Flow of polymers at interfaces

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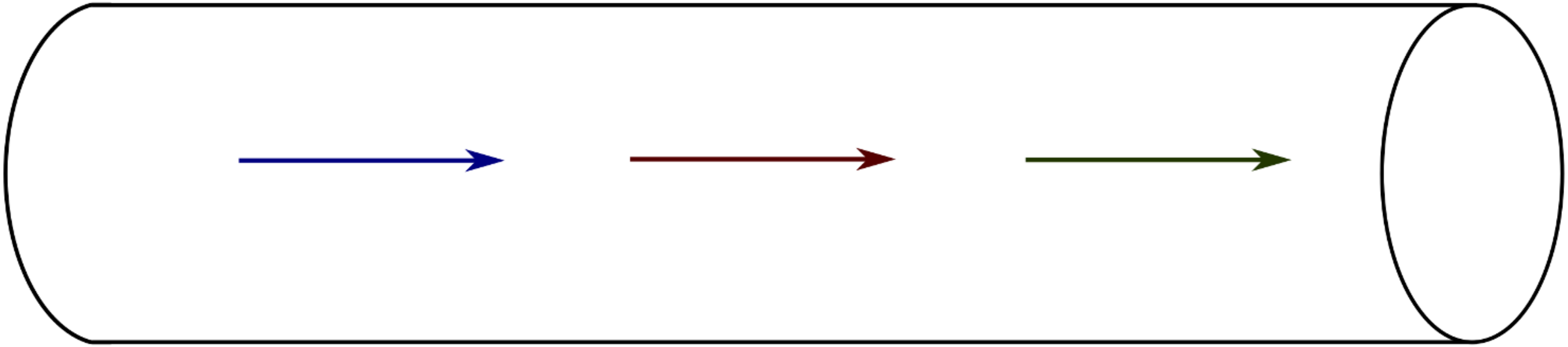
Liliane Léger
Collaborator: Alexis Chennevière

Fluid mechanics



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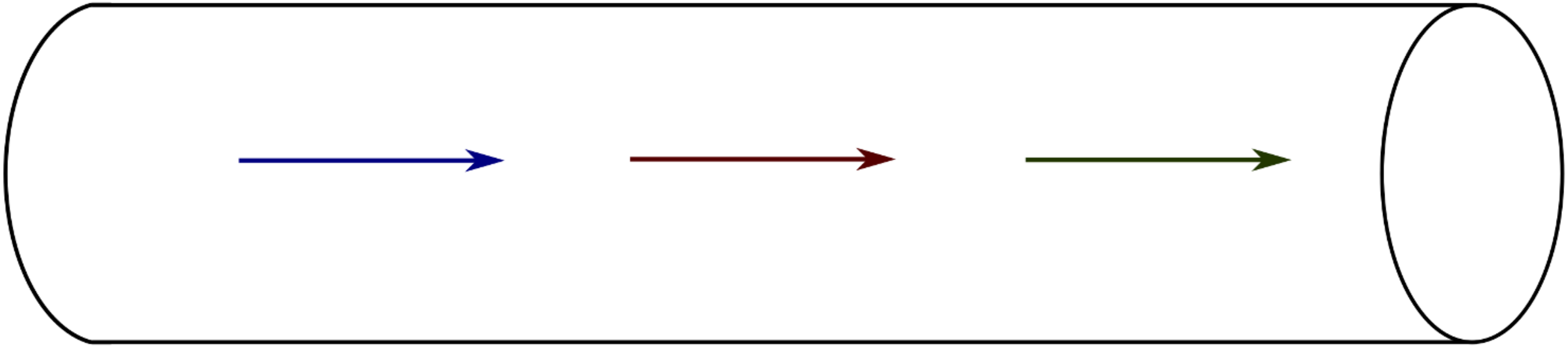

Navier-Stokes equation :

$$\rho(\partial_t + \boldsymbol{u} \cdot \nabla)\boldsymbol{u} = -\nabla p + \eta \nabla^2 \boldsymbol{u}$$

Incompressible flow :

$$\nabla \cdot \boldsymbol{u} = \boldsymbol{0}$$

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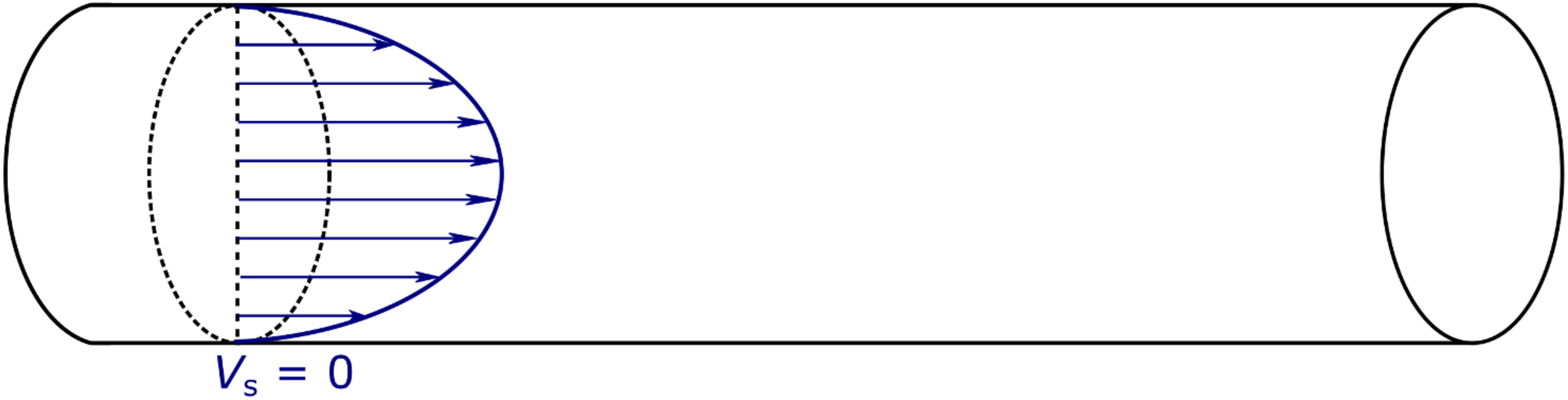

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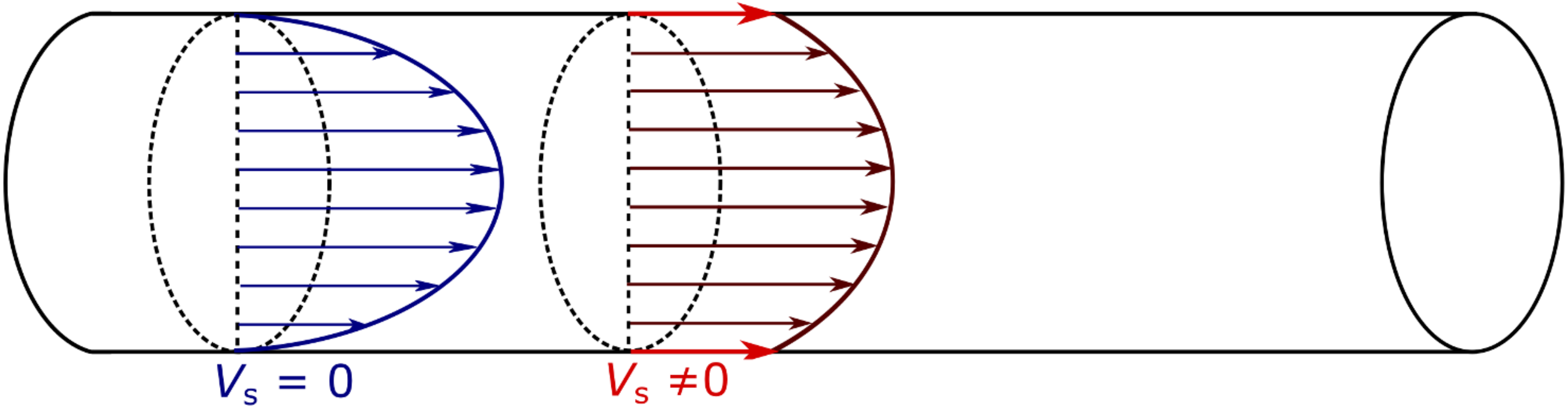

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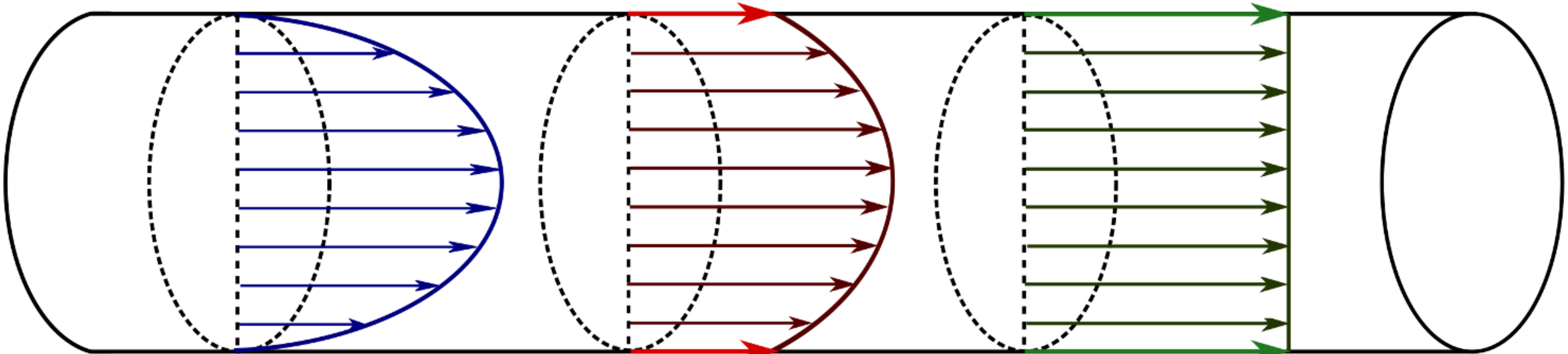
Stress at the wall $\sigma(z = 0) = k\, V_s$ Navier (1823)

Fluid mechanics



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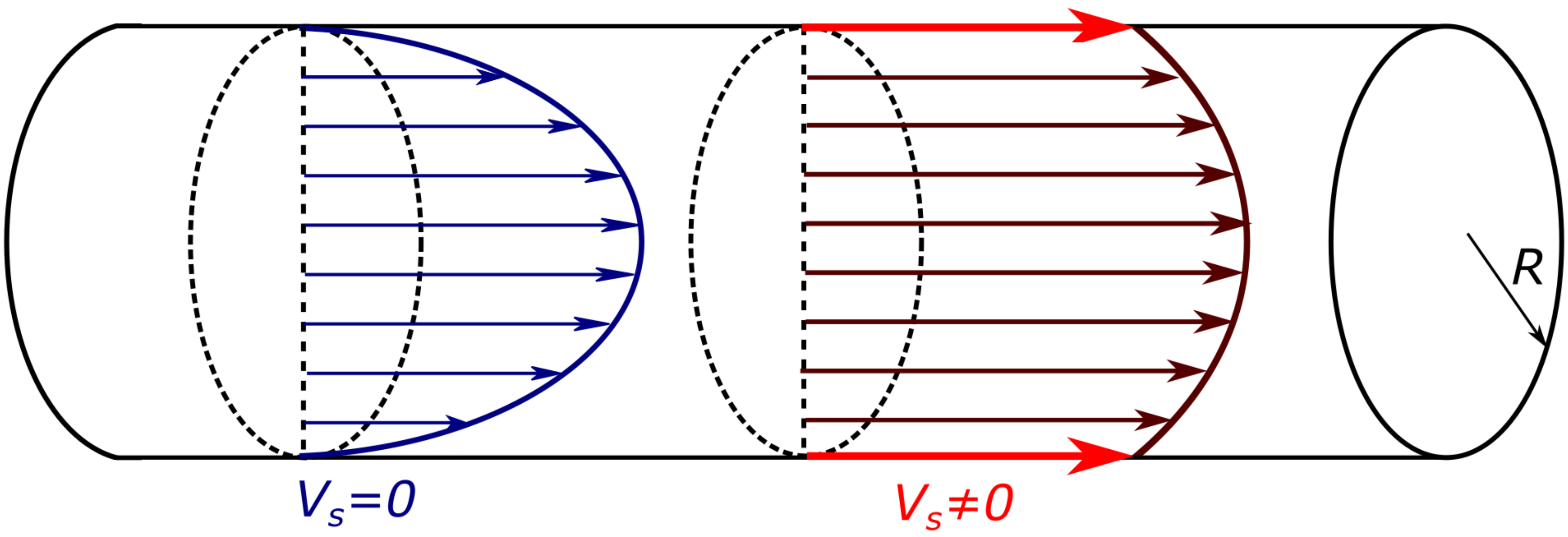

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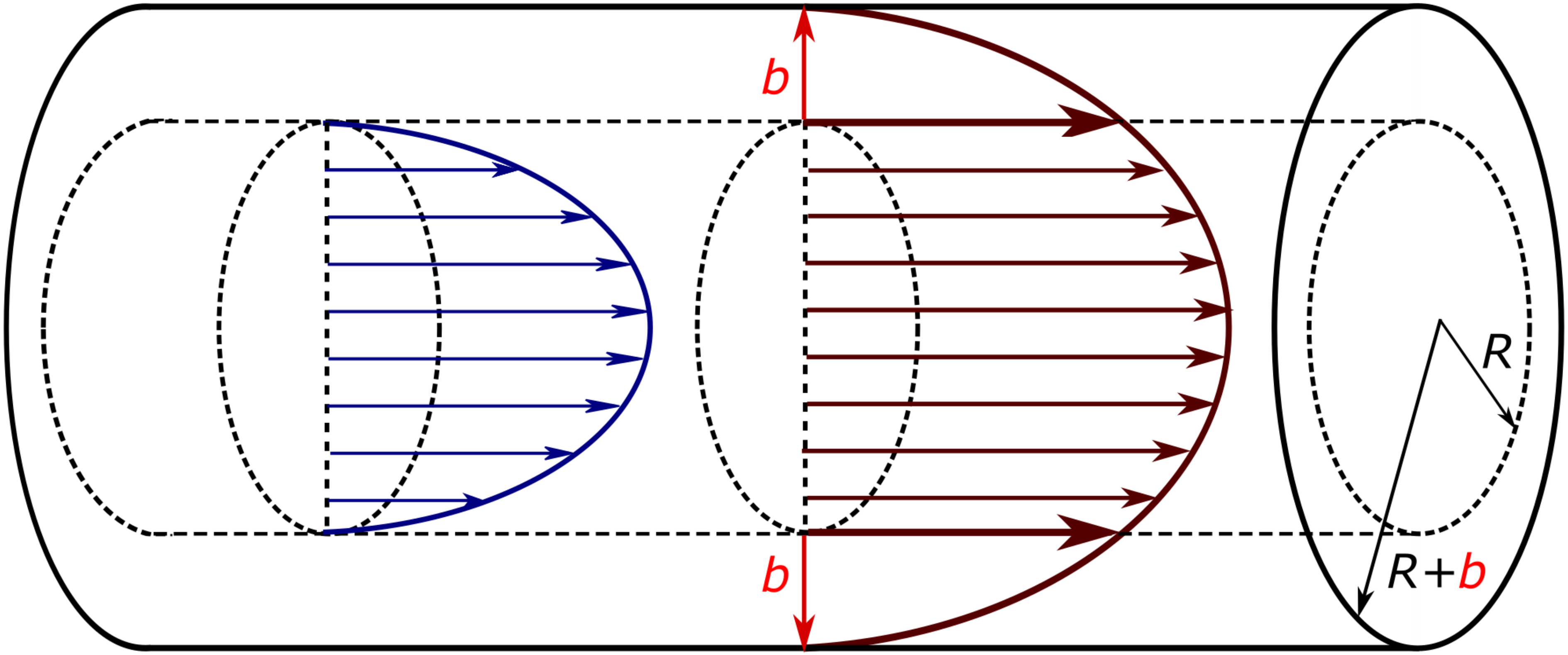

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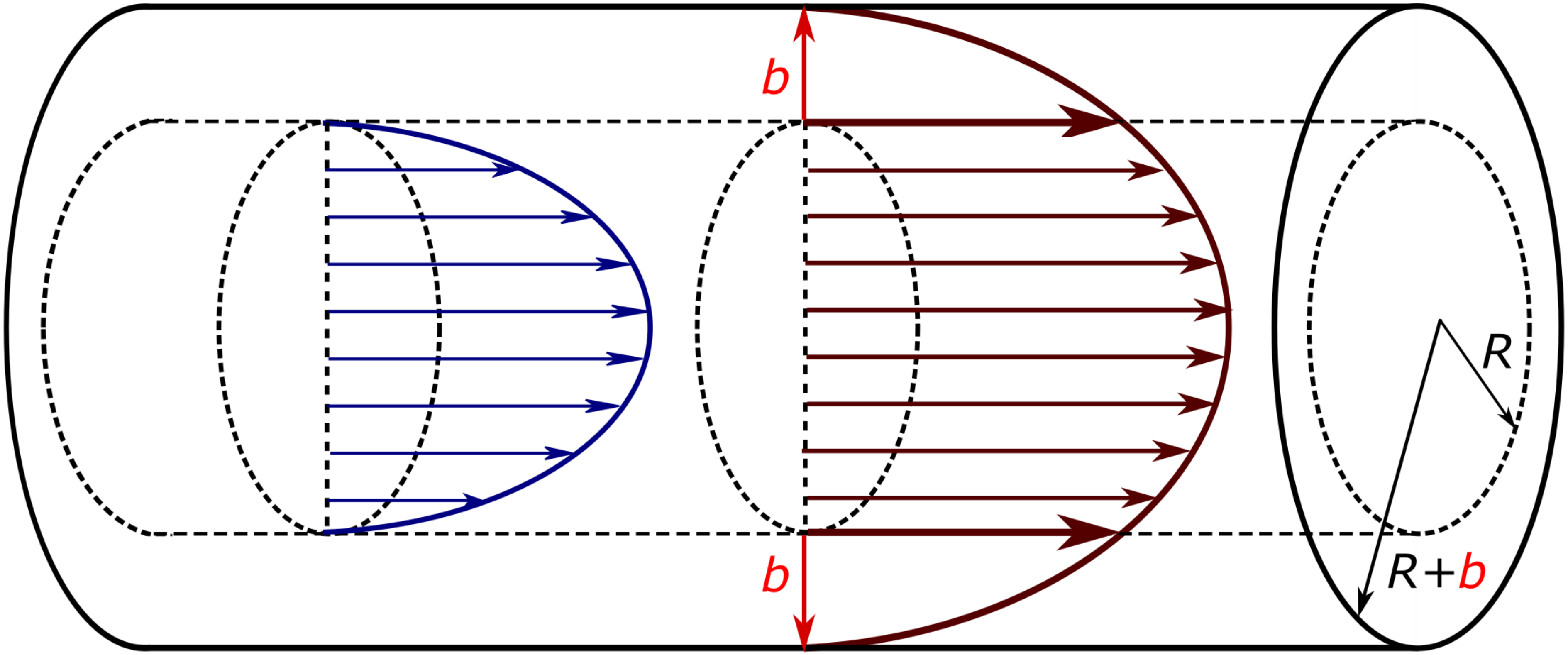
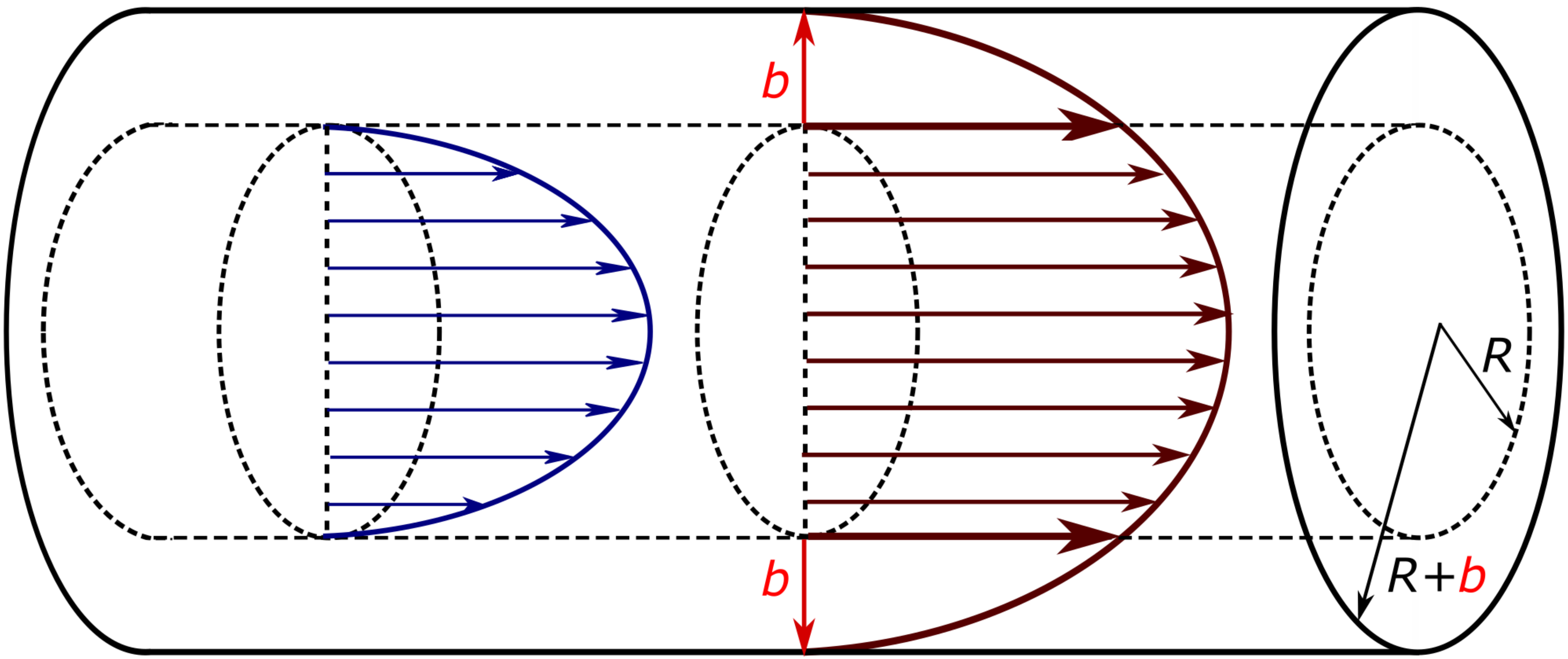


