Simple views in polymer dynamics

APS symposium honoring P.G. de Gennes

SLIPPAGE

Liliane Léger

Laboratoire de Physique des Solides,
UMR 8502 CNRS – Université Paris Sud-XI
leger@lps.u-psud.fr

LPS ORSAY

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An Old Problem

What causes resistance to the motion in a fluid?

Newton (1685), Bernoulli (1738), Euler (1755), Coulomb (1784), Navier (1821), Stokes (1842), Maxwell (1866), Brillouin, M. (1899)

- In bulk: liquid-liquid friction

→ *viscosity* η $\sigma = \eta\dot{\gamma}$

→ *Differential equation* (Navier-Stokes)

Fig. 2.

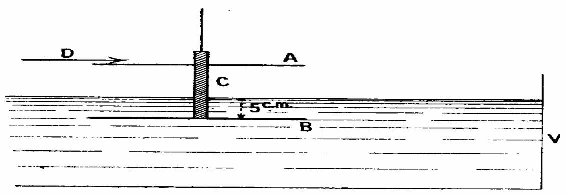
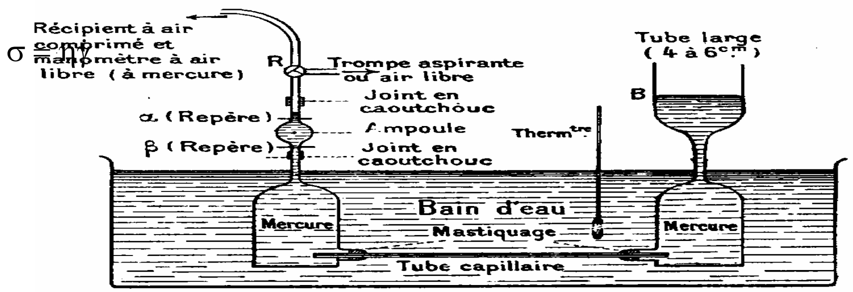


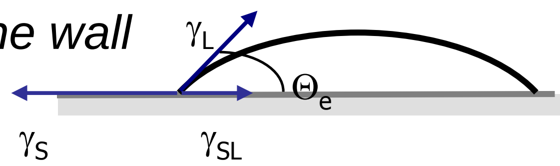
Fig. 32.



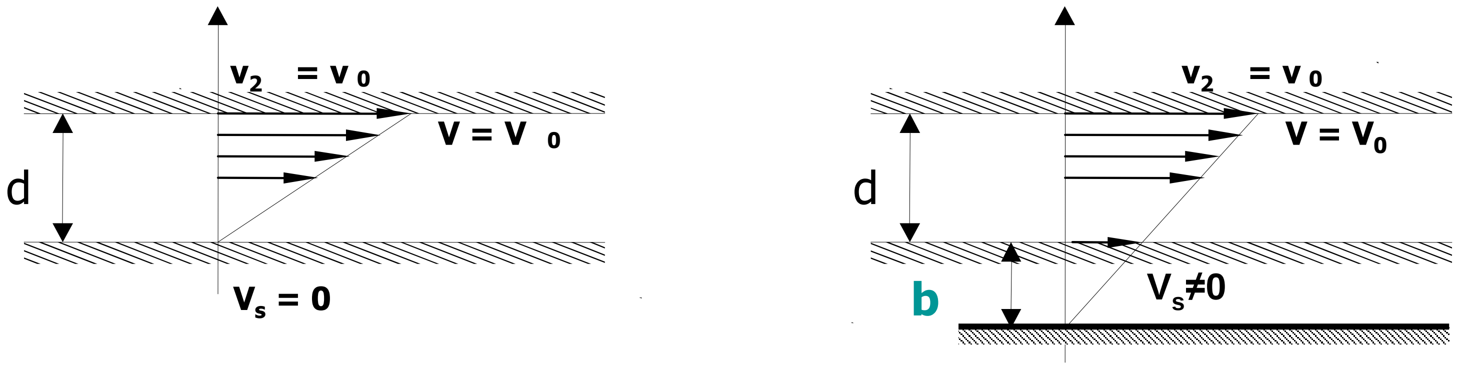
- At surface: liquid-solide friction

→ *Boundary condition for the velocity at the wall*

→ Interactions between fluid molecules and solid ↔ Wetting ?



Boundary condition for the velocity at the wall



Stress at interface:

$$\sigma = k_{FV}\ v_S = \eta\,\dot{\gamma}$$

$$\dot{\gamma} = \left.\frac{\partial v_x}{\partial z}\right|_{z=0} = \frac{v_S}{b}$$

Navier (1823)

Slip length *b*

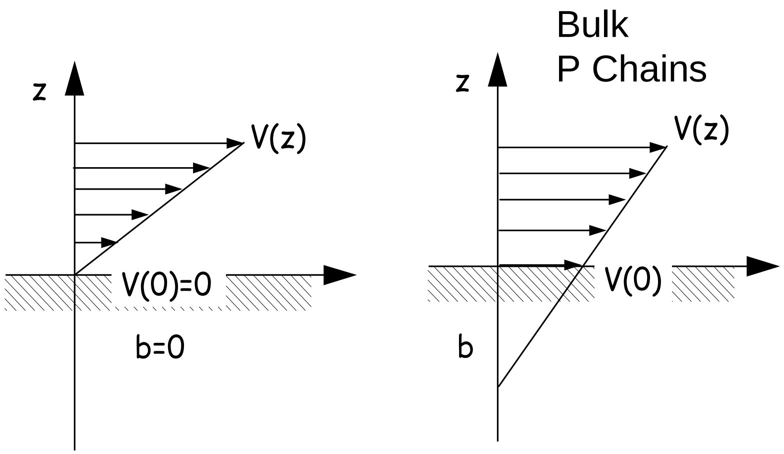
$$b = \frac{\eta}{k_{FV}}$$

Commonly admitted: b≈ molecular size

Friction at polymer interfaces: interfacial slip

P. G. de Gennes C. R. Acad. Sci. Paris, <u>288</u> B, 219 (1979)

Ideal surface +
polymer melt



$$\sigma = kV(0) = \eta \left.\frac{dV}{dz}\right|_{z=0} = \eta \frac{V(0)}{b}$$

$$\mathbf{k} = \frac{\sigma}{\mathbf{V(0)}} \qquad k \propto \frac{\eta}{b}$$

k= friction coefficient at interface

Fluid of monomers : $b = \frac{\eta_1}{k} \approx a$ $\quad a \approx$ few Å

Polymer : $b = \frac{\eta(P)}{k} = \frac{\eta(P)}{\eta_1} a$

Polymer : $\frac{\eta(P)}{\eta_1} \approx 10^5$ to 10^6

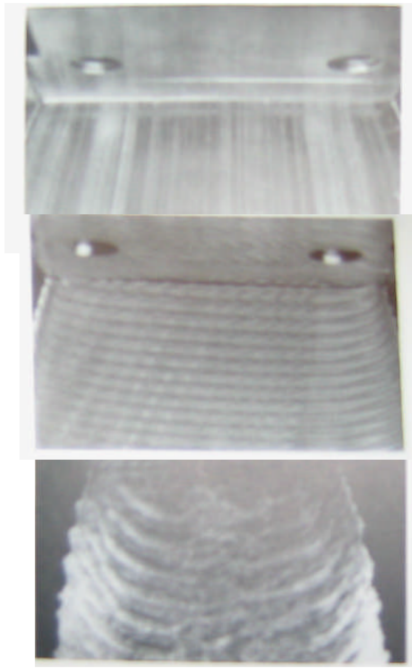
b ≈ 10 to 100 µm
Huge slip

Experimental indications:

- Polymer melt extrusion:

J.J. Bembow, P. Lamb, SPE trans. 3, (1963), 7
A.M. Kraynik, W.R. Schowalter, J. Rheol. 25, 95 (1981)
R.H. Burton, M.J. Folkes, K.H. Narh, A. Keller, J. Mater. Sci. 18, 315 (1983)
G.V. Vinogradov, V.P. Protasov, V.E. Dreval, Rheol. Acta, 23 (1984) 46
A.V. Rammamurthy, J. rheol., 30, (1986) 337
N. El Kissi, J.M. Piau, C.R. acad. Sci. 309, 7 (1989) and J. non Newtonnian Fluid Mechanics, 37, (1990) 55 – 94
S. G. Hatzikiriakos, J.M. Delay, J. rheol. 36, 703 (1992)
……

