Surfactant/polymer boundary lubricant films: passive and active control of friction and adhesion

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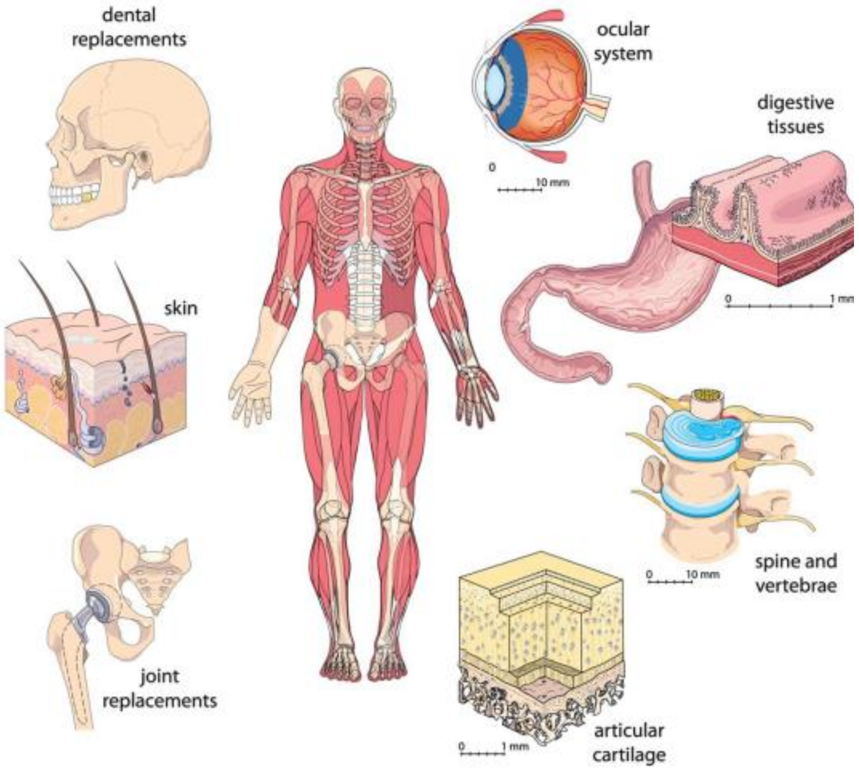
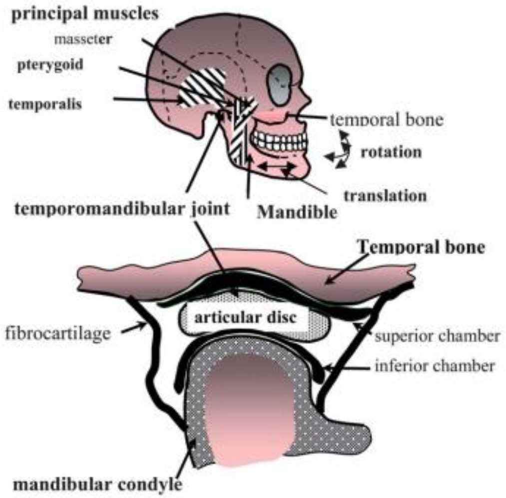
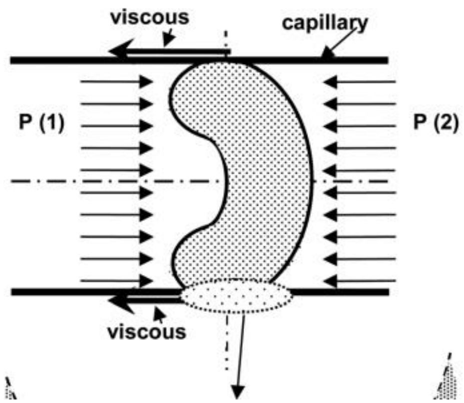
GDR TACT. November 2020



Angelini, *Faraday Discuss.*, 2012



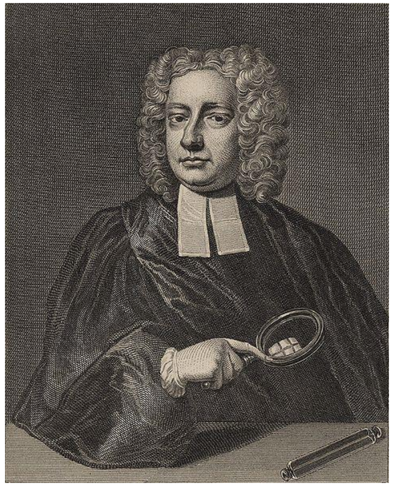
Dowson, *Faraday Discuss.*, 2012



Friction…

- …is not a fundamental force
- …is present only if a tangential movement (or a tendency to such motion) occurs
- …is a complex phenomena, with multiple intermingled causes

Objective: to understand the fundamental mechanisms of energy dissipation



Tho' there are ſo many Circumſtances in the Friction of Bodies, that the ſame Experiment does not always ſucceed with the ſame Bodies, ſo that a Mathematical Theory cannot be eaſily ſettled; yet we may deduce a Theory ſufficient to direct us in our Practice from a great Number of Experiments, always taking a Medium between Extremes.

"A course of Experimental Philosophy", J.T. Desaguliers, 1745

Friction… is much diversified, according to circumstances, and can be discovered in any particular case, only by experiments conducted in a scale of sufficient magnitude. *"Elements of natural philosophy"*, Sir John Leslie, 1829

To consider…

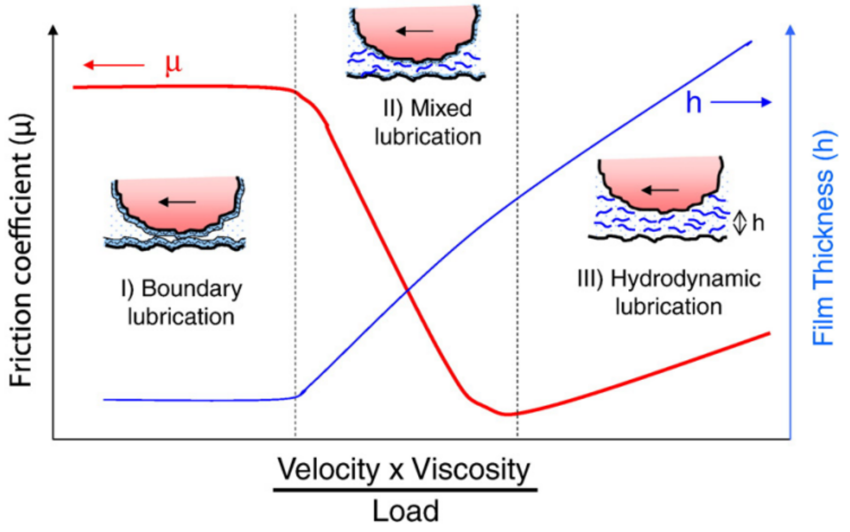
- 3 Bodies: two surfaces+everything in between
- Surfaces/contact
    - Roughness and chemical heterogeneity
    - Elastic/plastic deformation
- Interface
    - Lubricant
    - Adhesion
- Characteristic times (system/external stimuli)
- History (wear/tribochemistry)

Outline

- Aqueous boundary lubrication:
  - Mechanisms responsible for friction (rigid walls+boundary lubricant)
  - Compliant boundaries: static and dynamic effects

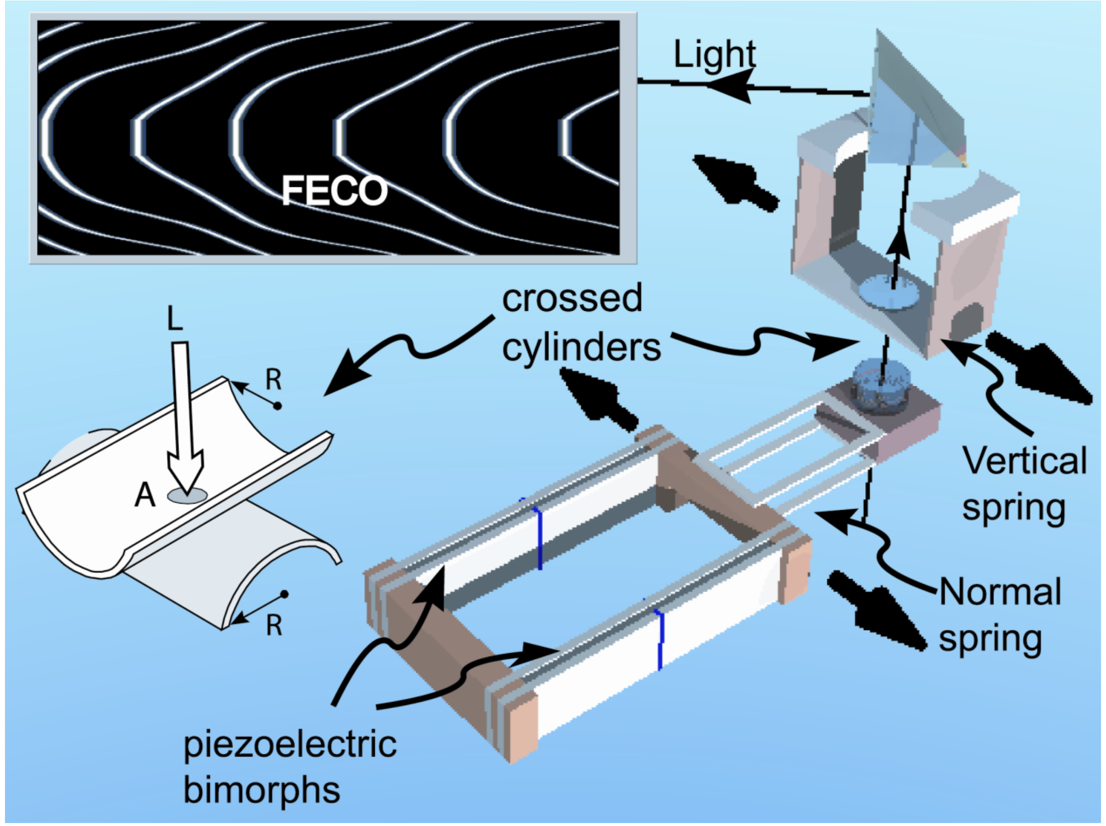
- Active control of surface properties:
  - Electro-responsive lubrication

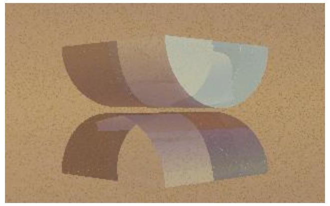
Lubrication: Stribeck's curve

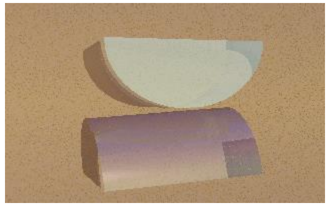


Coles et al, *Curr. Opin. Coll. Interf. Sci.*2010

Surface Forces Apparatus-Nanotribometer







Richetti, Drummond, Images de la Physique 2005

Boundary lubrication: Energy Dissipation

- Adhesive Surfaces: rupture of adhesive nanojunctions
- Wall/boundary lubricant deformation: thermal activation and multistability
- Wear
- Rheology of lubricant film

"It is found by experience that the flat Surface of Metals or other Bodies may be so far polished as to increase Friction; and this is a mechanical Paradox; **but the Reason will appear when we consider that the Attraction or Cohesion becomes sensible as we bring the Surfaces of Bodies nearer and nearer to Contact.**"

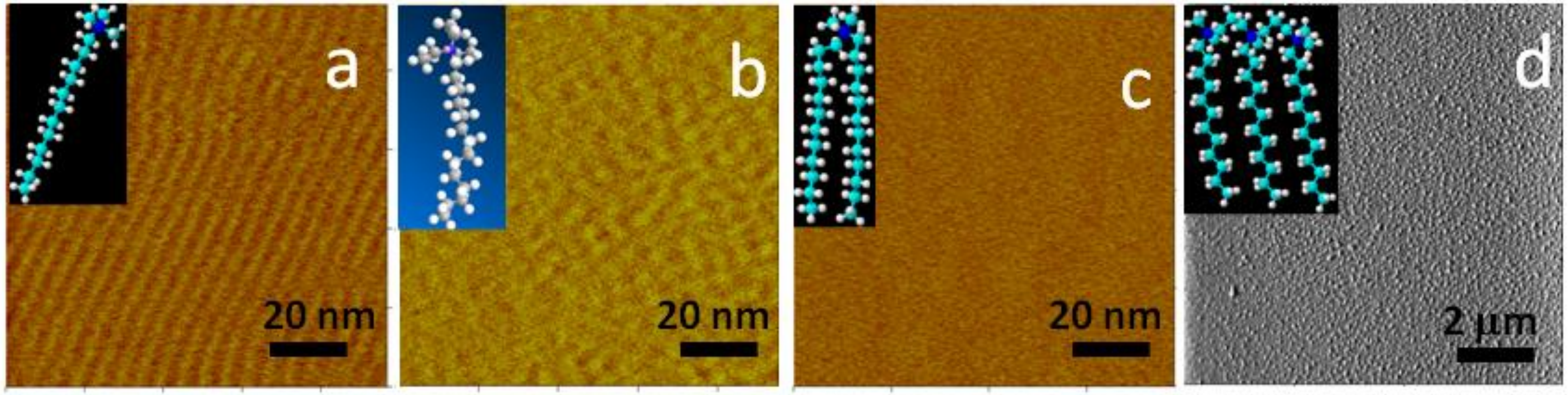
"*A course of Experimental Philosophy*", J.T. Desaguliers, 1745

Adhésion : Formation et cisaillement de jonctions

"Le frottement ne peut venir que de l'engrenage des aspérités des surfaces, et la cohérence ne doit y influer que très peu : car nous trouvons que le frottement est, dans tous les cas, à peu près proportionnel aux pressions, et indépendant de l'étendue des surfaces... **Nous trouvons cependant que cette cohérence n'est pas précisément nulle** "

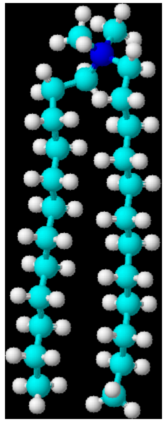
"*Théorie des machines simples, en ayant égard au frottement de leurs parties et à la roideur des cordages*".
Charles-Augustin de Coulomb, 1785

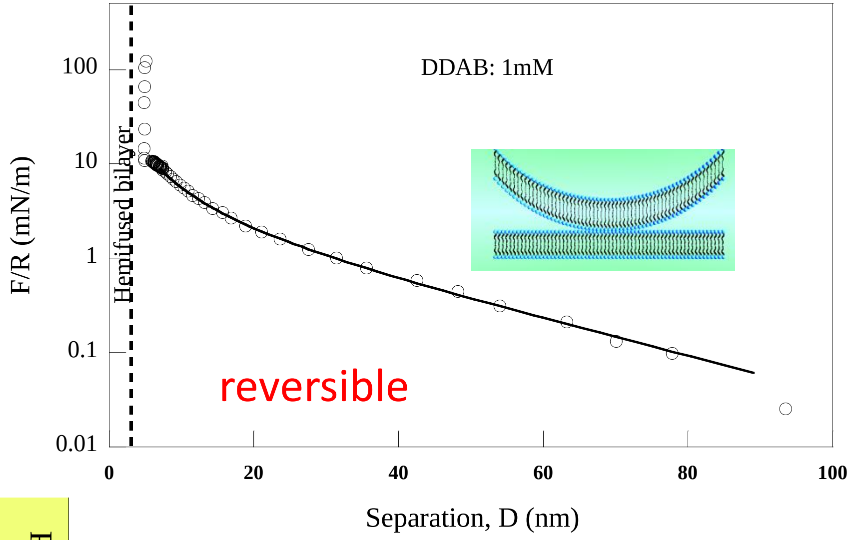
Self-assembled surfactant layers

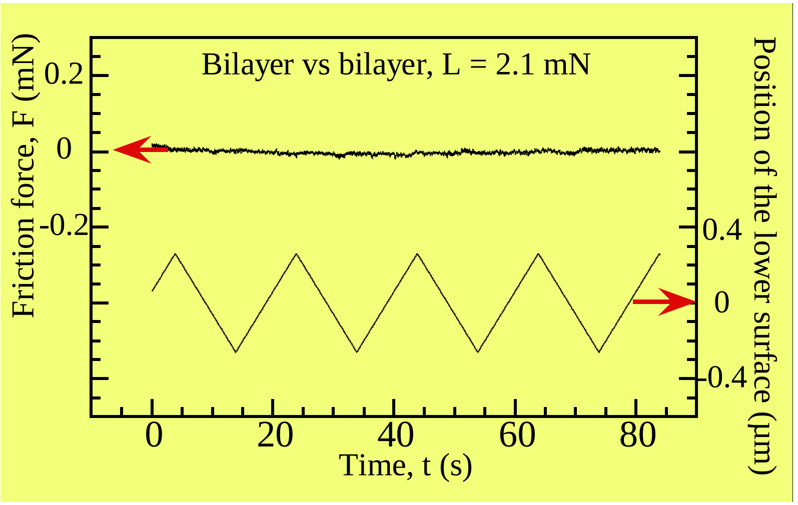


Cylinder/globular: DTAB, TTAB, CTAB
Bilayer: DDAB, DMDAB, 12-3-12-3-12 trimer, trimer + nonionic, CTAC, 12-3-12 gemini, DDAB+ nonionic