Slip length *b*:

$$V_s = b\frac{\partial v}{\partial z}$$

Slip length



Slip length *b*:

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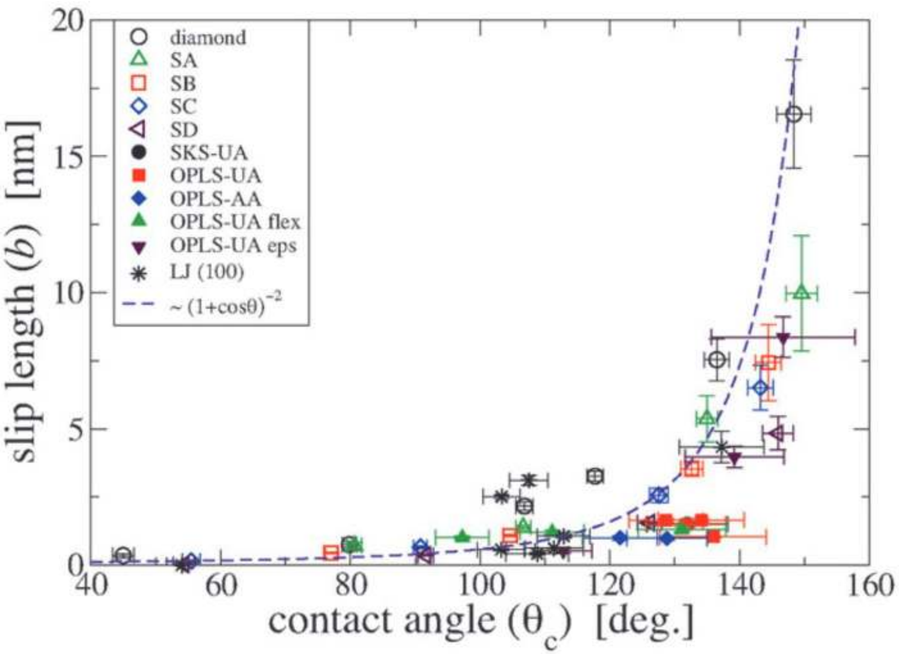
Flow rate:

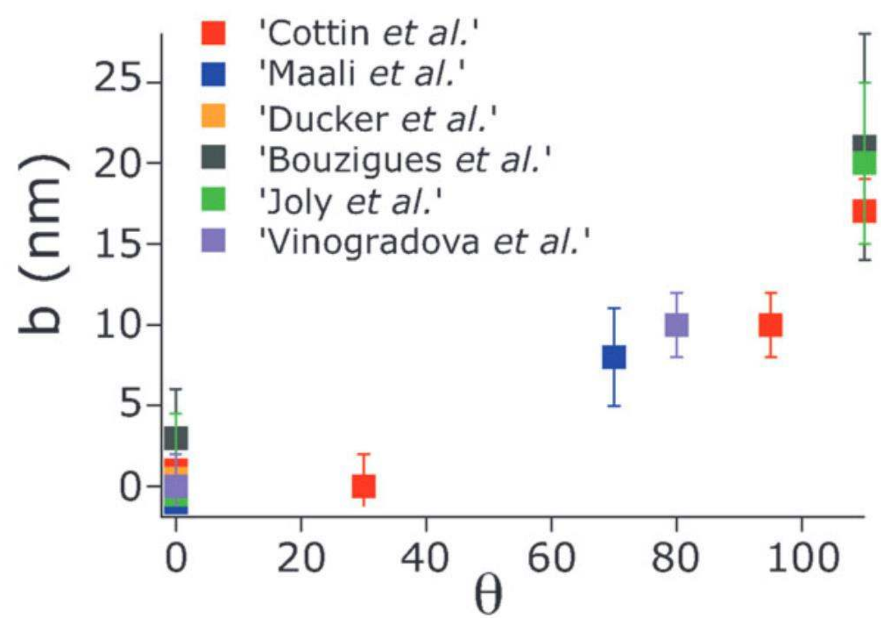
$$Q \propto radius^4$$

Slip length for simple fluids

Molecular Dynamics simulation



Experimental results



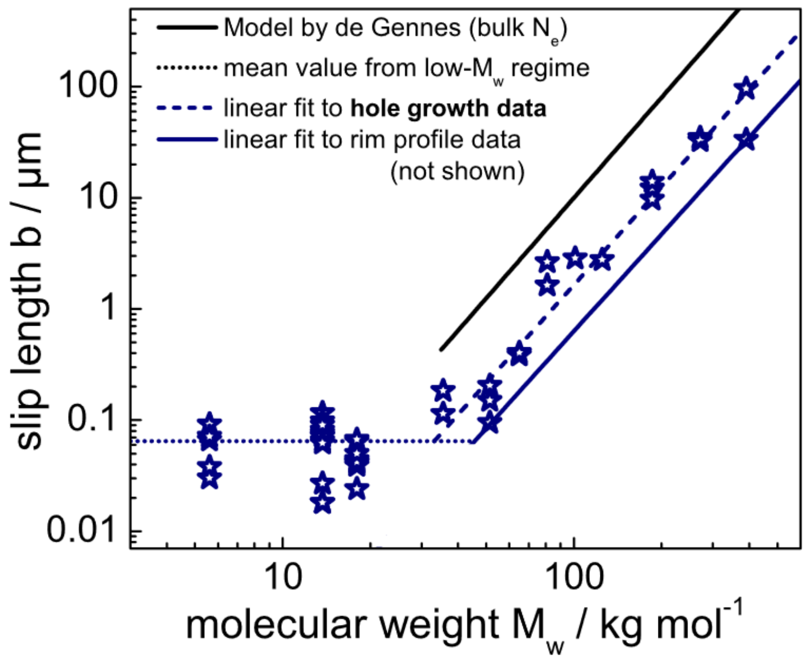
Orders of magnitude:

$b_{water/glass}$ ≈10 nm

But quite a mess…

L. Bocquet and E. Charlaix, *Chemical Society Reviews*, 2010

Slip length for polymer melts



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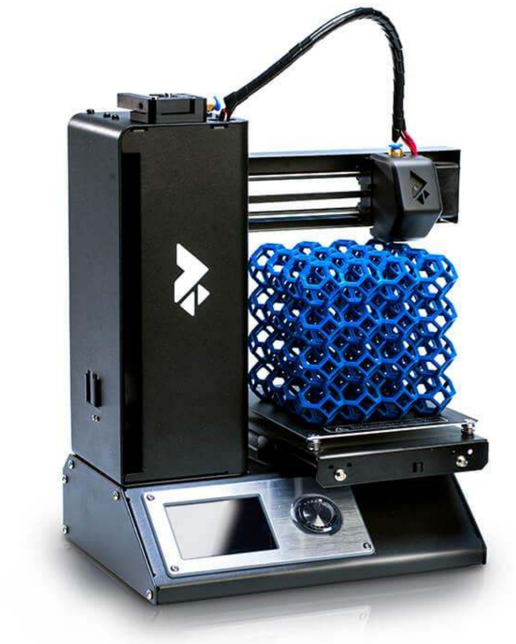
O. Bäumchen et *al.*, *Journal of Physics: Condensed Matter*, 2012

PhD's daily life



Videos for Q.S Wang on Youtube

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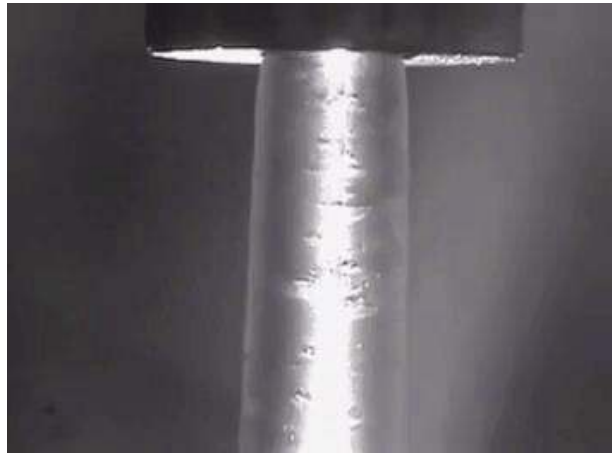
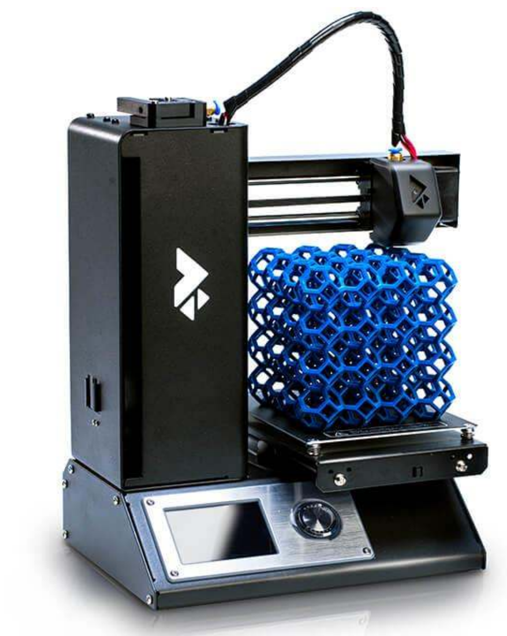


No slip



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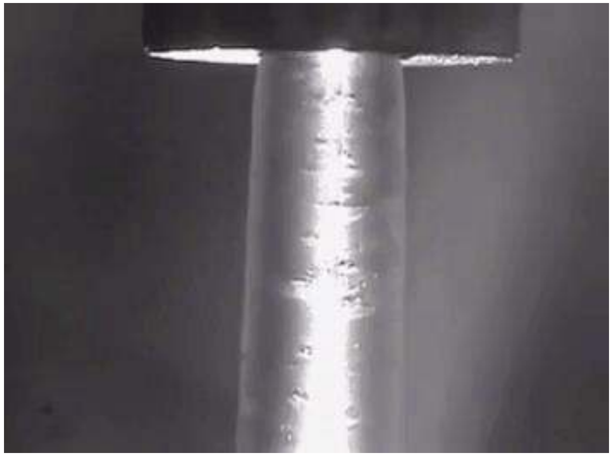

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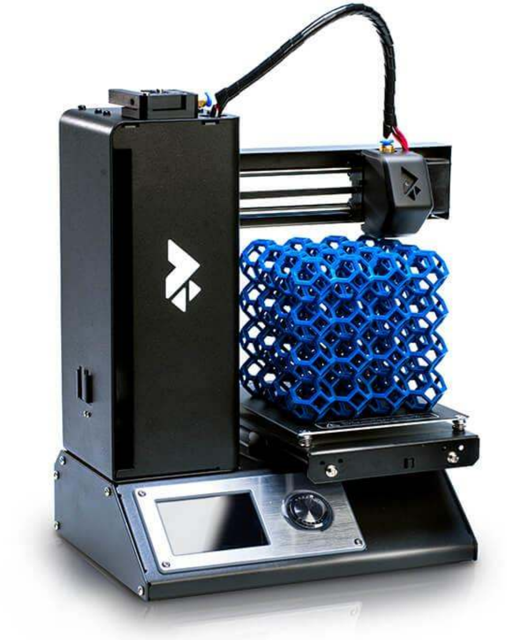
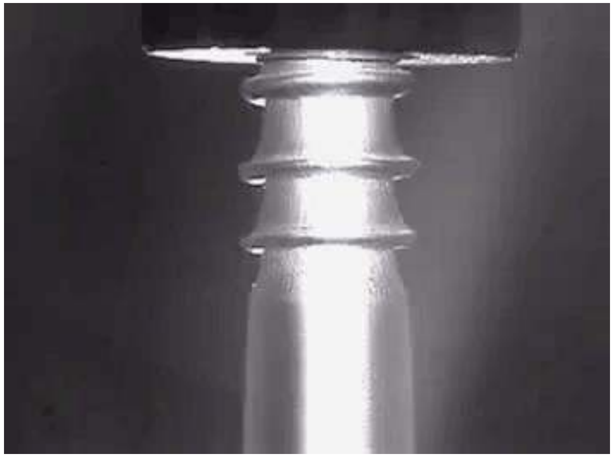


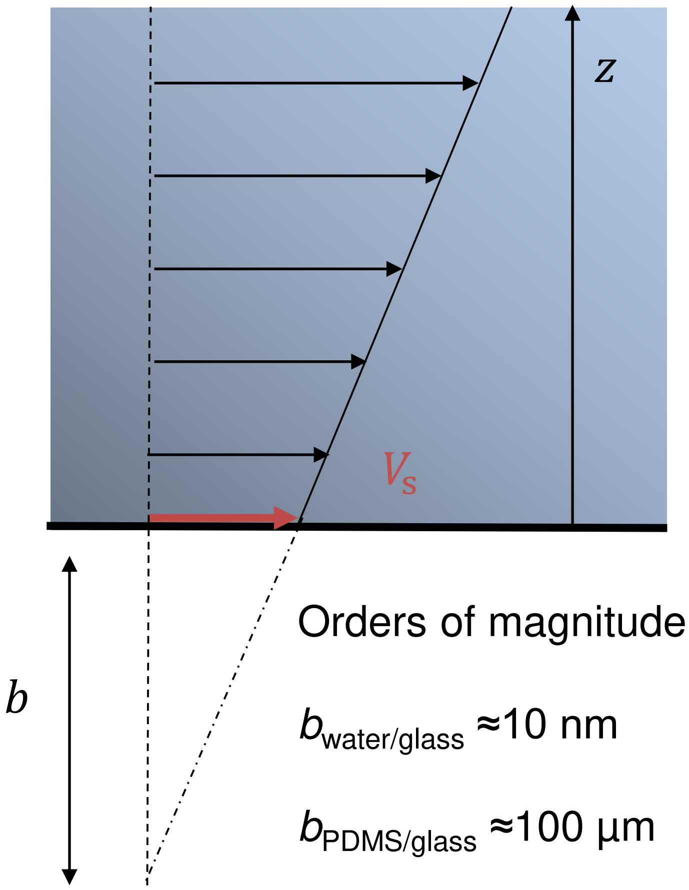


Stick slip

Videos for Q.S Wang on Youtube

Slippage of polymers

General case :



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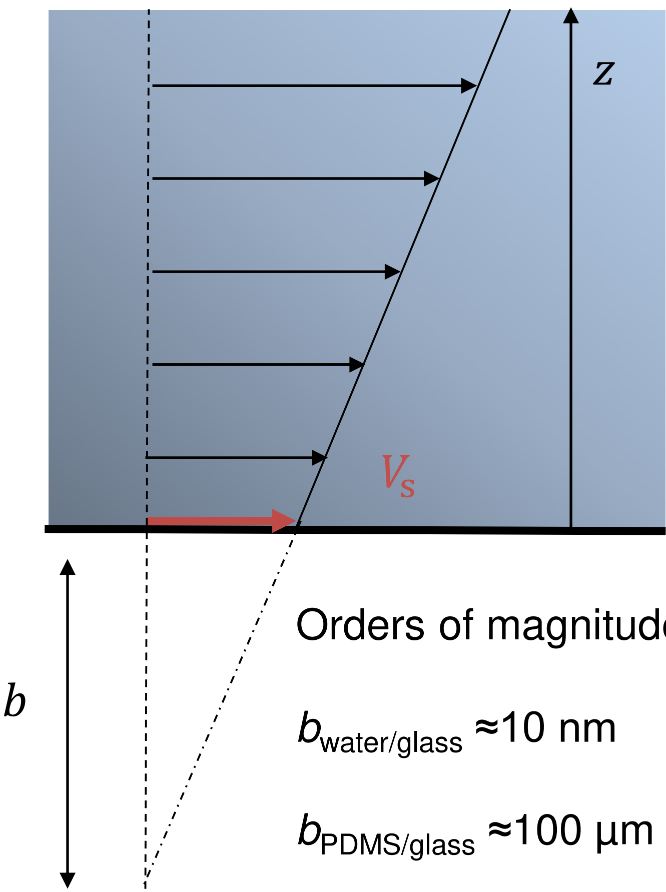