- Some evidences of slip (pressure drop versus flow rate and thickness dependences)
- depending on the nature of the wall
- evidences of the shear rate threshold
- relation to extrusion defects



- Direct characterization of the flow velocity at interface:
  - tracer particles *Atwood and Schowalter, Rheol. Acta 28, 134 (1989)*
  - near field laser velocimetry

Experiment: Near Field laser Velocimetry

Léger, Hervet, Massey, in Rheology of melt processing
J.M. Piau, J.F. Agassant Edt, Elsevier (1996)

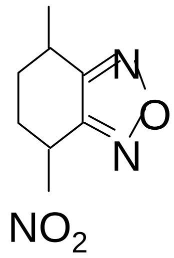
Polymer : (PDMS)

M_w = 200 to 970 kg/mol ($M_w/M_n \approx 1.1$)
P = 2700 to 13100.
$D^* = N_e^{1/2} a$ (N_e PDMS≈ 100)

} Entangled

End labeled with NBD
(5% by weight)

λ_{exc}=476 nm
Λ_{em}=510 nm
Photobleachable

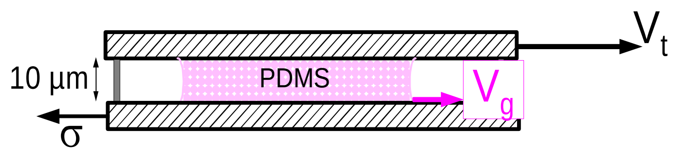


Surface:

PDMS on SiO2 (Prism)
OTS layer (ideal non adsorbing surface?)

Experiment:

simple shear



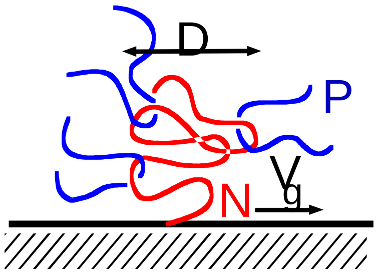
+ evanescent waves ⟹ sensitivity to the surface (Λ≈50 nm)

K.B. Migler, H. Hervet, L.L., Phys. Rev. Lett. 70, 3, (1993) 287: 3 different slip regimes

Model: entanglements driven friction

F. Brochard , P.G. de Gennes Langmuir 8 p3033 (1992): Shear dependent slippage at a polymer/solid Interface
*A. Ajdari et al J. Phys. II France **5** p491 (1995): Drag on a polymer chain moving in a polymer melt*
A. Ajdari, F. Brochard Wyart, P. G. de Gennes, L. Leibler, J.L. Viovy, M. Rubinstein, Physica A 204, 17 (1994)
*F. Brochard et al. Macromol. **29** p377 (1996): slippage of polymer melts on grafted surfaces*
C. Gay, Thesis University Paris VI, 1997

- **D>D***: weak deformation of surface chains → Fixed number of entanglements

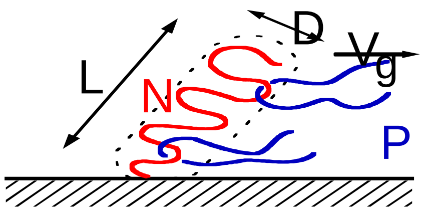


$$\sigma \propto V_S$$

$$b = \frac{\eta_P V_S}{\sigma} = cte$$

Linear Friction

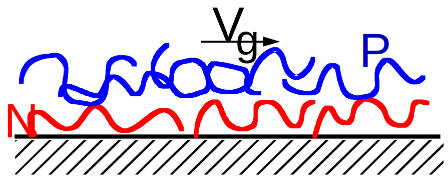
- **D=D***: marginal regime



- $\dot{\gamma}^* = \Sigma \frac{kT}{\eta_P a^2 D^*} \propto \Sigma$
- $V_S^* = \frac{kT}{\eta_P N a^2} \propto P^{-3.3} N^{-1}$
- $b = \frac{V_S}{\dot{\gamma}^*}$

Non linear Friction

- **D<<D***: disentangled regime

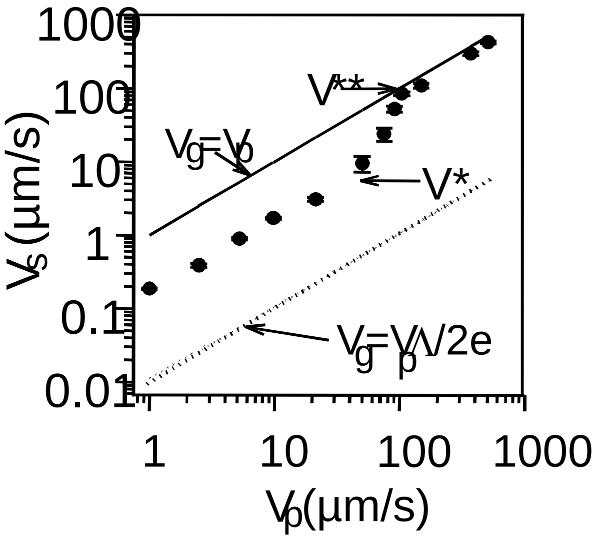


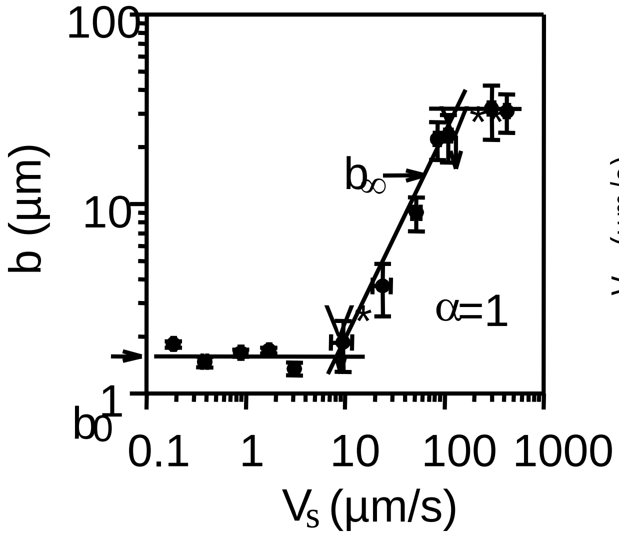
- $\frac{V_S}{D^*} \geq \frac{1}{\tau_{rep}}$
- $b = b_\infty \cong \frac{a\eta_P}{\eta_0}$
- $V_S \propto \dot{\gamma}$

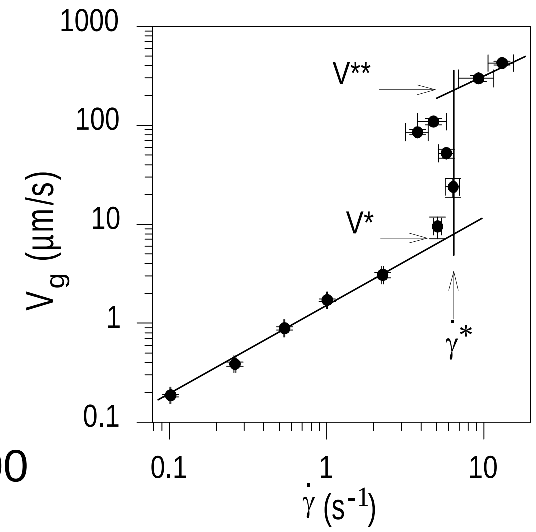
Linear, low friction

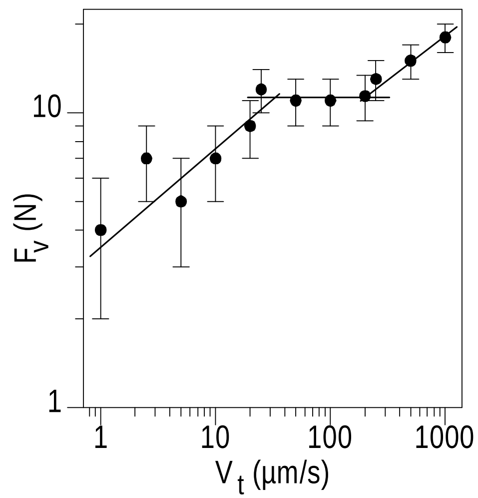
Typical results :

