The Abdus Salam International Centre for Theoretical Physics

2063-15

ICTP/FANAS Conference on trends in Nanotribology

19 - 24 October 2009

Hydration lubrication: exploring a new paradigm

KLEIN Jacob

The Weizmann Institute of Science
P.O.Box 26
IL-76100 Rehovot
ISRAEL

ICTP/FANAS Trends in Nanotribology, Trieste, 20.10.2009

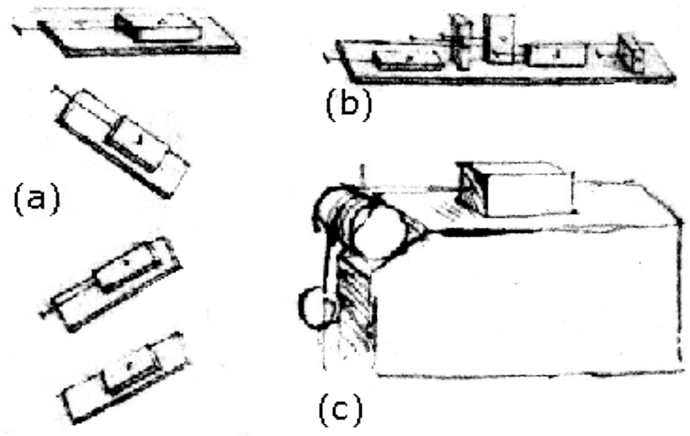
Hydration Lubrication: exploring a new paradigm

Jacob Klein
Weizmann Institute

Nir Kampf	Liraz Chai	
Ronit Goldberg	Jasmine Seror	(Weizmann)
Gilad Silbert	Yael Dror	
Irit Goldian	Raya Sorkin	
Susan Perkin	Wuge Briscoe	
Meng Chen		(Oxford)
S. Armes		Sheffield
R.K. Thomas		Oxford

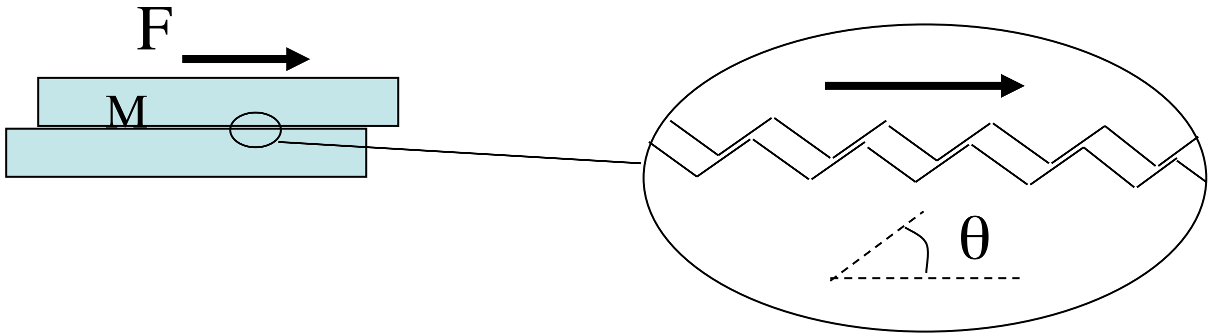
Funding: EPSRC (UK), Israel Science Foundation, Minerva Foundation

- Leonardo da Vini, ca. 1500



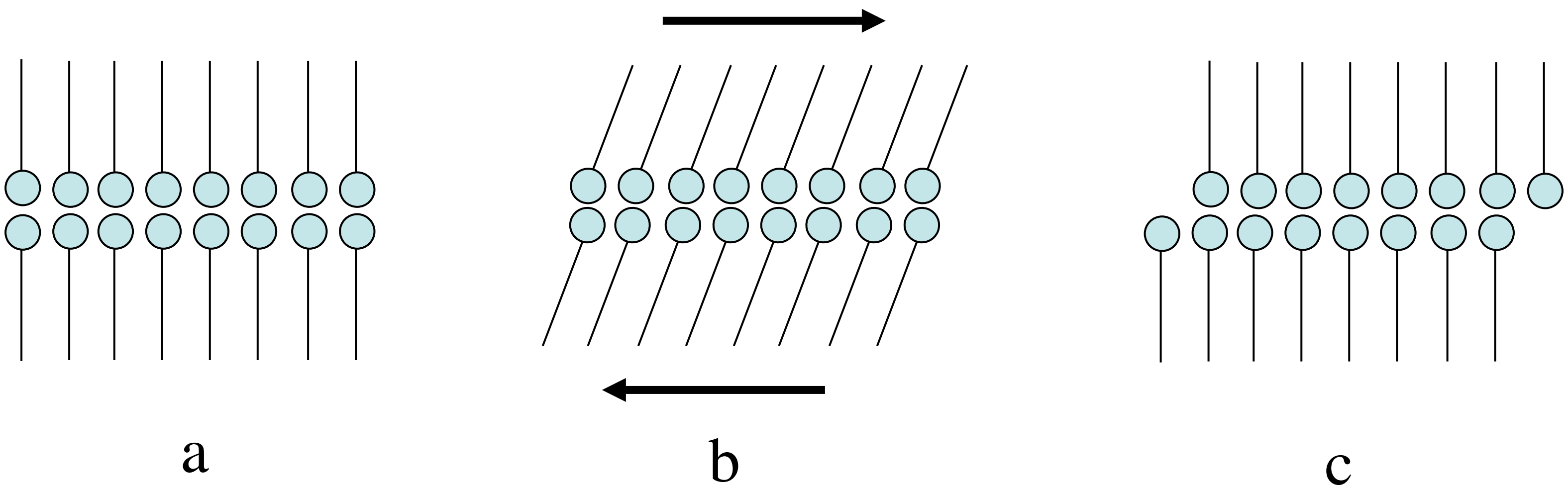
- Amonton, 1699 - classic laws of friction: μ= (Force to slide)/Load