Navier's hypothesis at the wall (1823) : $\sigma(z=0) = k\,V_s$

Friction coefficient

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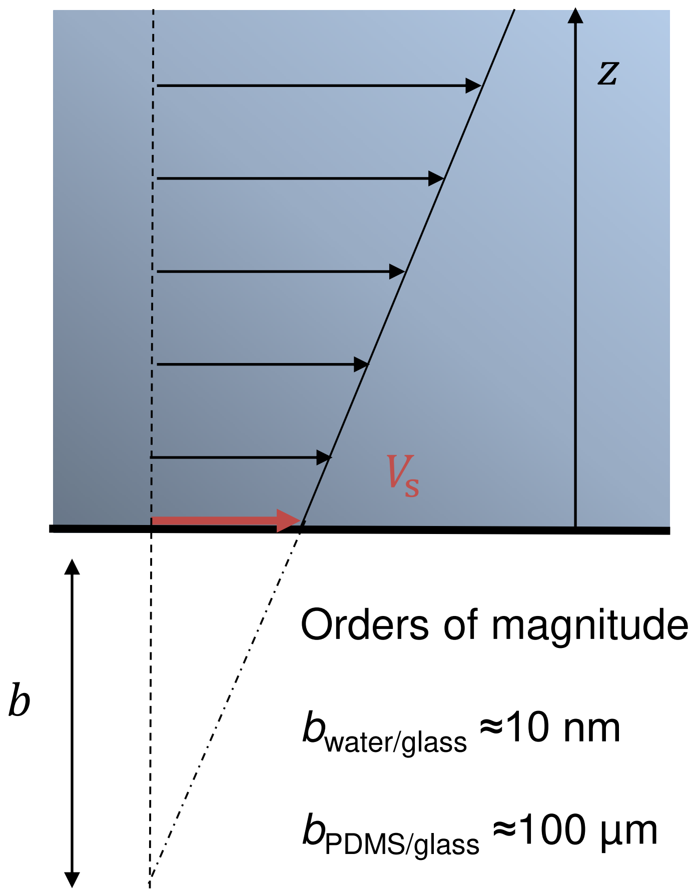

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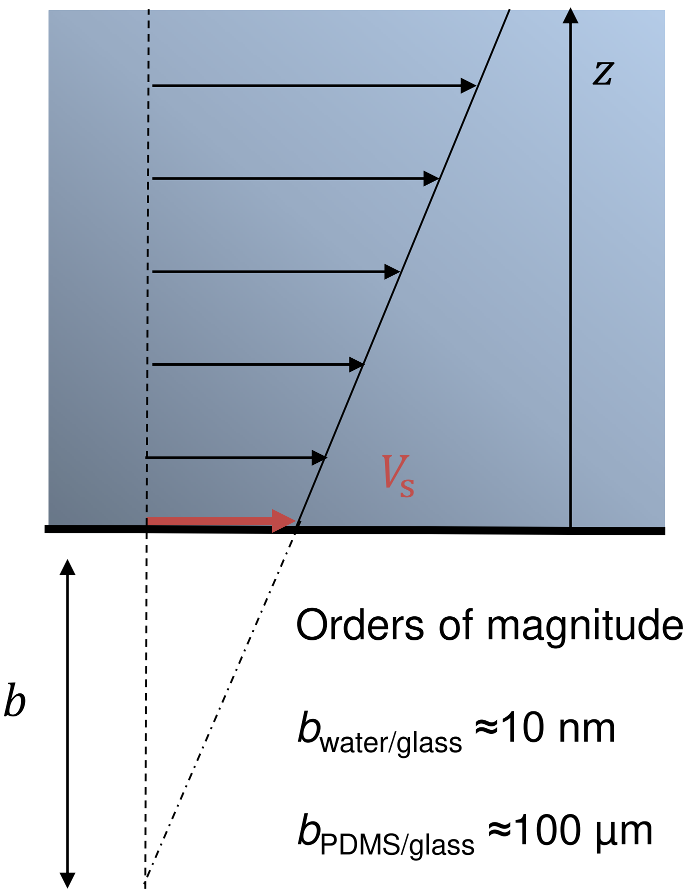

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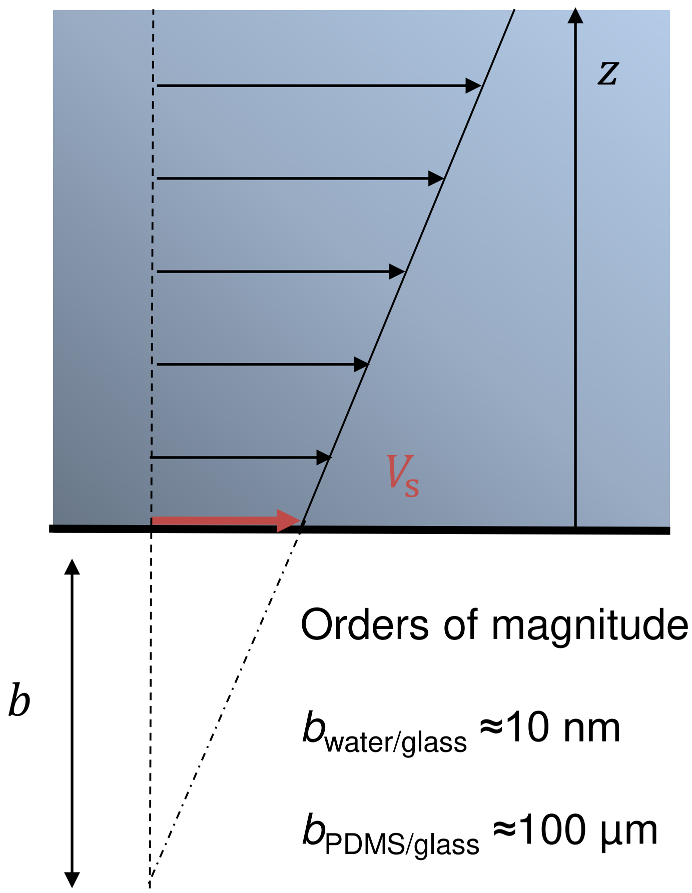

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k independent of *N*,
N number of monomers per chain

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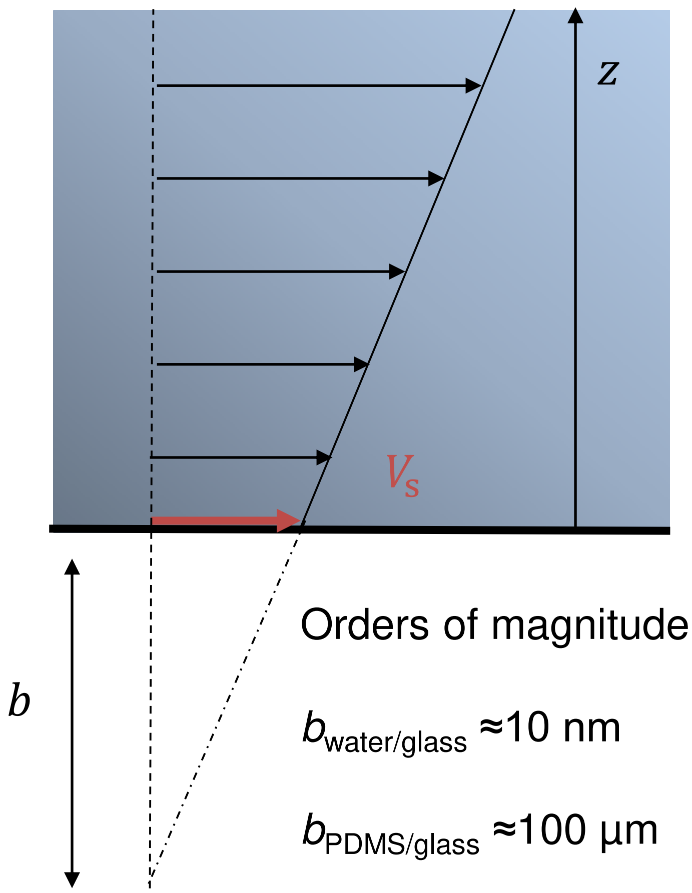

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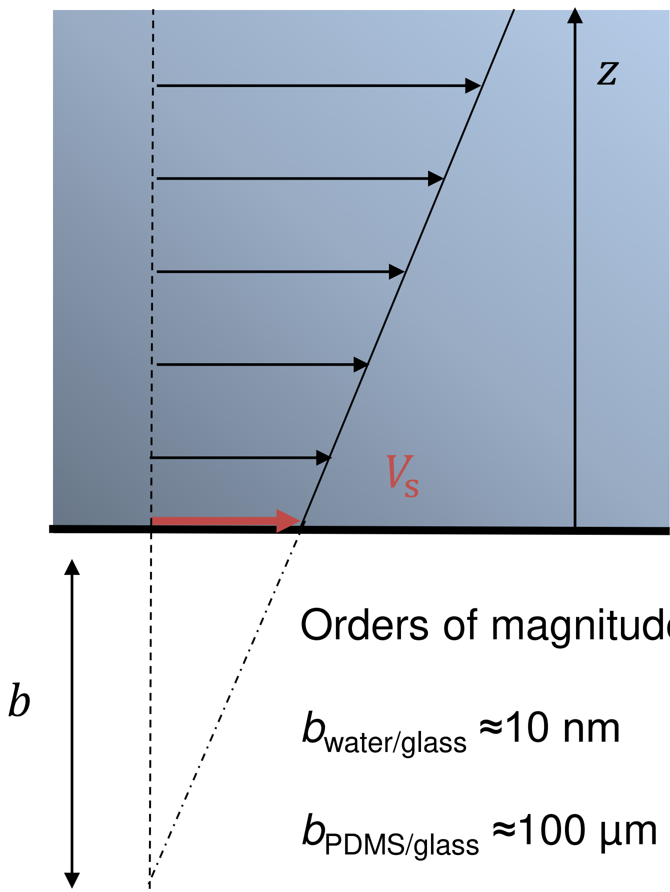

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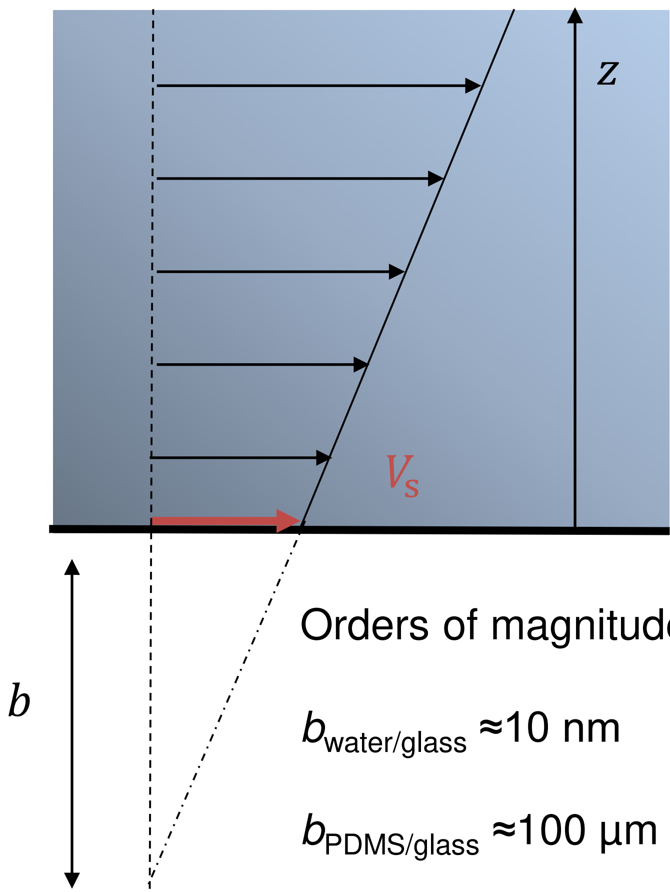

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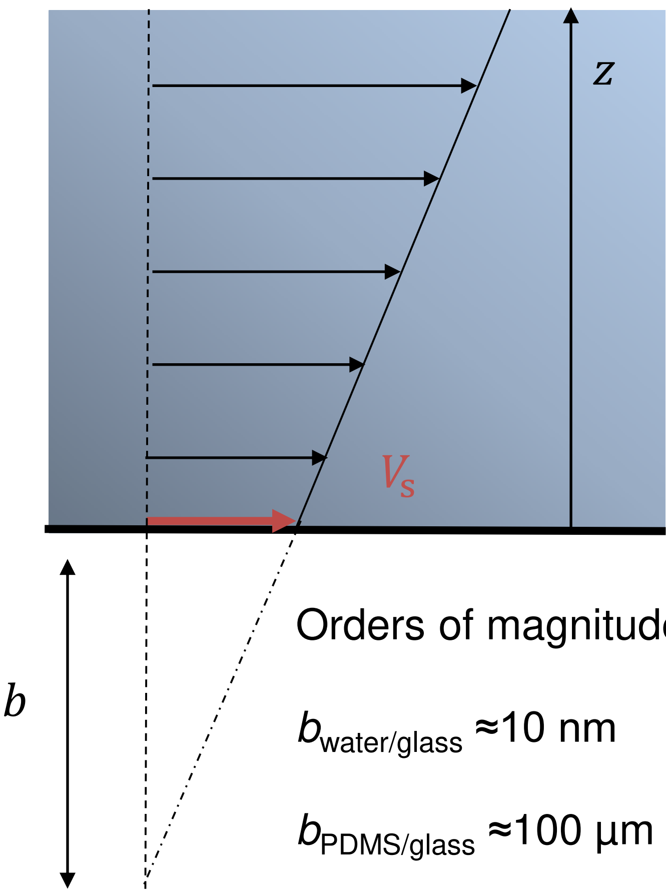

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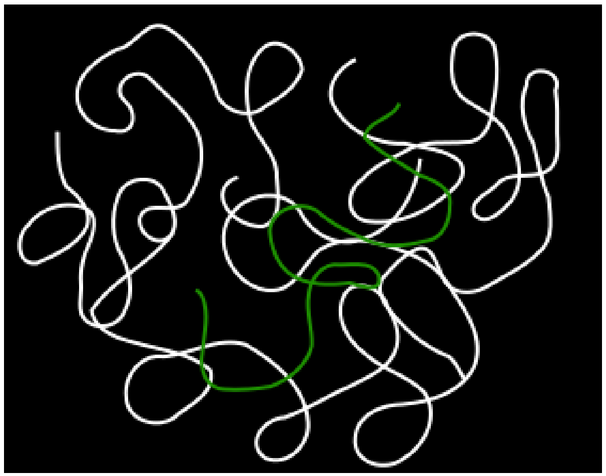
How to measure slippage of polymers ?

Velocimetry using photobleaching

Linear model polymers,
PolyDiMethylSiloxane (PDMS)



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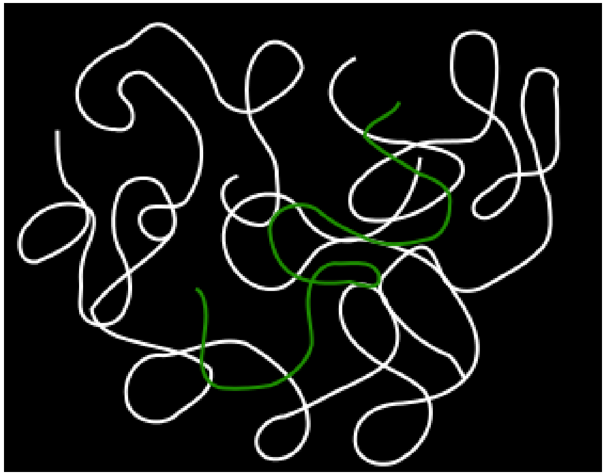
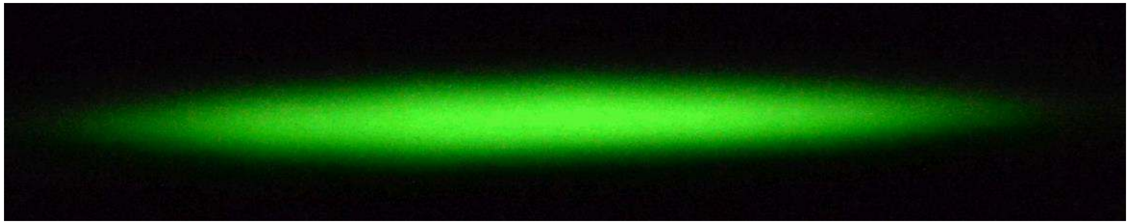
Mix of normal and fluorescent, photobleachable polymers





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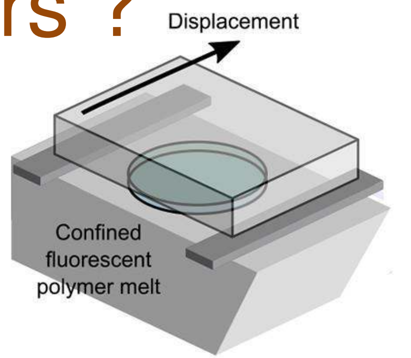