Self-assembled surfactant bilayers





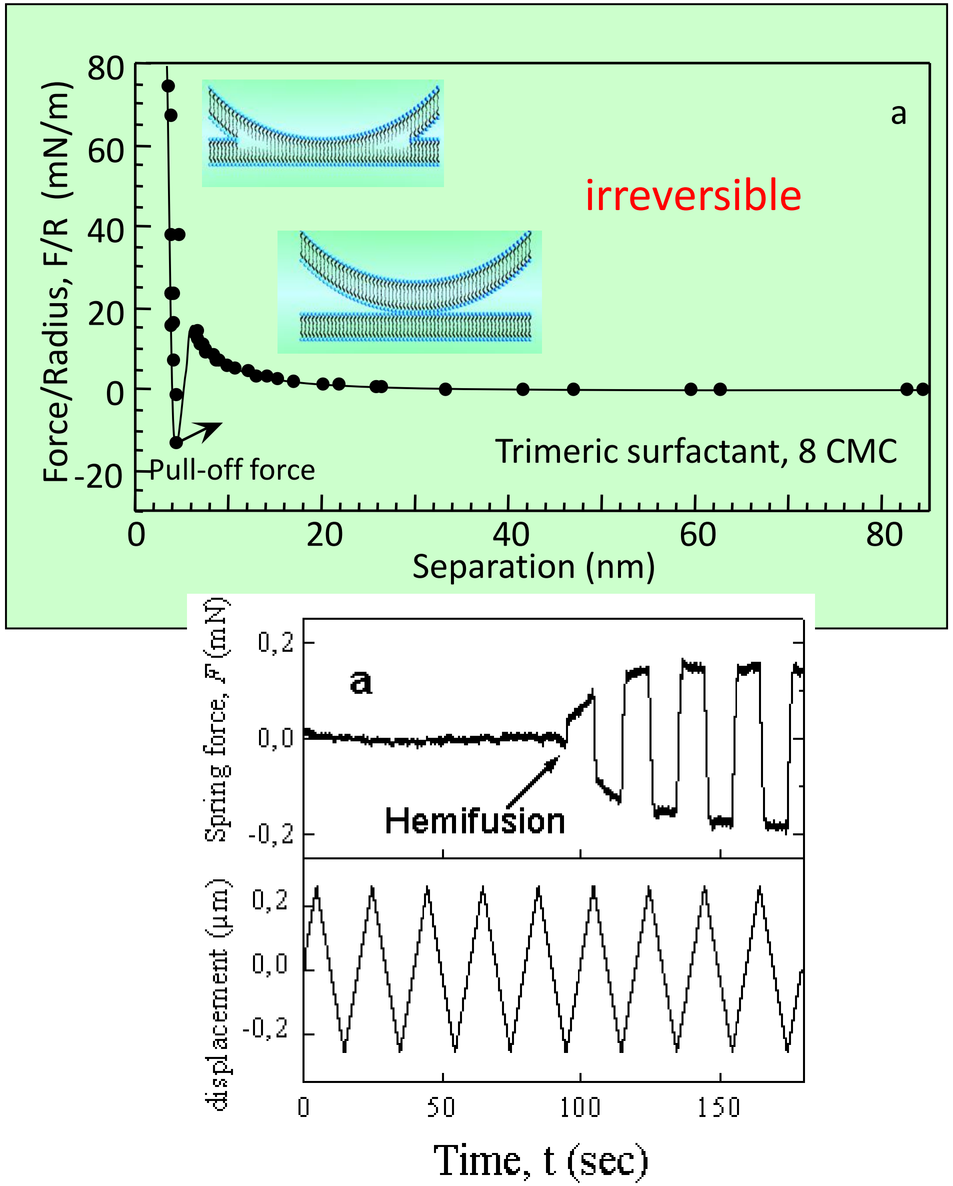


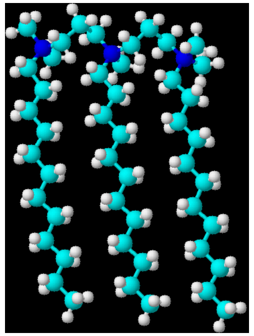
G. Warr

E. Wanless

Blom, Drummond, Warr, Wanless, Richetti, *Langmuir*, 2005

Hemifusion: adhesive contact

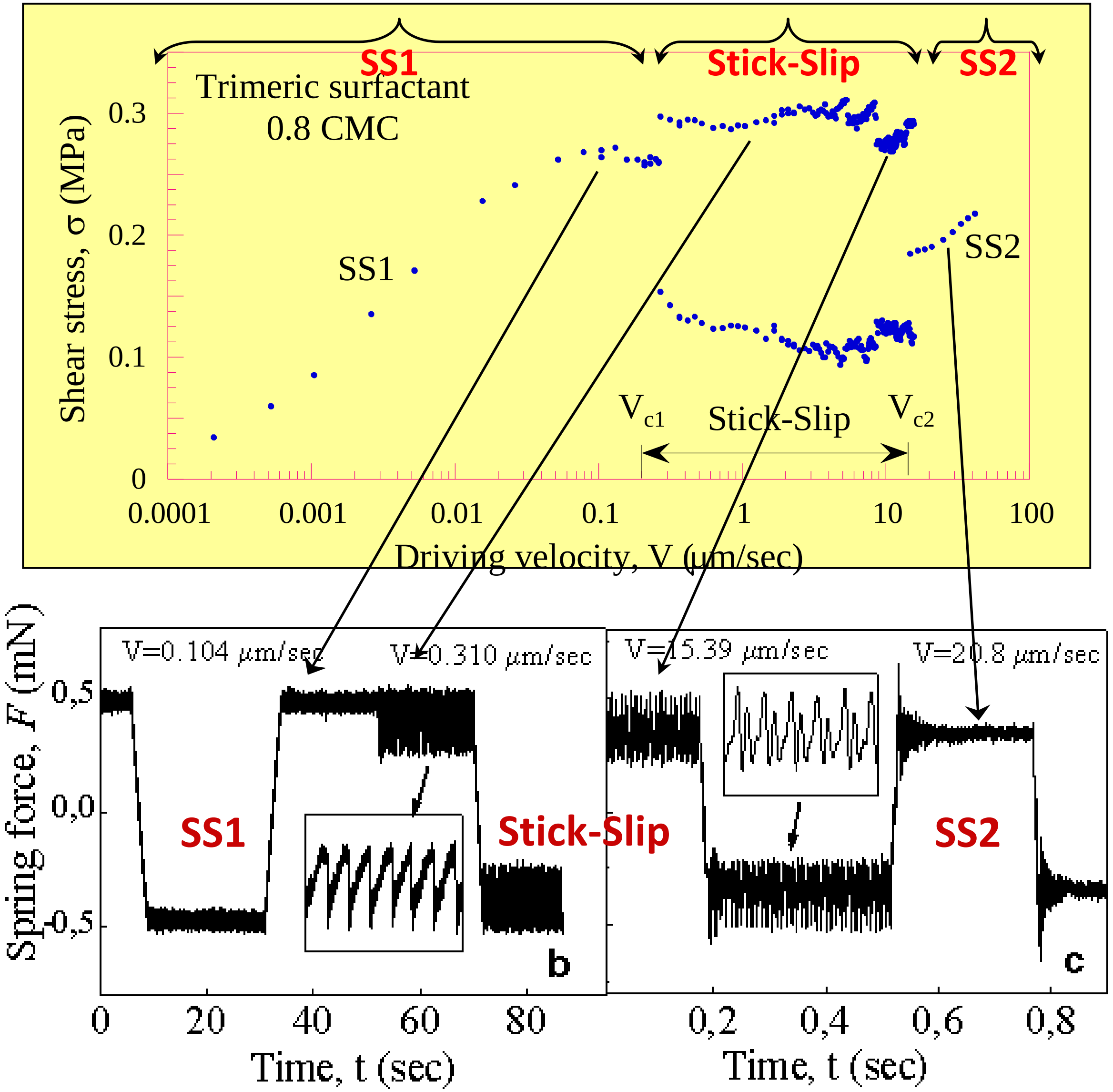




J. Israelachvili

Richetti, Drummond, In, Zana and Israelachvili, *Europhys. Lett.* 2001

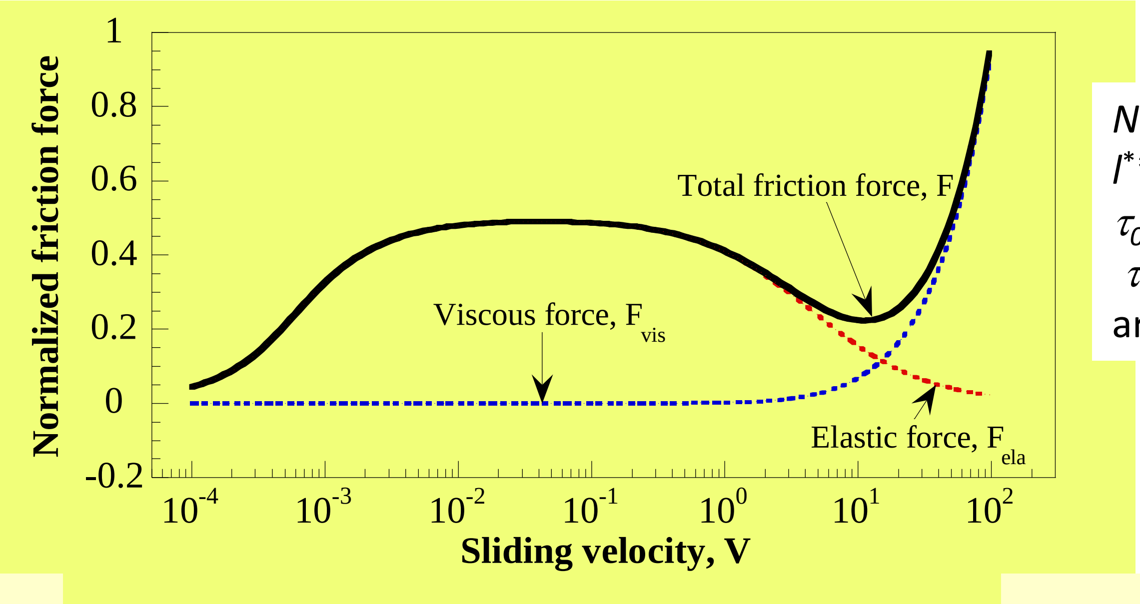
Hemifusion: sliding curve



Drummond, Elezgaray and Richetti, *Europhys. Lett.* 2002

Constitutive friction law

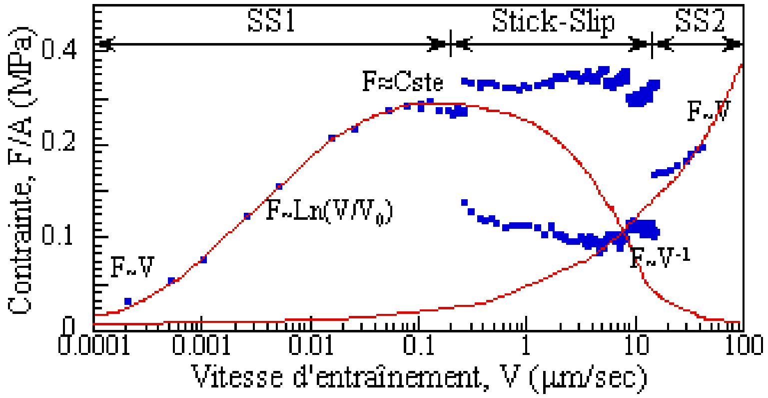
$$F(V) = \phi(V)N\, f_{Elas}(V) + (1-\phi(V))N\, f_{Vis}(V)$$



Nanojunctions
$l^{**} \approx 0.5$ nm
$\tau_0 \approx 0.1$ s
$\tau \approx 100$ µs
area ≈ 10 nm²

SS1
Equilibrium
adhesive contact

SS2
Out-of-equilibrium
non-adhesive contact



Drummond, Israelachvili and Richetti, *Phys. Rev. E* 2003

"Théorie des machines simples, en ayant égard au frottement de leurs parties et à la roideur des cordages".
Charles-Augustin de Coulomb, 1785

l'avons trouvé par nos expériences (*art.* 55 *et suiv.*) : lorsque le traîneau sera mu avec une vitesse quelconque, pour lors, comme les cavités de la surface du métal ont de l'étendue, relativement à la grosseur des fibres du bois, les fibres, après avoir passé sur les sommités des inégalités des surfaces métalliques, se relèveront en partie comme des faisceaux de ressort. Il faudra donc les plier de nouveau, pour leur faire franchir l'inégalité suivante. Plus la vitesse sera grande, plus il faudra plier de fois les fibres : ainsi, le frottement doit croître suivant une loi de la vitesse; mais cependant on les pliera sous un moindre angle, à mesure que la vitesse augmentera, parce qu'en passant d'une sommité à l'autre, les fibres n'ont pas le temps de se redresser en entier.

Fig. 8.

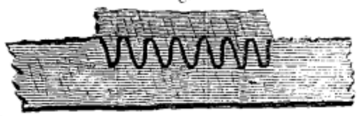


Fig. 9.

Fig. 10

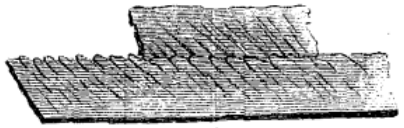


Fig. 13. N° 1.

Fig. 11

Fig. 13 N° 2.

Wall/boundary lubricant deformation

"To explain friction it is necessary to suppose the existence of some irreversible stage in the passage of one atom past another, in which heat energy is developed at the expense of external work"
Tomlinson 1929

Microscope. Friction is, therefore, commonly explained on the principle of the inclined plane, from the effort required to make the incumbent weight mount over a succession of eminences. But this explication, however currently repeated, is quite insufficient. The mass which is drawn along is not continually ascending; it must alternately rise and fall, for each superficial prominence has a corresponding cavity; and since the horizontal boundary of contact is supposed to be horizontal, the total elevation will be equal to their collateral depressions. Consequently, though the actuating force might suffer a perpetual diminution in lifting up the weight, it would, the next moment, receive an equal increase by letting it down again; and those opposite effects, destroying each other, would have no influence whatever on the general motion.

" Adhesion appears still less capable directly of explaining the source of Friction. A perpendicular force acting on a solid, can evidently have no effect to impede its advance; and though this lateral force, owing to the unavoidable inequalities of contact, must be subject to a certain irregular obliquity, the balance of chances must on the whole have the same tendency to accelerate as to retard the motion. If the conterminous surfaces were hence to remain absolutely passive, no Friction could ever arise. Its existence betrays an unceasing mutual change of figure, the opposite planes, during the passage, continually seeking to accommodate themselves to all the minute and accidental varieties of contact. The one surface, being pressed against the

tion. If the conterminous surfaces were hence to remain absolutely passive, no Friction could ever arise. Its existence betrays an unceasing mutual change of figure, the opposite planes, during the passage, continually seeking to accommodate themselves to all the minute and accidental varieties of contact. The one surface, being pressed against the
other, becomes, as it were, compactly indented, by protruding some points and retracting others. This adaptation is not accomplished instantaneously, but requires very different periods to attain its *maximum*, according to the nature and relation of the substances concerned. In some cases, a few seconds are sufficient; in others, the full effect is not produced till after the lapse of several days. While the incumbent mass is drawn along, at every stage of its progress, it changes its external configuration, and approaches more or less to a strict contiguity with the under surface. Hence the effort required to put it first in motion, and hence too the decreased measure of Friction, which, if not deranged by adventitious causes, attends generally an augmented rapidity.

" Friction, then, consists in the force expended in raising continually the surface of pressure by an oblique action. The upper surface travels over a perpetual system of inclined planes; but the system is ever changing, with alternate inversion. In this act, the incumbent weight makes incessant, yet unavailing efforts to ascend; for the moment it has gained the summits of the superficial prominences, these sink down beneath it, and the adjoining cavities start up into elevations presenting a new series of obstacles which are again to be surmounted; and thus the labours of Sisyphus are realized in the phenomena of Friction.

Elements of natural philosophy

Sir John Leslie

(1829)

Wall/boundary lubricant deformation

Robert Hooke

Dr. HOOK's *Diſcourſe of Carriages before the* Royal Society, *on* Feb. 25. 1684-5. *with a Deſcription of* Stevin's *Sailing Chariot, made for the Prince of* Orange.