- Euler, ca. 1750, and Coulomb, ca. 1780



$$\mu = F/Mg = \tan\theta$$

- Leslie, 1804 (pointed out that the Euler/Coulomb mechanism results in no energy dissipation)



Basic Tomlinson model (1929)

a - in equilibrium
b - lattice sheared
c - strain energy dissipated as surfaces jump to new equilibrium position (vibrations of released atoms lost as phonons - heat up lattice) - related to adhesion hysteresis

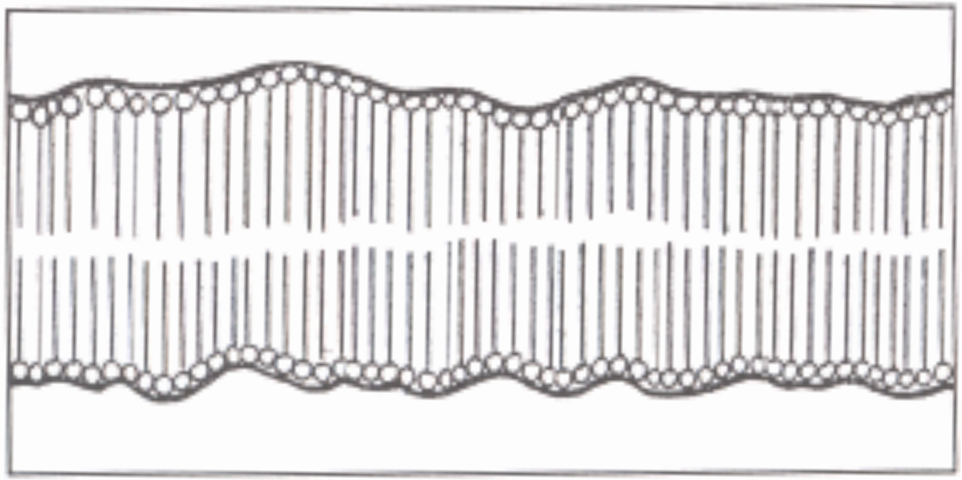
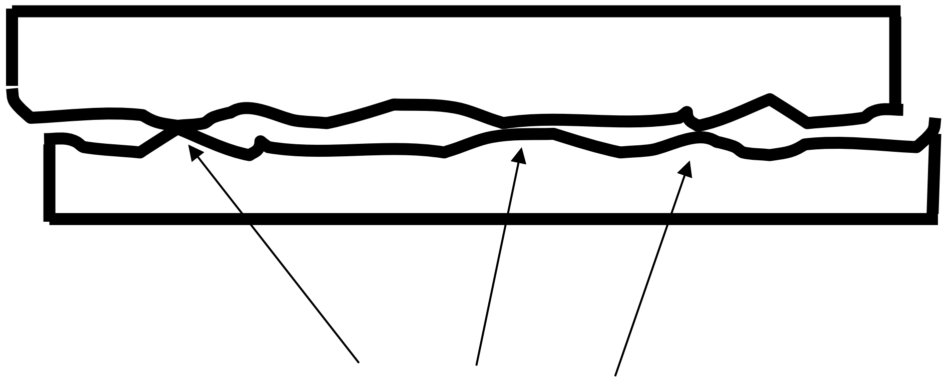


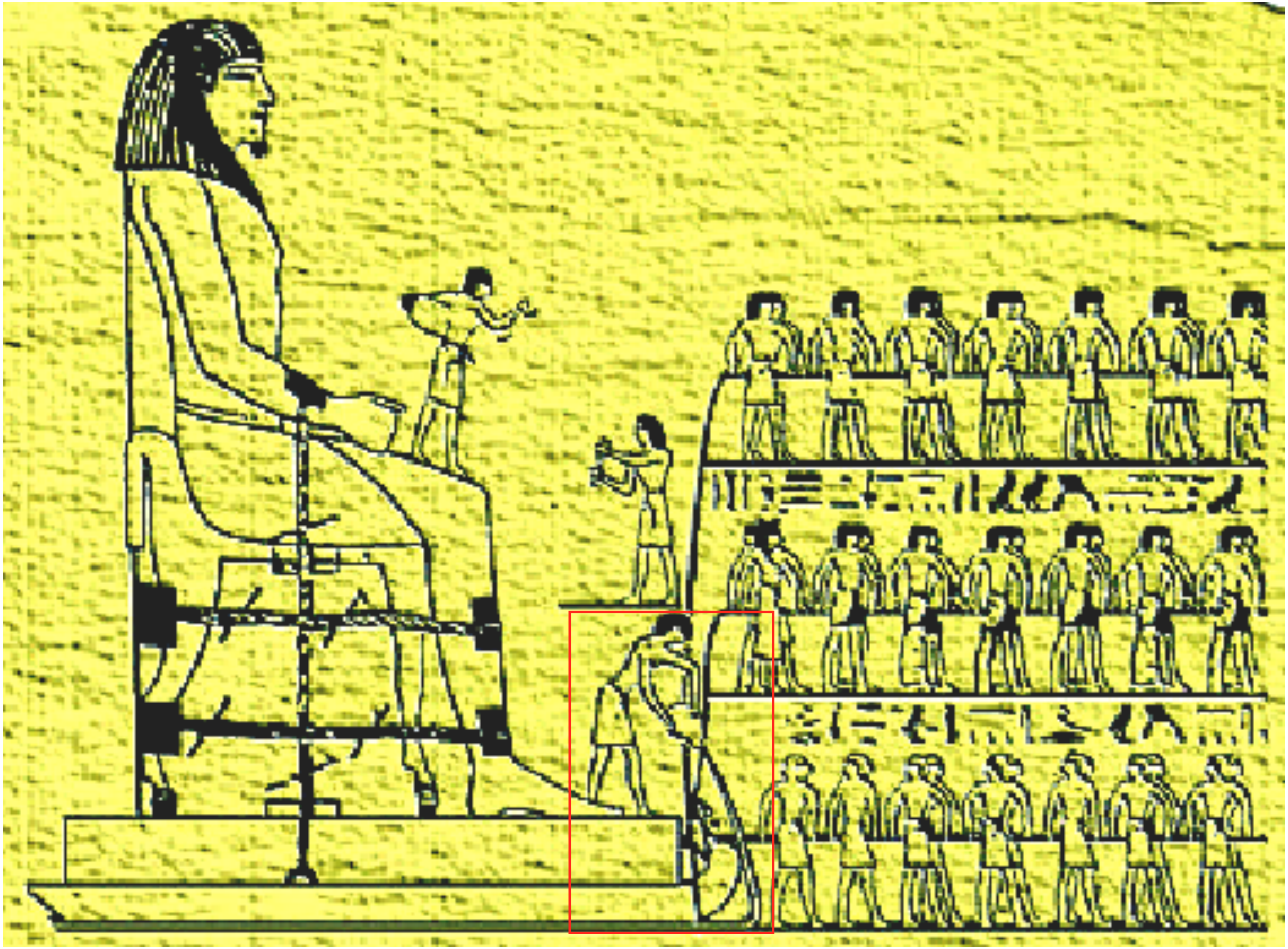
Figure 2 Sir William Bate Hardy': Concept of Boundary Lubrication