Velocimetry using photobleaching

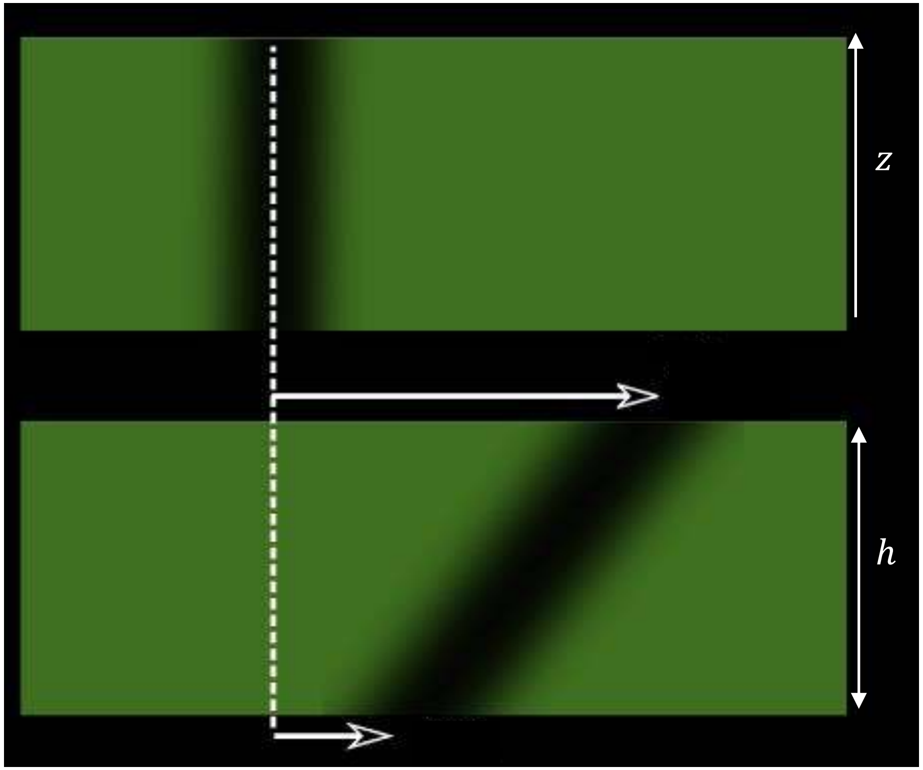
Side view

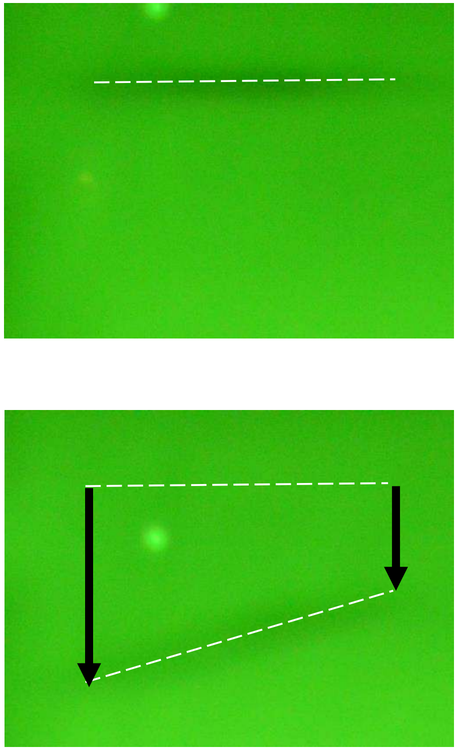
Top view

Photobleached pattern

Before shearing

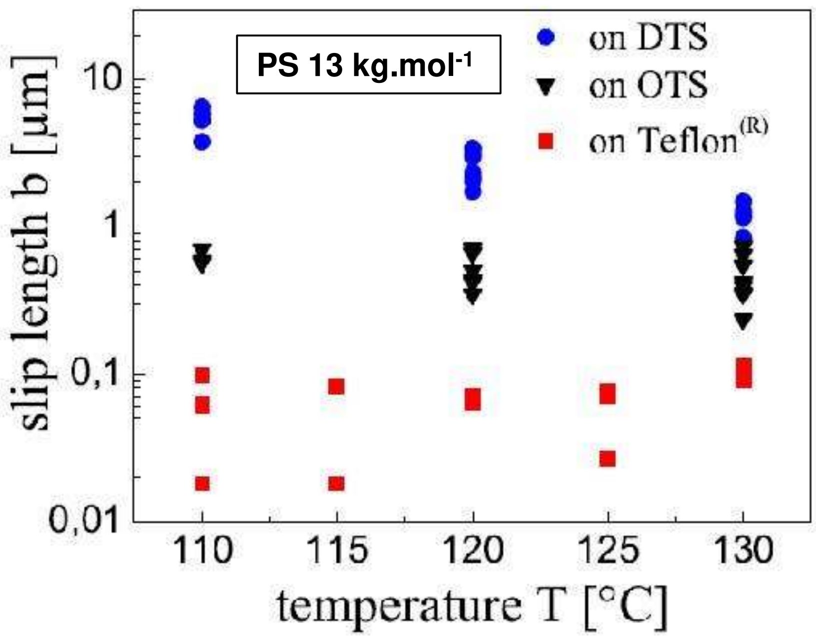
After shearing



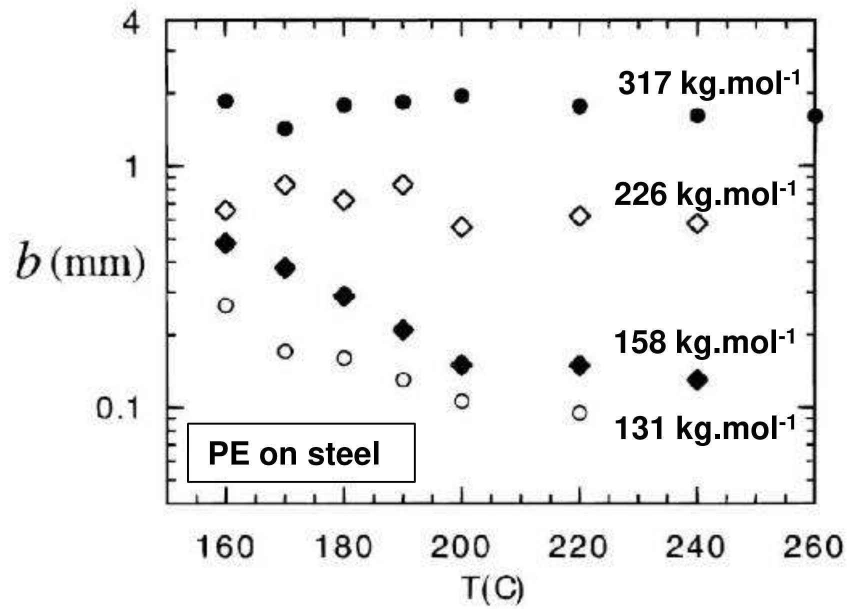


Temperature dependence of the slippage?

The higher the temperature, the easiest the slippage?



Bäumchen *et al.*, *J. Phys. Conf. Ser.*, 2010



Wang *et al.*, *Macromolecules*, 1996

Temperature-Controlled Slip of Polymer Melts on Ideal Substrates

PDMS melt 685 $kg.mol^{-1}$ on OTS and PDMS 2 $kg.mol^{-1}$ grafted layer

Hénot *, Grzelka *, *et al., Phys. Rev. Letters,* 2018

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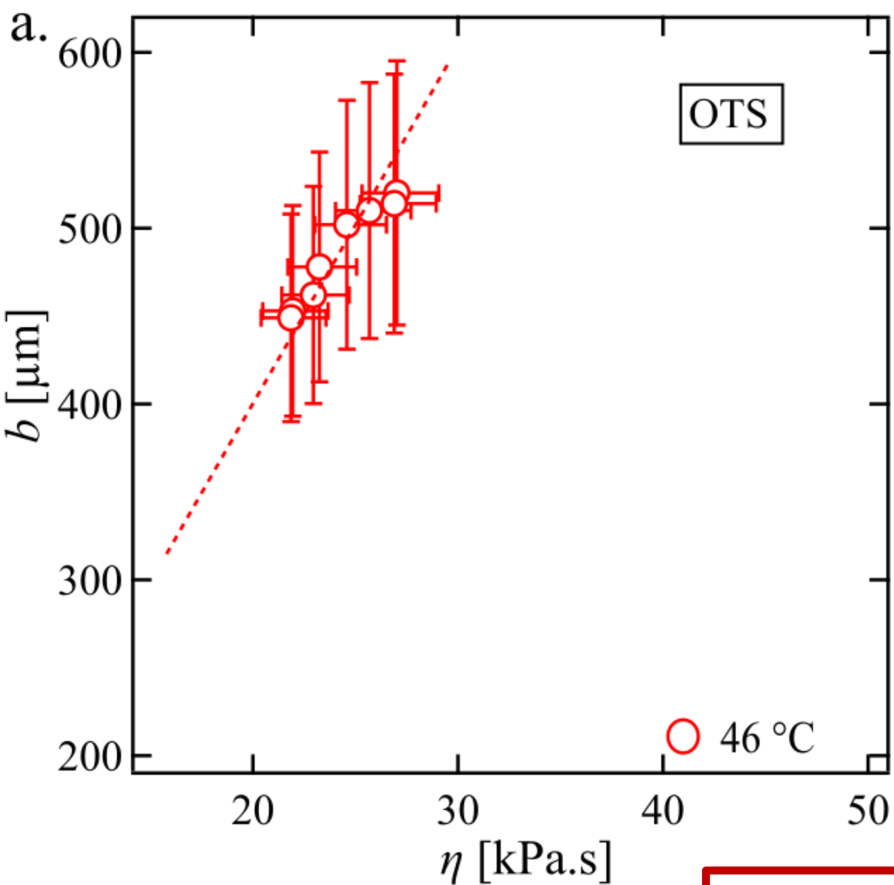

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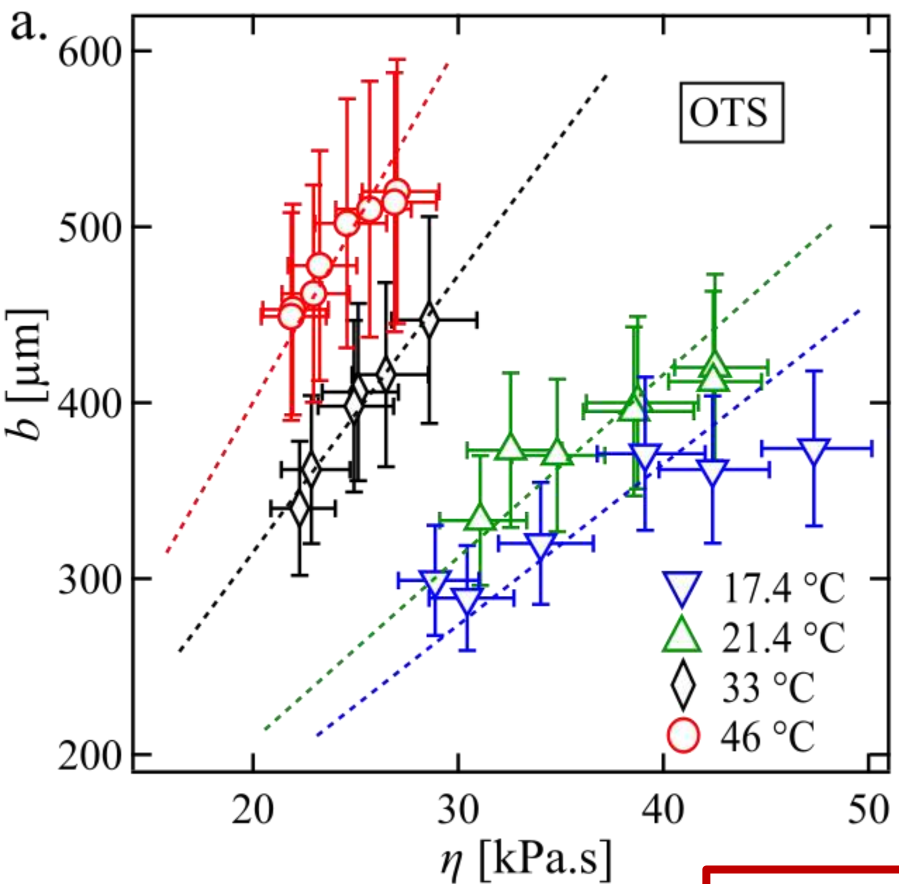

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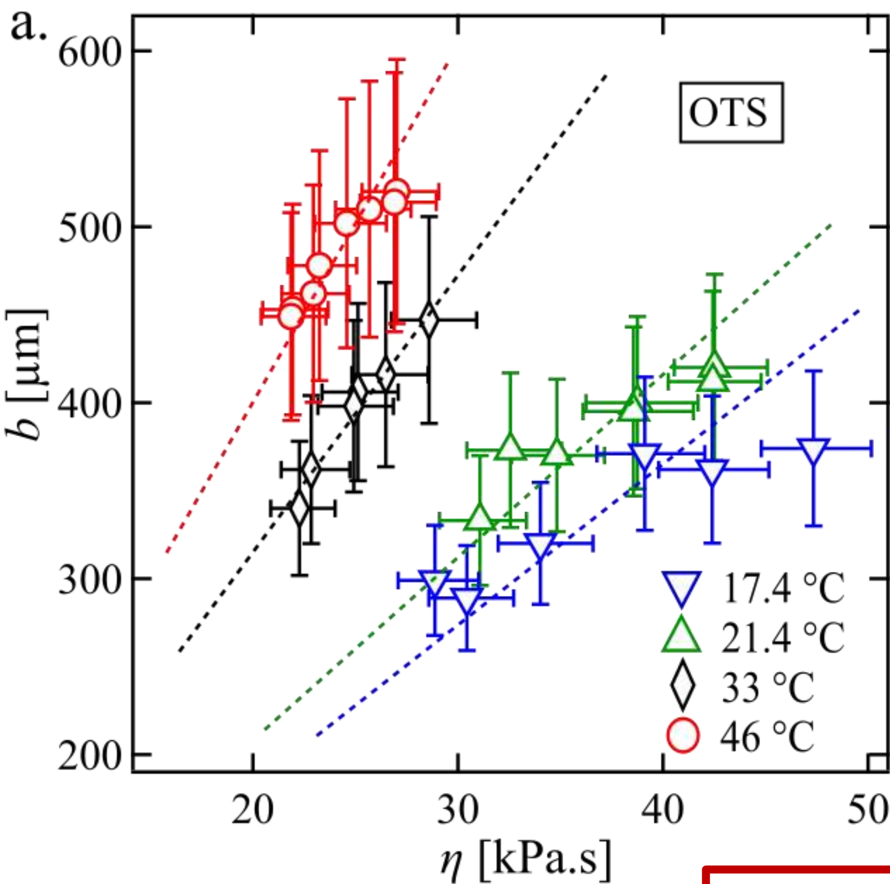

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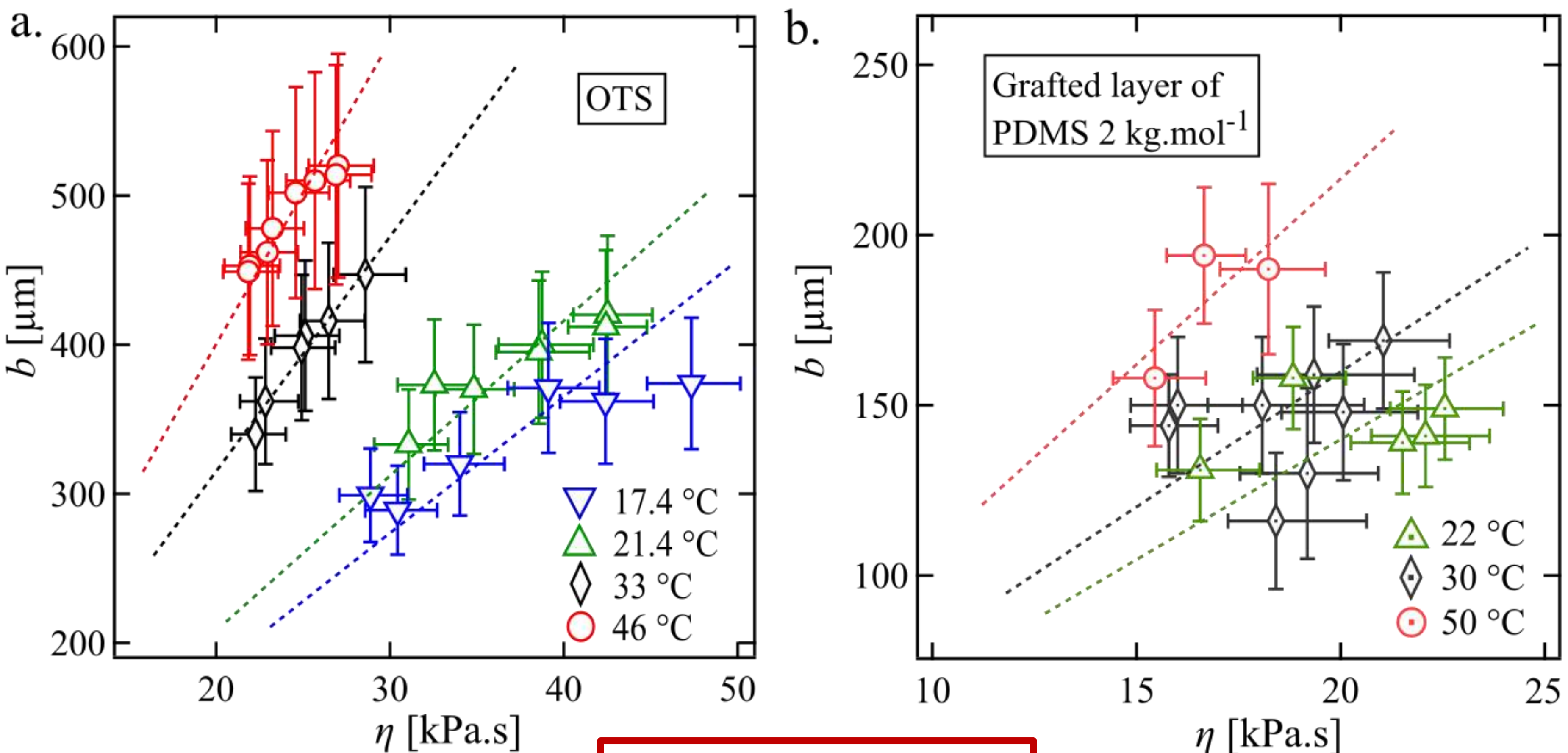

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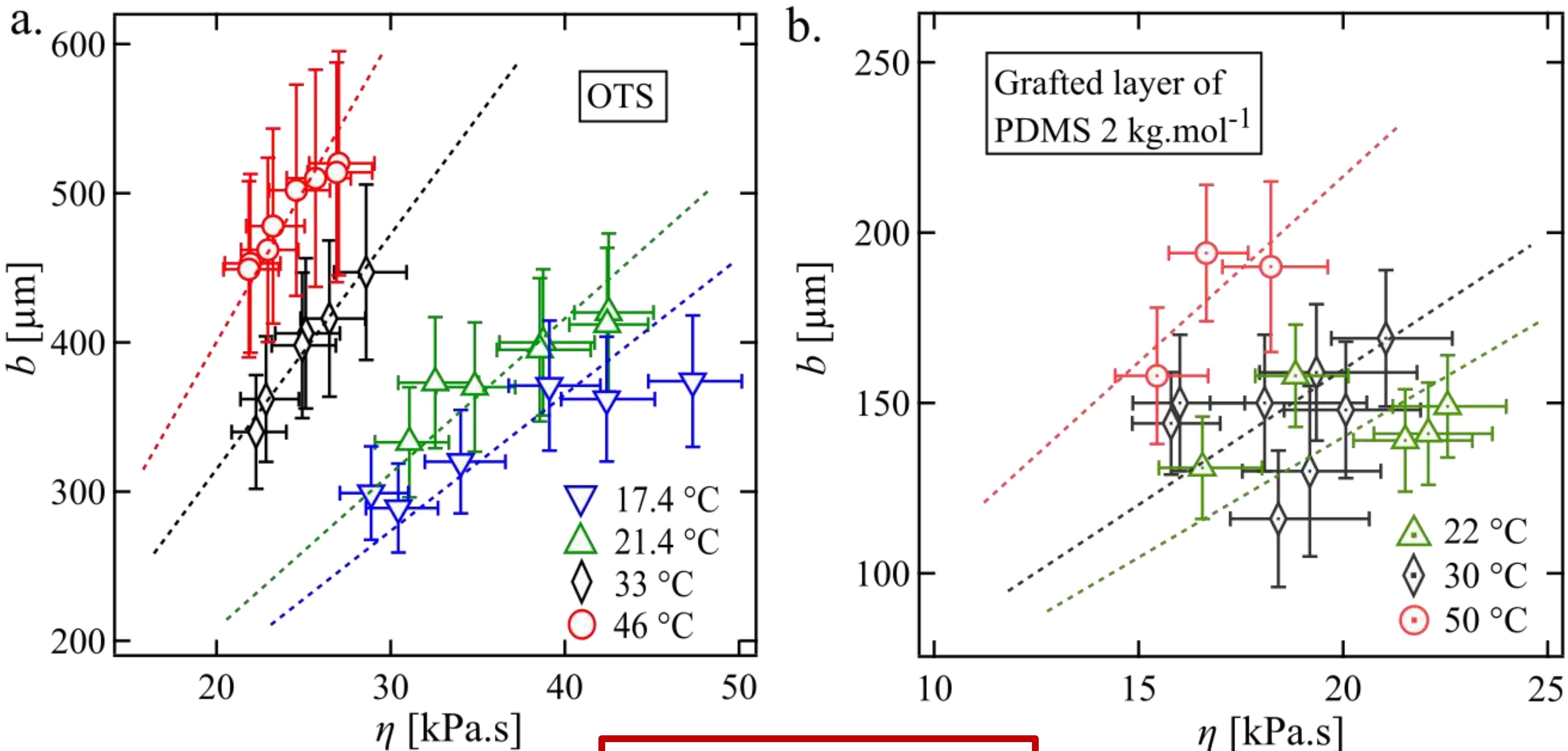