NEXT, we are to conſider, what Impediment to its Motion, a Wheel, thus roll'd upon a Floor, receives from that Floor. There may be two impediments then, that a Wheel, ſo roll'd, may receive from a Floor according to the Nature thereof. The firſt and chiefeſt, is the yielding, or opening of that Floor, by the Weight of the Wheel ſo rolling and preſſing; and the ſecond, is the ſticking and adhering of the Parts of it to the Wheel; to which two may be referr'd all others, all of which proceed from the yielding or giving Way of the Parts of the Floor, and the not returning again to their bended Poſture; for, if the Floor be perfectly hard (as alſo the Parts of the Wheel) tho' it be very unequal, yet is there little or no Loſs, or conſiderable Impediment to be accounted for; for whatever Force is loſt, in raiſing or making a Wheel paſs over a Rub, is gain'd again by the Wheel's deſcending from that Rub, in the ſame Nature as a Ship on the Sea is promoted by the deſcending down of a Wave, as much as impeded by its aſcending, or a *Pendulum* is promoted by its Deſcent, as much as impeded by its Aſcent.

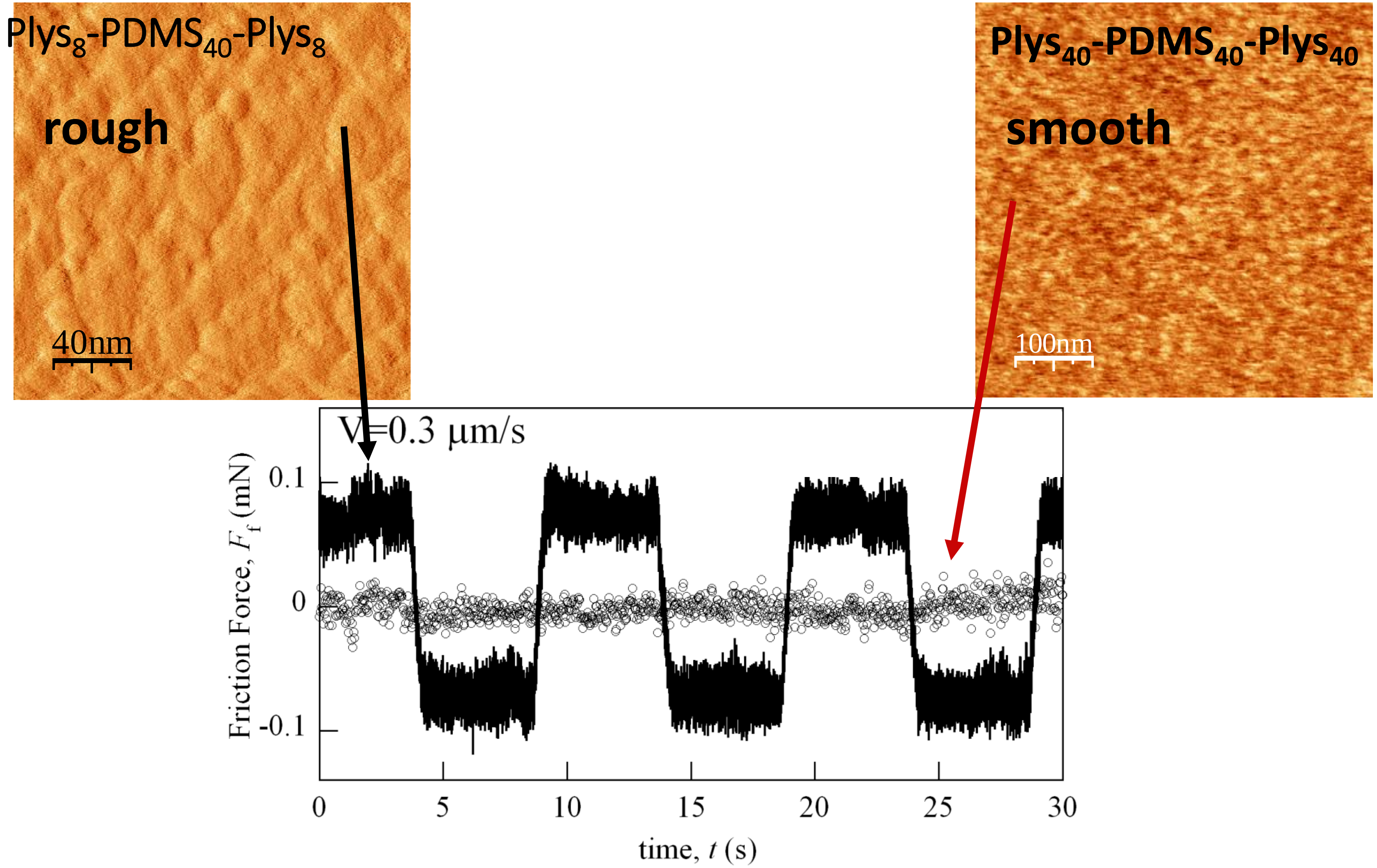
NOR is the yielding of the Floor any Impediment, if it returns and riſes againſt the Wheel, for the ſame Reaſon; but the yielding, or ſinking of the Floor, and its not returning again, is the great

great Impediment from the Floor; for ſo much of Motion is loſt thereby, as there is Force requiſite to ſink ſuch a Rut into the ſaid Floor by any other Means; whether by Weight, Preſſure or thruſting directly down, or any Ways obliquely.

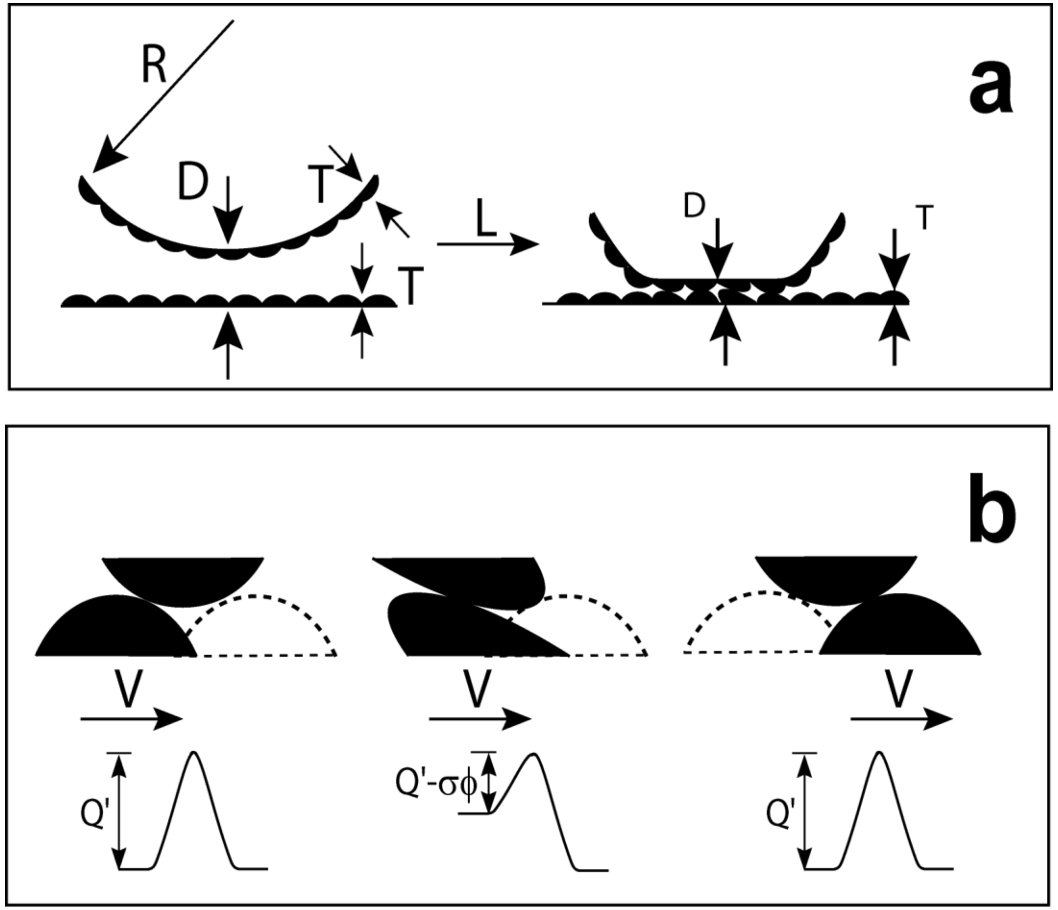
AND it may alſo be calculated, by drawing on the Wheel, whoſe Weight, at the mean Time, ſinks the Floor it rolls over. Either Way it will be eaſy to bring it under Calculation, which is the Deſign of this Diſcourſe.

THE Second Impediment it receives from a Floor, or Way, is the ſticking and adhering of the Parts of the Way to it; for by that Means, there is a new Force requiſite to pull it off, or raiſe the hinder Part of the Wheel from the Floor, or Way, to which it ſticks, which is moſt conſiderable in moiſt clayie Ways, and in a broad rimm'd Wheel. For in ſuch Ways, the Wheel doth not only loſe a Part of its Motion, by the yielding and preſſing of the Clay againſt the fore Parts of the Wheel, but by the cleaving to, and holding of it to the hinder Parts, which makes all Carriages move very ſluggiſhly and heavily in ſuch Ways.

Non-adhesive contact: Self-assembled copolymers



Drummond, Rodríguez-Hernández , Lecommandoux , Richetti. *JCP*, 2007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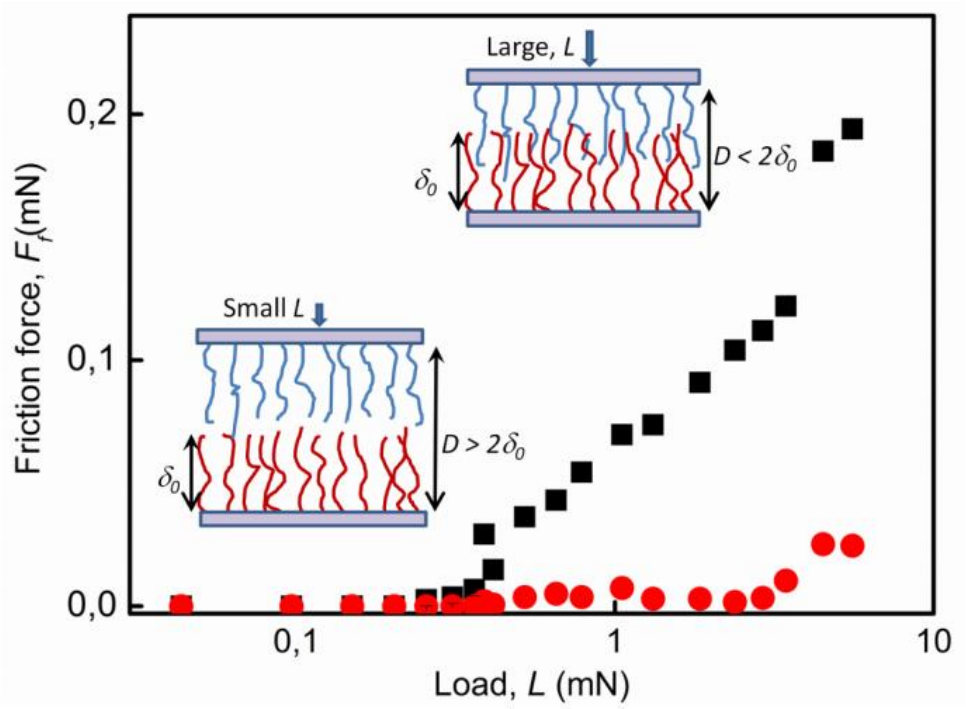
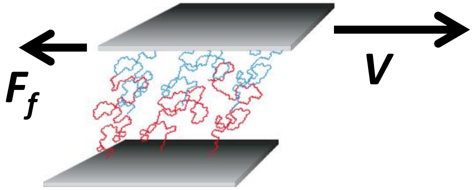
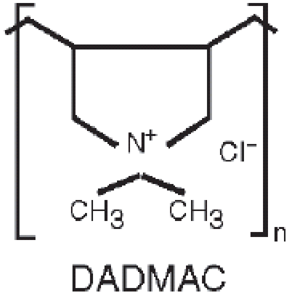
Polyelectrolyte brush (PAA)