Bulk PDMS melt: M_w=970 kg/mol
Surface: silica + end grafted PDMS
M_w=96 kg/mol, Σ=0.0055







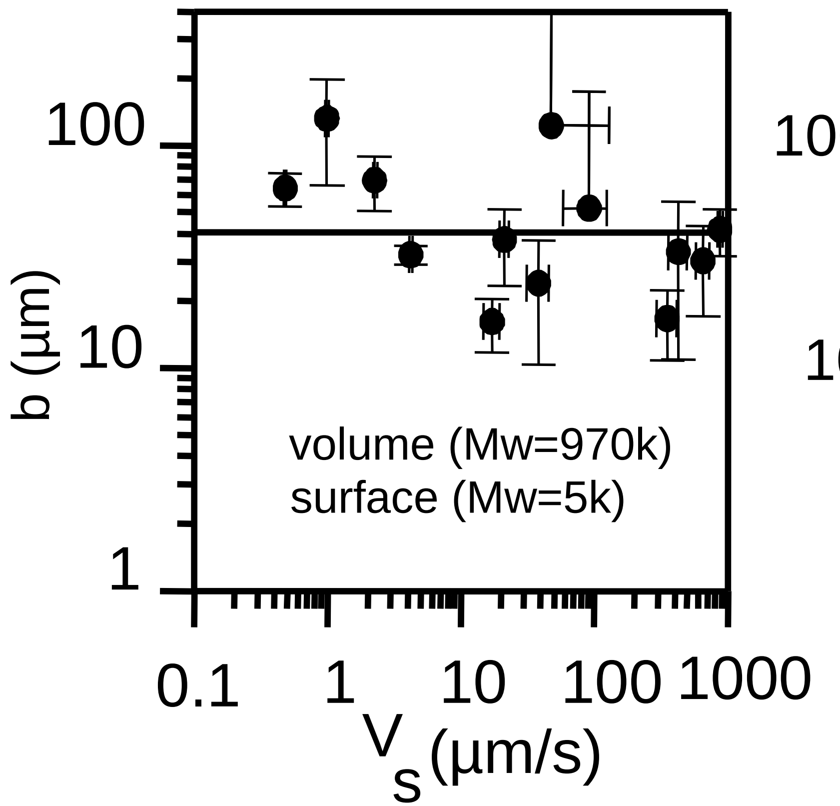


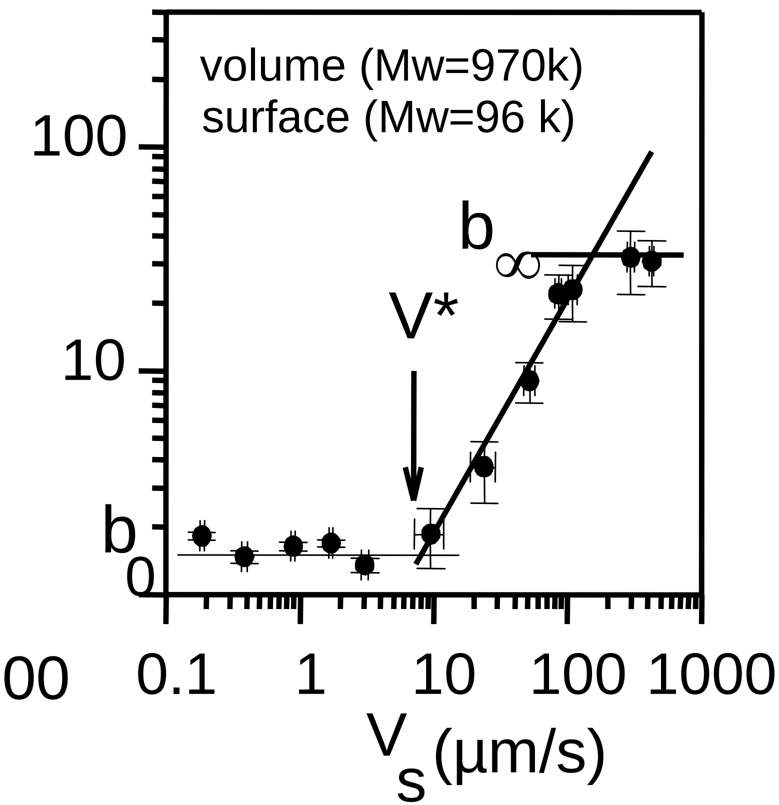
E. Durliat Thesis Univ. Paris VI (1997)
E. Durliat et al. Europhys. Lett ***38****, 383 (1997) and*
J. Phys. Condens. Matter ***9****, 7719 (1997)*
L. Léger et al. Advances in Polymer Sci. ***138****, 185 (1999)*

Entanglements driven friction

Bulk Polymer : PDMS $P>N_e$
Surface: PDMS brush

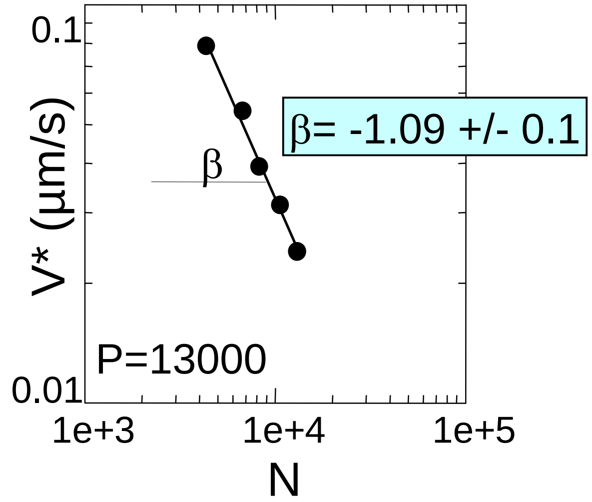
Short grafted chains:
Only high slip regime

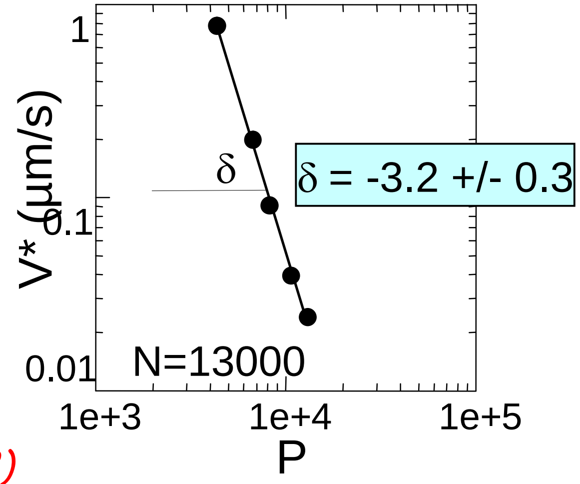




Effects of molecular weights on V*

$$V^* = \frac{kT}{\eta_P a^2 N} \propto N^{-1} P^{-3,3}$$



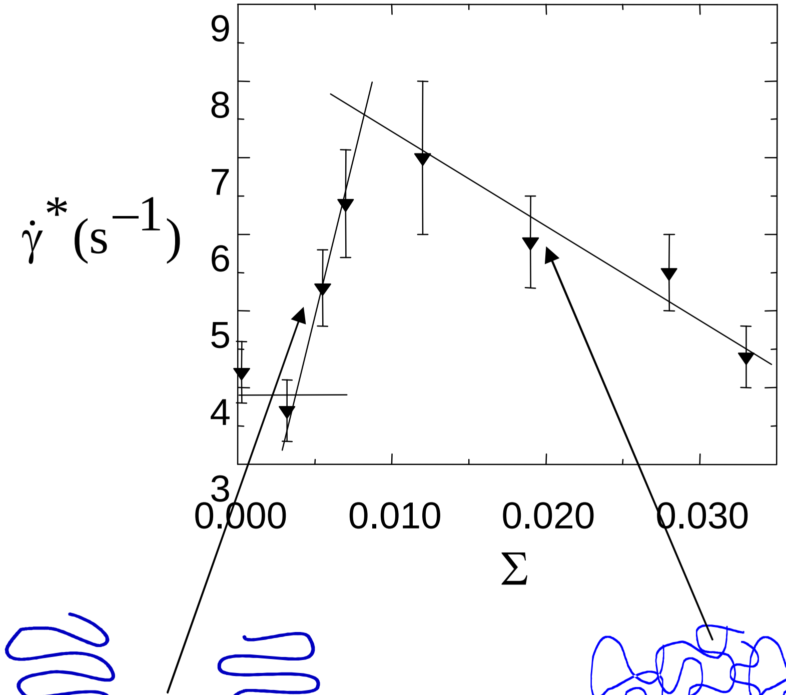


Massey G., Hervet H., Léger L. Europhys Lett 43, 83 (1998)