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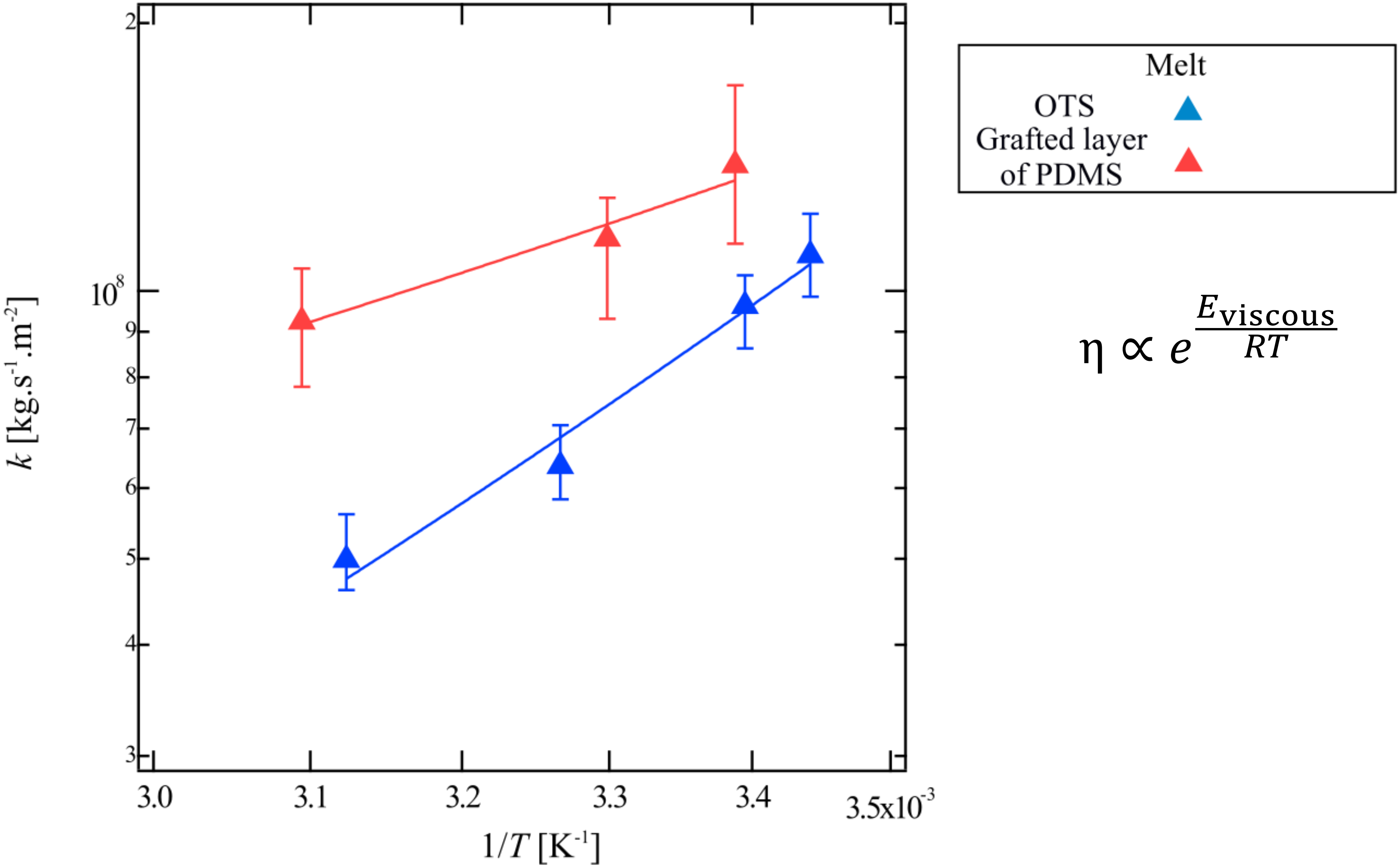
Hénot *, Grzelka *, *et al., Phys. Rev. Letters,* 2018

The higher the temperature, the less friction!



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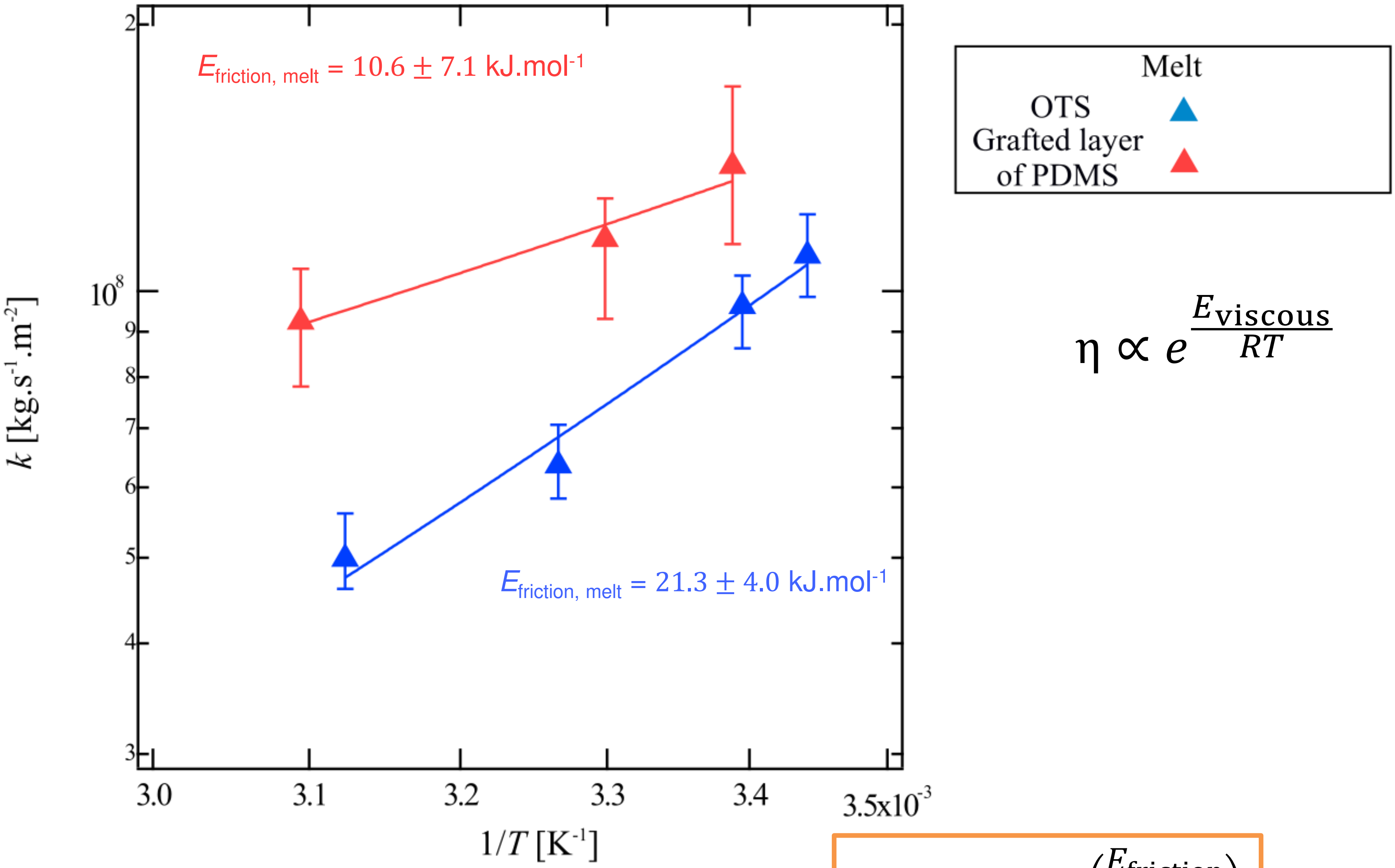

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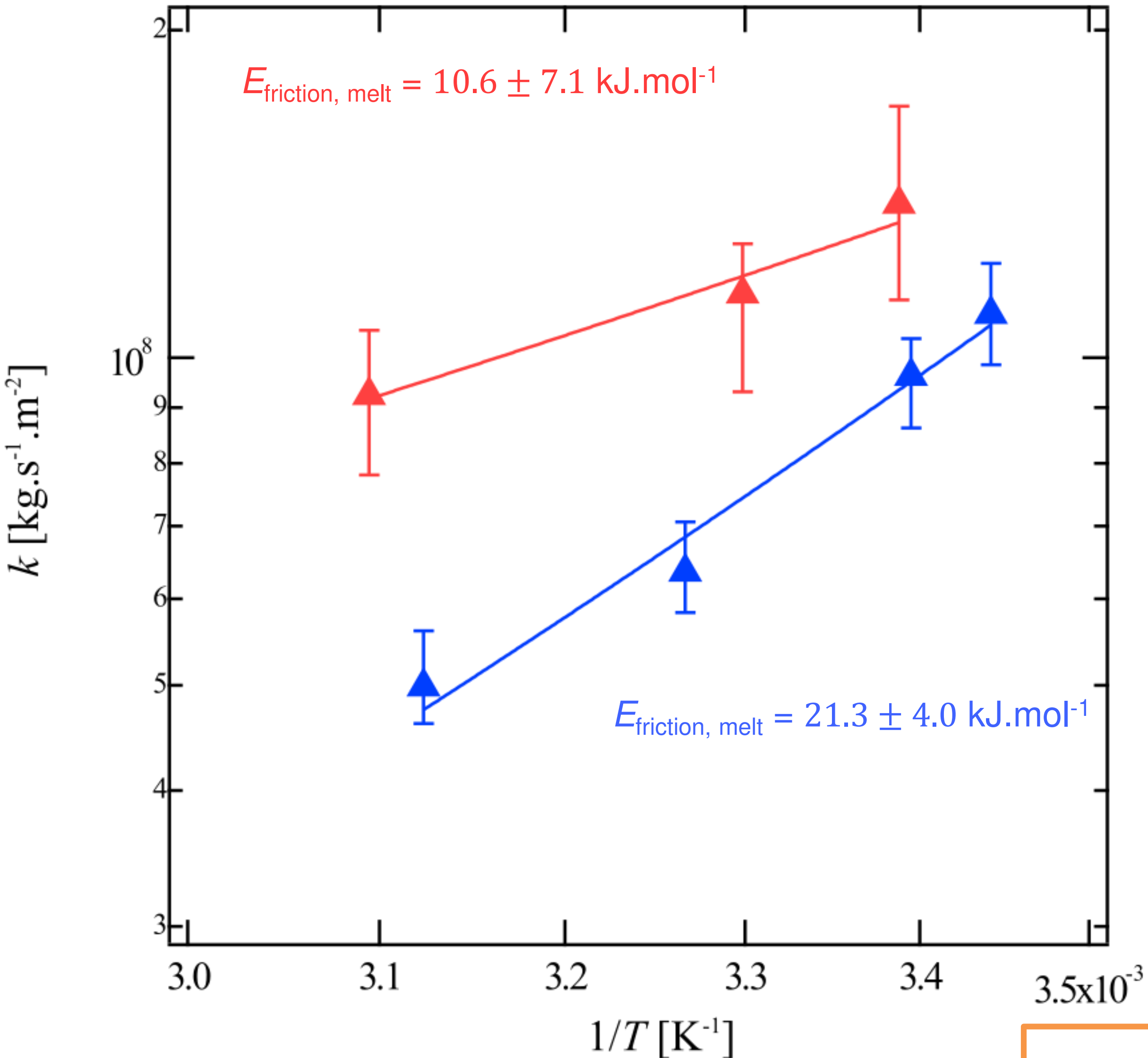

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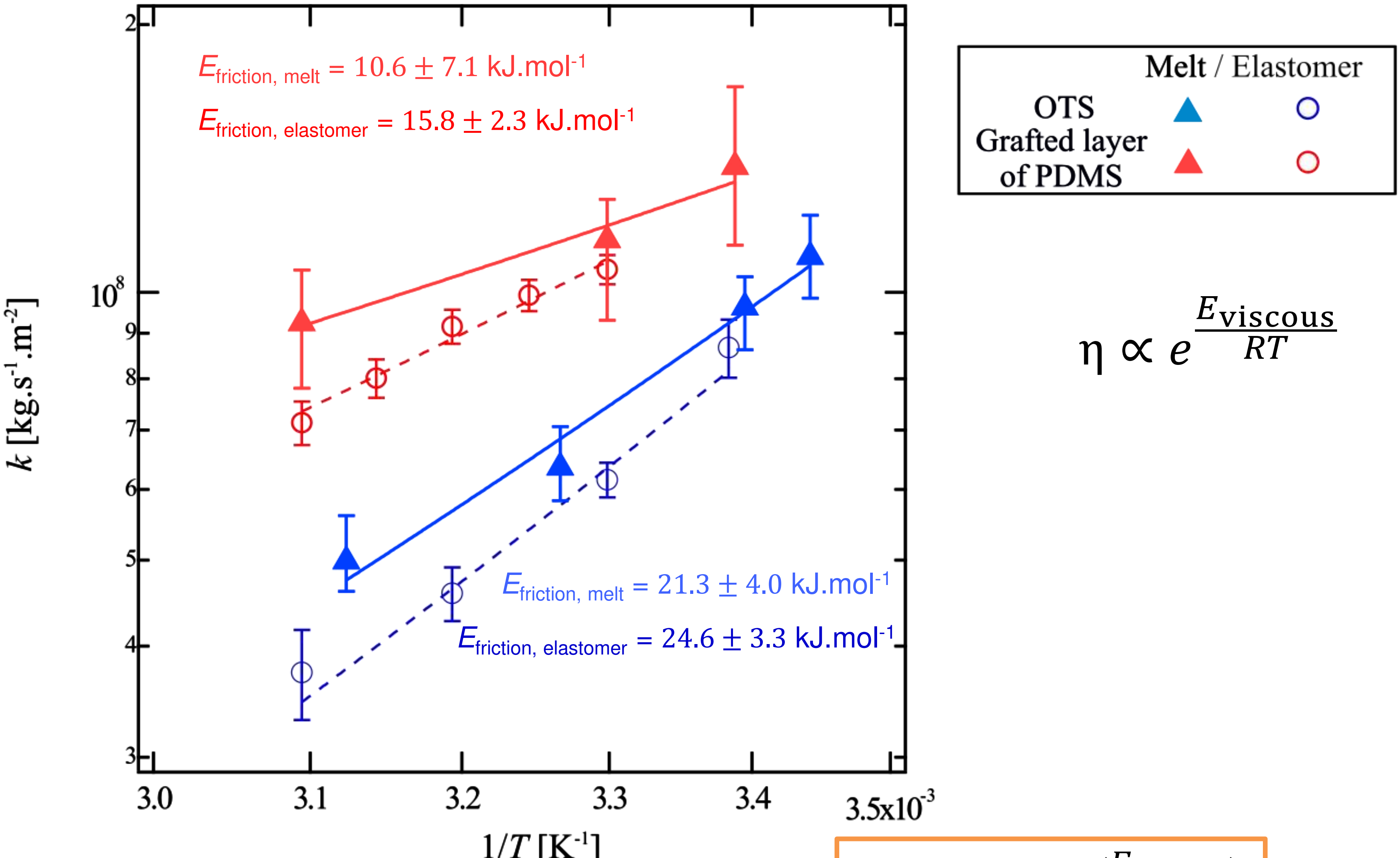

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Grafted PDMS layer

$E_{\text{viscous}} = 16.3 \pm 2.8$ kJ.mol^{-1}

$E_{\text{friction}} = 15.8 \pm 2.3$ kJ.mol^{-1}

$E_{\text{viscous}} \sim E_{\text{friction}}$

$b\ (T) \sim$ constant

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$$b \propto e^{\frac{E_{\text{viscous}} - E_{\text{friction}}}{RT}}$$

Grafted PDMS layer

$E_{\text{viscous}} = 16.3 \pm 2.8$ kJ.mol^{-1}

$E_{\text{friction}} = 15.8 \pm 2.3$ kJ.mol^{-1}

$E_{\text{viscous}} \sim E_{\text{friction}}$

$b\ (T) \sim$ constant

OTS layer

$E_{\text{viscous}} = 16.3 \pm 2.8$ kJ.mol^{-1}

$E_{\text{friction}} = 24.6 \pm 3.3$ kJ.mol^{-1}

$E_{\text{viscous}} < E_{\text{friction}}$

b increases with T

The higher the temperature, the easiest the slippage?

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PS on DTS layer

$E_{\text{friction}} \sim 250$ kJ.mol^{-1}

250 kJ.mol^{-1} < E_{viscous} < 500 kJ.mol^{-1}

$E_{\text{viscous}} > E_{\text{friction}}$

b decreases with T

Conclusion

- Experimental technique to measure $b > 1\ \mu\text{m}$

- Possible to study of molecular effect :

The friction is a thermodynamically activated process far above T_g

$$k_{\text{friction}} \propto \exp\left(\frac{E_{\text{friction}}}{RT}\right)$$

The higher the temperature, the less friction

→ Validity for simple liquids?

k_{friction} local, independent of *N*, so should be valid for simple liquid too

Acknowledgements

Laboratoire Ingénierie des Matériaux Polymères, Lyon

E. Drockenmuller
I. Antoniuk

Laboratoire de Physique des Solides, Orsay

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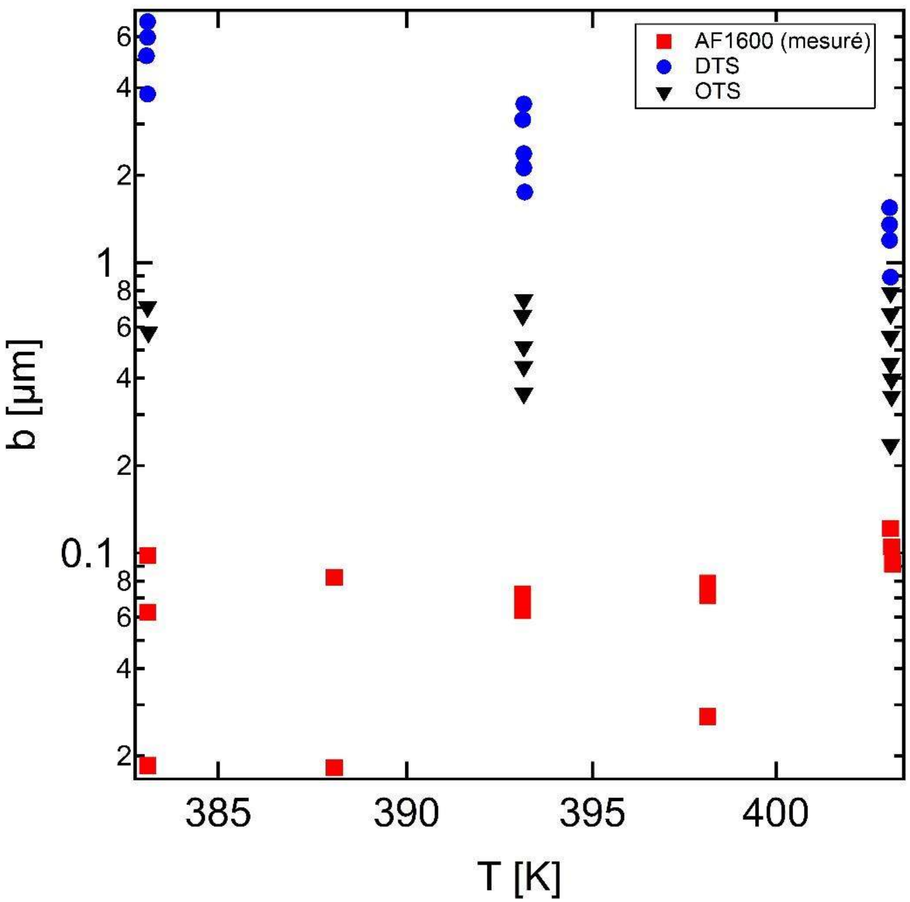
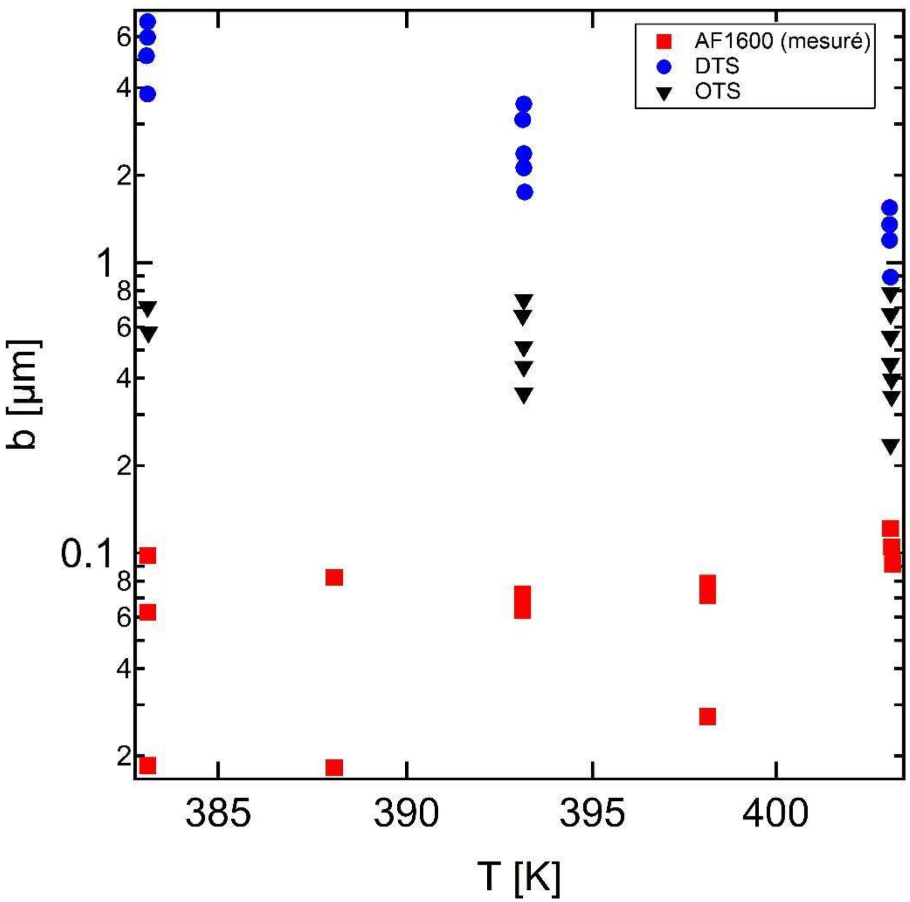
Thank you for your attention!

