plasticizer performance agrees with all known experiments.

Lu Zhu 朱路

Dongyang Li 李东洋

Kushal Panchal

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