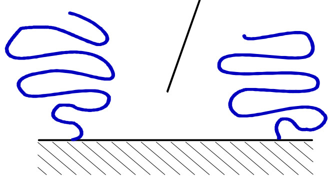
Role of the surface grafting density : Σ

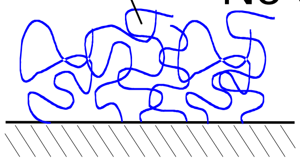
M(P) = 970 kg/mole
M(N) = 96 kg/mole

E. Durliat et al. Europhys. Lett 38, 383 (1997)



$$\dot{\gamma}^* = \frac{\Sigma kT}{a^2 D^*} \propto \Sigma$$





No quantitative predictions

$$\dot{\gamma}^* \propto \Sigma$$

Non independent surface chains :
Easier decoupling: bulk chains expelled from grafted layer
Entaglements inside the grafted layer: less defromable

- Qualitative agreement between model and experiments
- Can we do more than get a qualitative agreement?

Direct measurement of the friction force on one grafted chain, as a function of sliding velocity

Friction force on one chain

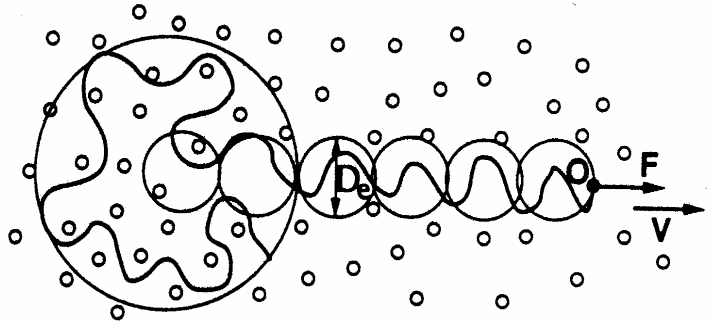
Ajdari et al., Physica A 204 (1994) 17 - 39

One chain Z, pulled out of an elastomer or a melt N, under the force F

Dynamics driven by arm retraction:

$$\tau_{arm}(Z) = \tau_1 Z^2 \exp(\mu Z / N_e)$$

compare D_e/V to τ_{arm}



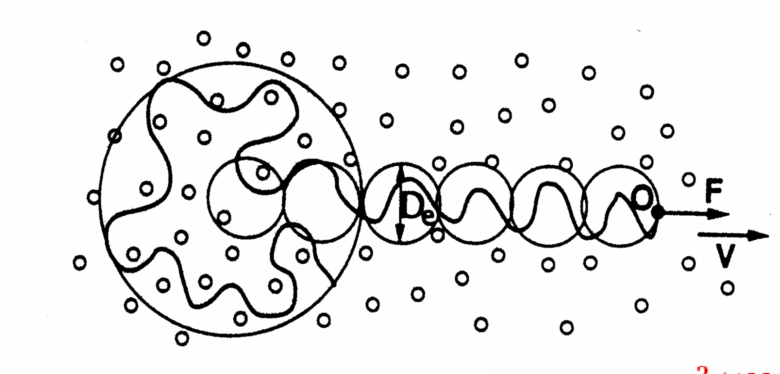
1) $V < V_1 = D_e/\tau_{arm}(Z)$: $F = \frac{kT}{D_e}\frac{V}{V_1}$ chain fully relaxed

2) $V_1 < V < V_2 = D_e/\tau_1 Z^2$: $F = \frac{kT}{D_e} + (Z-q)\zeta_1 V$ relaxed tail, q monomers q(V) such that $v\tau_{arm}(q) = D_e$

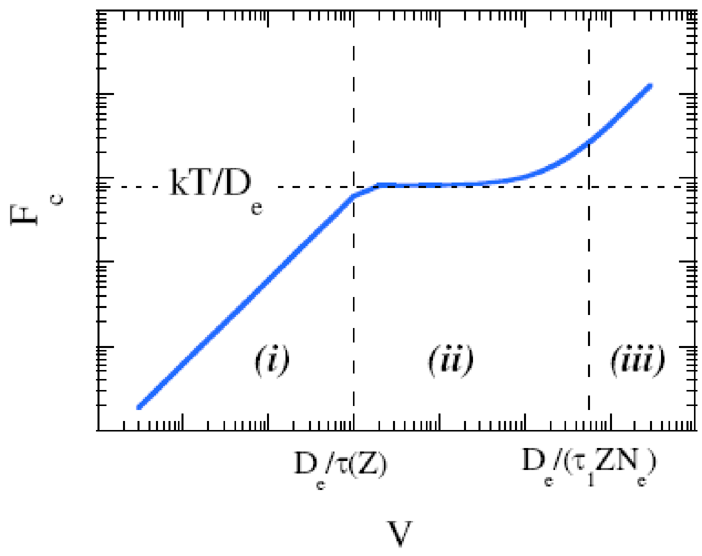
3) $V_2 < V < V_3 = V_2(Z/N_e)^2$: $F = \frac{kT}{D_e} + (Z-q)\zeta_1 V$ Force ≈ V independent

4) $V_3 < V$: $F = Z\zeta_1 V$ ζ_1 monomer friction coefficient

Pull-out friction on one chain



Compare D_e/V to $\tau \sim \tau_1 Z^2 e^{q^2/(N_e Z)}$



$(i)\ F_c \propto V$

$(ii)\ F_c = \frac{kT}{D_e} + (Z - q)\zeta_1 V$

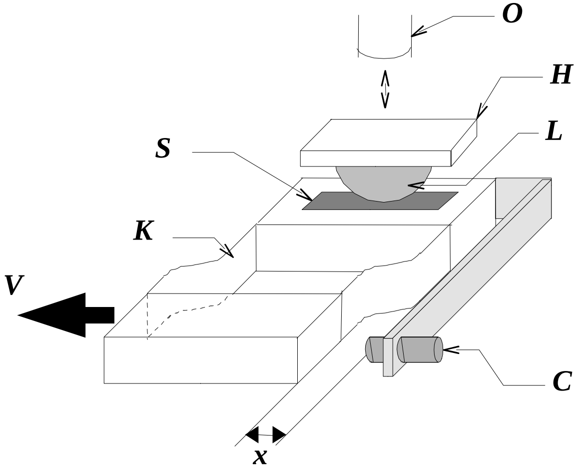
$(iii)\ F_c \propto V$

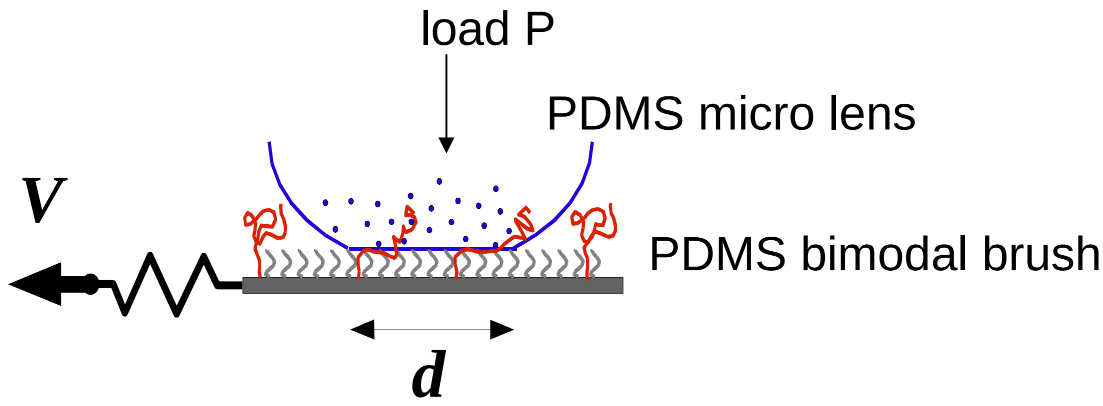
Experimentally $F_c = (\sigma - \sigma_{short})/\Sigma$