Slippage of polymer melts close to T_g?



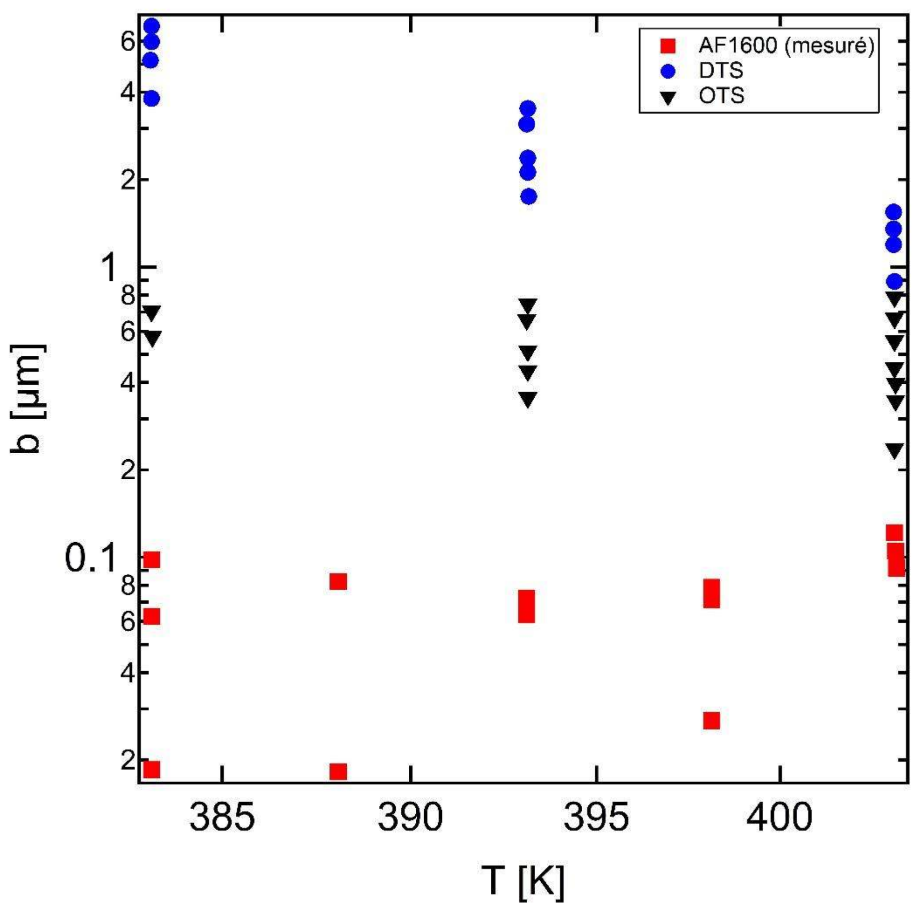
$$k_{\text{friction}} \propto e^{\frac{E_{\text{friction}}}{RT}}$$?

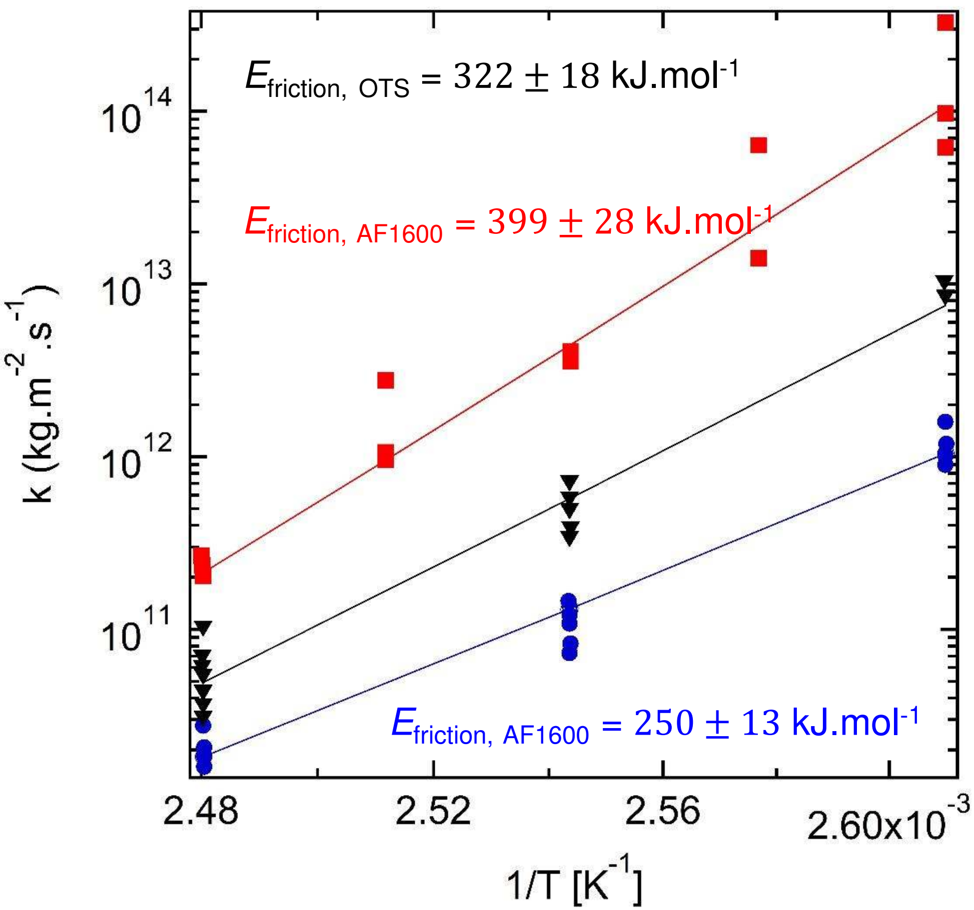
Slippage of polymer melts close to T_g?



$$k_{\text{friction}} \propto e^{\frac{E_{\text{friction}}}{RT}} \quad ?$$

Slippage of polymer melts close to T_g?





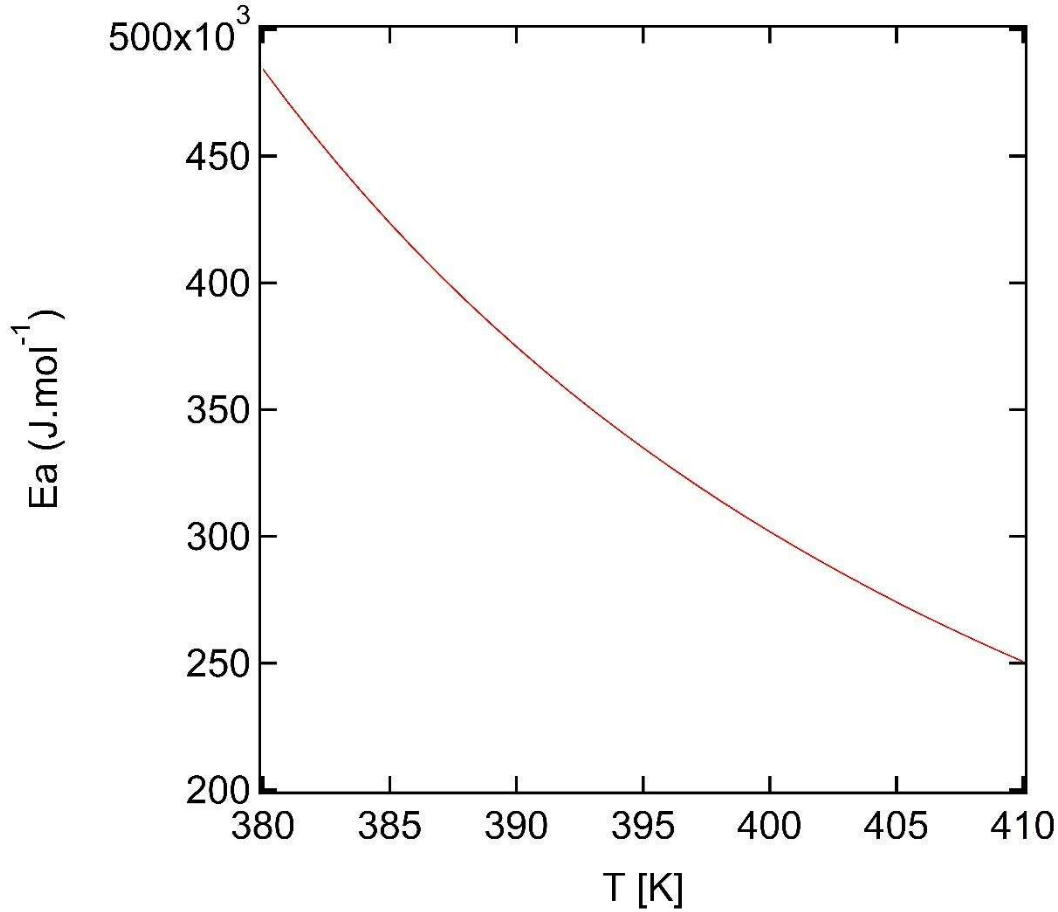
$$k_{\text{friction}} \propto \exp\left(\frac{E_{\text{friction}}}{RT}\right)$$

Slip of polymer melt close to T_g?

Williams–Landel–Ferry equation

$$\log\left(\frac{\eta_T}{\eta_{T_g}}\right) = -\frac{c_1(T - T_g)}{c_2 + T - T_g}$$

$$E_a = \ln(10)\, R c_1 c_2 \frac{T^2}{(c_2+T-T_g)^2}$$



For calculations, see Ferry

Temperature-Controlled Slip of Polymer Melts on Ideal Substrates

$$k_{\text{friction}} \propto e^{\frac{E_{\text{friction}}}{RT}}$$

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$E_{\text{viscous,PDMS}} = 15$ kJ.mol^{-1} Barlow *et al.*, 1964

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Grafted PDMS layer

E_{friction} = 15 kJ.mol^{-1}

$\sim 6\ k_B T$

$E_{\text{viscous}} \sim E_{\text{friction}}$

$b\ (T) \sim$ constant

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$b\ (T) \sim$ constant

OTS layer

E_{friction} = 23 kJ.mol^{-1} $\sim 9\, k_B T$

$E_{\text{viscous}} < E_{\text{friction}}$

b increases with T

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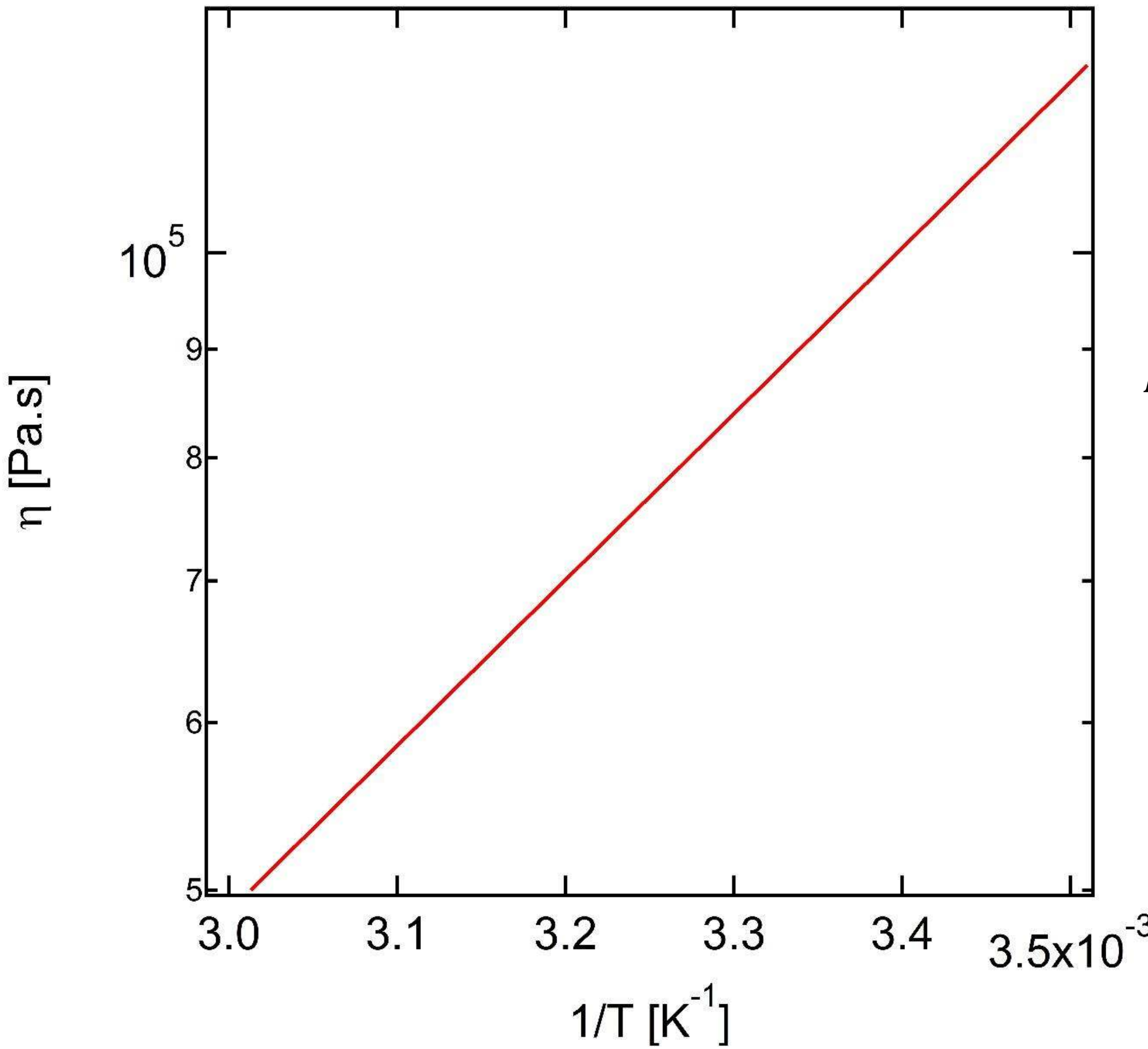
Temperature-Controlled Slip of Polymer Melts on Ideal Substrates



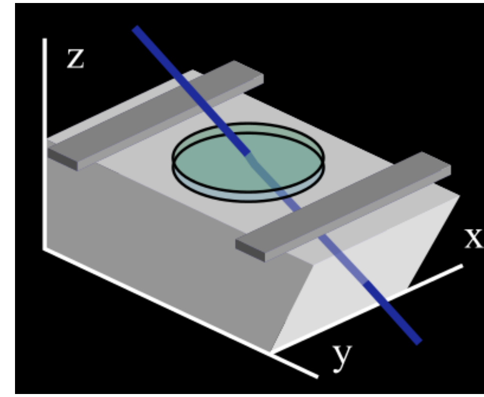
$$\eta \propto e^{\frac{E_{\text{viscous}}}{RT}}$$

$E_{\text{viscous,PDMS}} = 15$ kJ.mol^{-1}

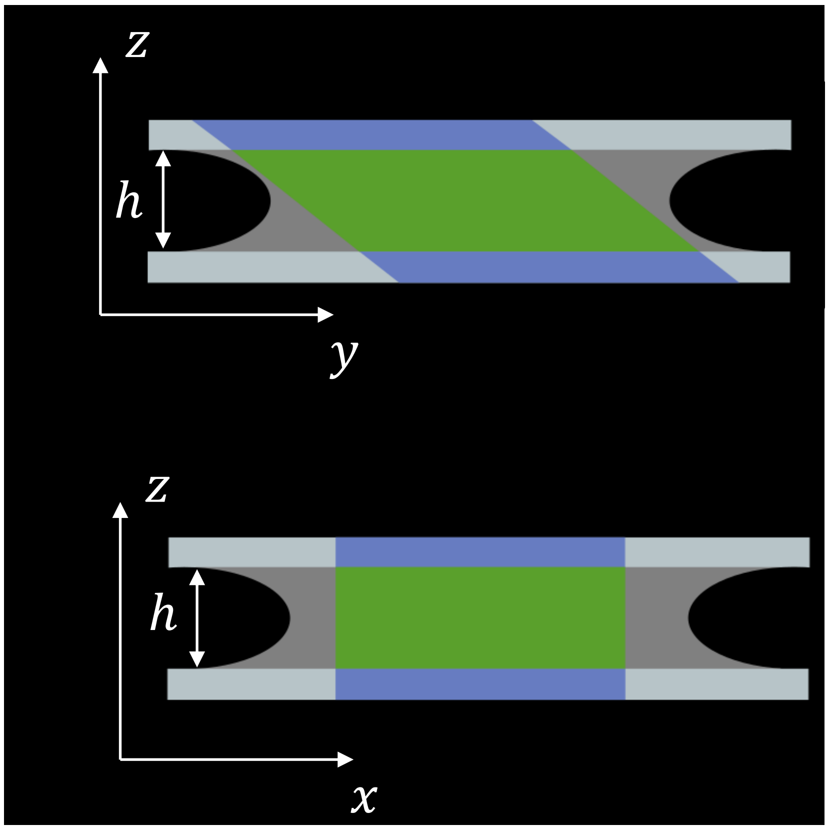
Barlow *et al.*, 1964

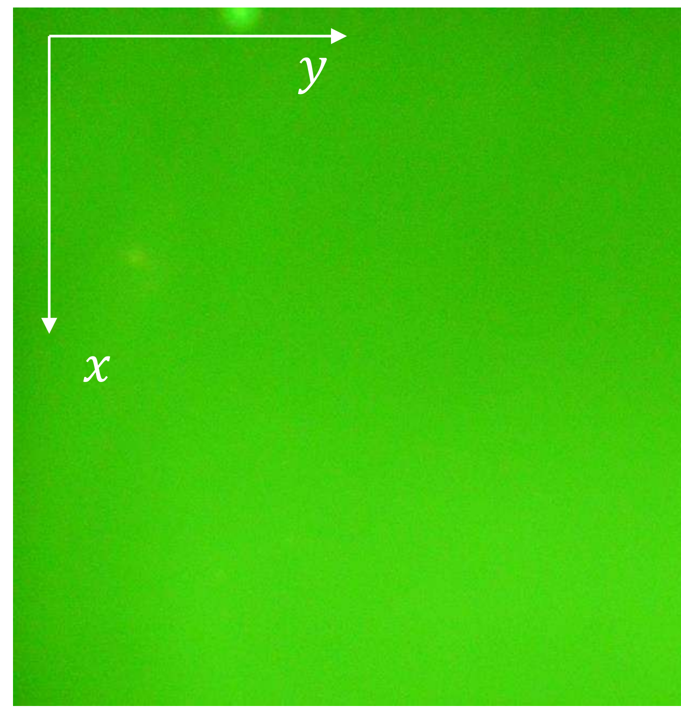
How to measure slippage of polymers ?