(1922)

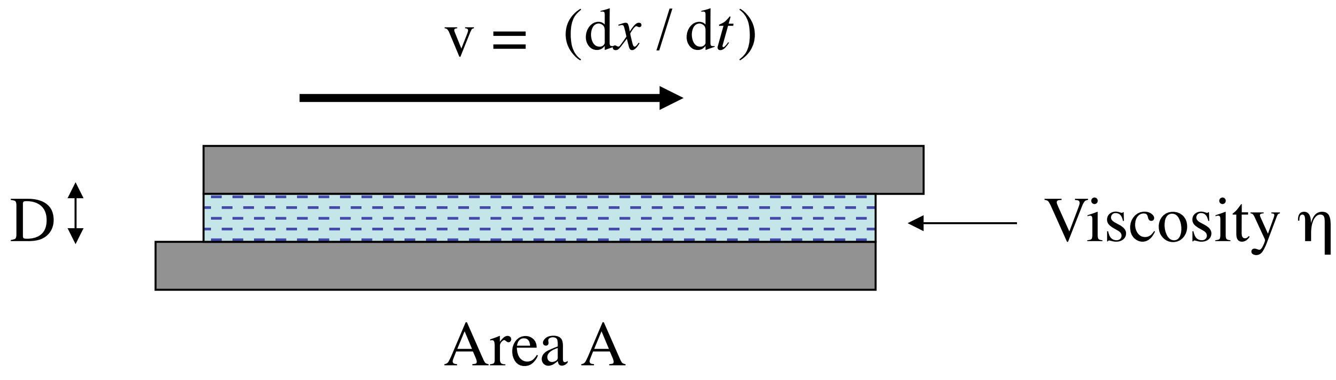
Under strong compressions, or at asperities, the situation is less straightforward (e.g. plastic flow)



Asperity contact



Liquids, such as oils - viscous dissipation in hydrodynamic lubrication



Shear stress = (friction force)/area = σ = ηv/D

$$\Delta E_{\text{viscous}} = \int \eta_{eff} \frac{(\mathrm{d}x / \mathrm{d}t)}{D} A.\mathrm{d}x$$

(assumes no slip of liquid at surface)

So what is the ‘new paradigm’?

It is the realization that, in contrast to classic mechanisms involving oils or boundary lubricants, water can provide remarkable lubrication between molecules or surfaces, due to its dipolar nature and orientational entropy properties.

1. Raviv, U.; Laurat, P.; Klein, J. **Nature** 413, 51-54 (2001).

2. Raviv, U.; Klein, J. **Science** 297, 1540 (2002).

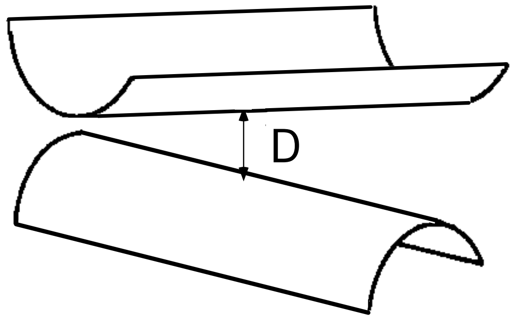
3. Raviv, U.; Giasson, S.; Kampf, N.; Gohy, J.-F.; Jerome, R.; Klein, J. **Nature** 425, 163 (2003).