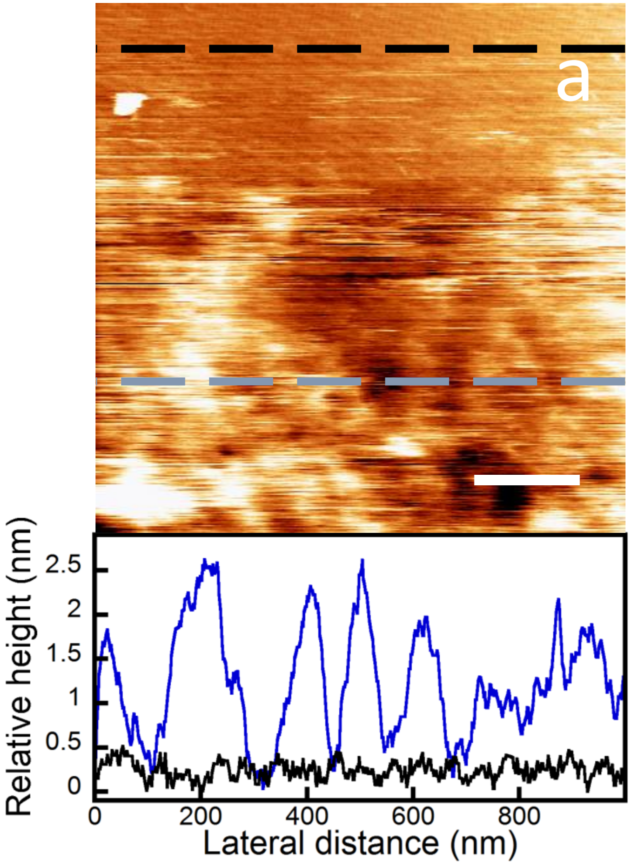


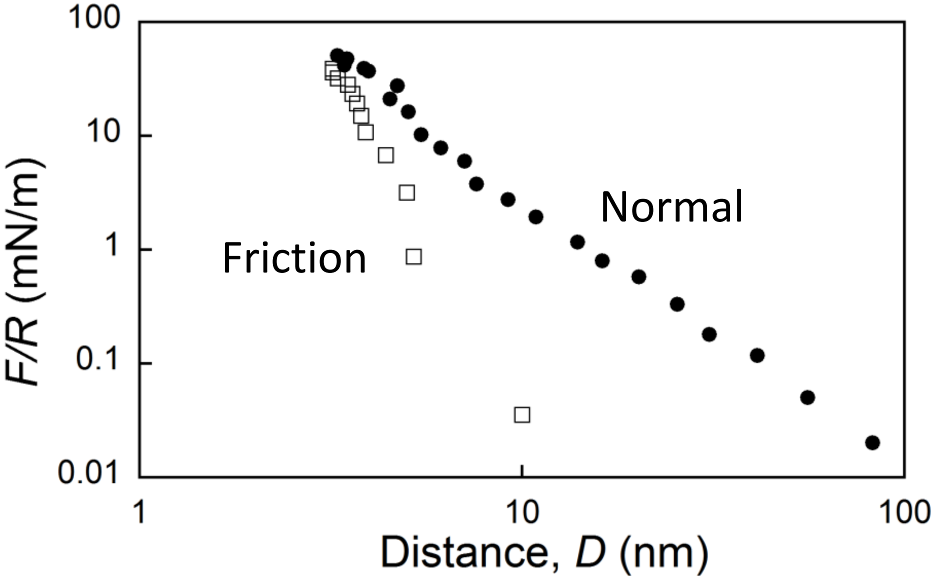


Drummond, *PRL* 2012

Non-adhesive contact: Adsorbed polyelectrolyte

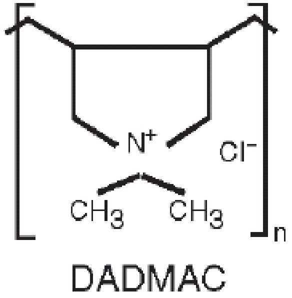


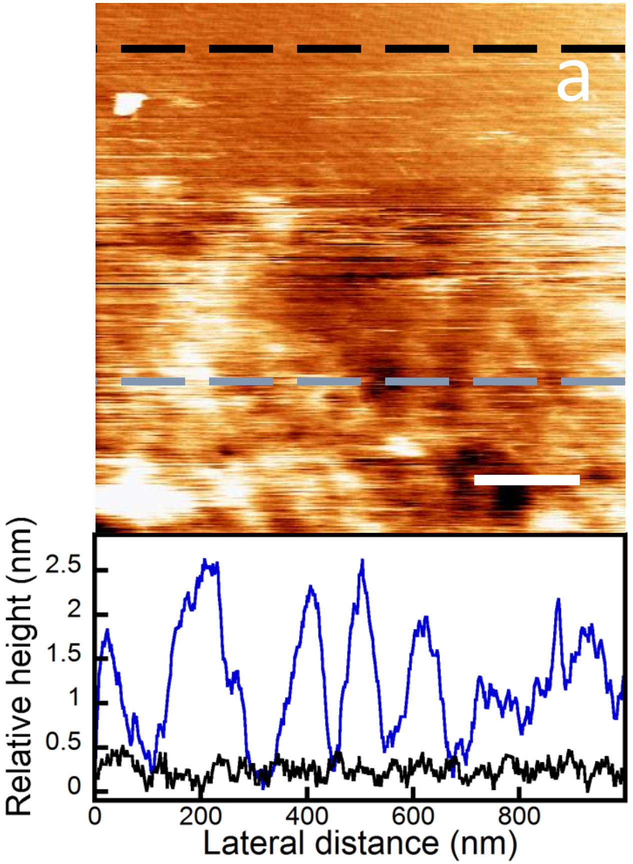


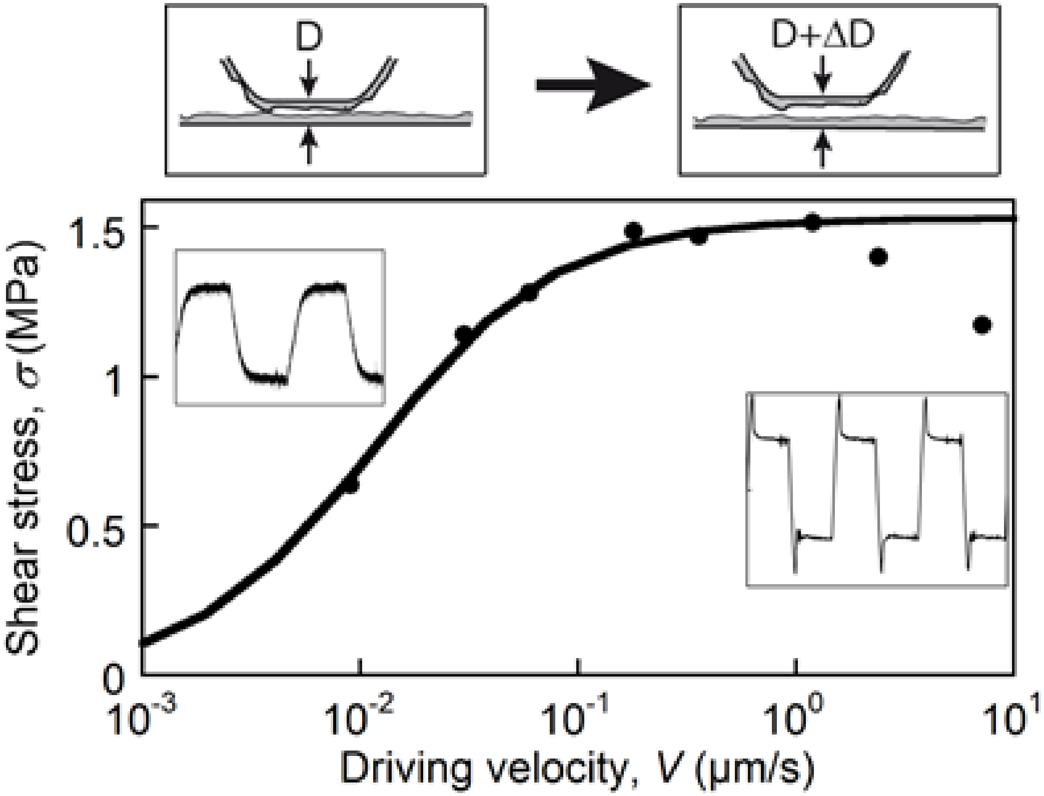


Bouchet, *et al*. *Macromolecules*, 2015

Non-adhesive contact: Adsorbed polyelectrolyte







$d^* \approx 1.5$ nm
$\tau_0 \approx 0.3$ s
$l^* \approx 1$ nm

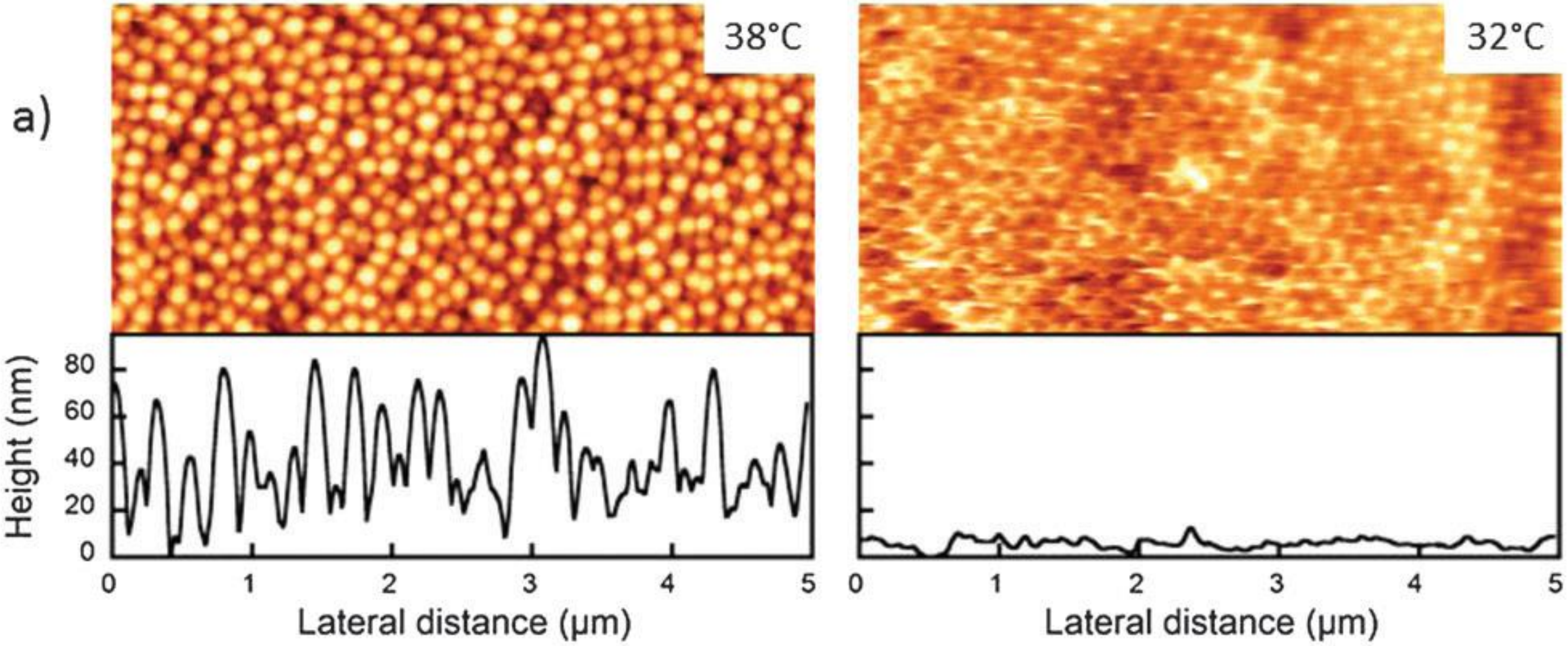
Bouchet, *et al*. *Macromolecules,* 2015

Boundary lubrication: Energy Dissipation

- Adhesive Surfaces: rupture of adhesive nanojunctions
- Wall/boundary lubricant deformation: thermal activation and multistability
- Wear
- Rheology of lubricant film

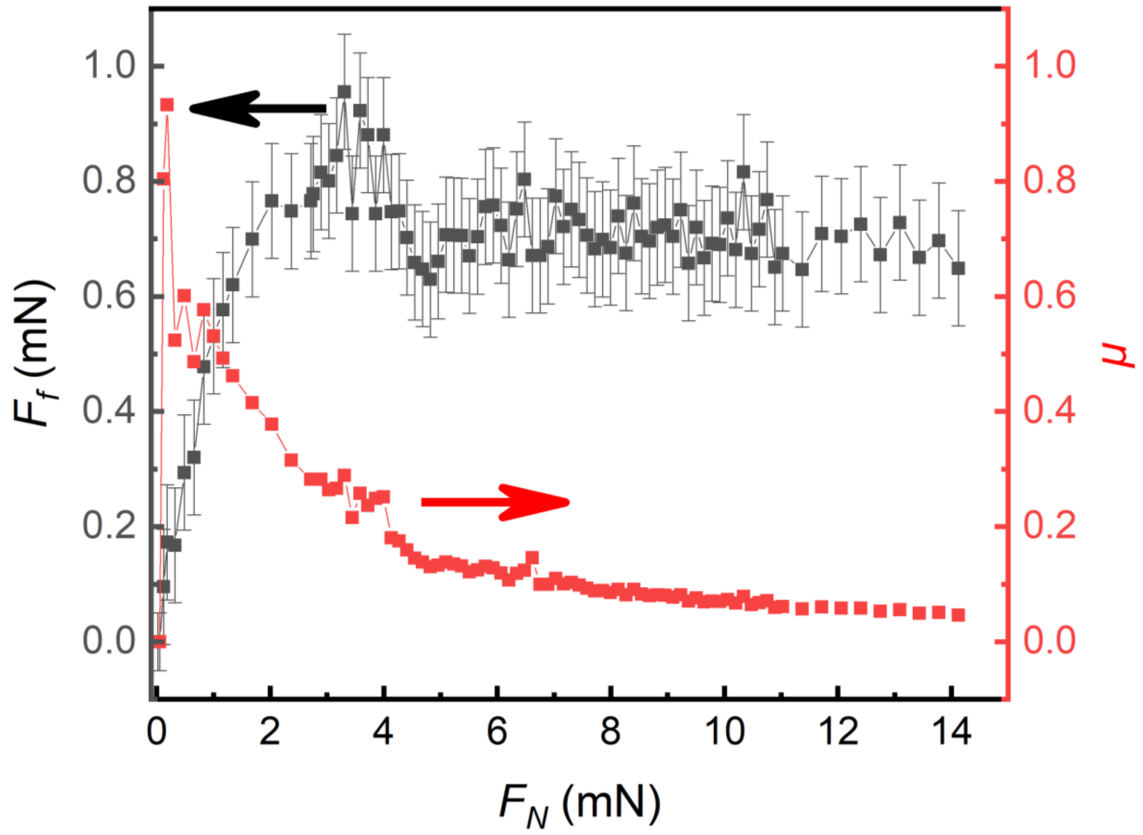
Soft boundaries: static and dynamic effects

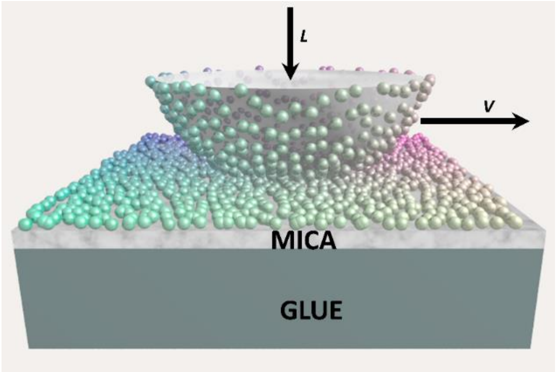
Thermoresponsive pNIPAM microgels



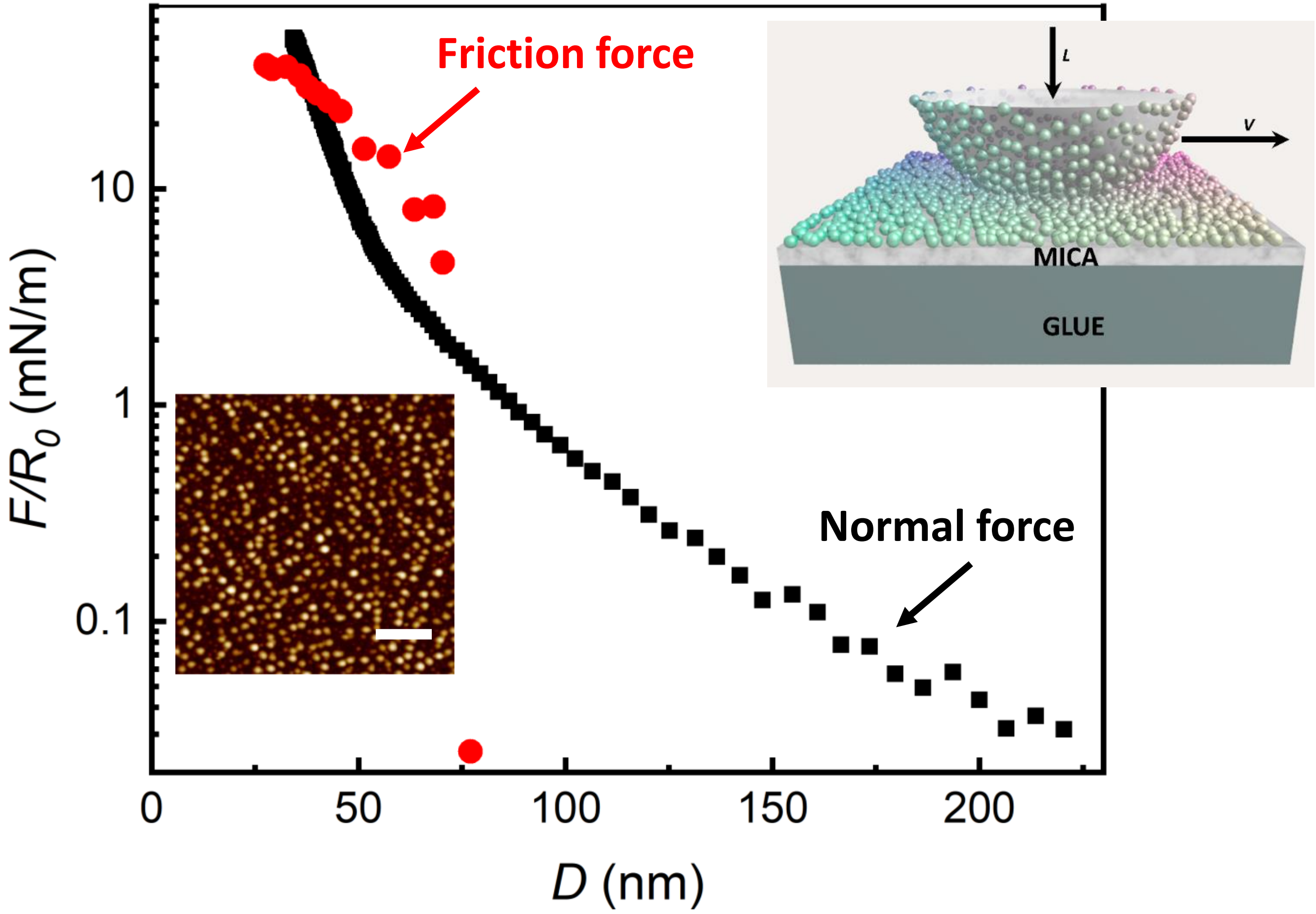
Pérez-Fuentes, et al; *Soft Matter*, 2015

Bastos-González et al. *Current Opinion in Colloid & Interface Science* (2016)