Measuring the fluorescence using a microscope and a camera



Reading mode





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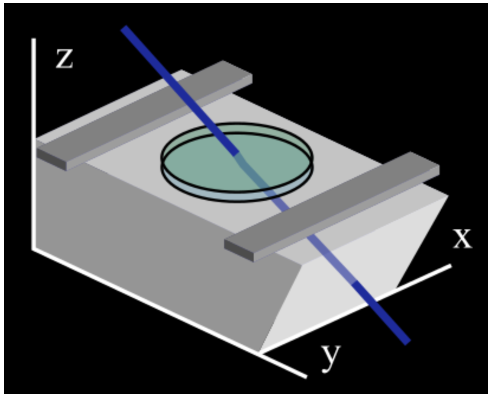
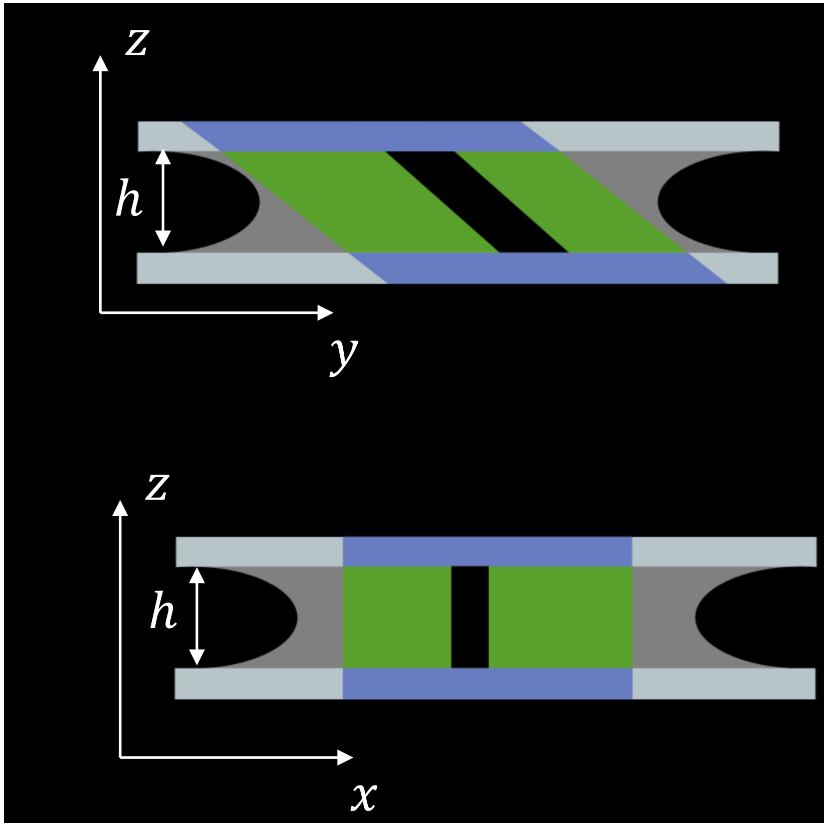
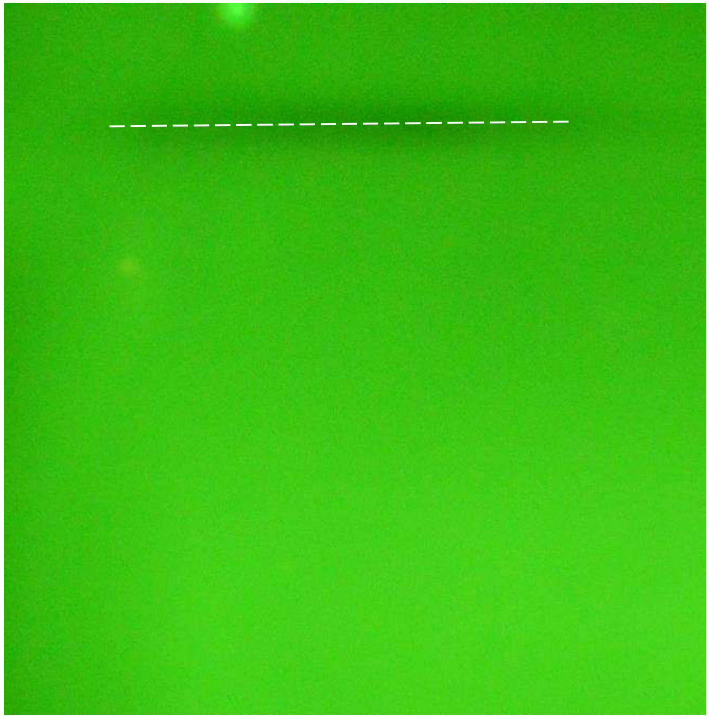


After bleach





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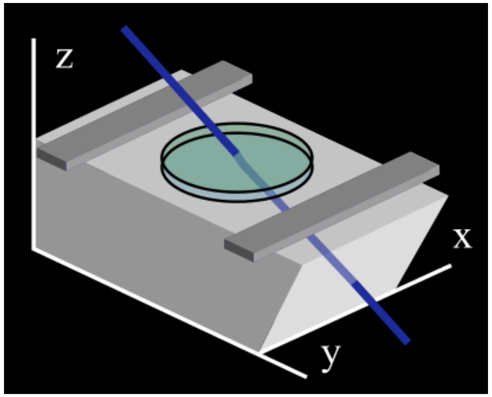
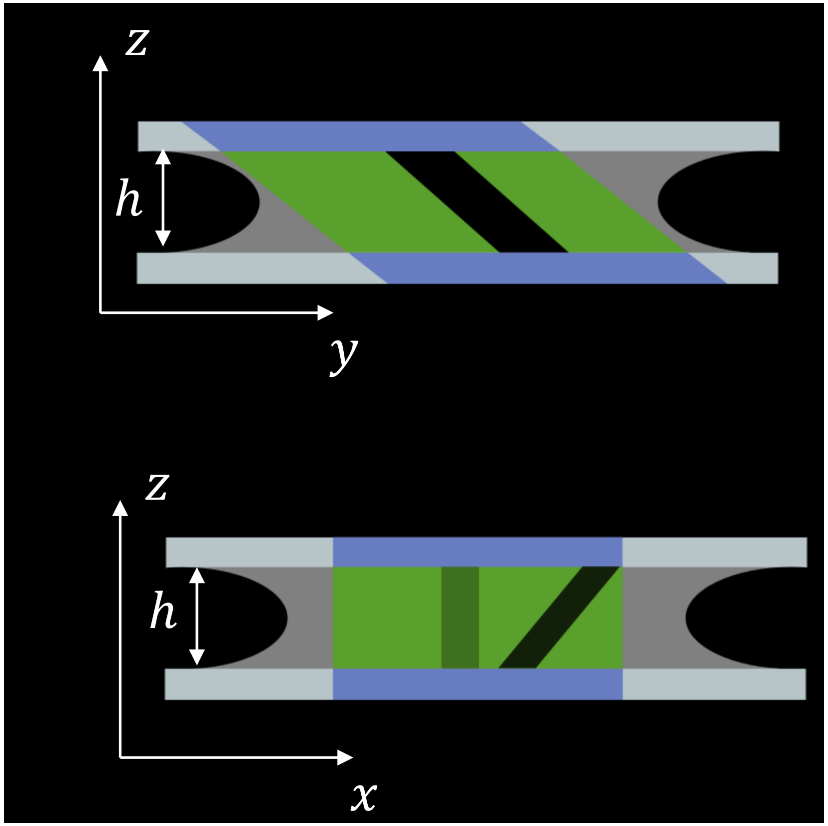
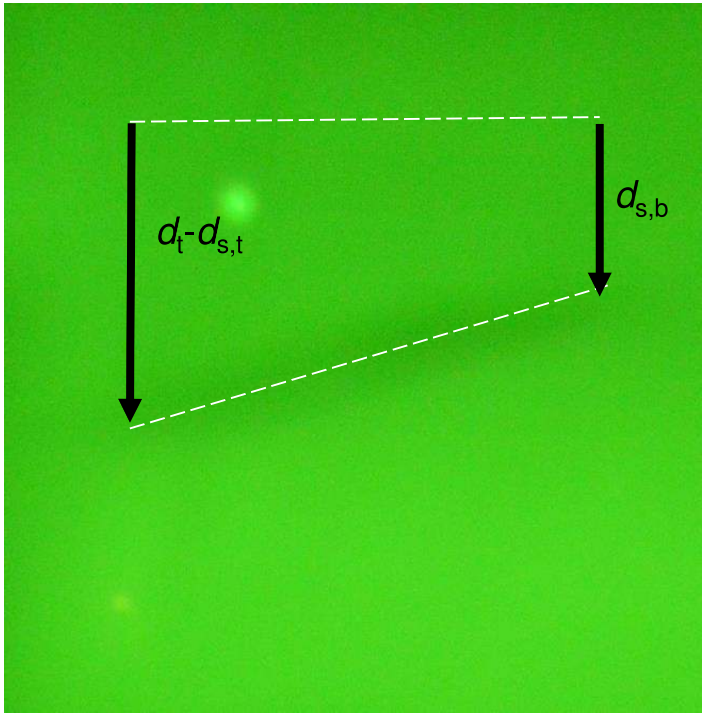
Measuring the fluorescence using a microscope and a camera



After shearing

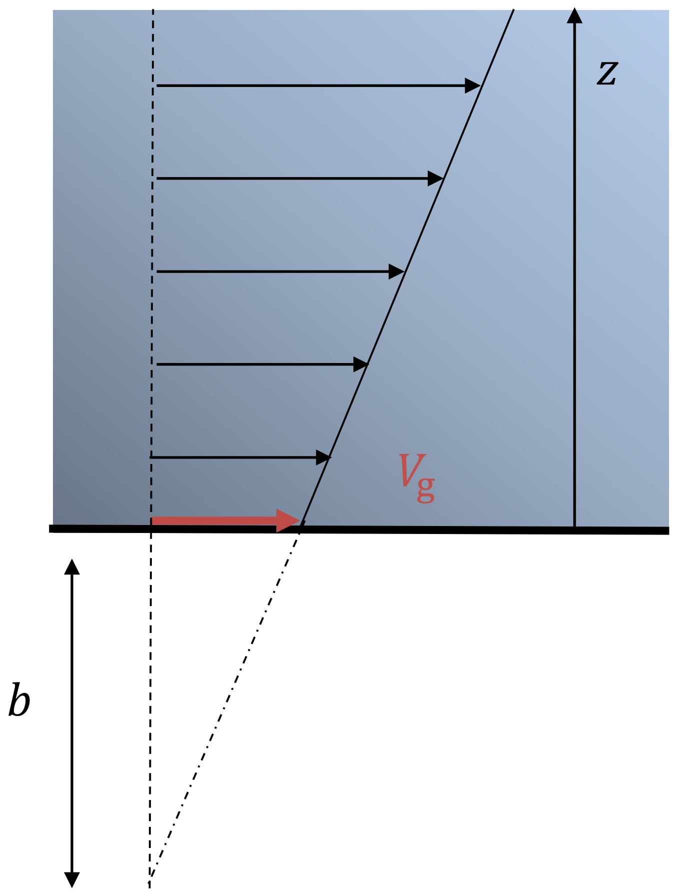




$$b = \frac{h\, d_{s,b}}{d_t - d_{s,t} - d_{s,b}}$$

Slippage of polymers

General case :



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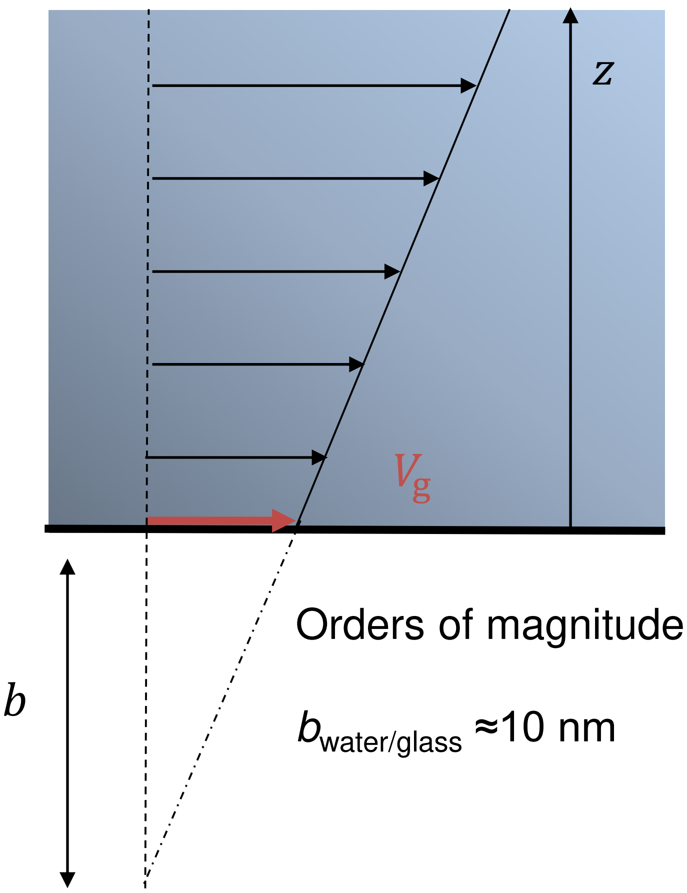

Orders of magnitude:

$b_{water/glass}$ ≈10 nm

Slippage of polymers

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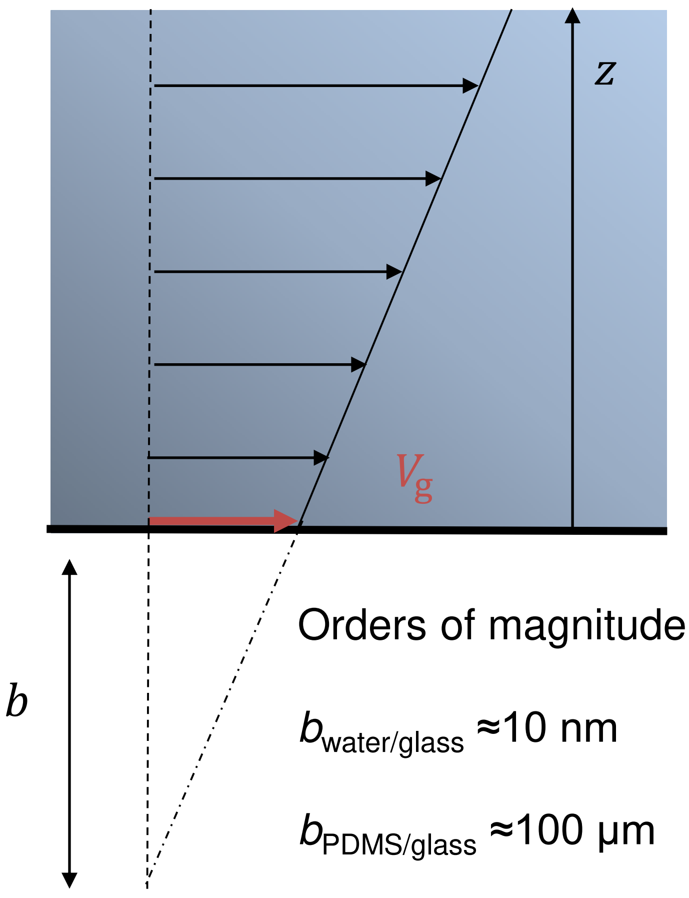

Orders of magnitude:

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Slippage of polymers

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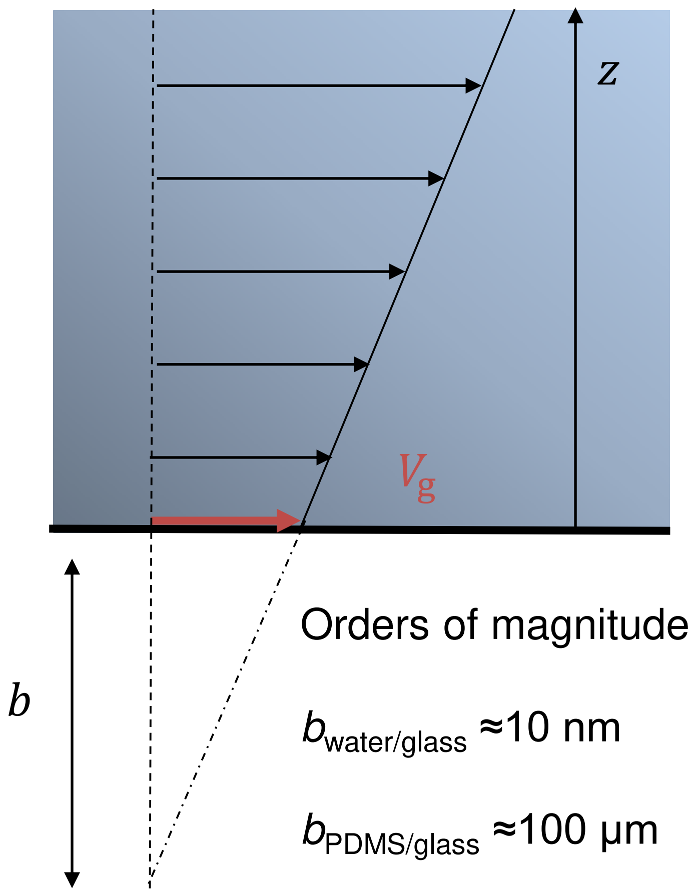