Direct measurements of the Friction force : Elastomer – grafted surface

L. Bureau, L. Léger, Langmuir (2004)

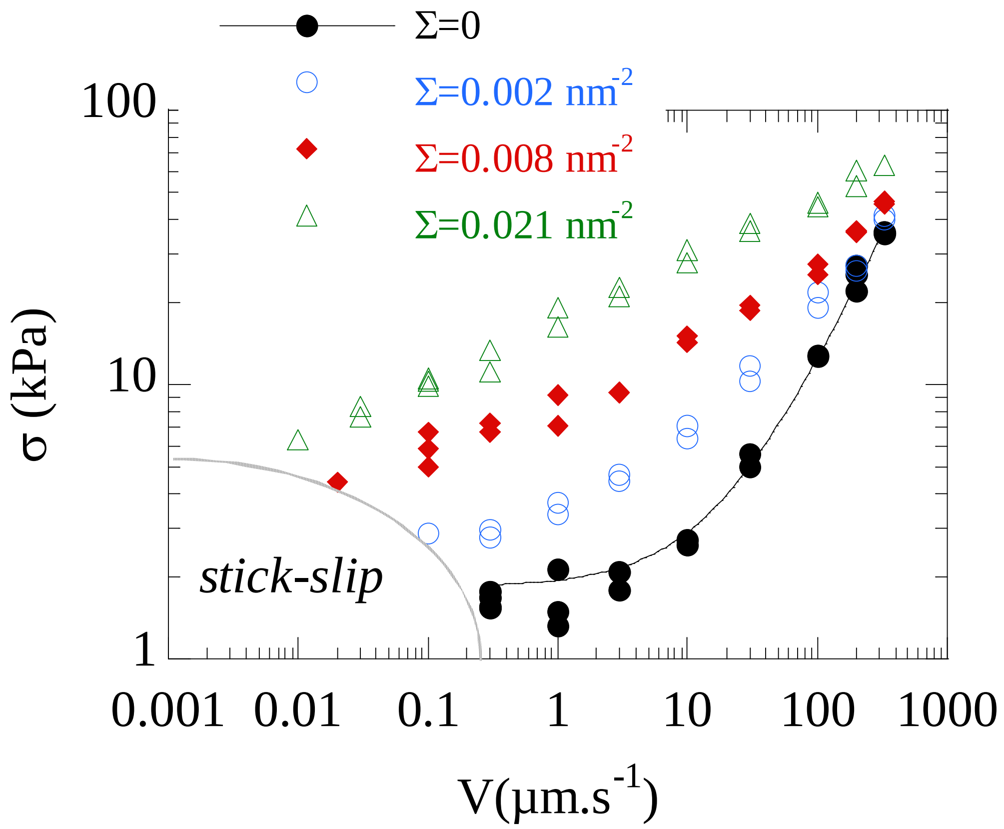
- JKR like experiments (fixed contact area)
- friction force measurement: spring translated at chosen velocity





3 nm/s < V < 330 µm/s; d = 200 – 400 µm; F = 50 µN – 50mN

Results:



M_{wlong} = 114 kg/mole

➢Two regimes:
- $V>V_c$ stationary slip motion
- $V<V_c$ Stick-slip

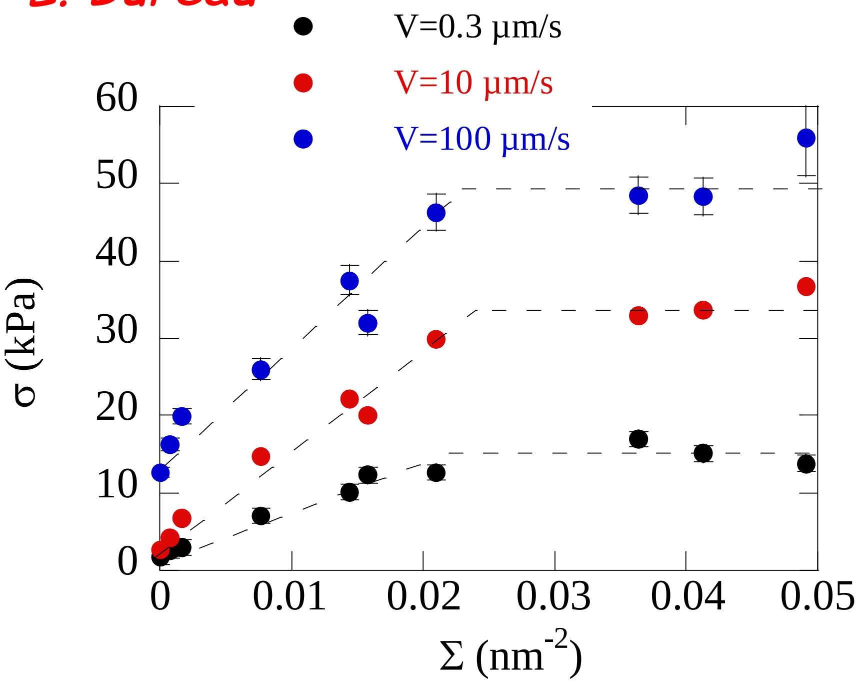
➢ σ(V) non linear

Effects of Surface density

Two regimes in Σ:

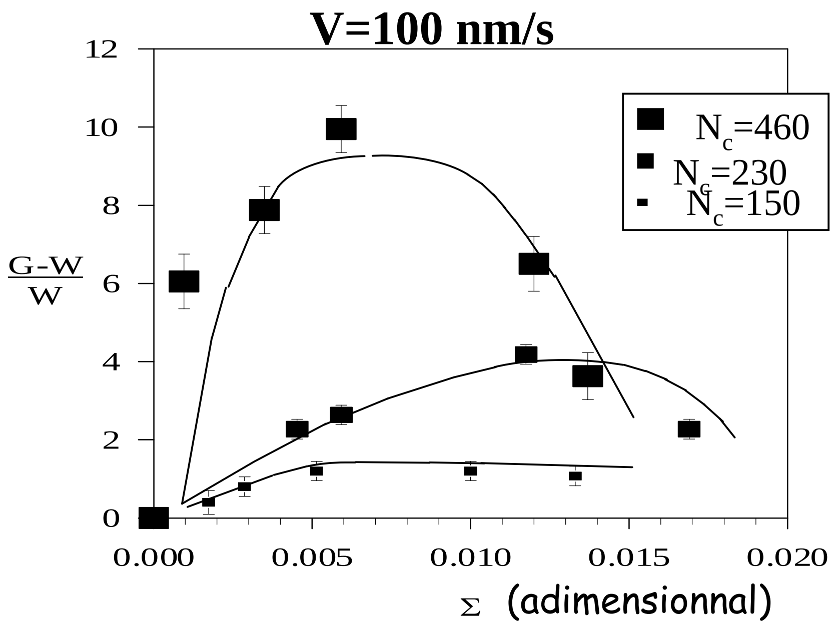
- Low Σ: σ increases linearly with Σ
- High Σ: saturation