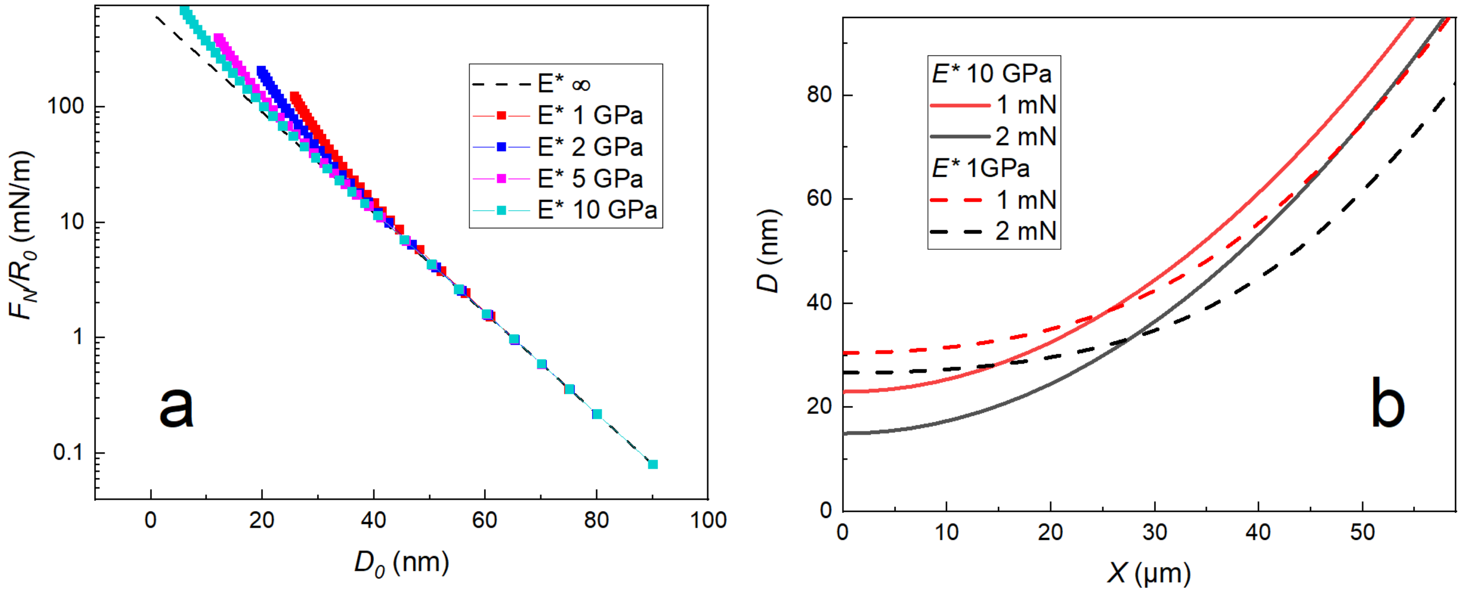




Vialar et al, *Langmuir* 2019

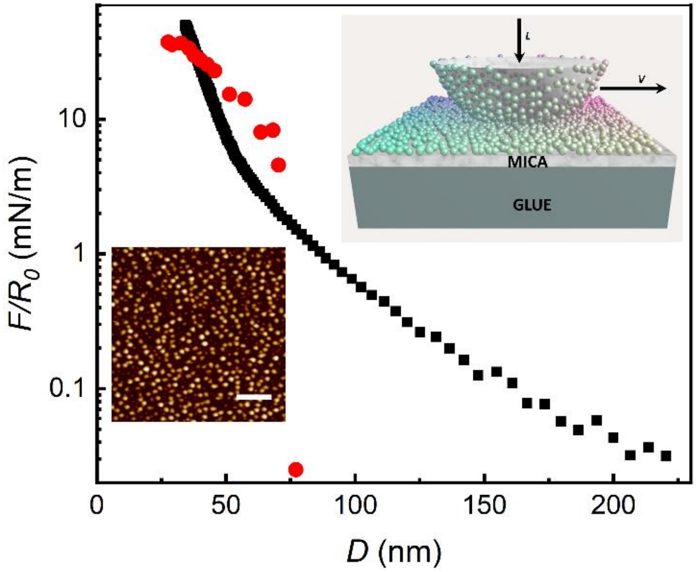


Vialar et al, *Langmuir* 2019



Numerical recipe from Barthel, *Thin Solid Films* 1998

Vialar et al, *Langmuir* 2019

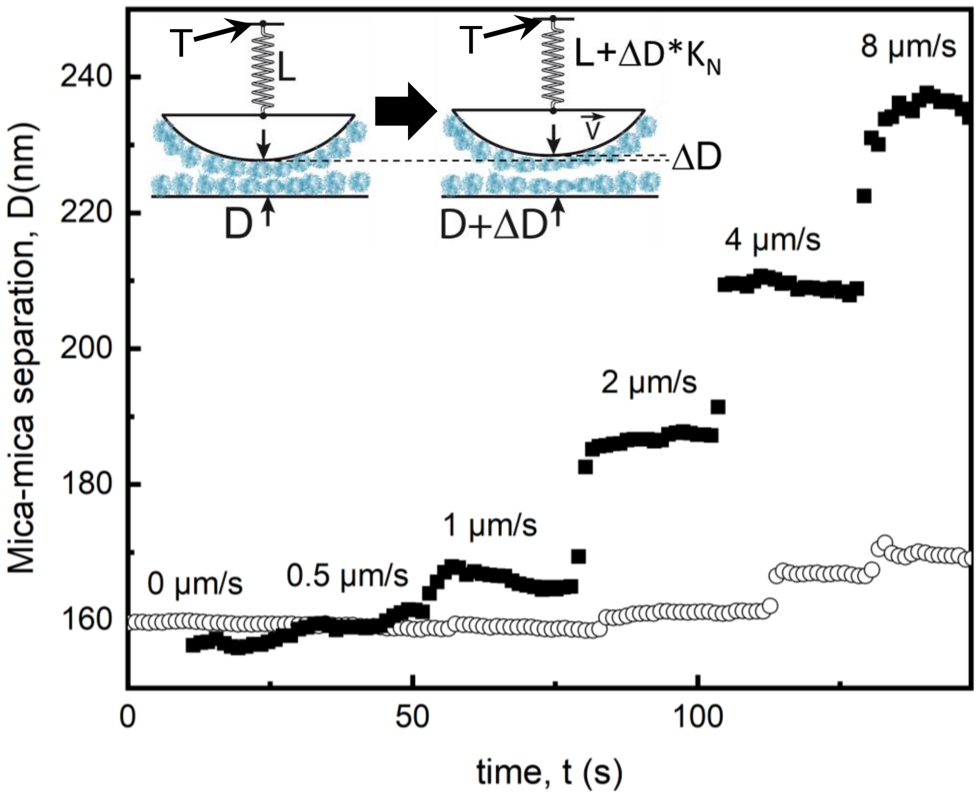


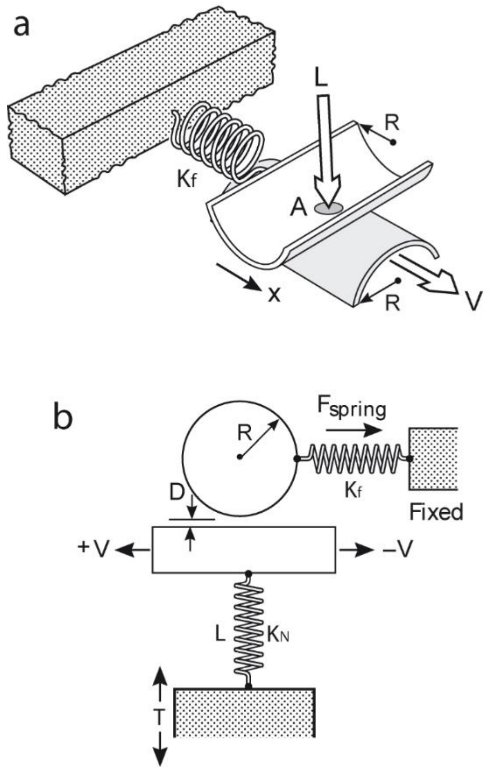
Long-range repulsive interaction

significantly surface deformation at finite separations

limited surface approach

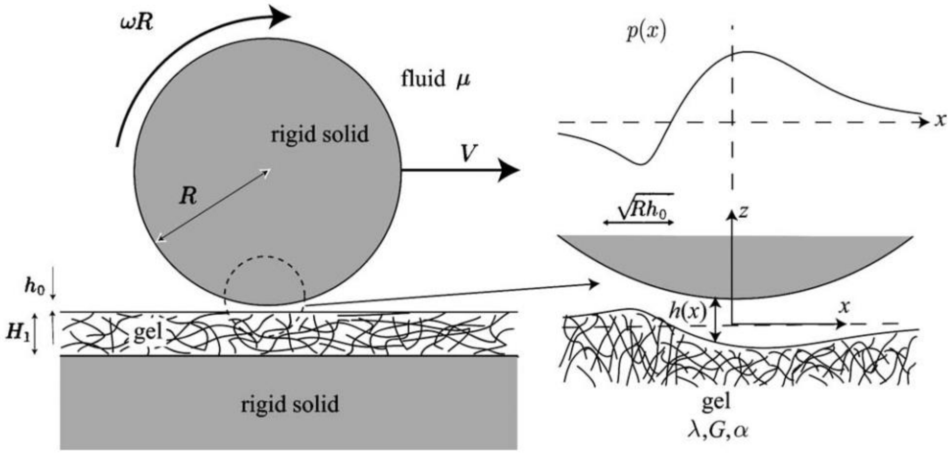
restriction of friction growth





Vialar et al, *Langmuir* 2019

$$F_{Lift} = \frac{\mu^2 V^2}{E} \frac{H_l R^2}{h_0^3}$$

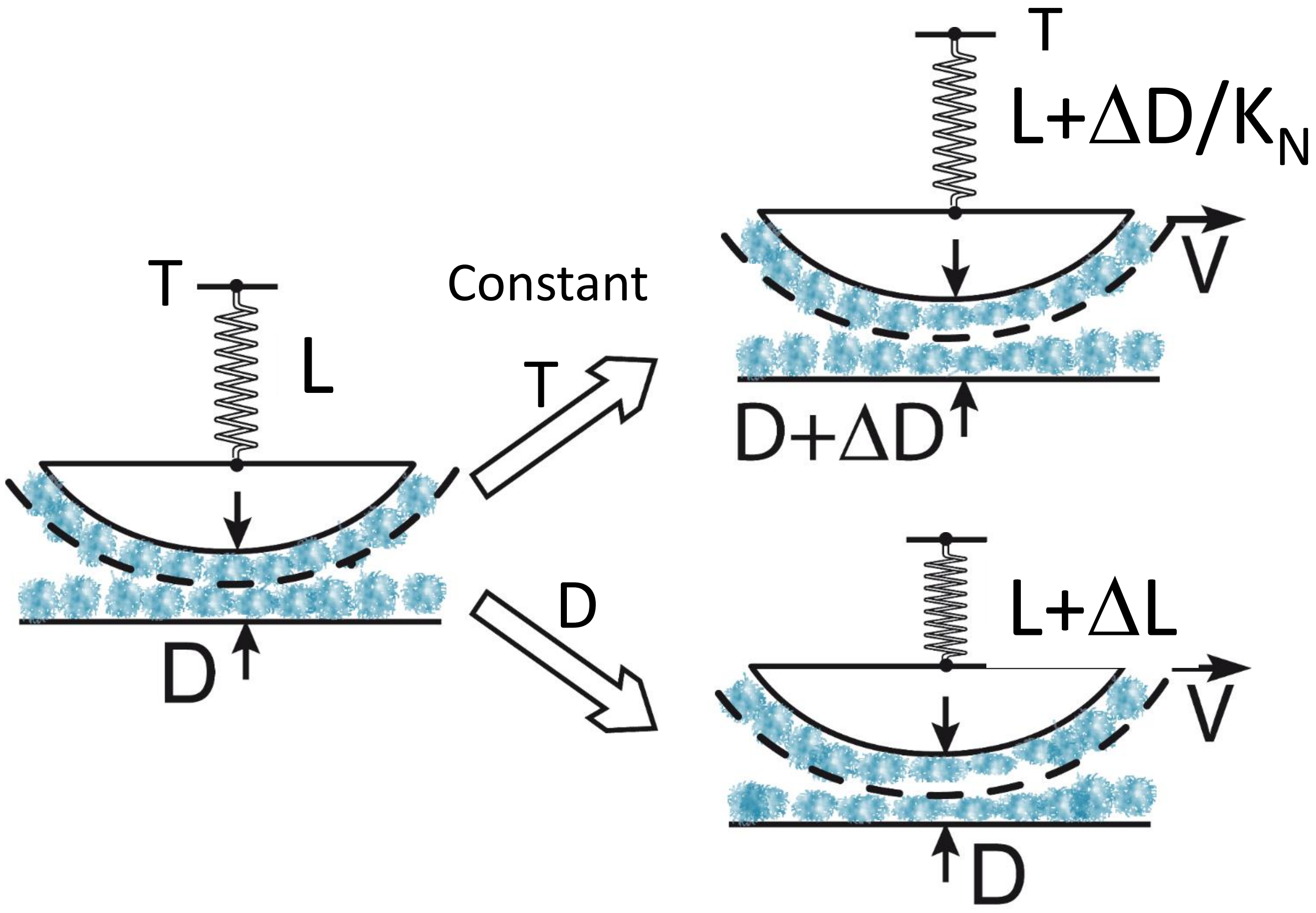


PHYSICS OF FLUIDS **17**, 092101 (2005)

Soft lubrication: The elastohydrodynamics of nonconforming and conforming contacts

J. M. Skotheim and L. Mahadevan

Sekimoto and Leibler, EPL 1993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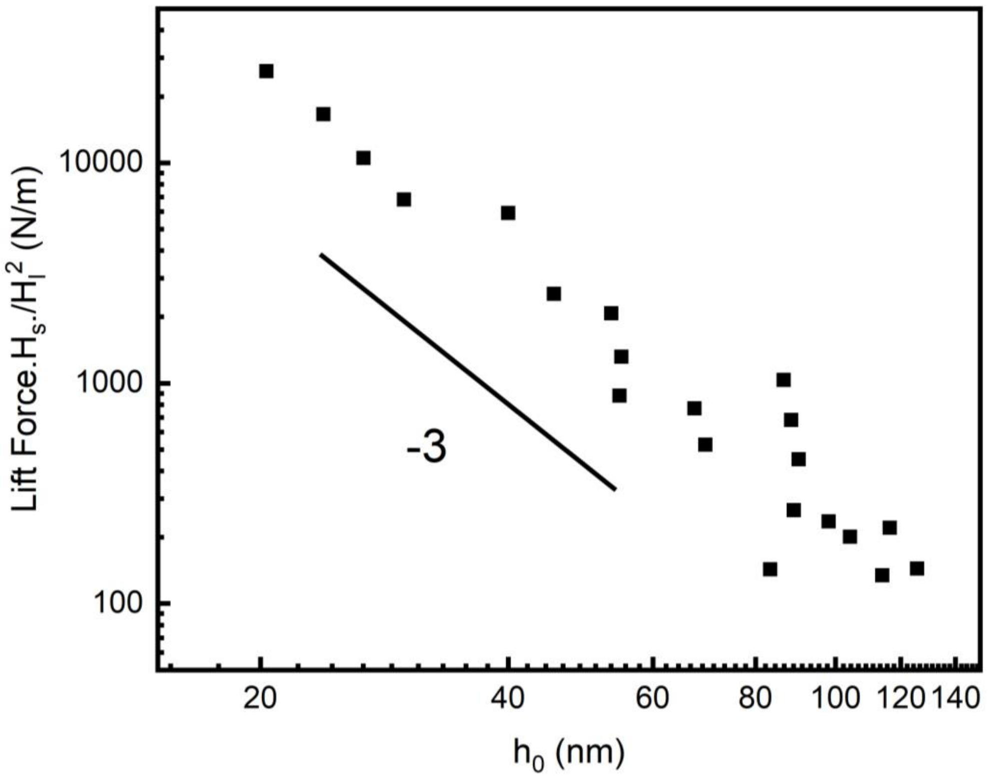
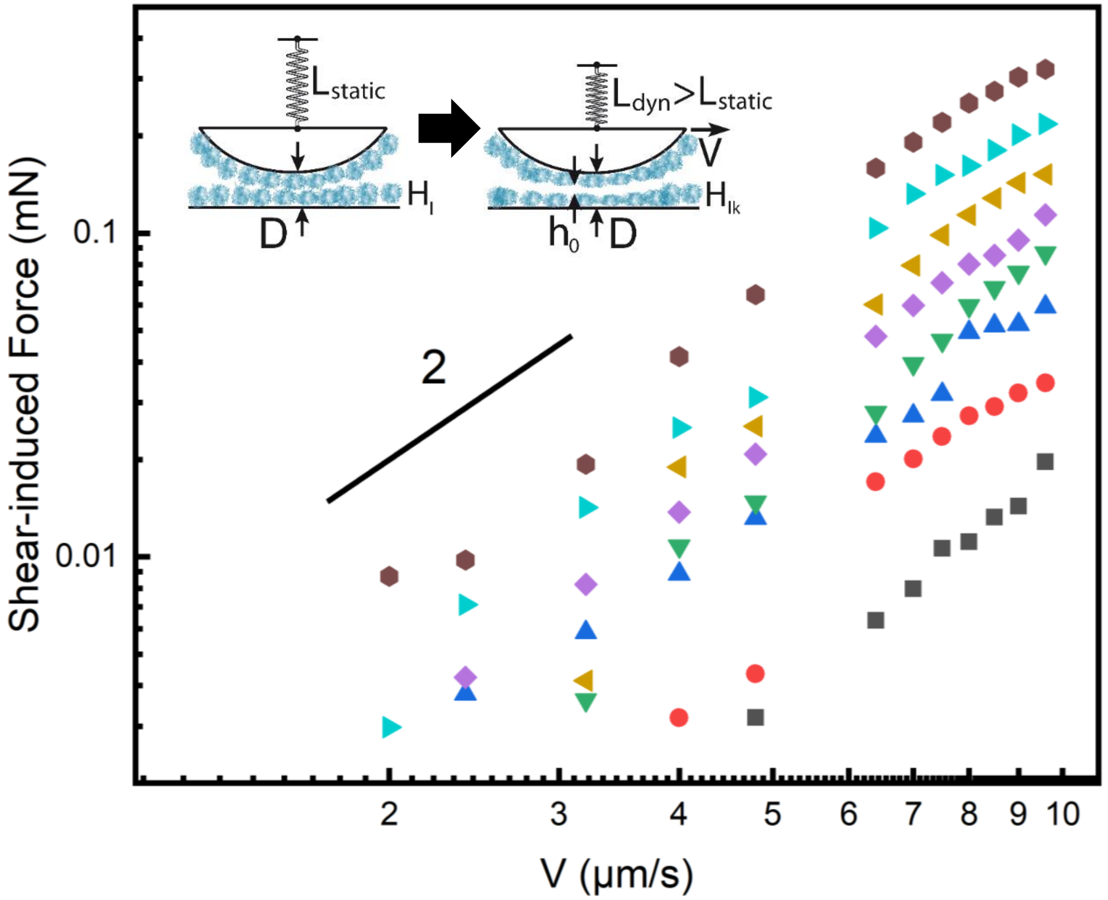