4. Briscoe, W. H.; Titmuss, S.; Tiberg, F.; Thomas, R. K.; McGillivray, D. J.; Klein, J. **Nature** 444, 191 (2006).

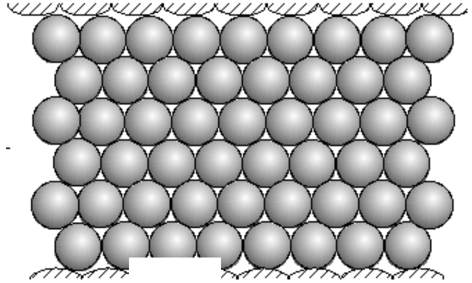
5. Klein, J. **Science,** 323, 47 (2009)

6. Chen, M.; Briscoe, W. H.; Armes, S. P.; Klein, J. **Science,** 323, 1698 (2009).

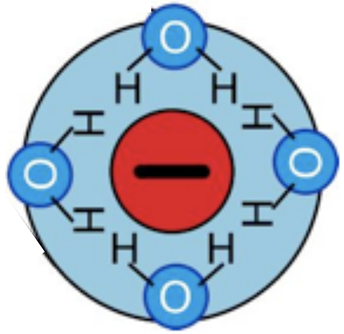
- Mechanical properties of liquids confined down to subnanometer levels



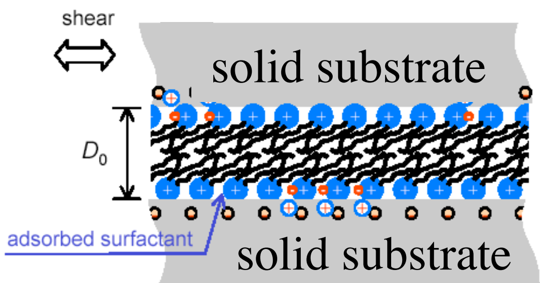
- Confined 'simple' liquids vs. confined water

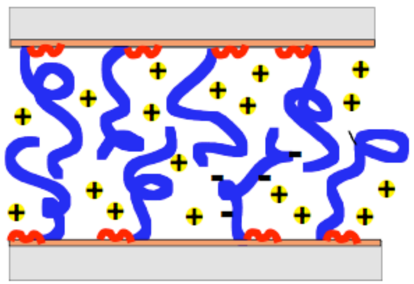


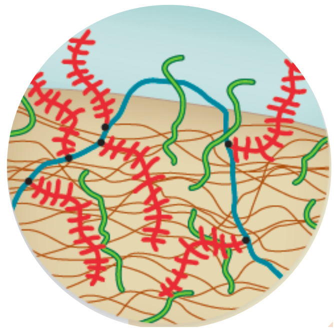
- Hydration layers: the ultimate confinement