L. Bureau



Adhesion: same systems

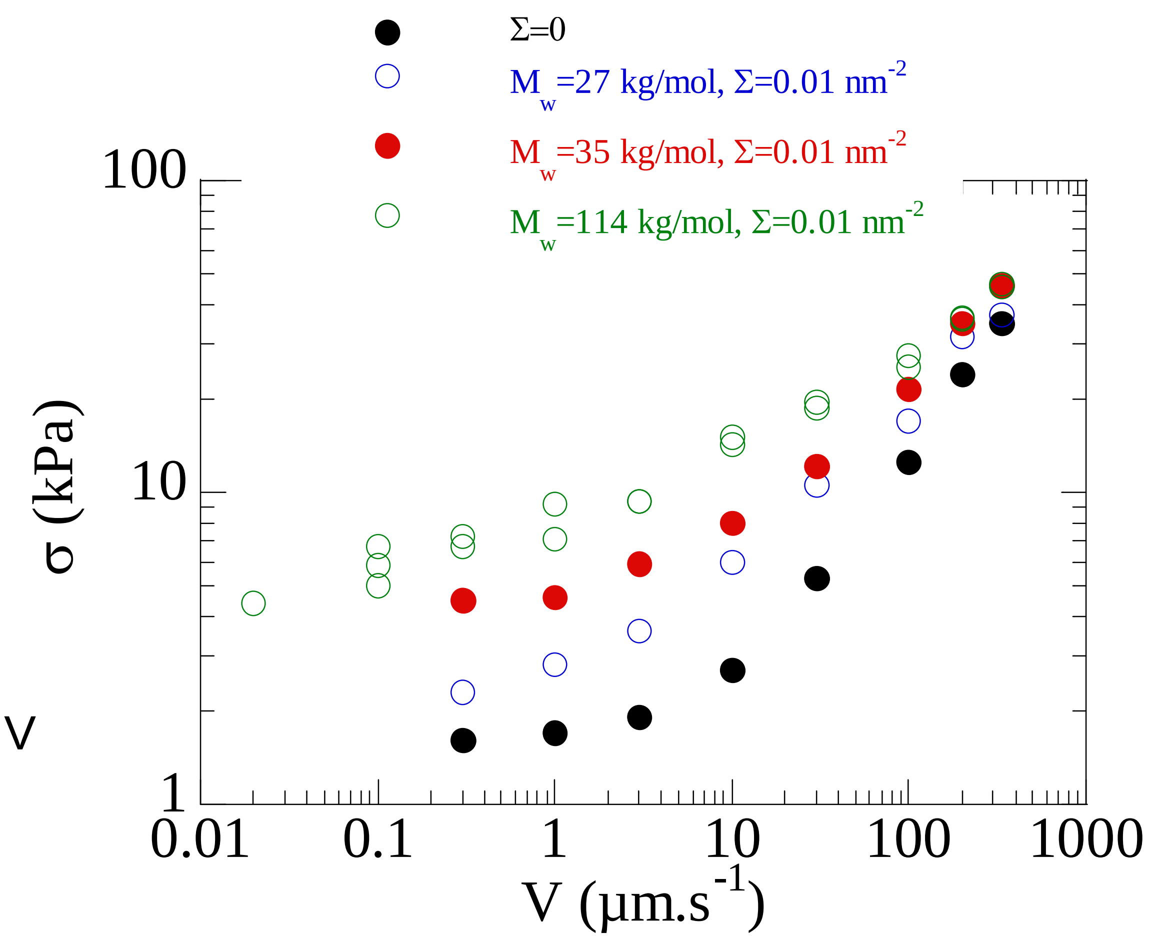
C. Tardivat



a= 0.5 nm

Molecular weight effects

low Σ regime:



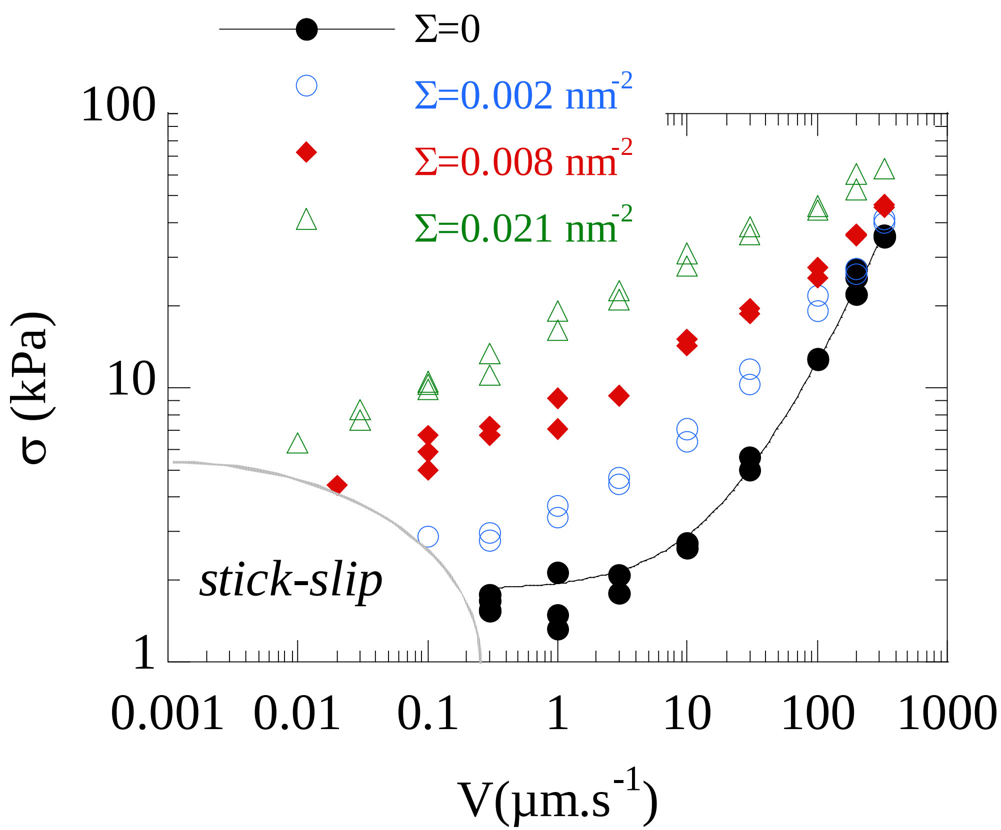
σ increases with M at small V

curves merge at large V

Friction for $\Sigma = 0$

$$\sigma = \sigma_0 + kV$$

$k = 10^8$ Pa.s.m^{-1}



Dense layer of short chains:
no entanglements:

monomer –monomer friction

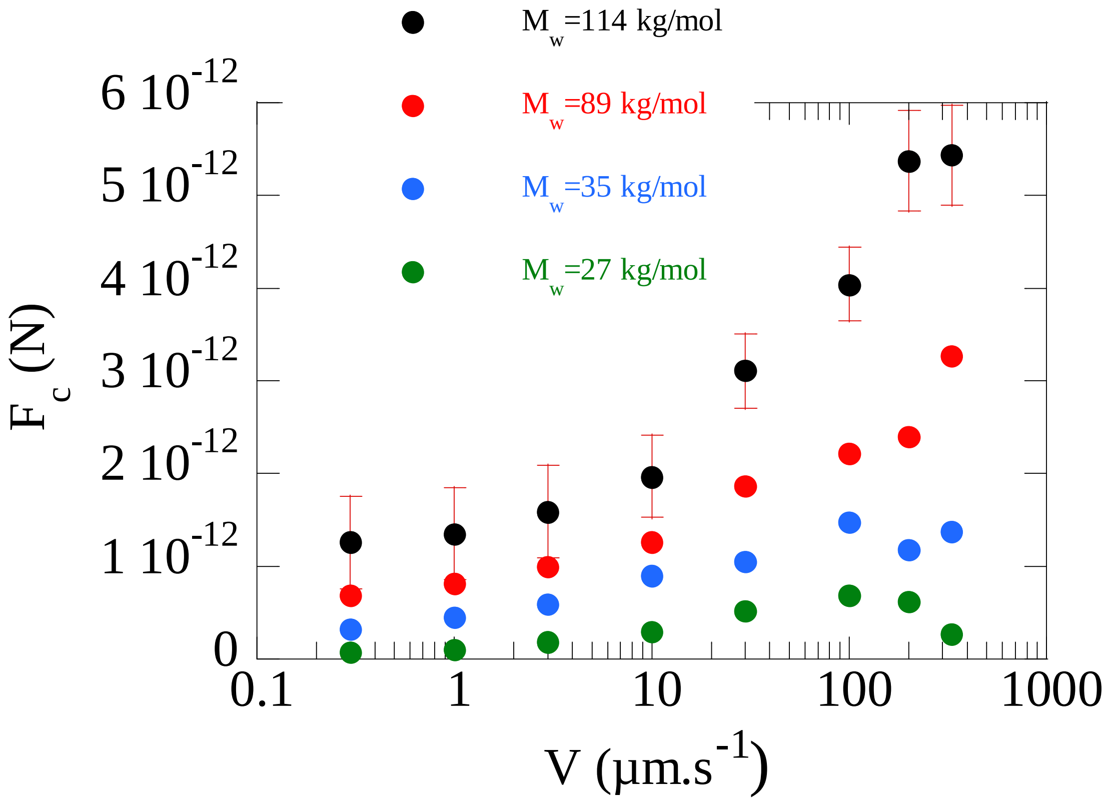
$\sigma = \sigma_{mono} = \zeta_1 V/a^2$
$\zeta_1 = ka^2 = 2.5.10^{-11}$ N.s.m^{-1}
compared to
$\zeta_1 = 10^{-11}$ N.s.m^{-1} (self diffusion)