$$F_{Lift} = \frac{\mu^2 V^2}{E} \frac{H_l R^2}{h_0^3}$$

Vialar et al, *Langmuir* 2019

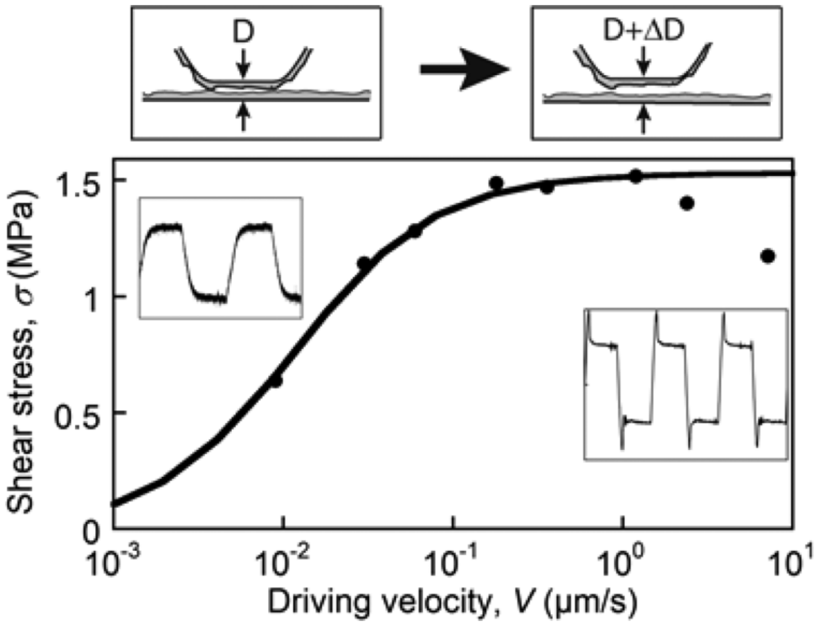


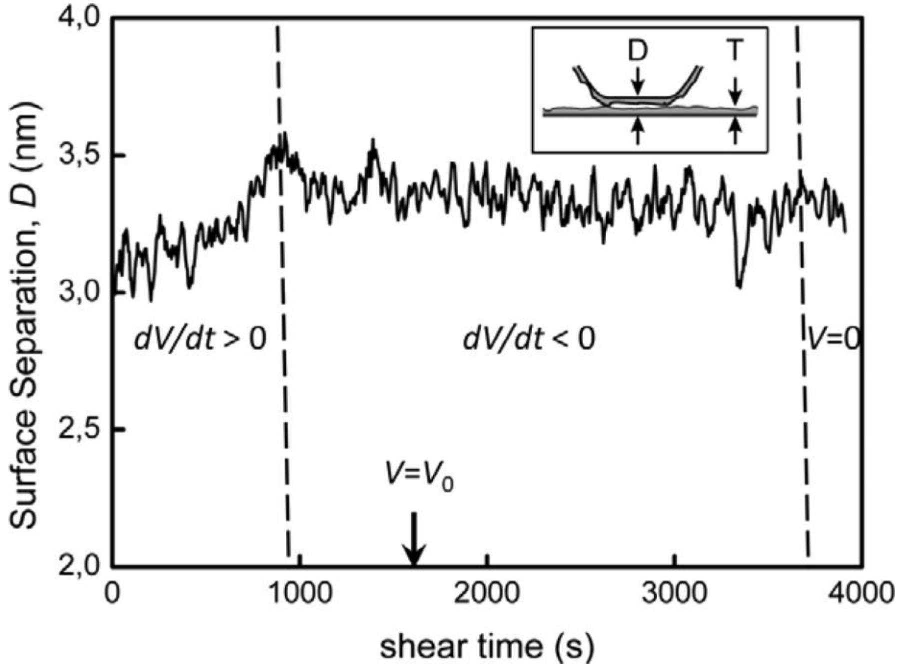
D= 130 nm

D= 300 nm

$$F_{Lift} = \frac{\mu^2 V^2}{E} \frac{H_l R^2}{h_0^3}$$

Vialar et al, *Langmuir* 2019





Self assembled polyDADMAC

Bouchet et al, *Macromolecules* 2015

Active friction control

- **Means:**
  - Lubricant “state”
  - Chemistry (lubricants, surfaces, boundary layers…)
  - Surface microstructure
- **Consider:**
  - Dynamics
  - Amplitude of changes of the material’s properties.
  - Reversibility
  - Reproducibility
  - Intensity of the external trigger

Stimuli

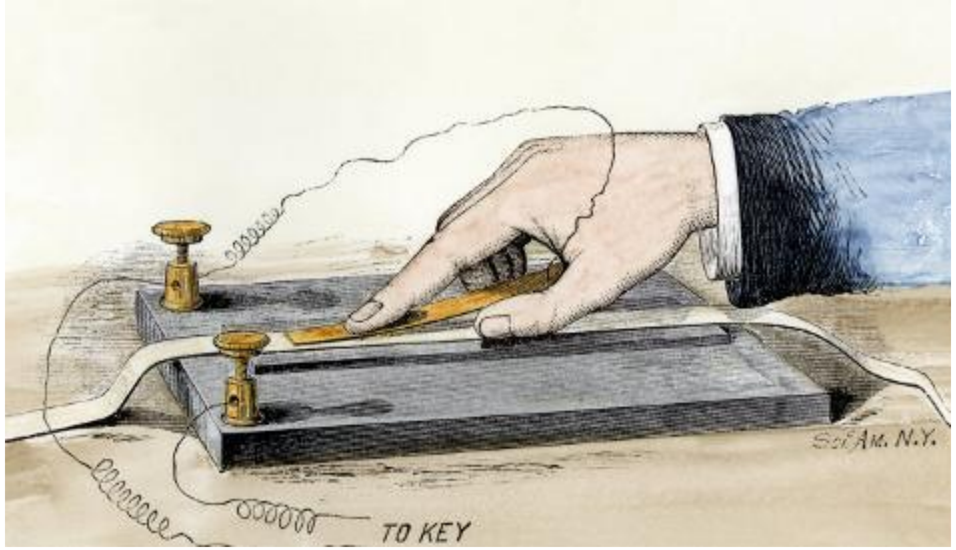
Physical	Chemical	Biological
• Thermal • Light • Electromagnetic • Mechanical	• pH • Ionic strength • Solvent quality • Redox prcess	• DNA • Protein • Glucose • Virus • bacteria

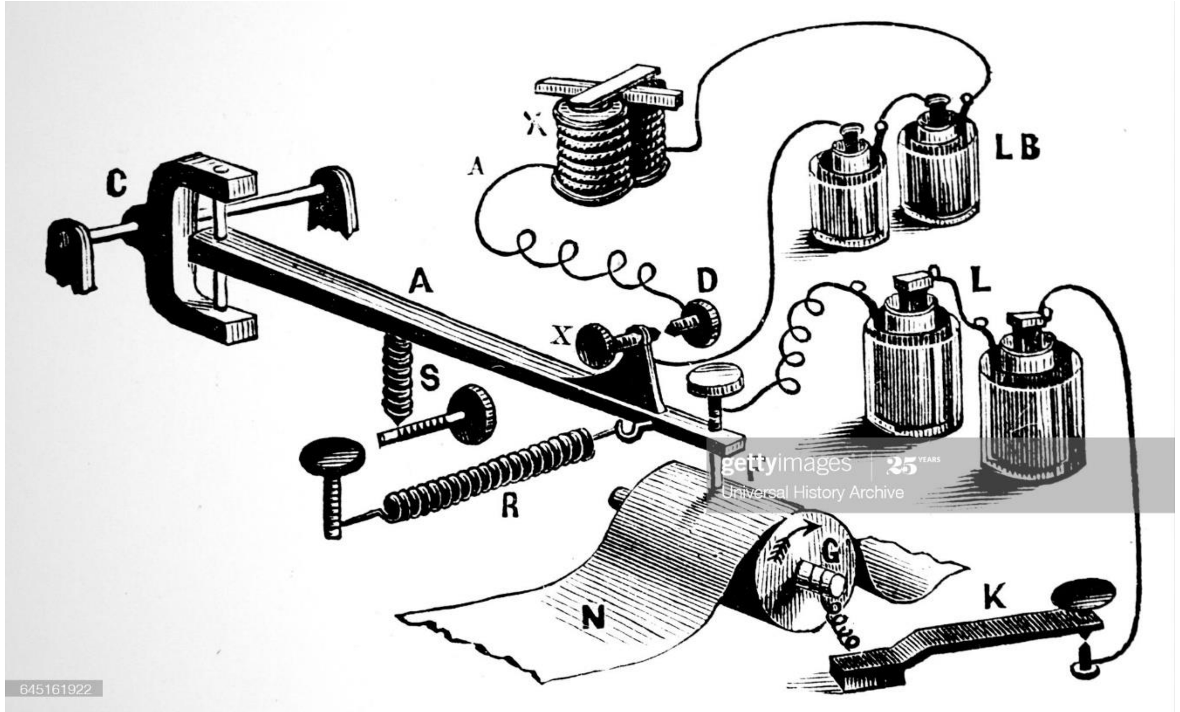
Single/multiple response

Controlling friction: electric fields

- Bulk lubricant changes
  - Electrorheological
  - Ionic liquids
- Contact changes
  - Field-induced repulsive force
  - Hysteresis reduction
- Boundary layer changes
  - Redox reactions: gas formation, tribofilm development, oxidation
  - Molecular rearrangement

The electromotograph (Edison)





Polaromicrotribometry: A Friction Method for the Study of Polarized Metal Solution Interfaces

Application to the Gold Electrode

J. E. Dubois and P. C. Lacaze

J. E. Dubois *et al* 1975 *J. Electrochem. Soc.* **122** 1454

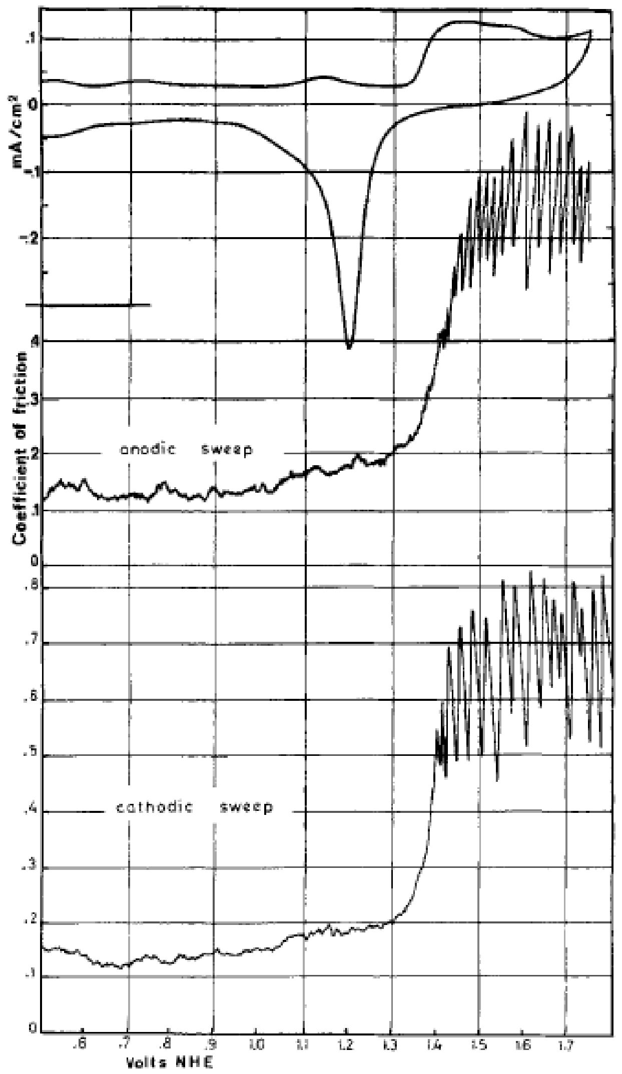
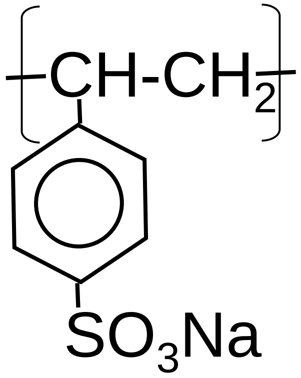
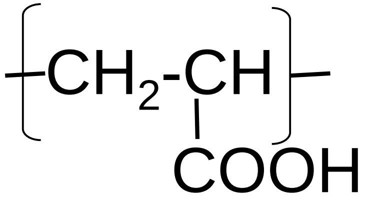


Fig. 3. Silica-gold friction in *N* sulfuric acid. Triangular sweep, 25 mV/sec, 3g load. Top, I-V curve; middle, coefficient of friction as a function of the interface potential: anodic sweep; and (bottom) cathodic sweep. The beginning of the friction rise is at the same potential as the beginning of oxidation.

Polyelectrolytes – polymers with charged groups

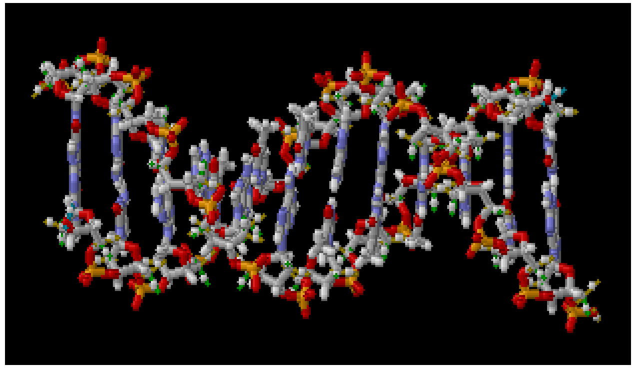




Strong: Poly(styrene sulfonate)

Weak: Poly(acrylic acid)

Biological DNA

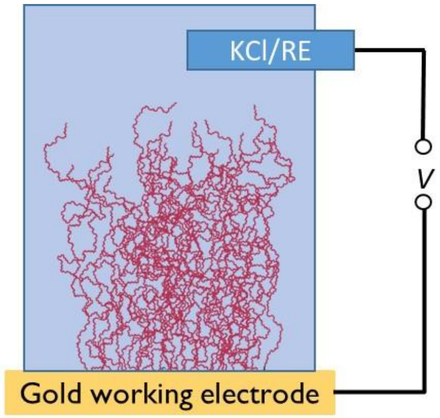


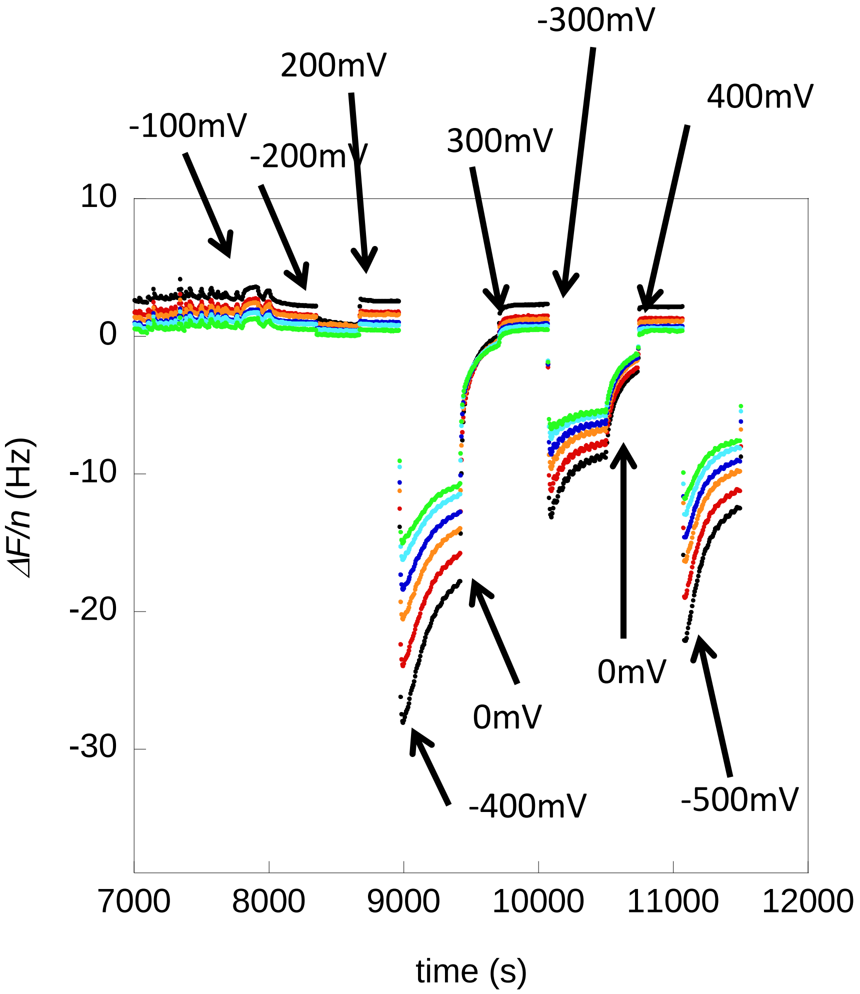
Conformation regulated by concentration of ions, pH, solvent quality, temperature…