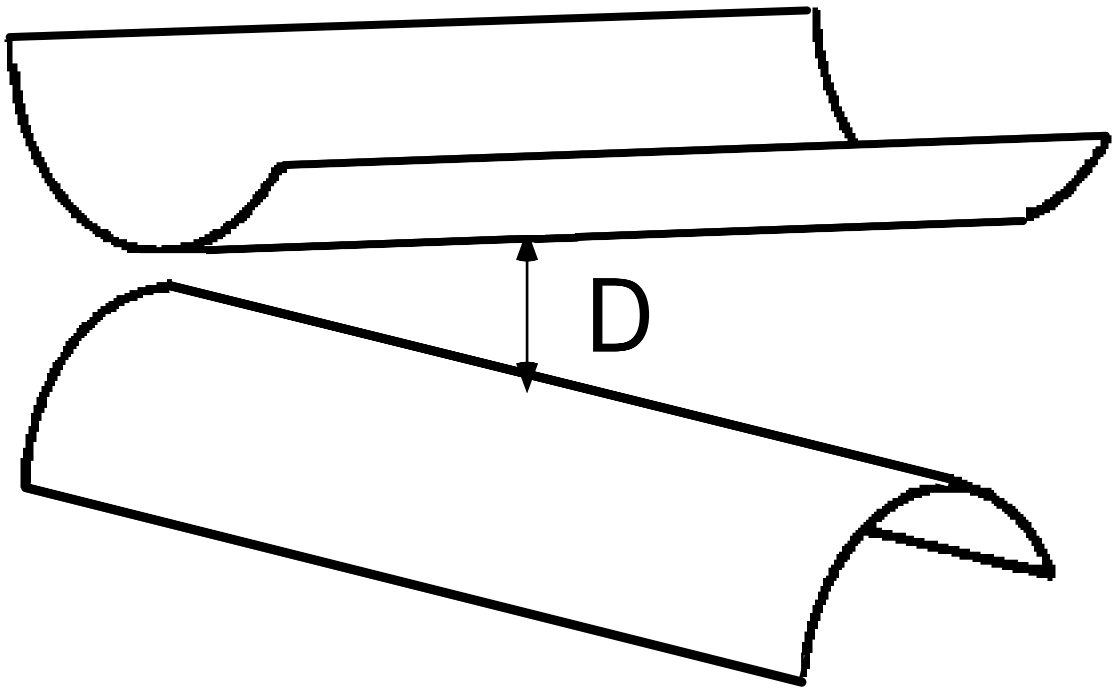
- Some implications

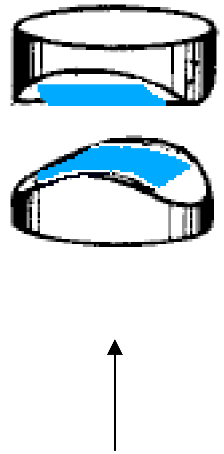




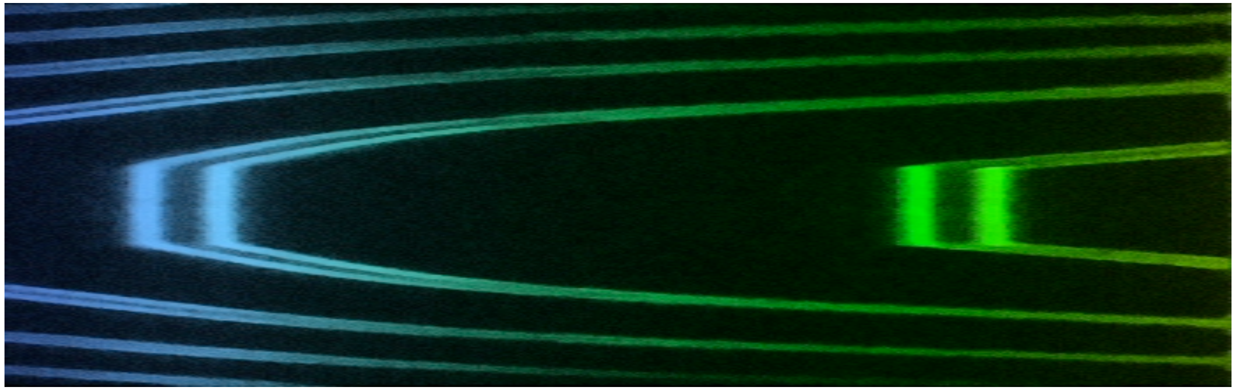


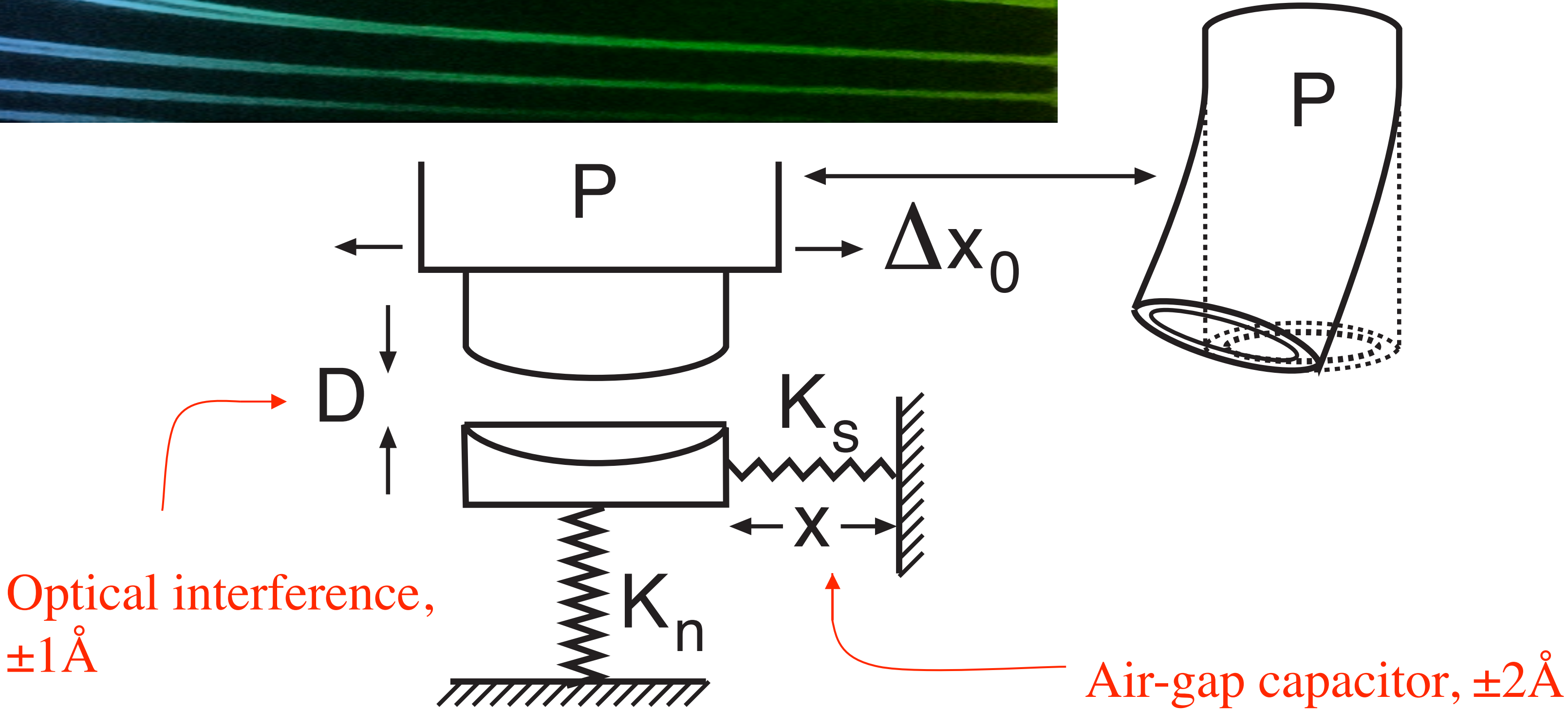
Forces F(D) between mica sheets are measured directly