⇩

OK with monomer – monomer friction

Experiments: Friction Force on one connector Fc

Λοω Σ regime: $$\sigma(V) = \sigma_{\Sigma=0}(V) + \Sigma F_c(V)$$



two different Σ for each M

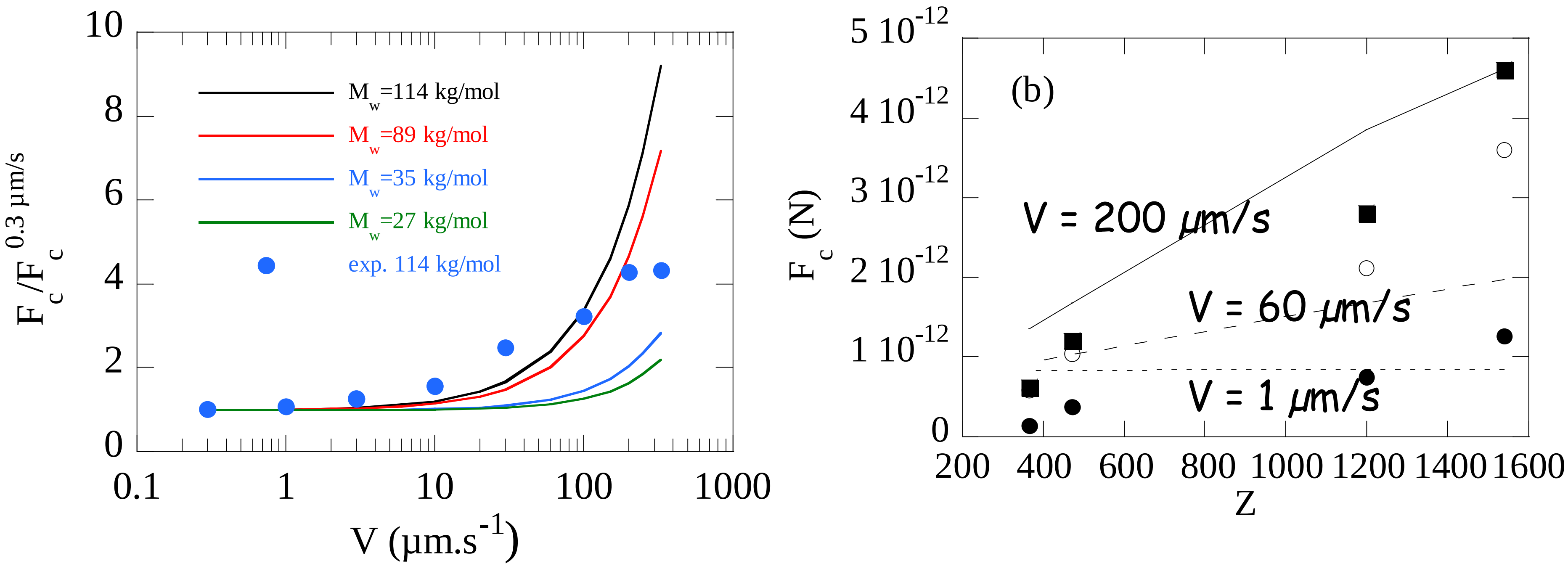
Σ independent†

$F_1 = kT/D_e \approx 8.10^{-13}$N

quantitative agreement with F_c(0,3 µm/s)

Molecular weight dependence at low V?

Comparison with Ajdari et al prediction



quantitative agreement, no adjustable parameter

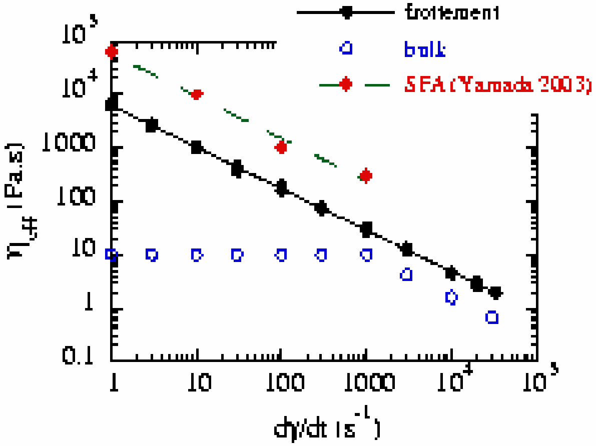
Chain pull out governs friction at low Σ

Friction mechanisms at large Σ

Chains are expelled from the elastomer at large enough Σ
(swelling elasticity of the elastomer, *P.G. de Gennes C.R. acad Sc. Paris 1994*)

$$\sigma \approx V^{0.2}$$

$$\eta_{eff} = \sigma h / V$$



Confined entangled layer of chains tethered to the surface,
thickness h, submitted to shear

σ(V) gives access to the nano-rheology of
the confined layer of tethered chains

Friction mechanisms: what have we learn?

- Tethered polymer chains deeply affect elastomer or melt– solid friction
- As soon as interdigitation is possible, the pull out mechanism leads to non linear frictions regimes, with transitions between regimes characterized by a central regime where the friction force is independent of the velocity
- Quantitative agreement with Adjdari et al. model for independent tethered chains
- It is then possible to design surfaces with adjusted friction
- At large grafting densities, the chains form a confined layer out of the elastomer. Macroscopic friction force measurements can lead to characterization of the rheology in the confined layer

Closely related problems

- Sliding molecules *at* polymer/polymer interfaces: *(weakly incompatible polymers)*
  F. Brochard Wyart, P.G. de Gennes, C.R. Acad. Sci. Paris, 317 serie II, 13 – 17 (1993)

- Supressing slippage at incompatible polymer interfaces with diblock copolymers:
  F. Brochard Wyart, P.G. de Gennes, P. Pincus, C.R. Acad Sci. Paris 314 serie II, 873 – 878 (1992)

- Nanorheology of polymer melts between grafted surfaces:
  F. Brochard Wyart, P.G. de Gennes, C.R. Acad. Sci. Paris, 317 serie II, 449 - 453 (1993)

- Wetting and de-wetting:
  Brochard F., de Gennes P.G., J. Phys. Lett. 45, L597 (1994)
  F. Brochard-Wyart, P.G. de Gennes, H. Hervet, C. Redon, Langmuir 10, (1994) 1566 – 1572
  Redon C., Brochard, F. Macromolecules 27, 468 – 471 (1994)
  Brochard F., Redon, C., Sykes C., A.R. Acad Sci. Paris 314, 19 (1992)