E-field control of PE

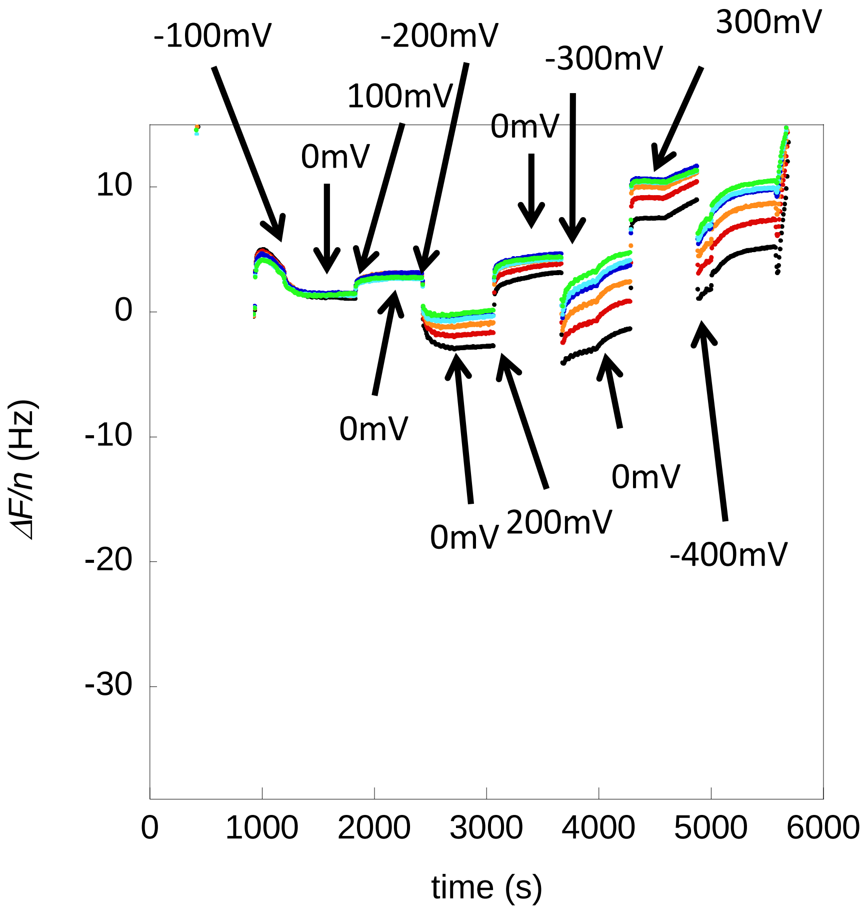
- Attraction/repulsion of ionomers: typically small changes (more important for rigid molecules; e.g. DNA orientation).
- Polarization/counterion cloud distorsion
- Conformational transition: coil-globule (pH-sensitive polyelectrolyte), helix-coil (polypeptides)…. More significant changes
- Redox reactions

$(PAA47)_2S_2$





pH 4.5: globule-coil transition

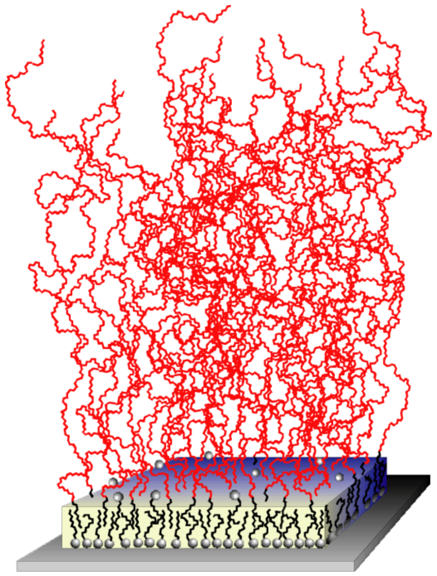


pH 10: coil-extended coil

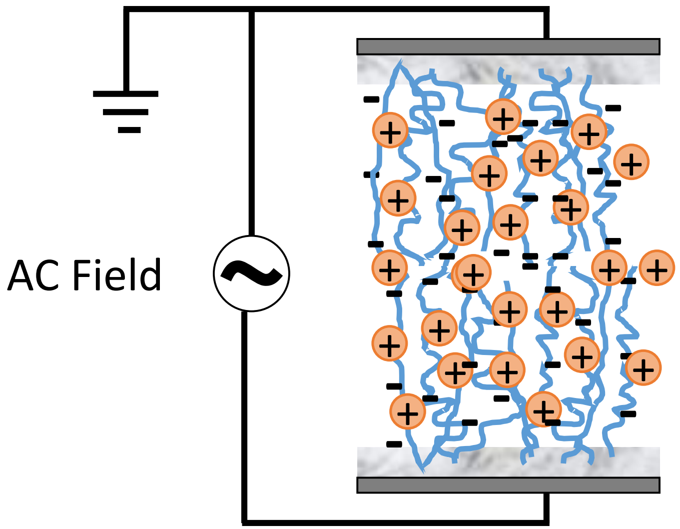
PE brush

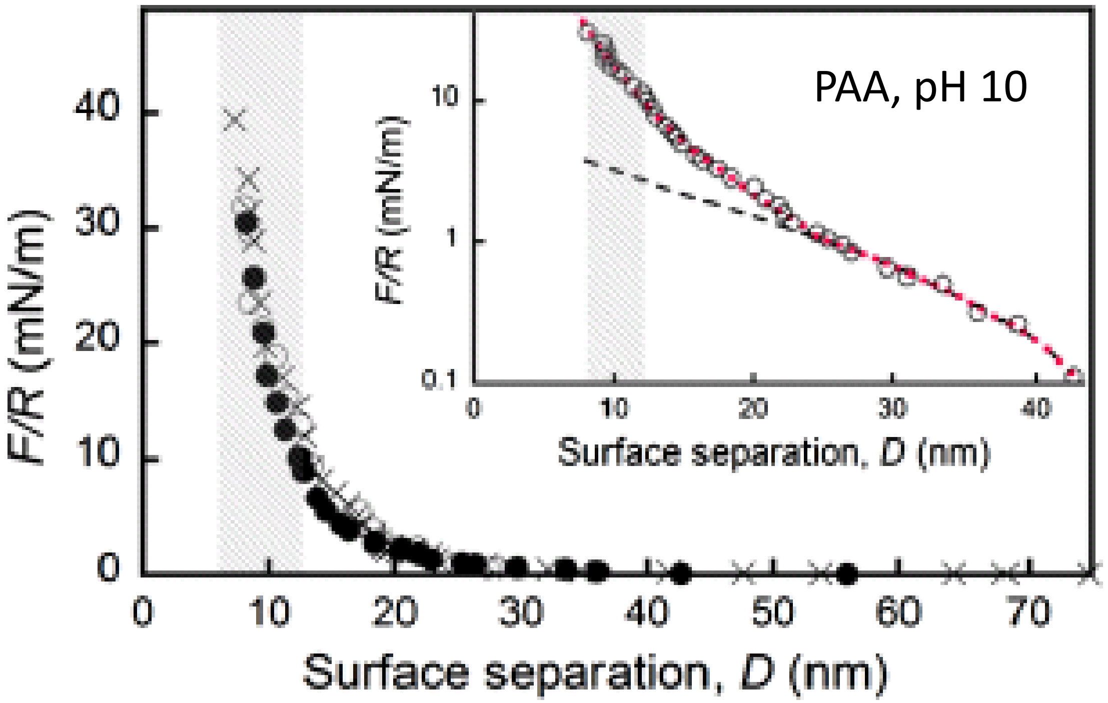
Conformational control → **Tuning of surface properties**

- Electroresponsive boundary lubricant
- Electroadhesion
- Electrowetting



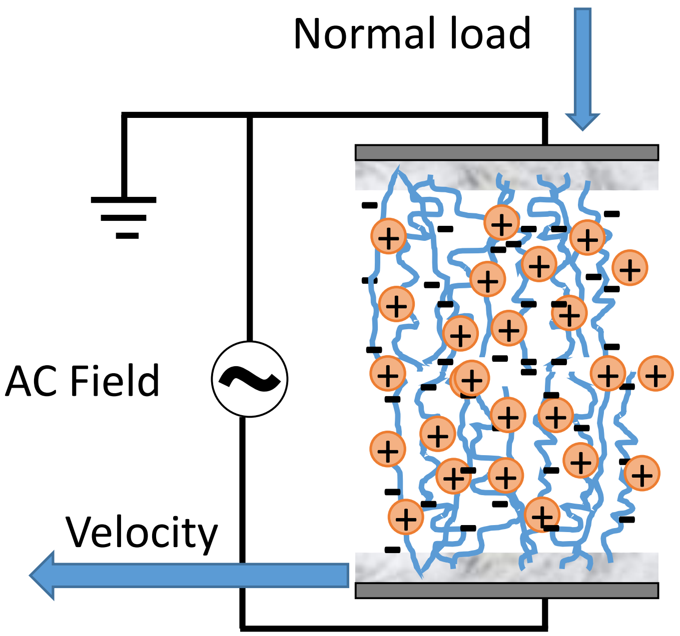
Self-assembled PE brush: normal forces

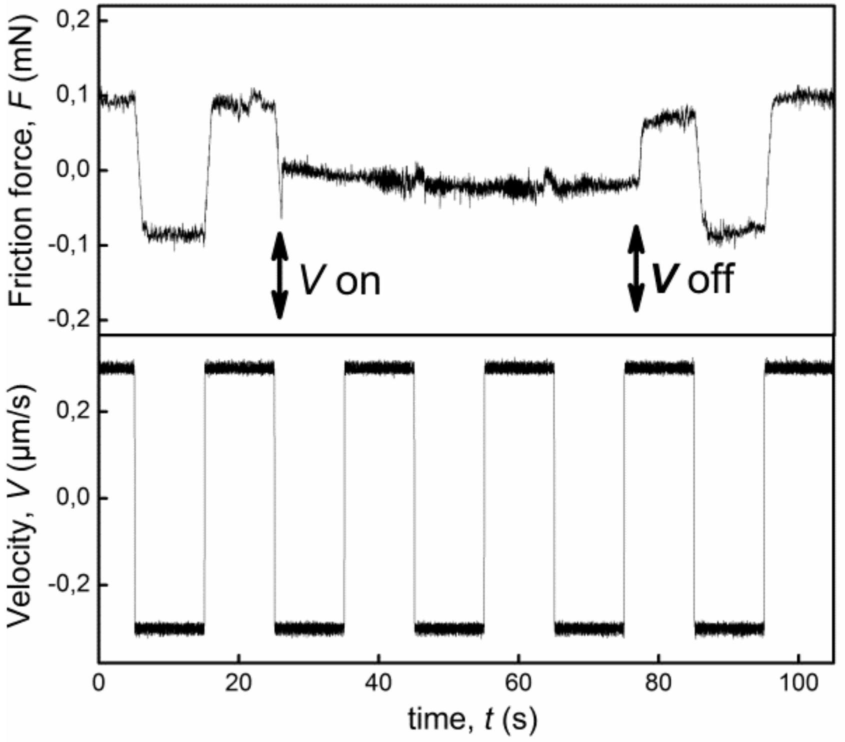




pH=10 (> pK_a)

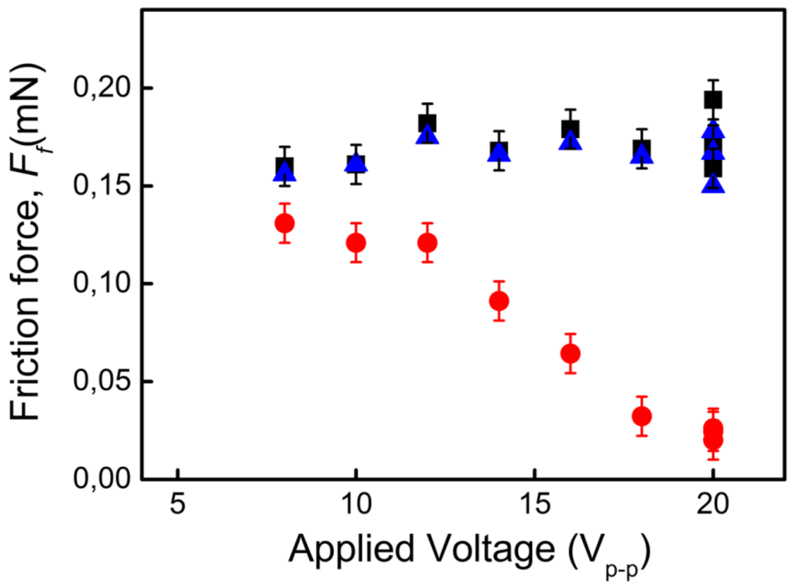
Polyelectrolyte brush: e-responsive boundary lubricant

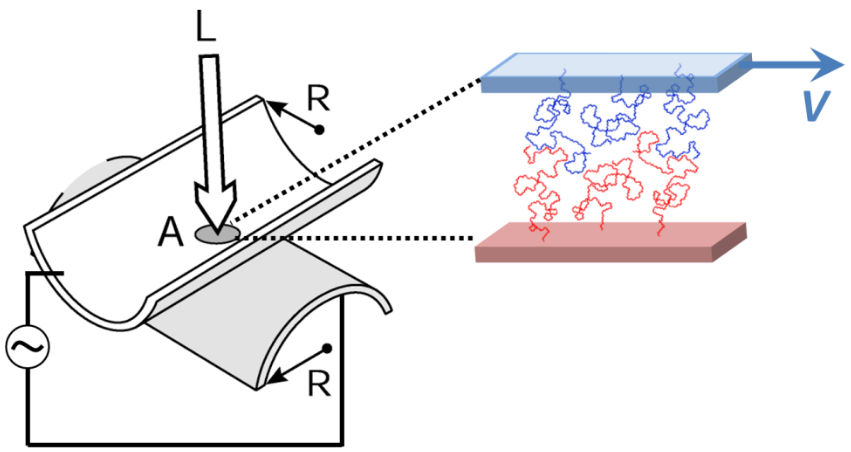




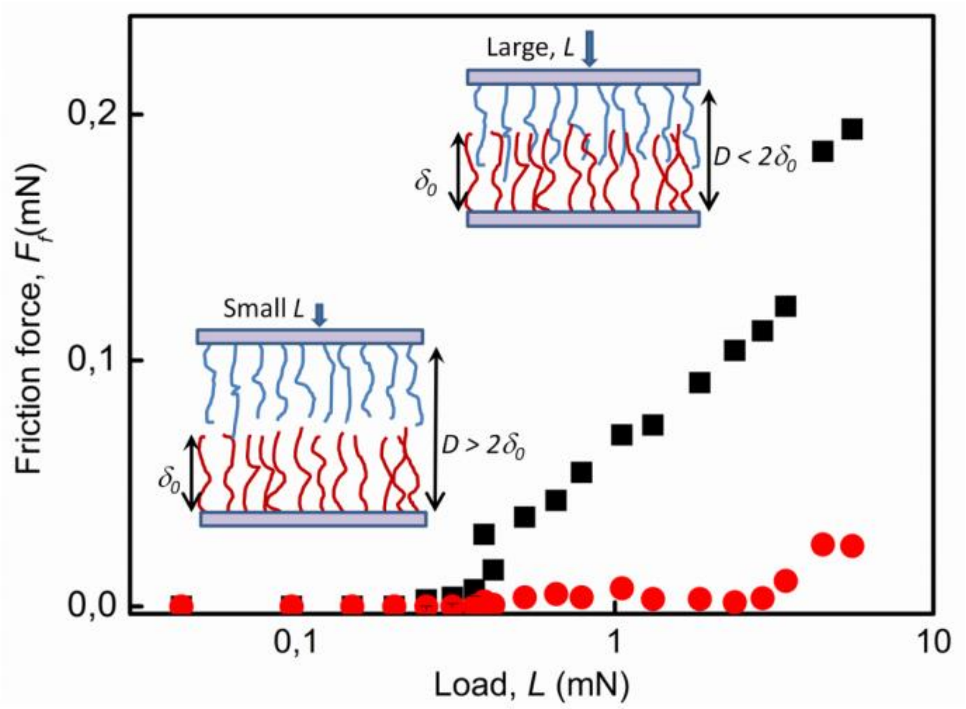
Drummond, *PRL* 2012

pH=10 (> pK_a)