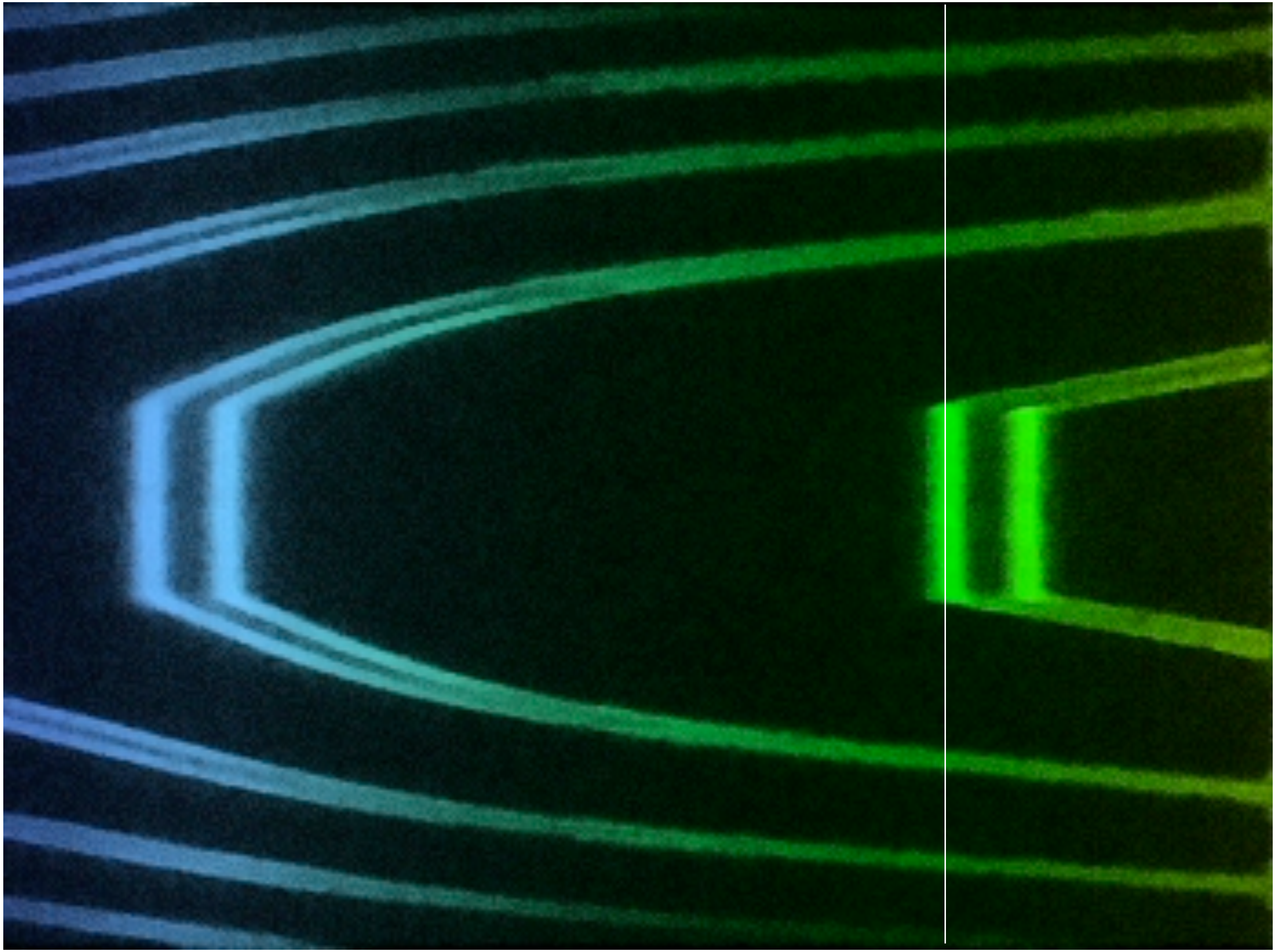
Crossed-cylindrical lenses

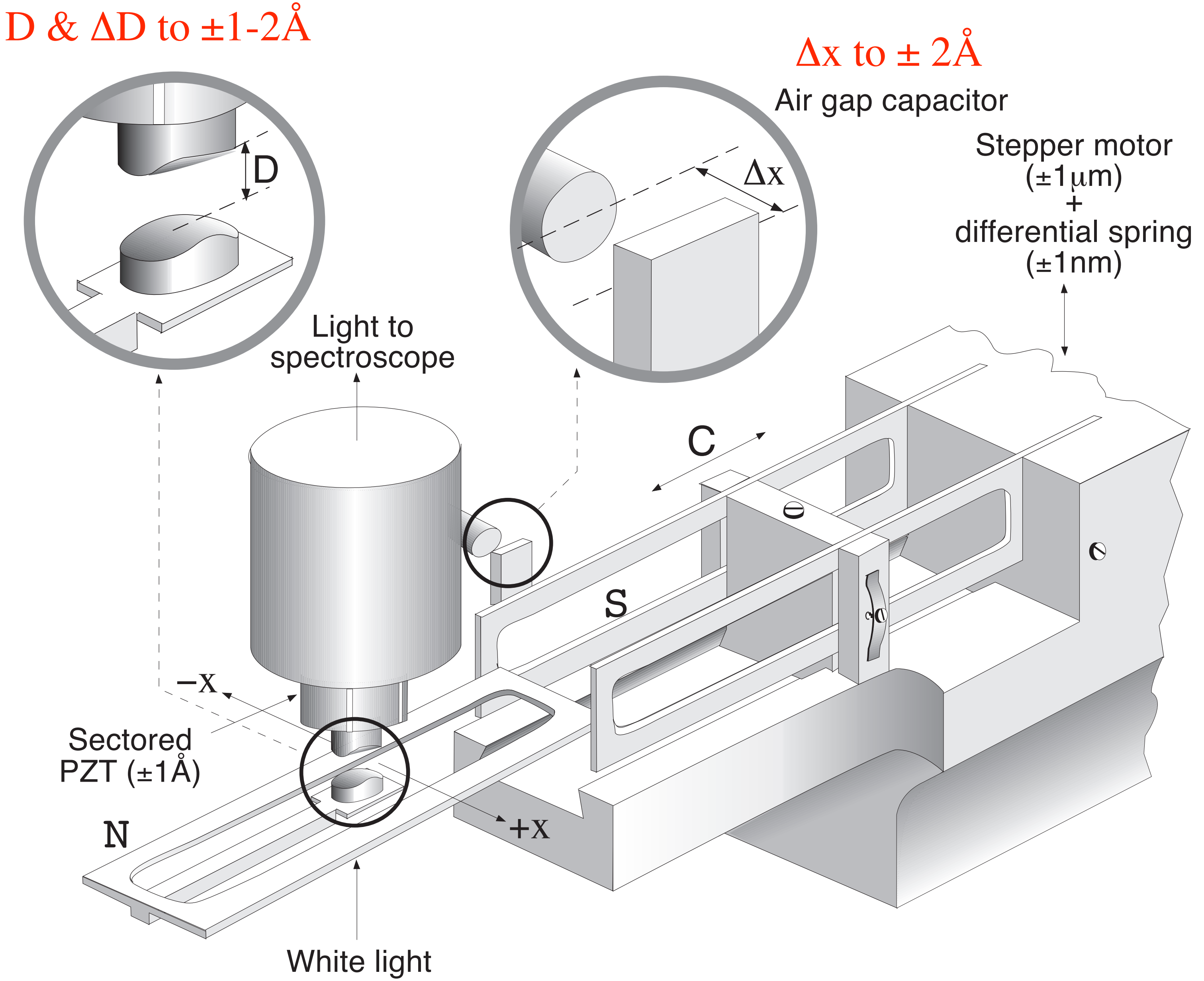




Nature **352**, 143 (1991)
Nature **370**, 634 (1994)
Science **269**, 816 (1995)
J. Chem. Phys. **108**, 6996 (1998)