Navier's hypothesis at the wall :

$$\sigma(z=0) = k\, V_g$$

Friction coefficient

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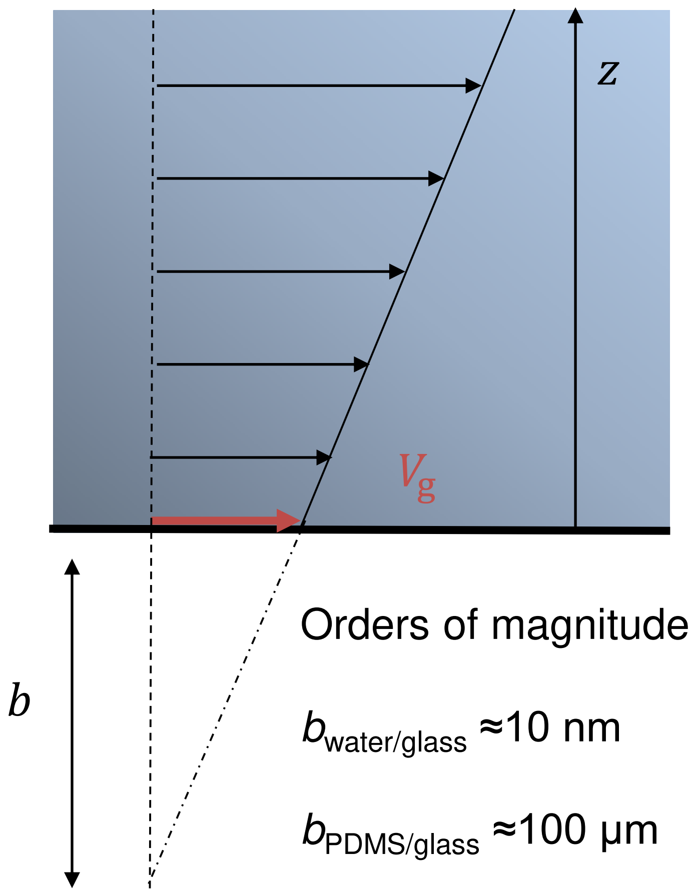

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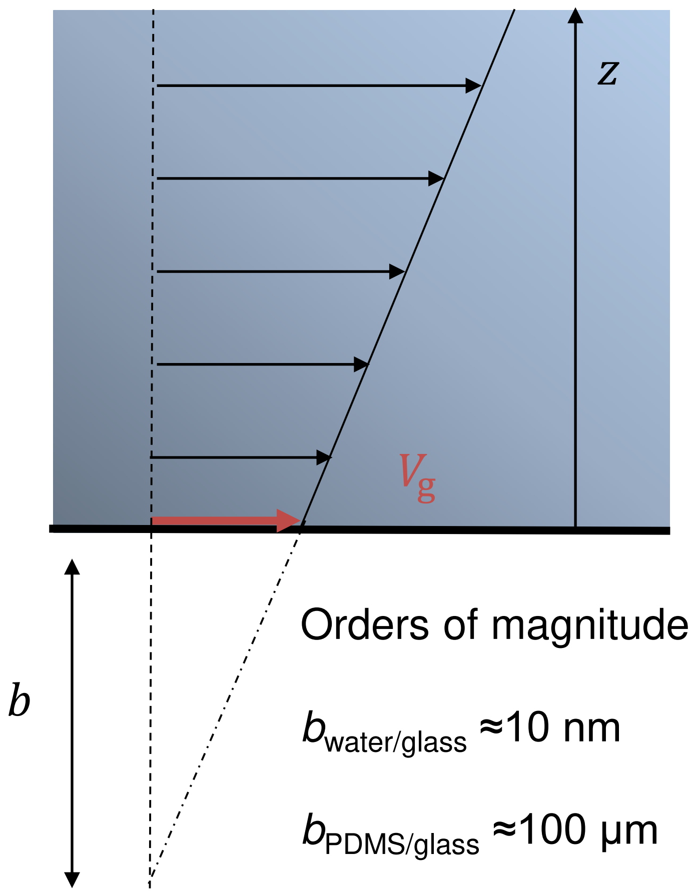

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In the bulk : $\sigma(z) = \eta_{bulk} \frac{\partial v}{\partial z} = \eta_{bulk} \frac{V_g}{b}$

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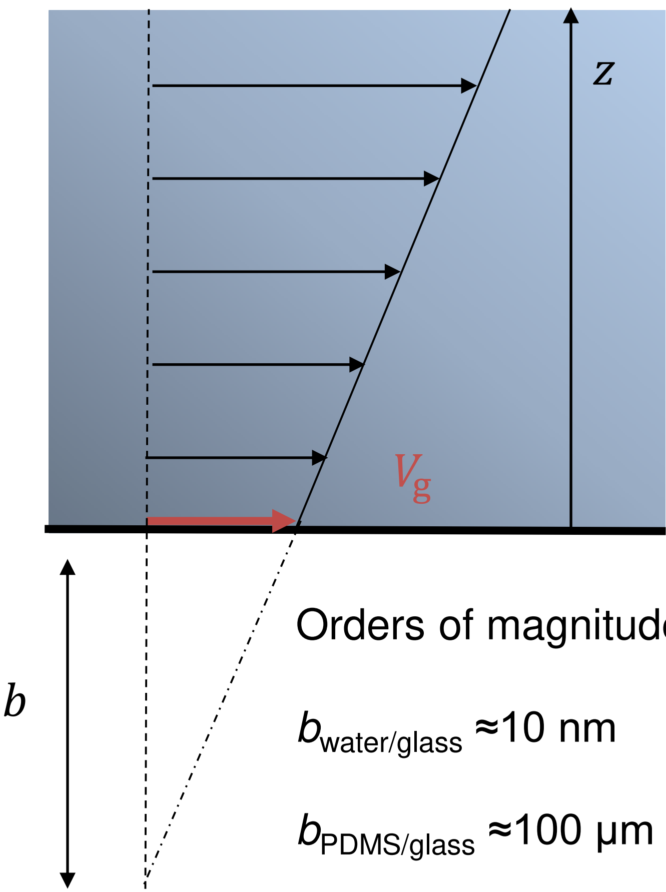

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Slip length : $$b = \frac{\eta_{\text{bulk}}}{k}$$

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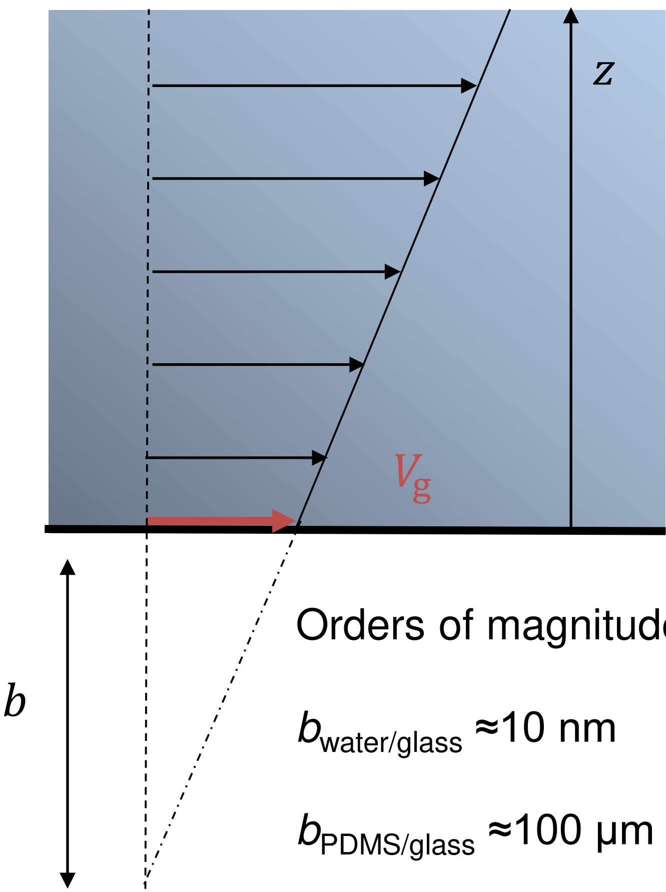

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Friction coefficient

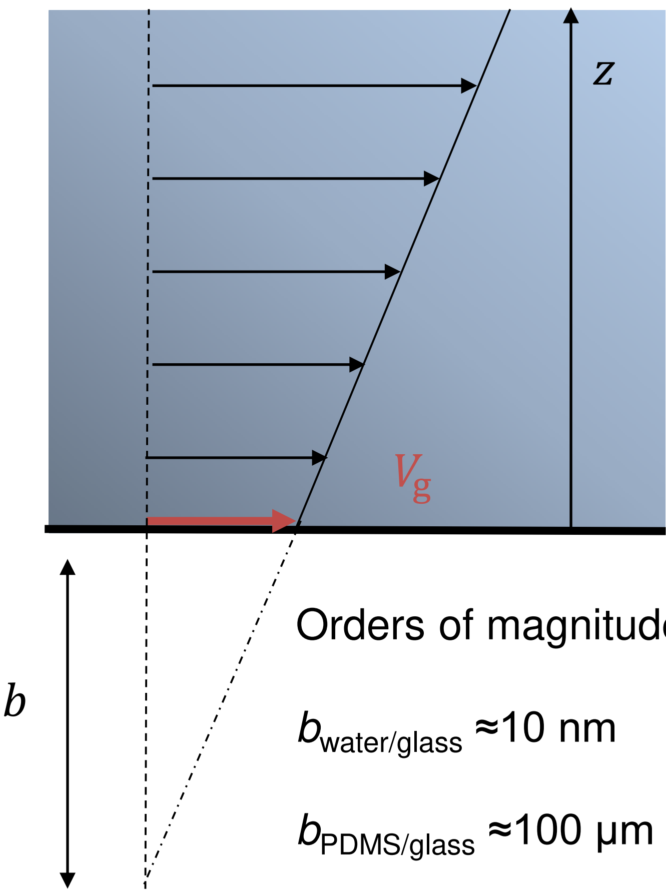
Slip length : $b = \dfrac{\eta_{\text{bulk}}}{k}$

Viscosity governed by entanglements.
$\eta \propto N^3$, N number of monomers per chain

de Gennes' hypothesis :
k independent of N

Slippage of polymers

General case :



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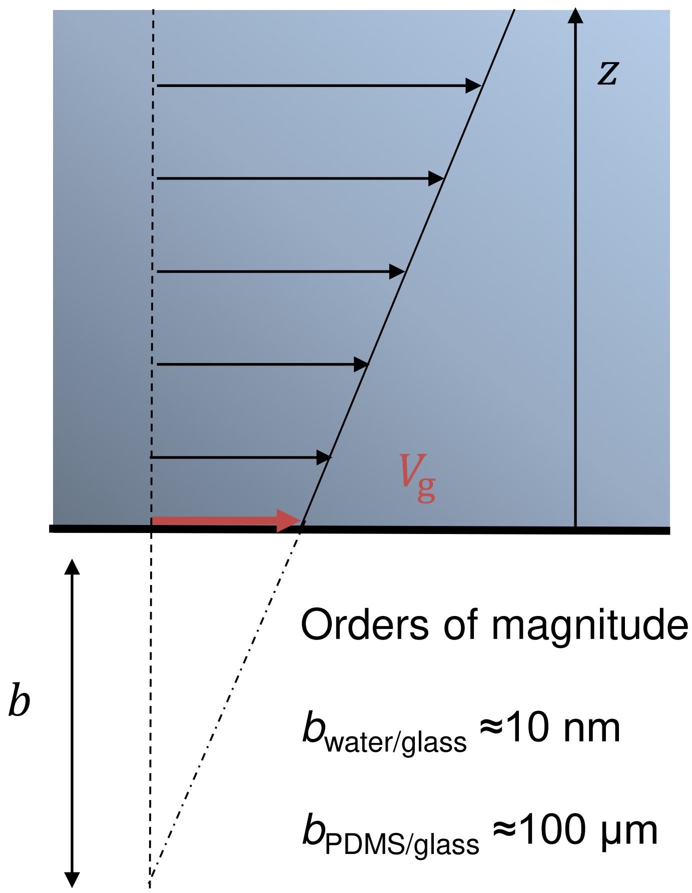

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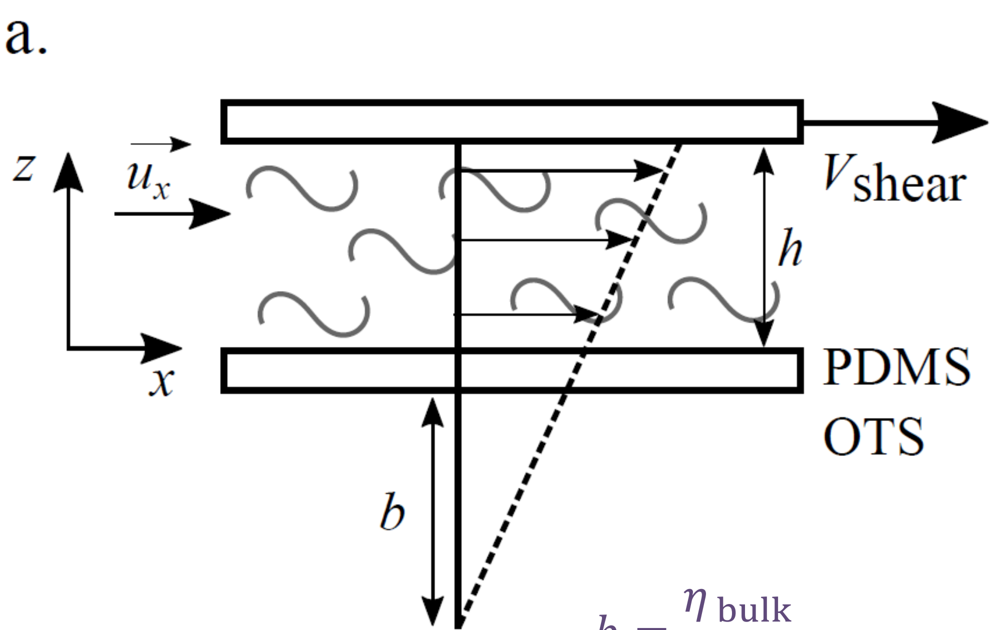
Viscosity governed by entanglements.
$\eta \propto N^3$, *N* number of monomers per chain

de Gennes' hypothesis :
k independent of *N*

$$b_{\mathrm{polymer}} = b_{\mathrm{monomer}} N^3$$

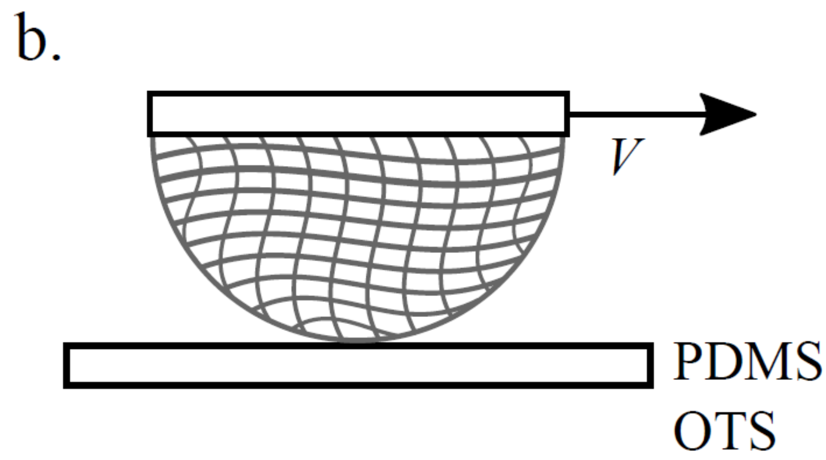
Temperature-Controlled Slip of Polymer Melts on Ideal Substrates

PDMS melt 685 kg.mol^{-1} on OTS and PDMS 2 kg.mol^{-1} grafted layer



$$b = \frac{\eta_{bulk}}{k}$$

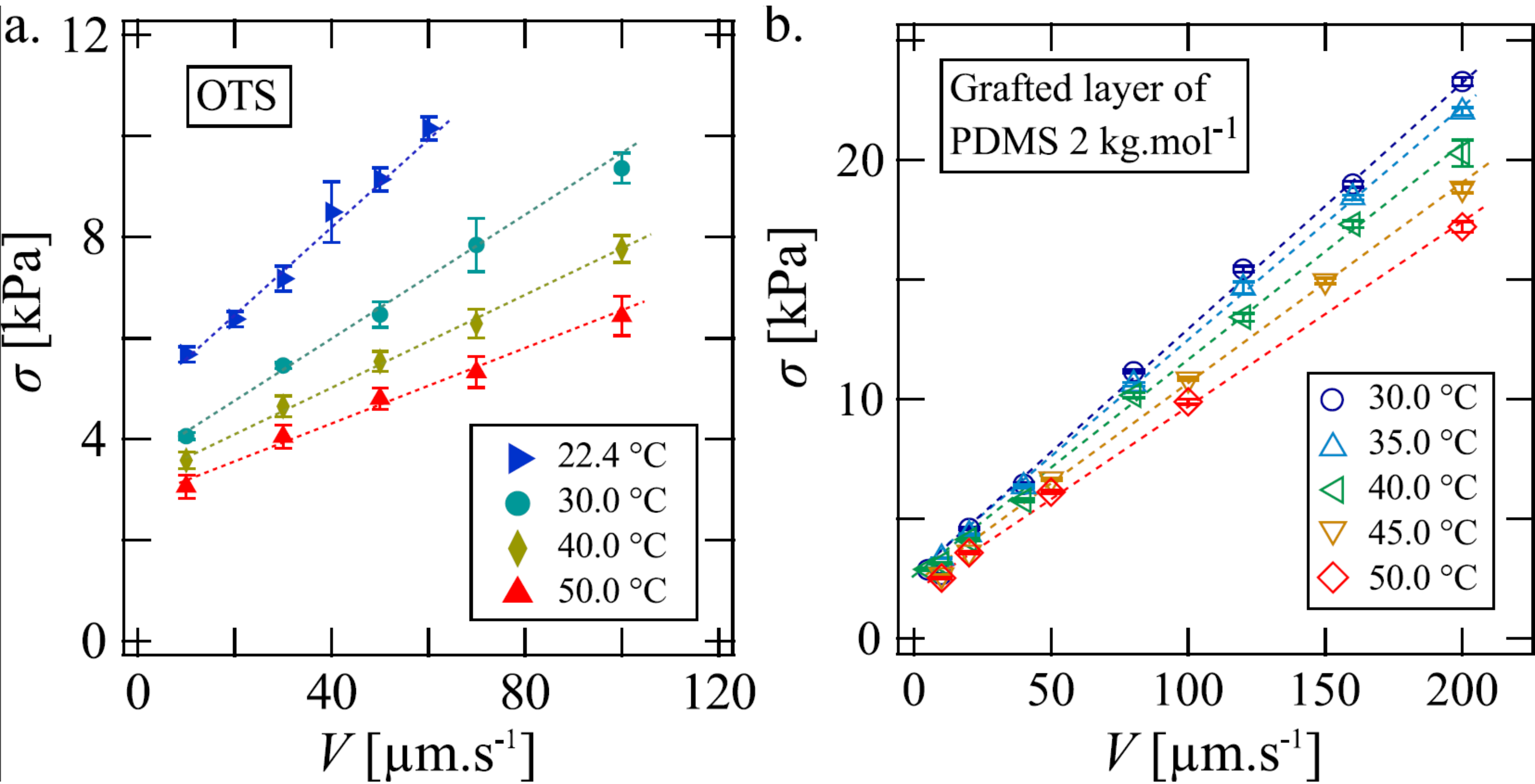
b and *η* measured, *k* deduced



$$\sigma(z=0) = k\,V$$

σ and V measured, *k* deduced

Temperature-Controlled Slip of Polymer Melts on Ideal Substrates



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