0,20
0,15
0,10
0,05
0,00
5
10
15
20
Friction force, F_f(mN)
Applied Voltage (V_{p-p})


L
R
A
R
V

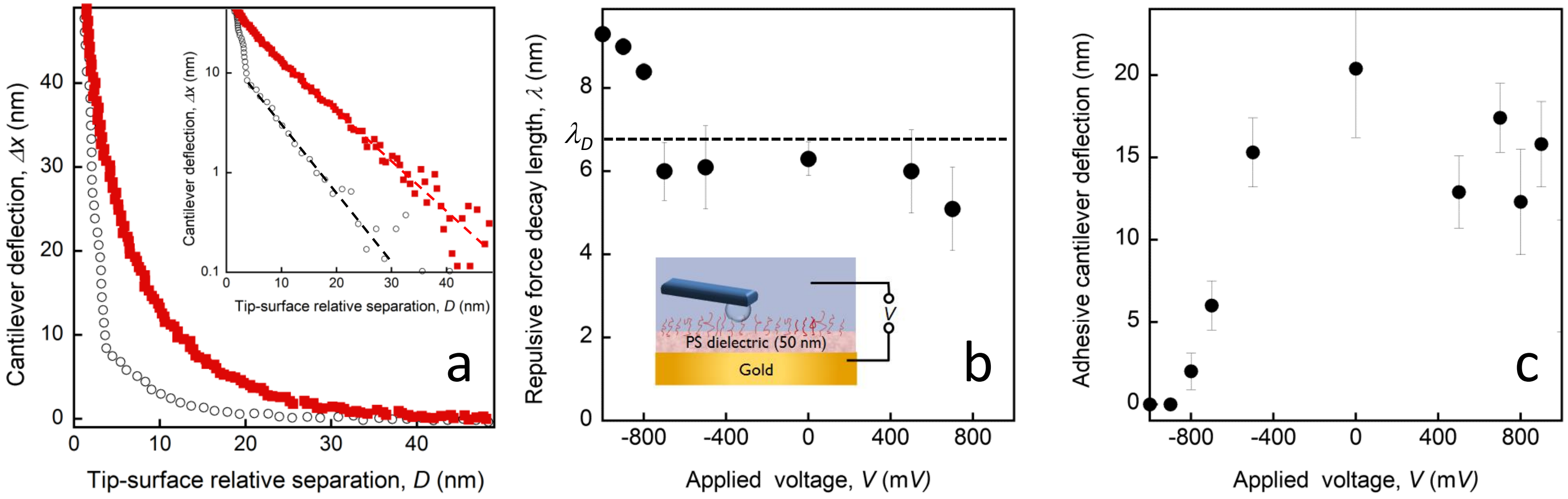
Polyelectrolyte brush: electro responsive lubricant



Drummond, *PRL* 2012

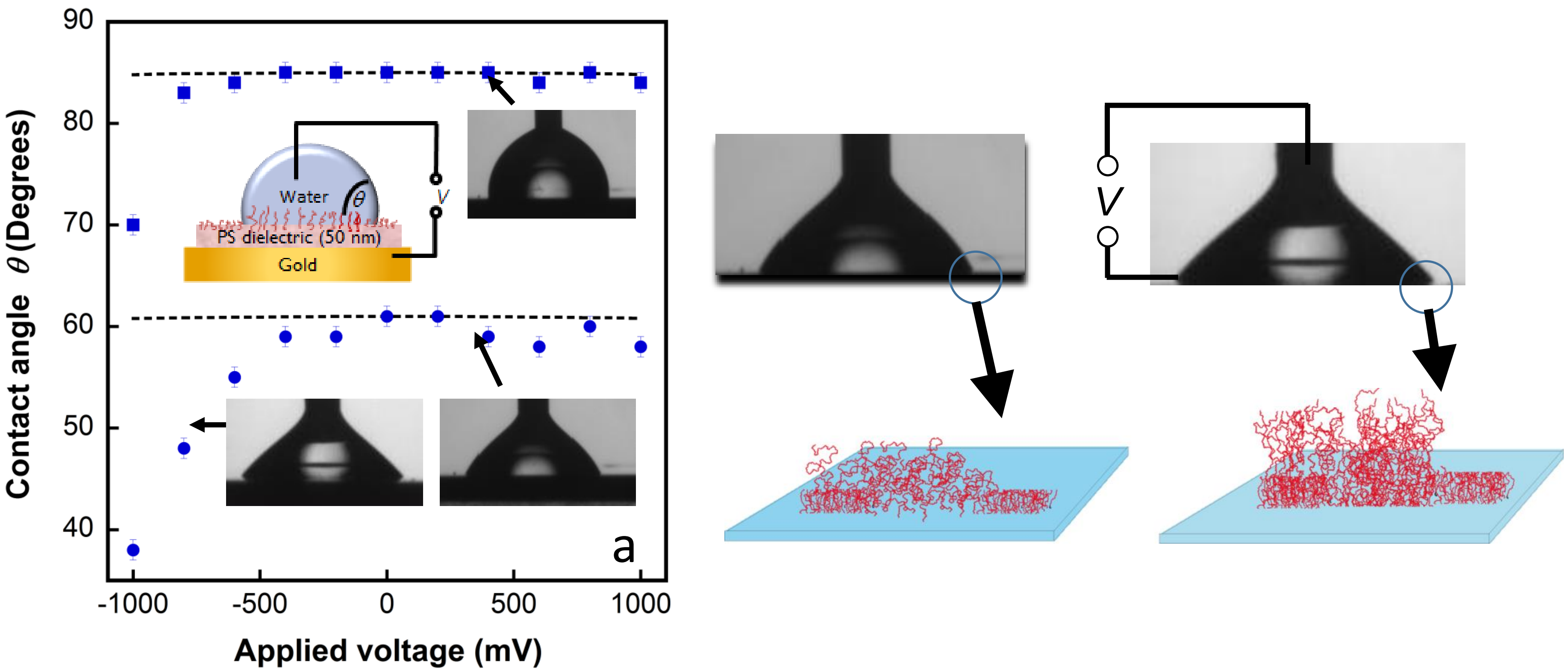
pH=10 (> pK_a)

Electroadhesion

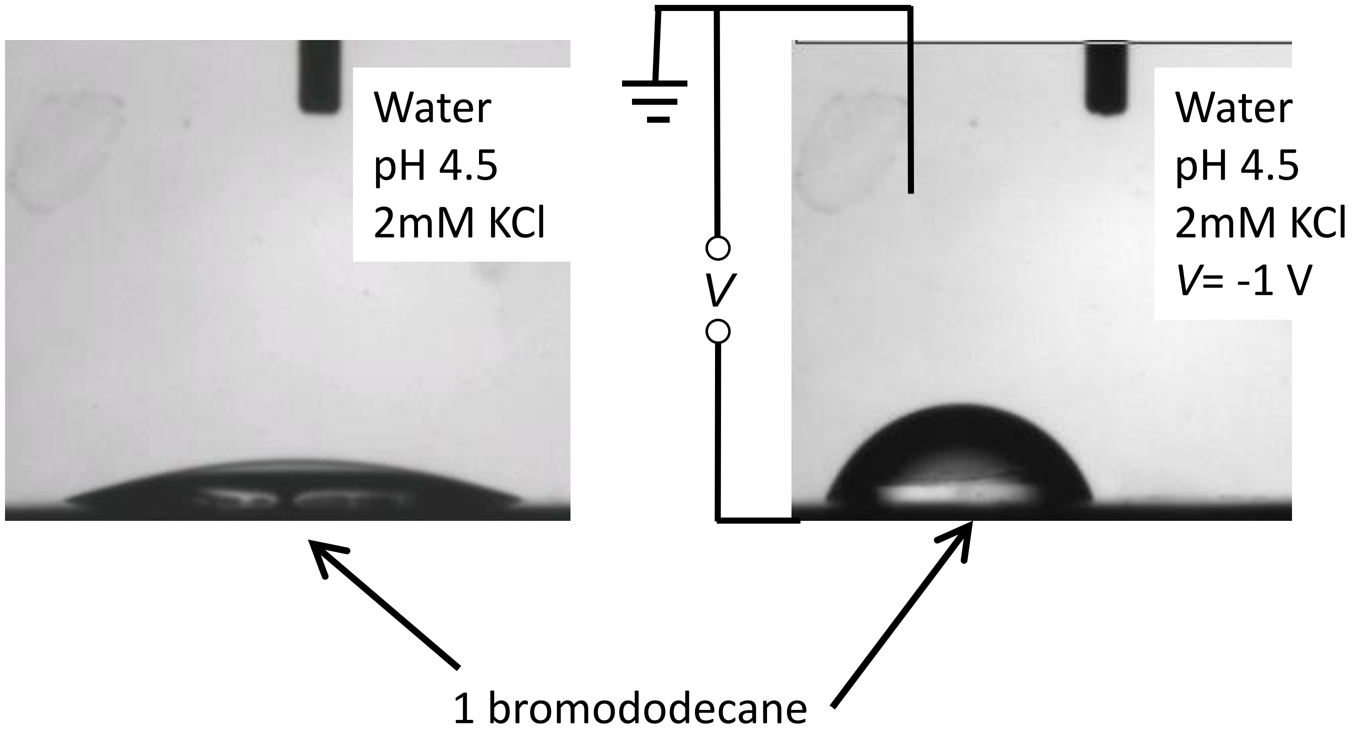


pH 4.5: DC field-induced globule-coil transition

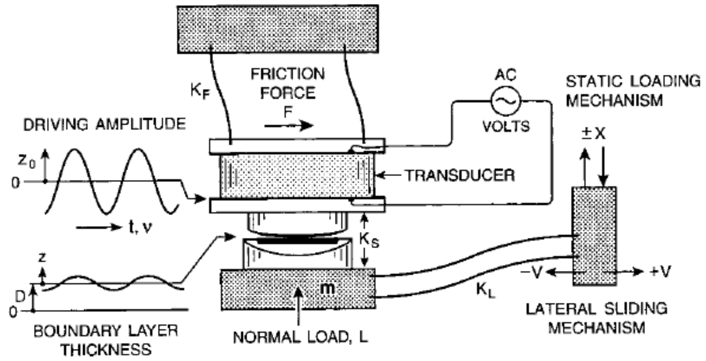
Electrowetting

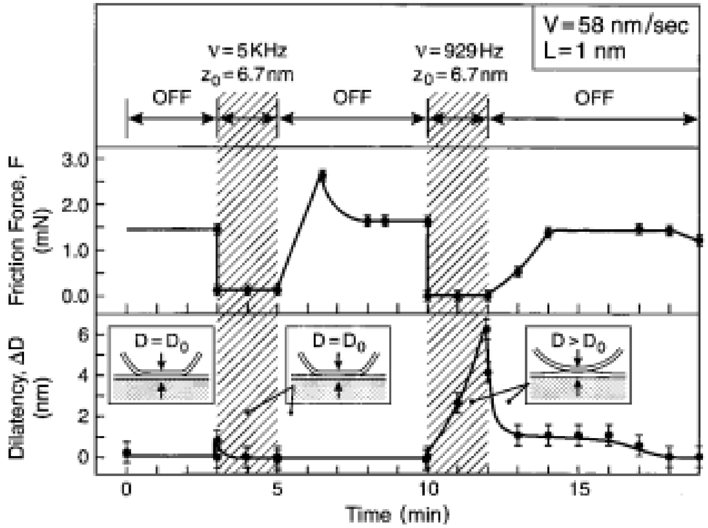


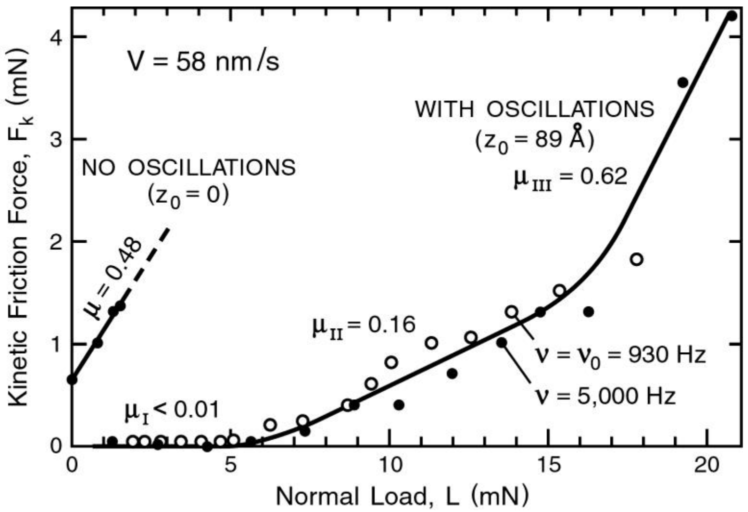
pH 4.5: DC field-induced globule-coil transition


Water
pH 4.5
2mM KCl
V
Water
pH 4.5
2mM KCl
V= -1 V
1 bromododecane

Friction control: sonolubrication





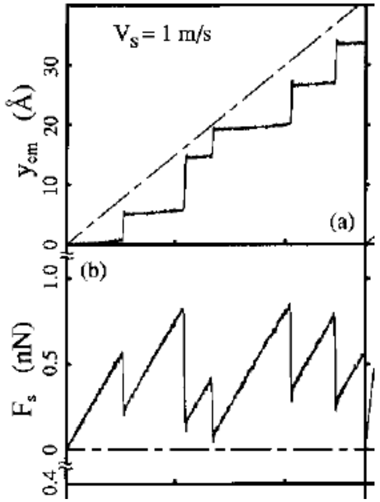


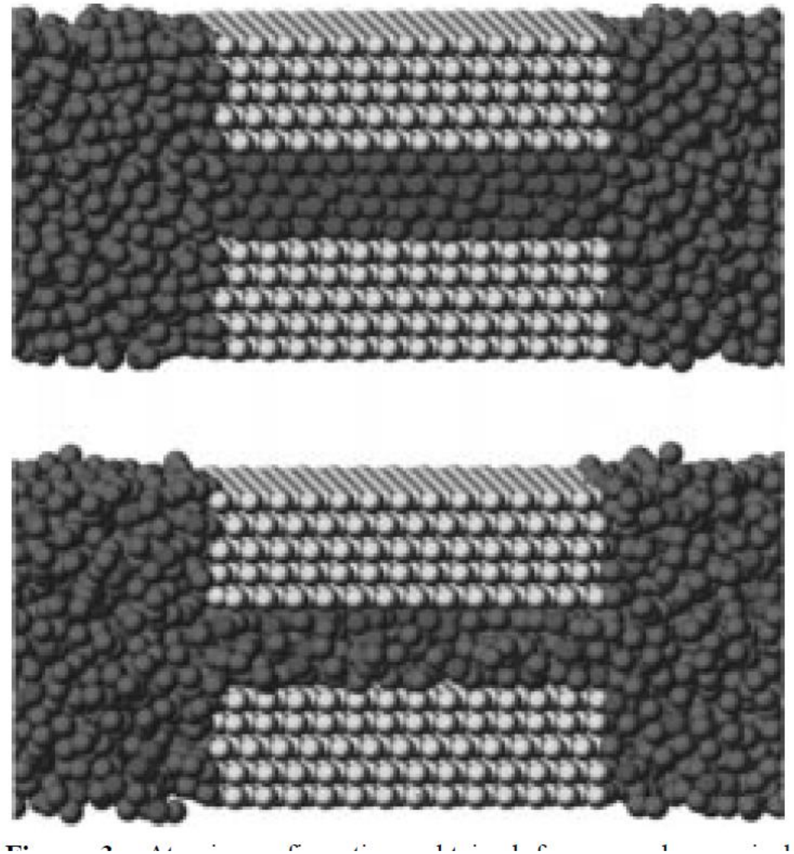
M. Heuberger, C. Drummond et J. Israelachvili, J. Phys. Chem. B, 1998

J. Phys. Chem. B 1998, 102, 5033−5037

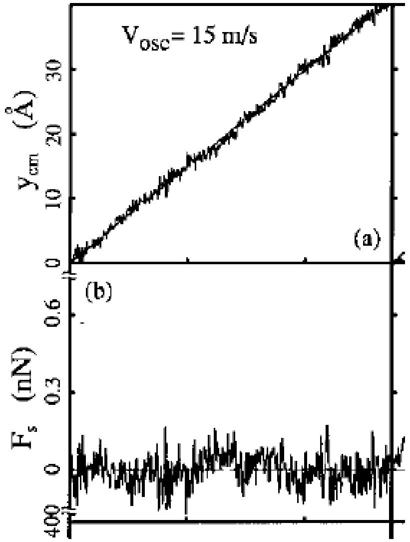
Friction Control in Thin-Film Lubrication

Jianping Gao, W. D. Luedtke, and Uzi Landman*





Small amplitude
(0.15nm) perturbation



Friction control: morphing

- Active (shaped tunable) microwrinkles
  - Electromechanical
  - Pressure
  - Strain
  - Light
  - Temperature
  - Chemically sensitive

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S. Giasson (U. Montréal)

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