Sensitivity and resolution in shear and normal stress is ca. 5-10,000-fold that of tipped AFM, STM



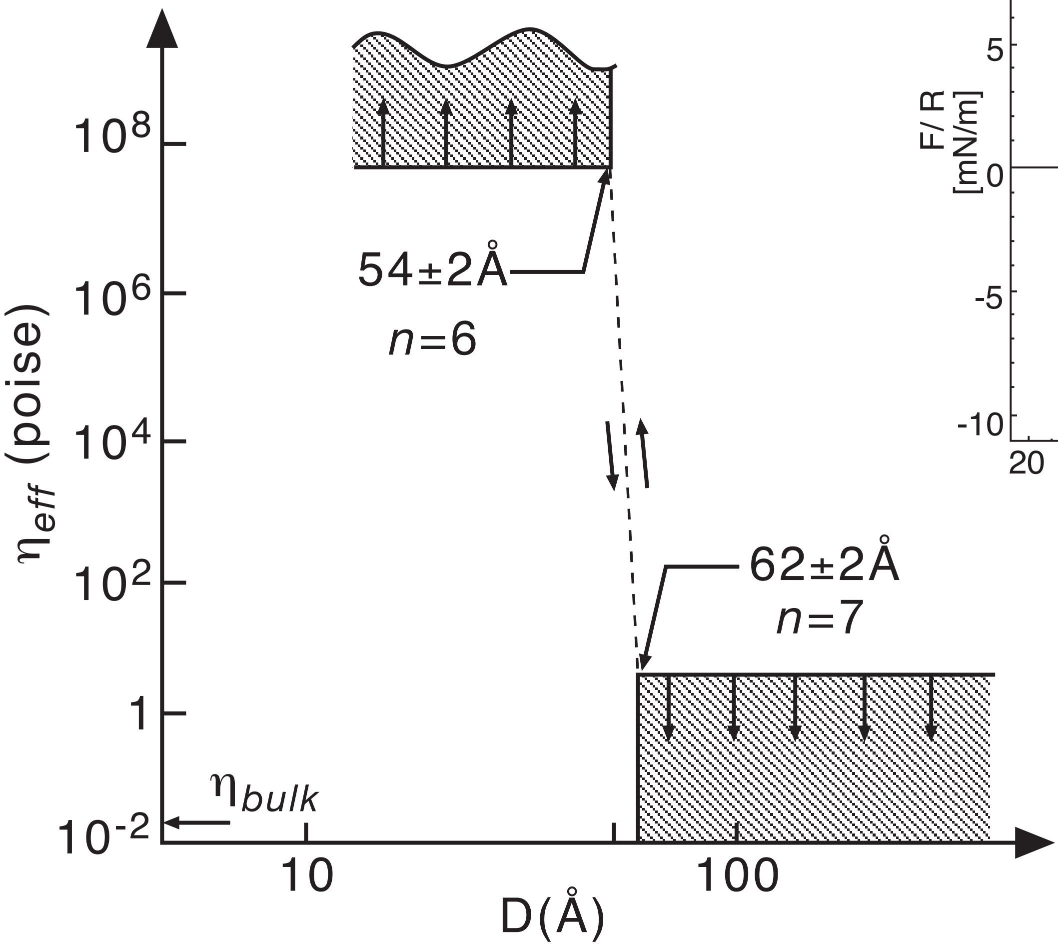


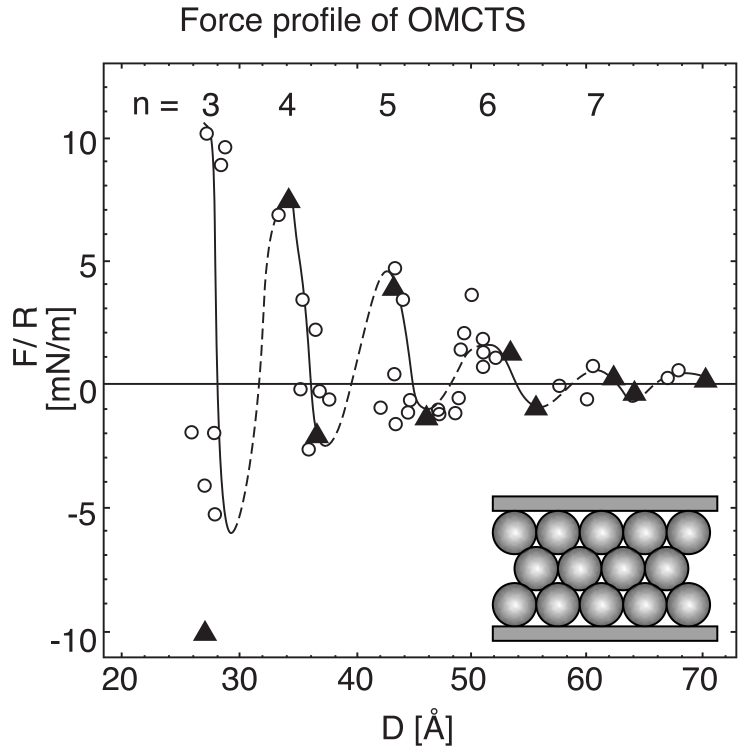
J. Phys. Chem. B
105, 8125 (2001)