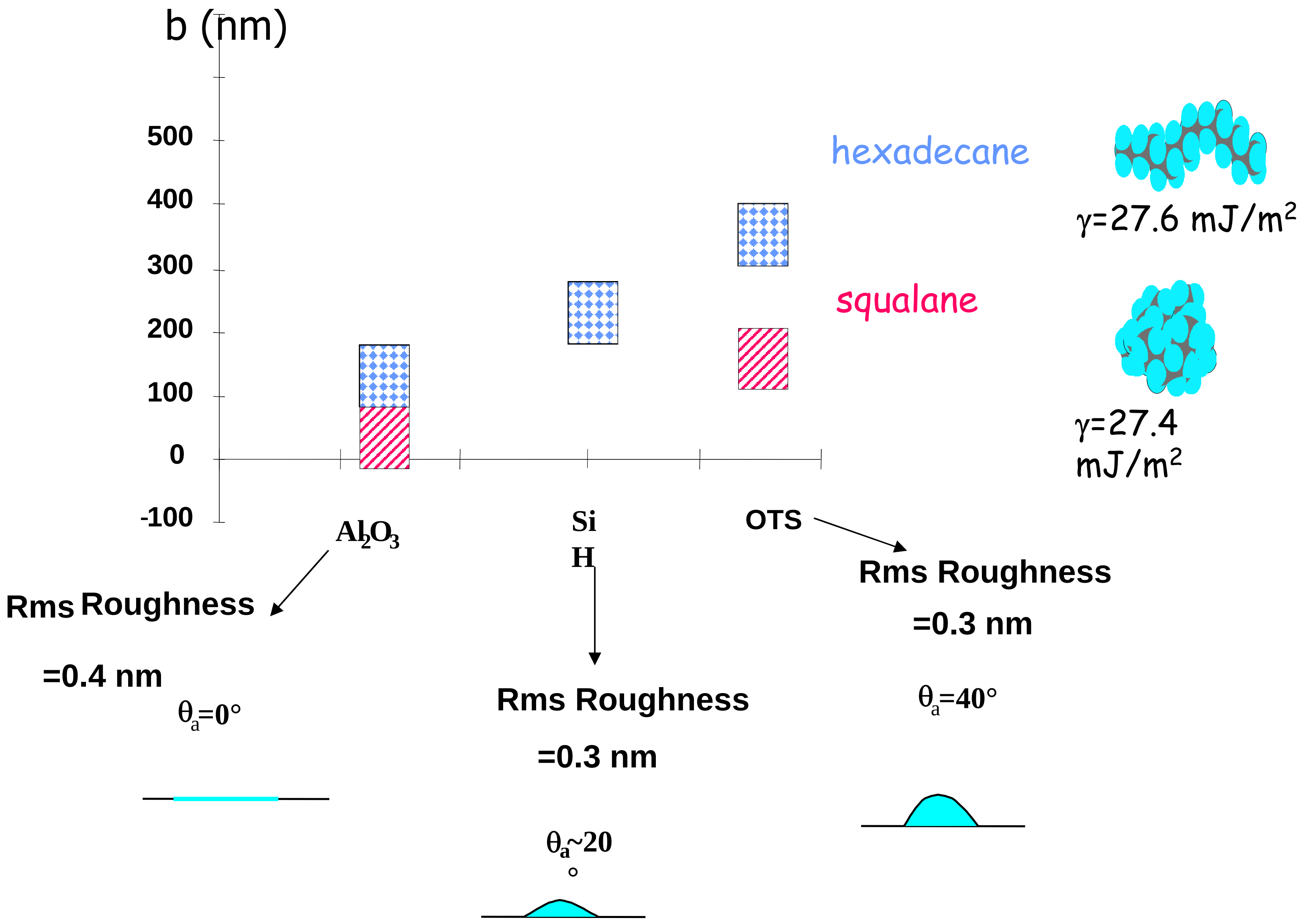
- Correlation to adhesion behavior:
  B. Z. Newby, M. Chaudhury, Langmuir 13, (1997) 1805 – 1809
  H. Brown, Faraday Discuss. 98, (1994) 47 – 54; Science, 263, 1411 (1994)

- Further theoretical work:
  Y. M. Joshi, A. K. Lele, J. Rheol. 46 (2002) 427: wall slip at high surface coverage
  J. L. A. Dubbeldam, J. Molenaar, Phys. Rev. E 67 011803 (2003): self consistent dynamics of wall slip

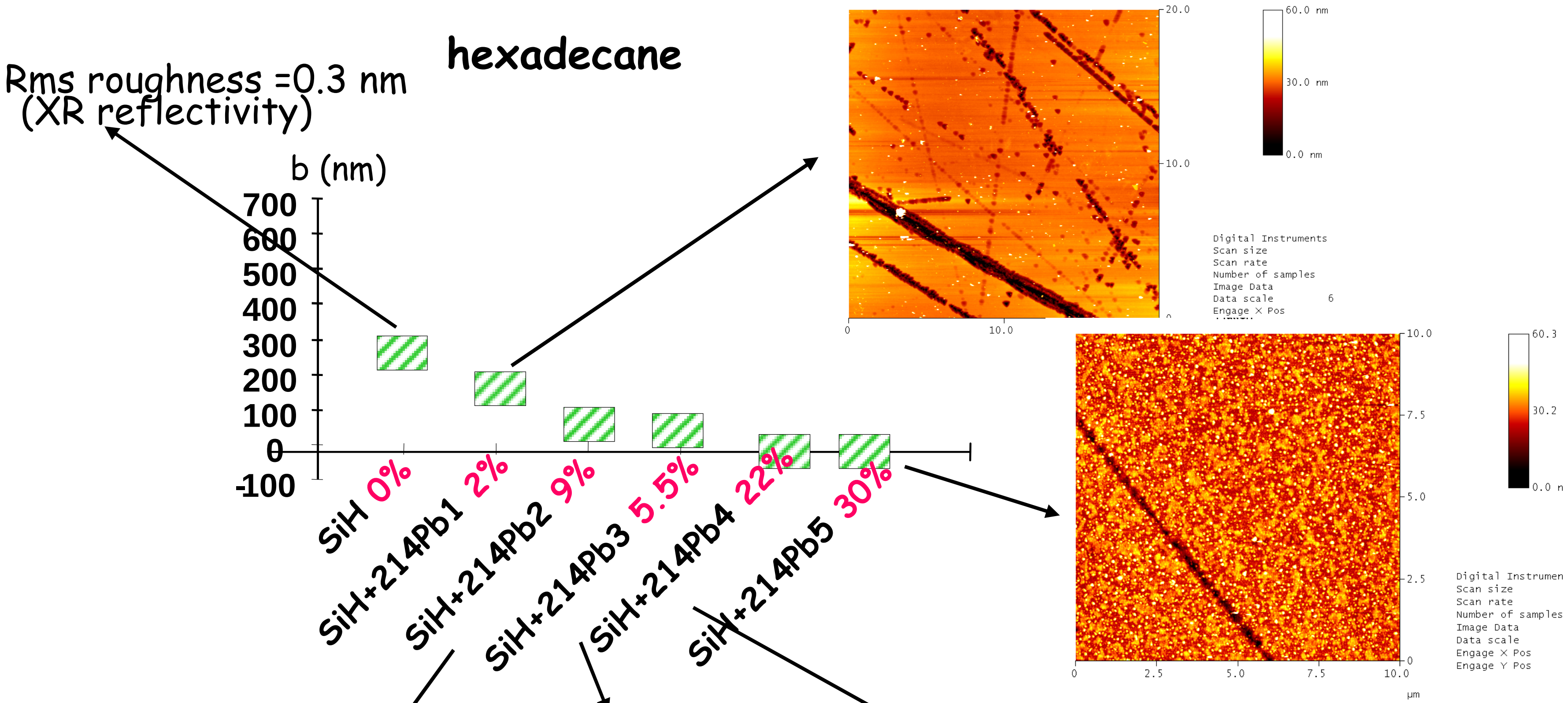
Open questions

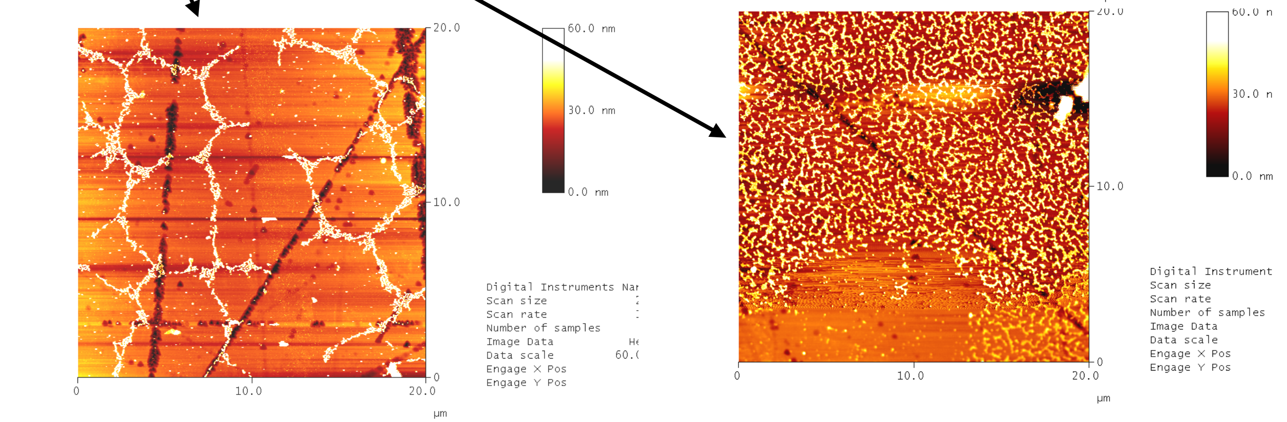
- Friction at grafted surfaces – polymer solution interfaces: shear banding?
- What happens with polyelectrolytes, with weakly associating polymers
- Melt fracture of entangled polymer melts: *P.G. de Gennes, Eur.Phys.J.E 23 3-5 (2007)*
  possible explanation of discontinuities in the flow field
- What finally fixes the value of k, the friction coefficient at the surface?
  experiments of near field laser velocimetry in simple fluids

. Schmatko et al. PRL 94, 244501 (2005)



High sensitivity to nano-roughness





Schmatko et al. Langmuir (2006)