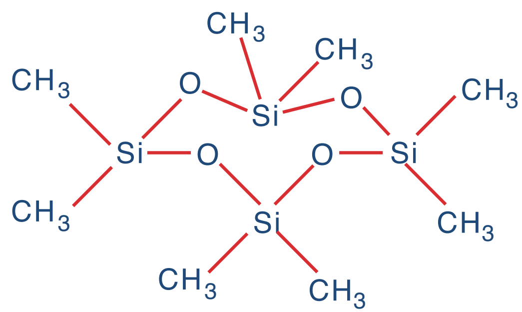
Sensitivity and resolution in shear and normal stress is ca. 5-10,000-fold that of tipped AFM, STM

- Confined ‘simple’ liquids vs. confined water

Organic liquids become solid-like under confinement







OMCTS

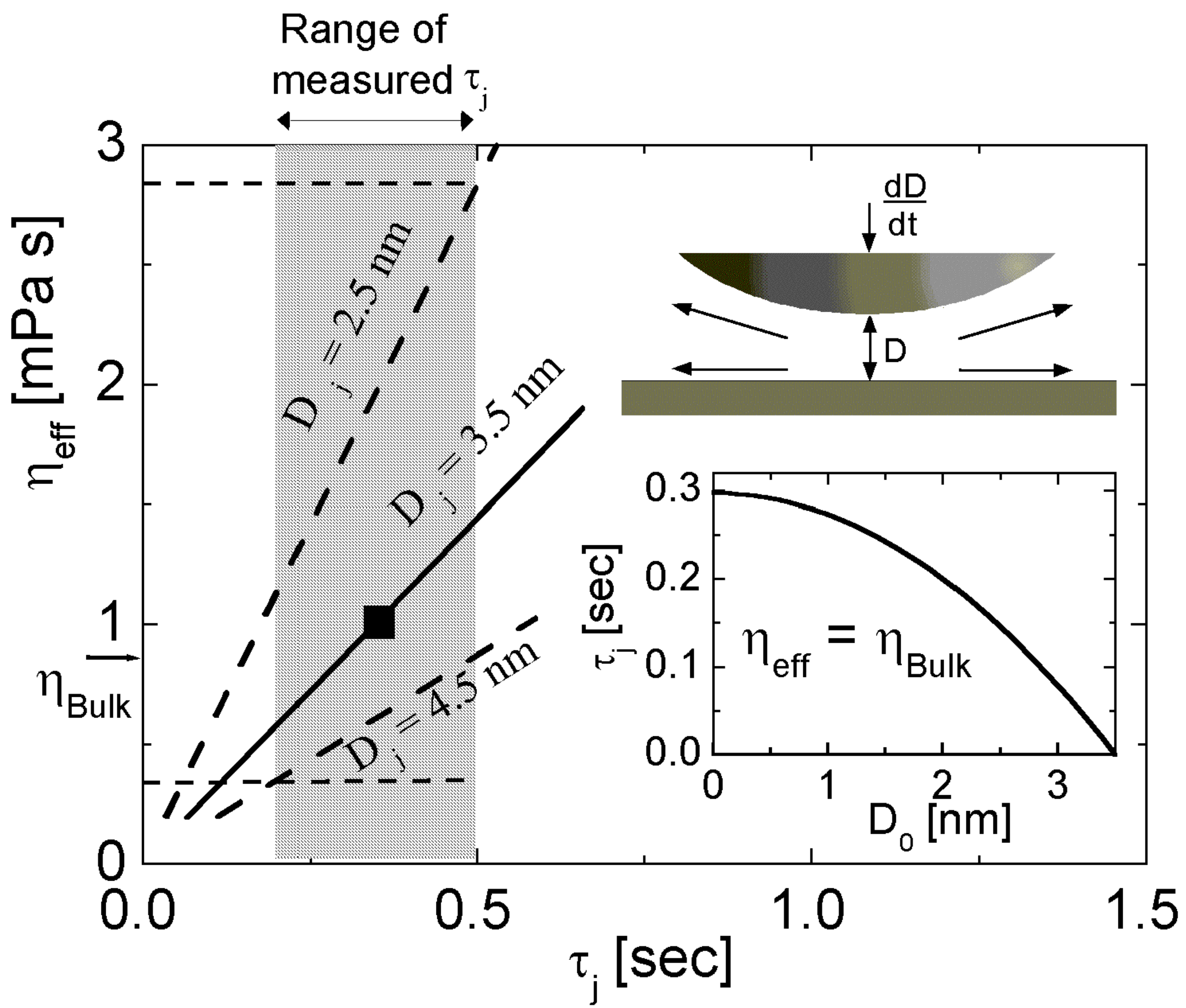
J.K. & E. Kumacheva *Science* **269,** 816 (1995)

J.Chem. Phys. **108,** 6996 (1998)

What happens in the case of confined water?

Raviv, Laurat, JK, *Nature*, **413**, 51-54 (2001); Raviv, Perkin,Laurat, JK *et al, Langmuir* **20**, 5322-5332 (2004); Goldberg, JK et al. *PCCP* **10**, (32),4939-4945 (2008); Perkin et al., Langmuir **22**, 6142-6152 (2006) & Faraday Disc., **141**, 399 (2009);

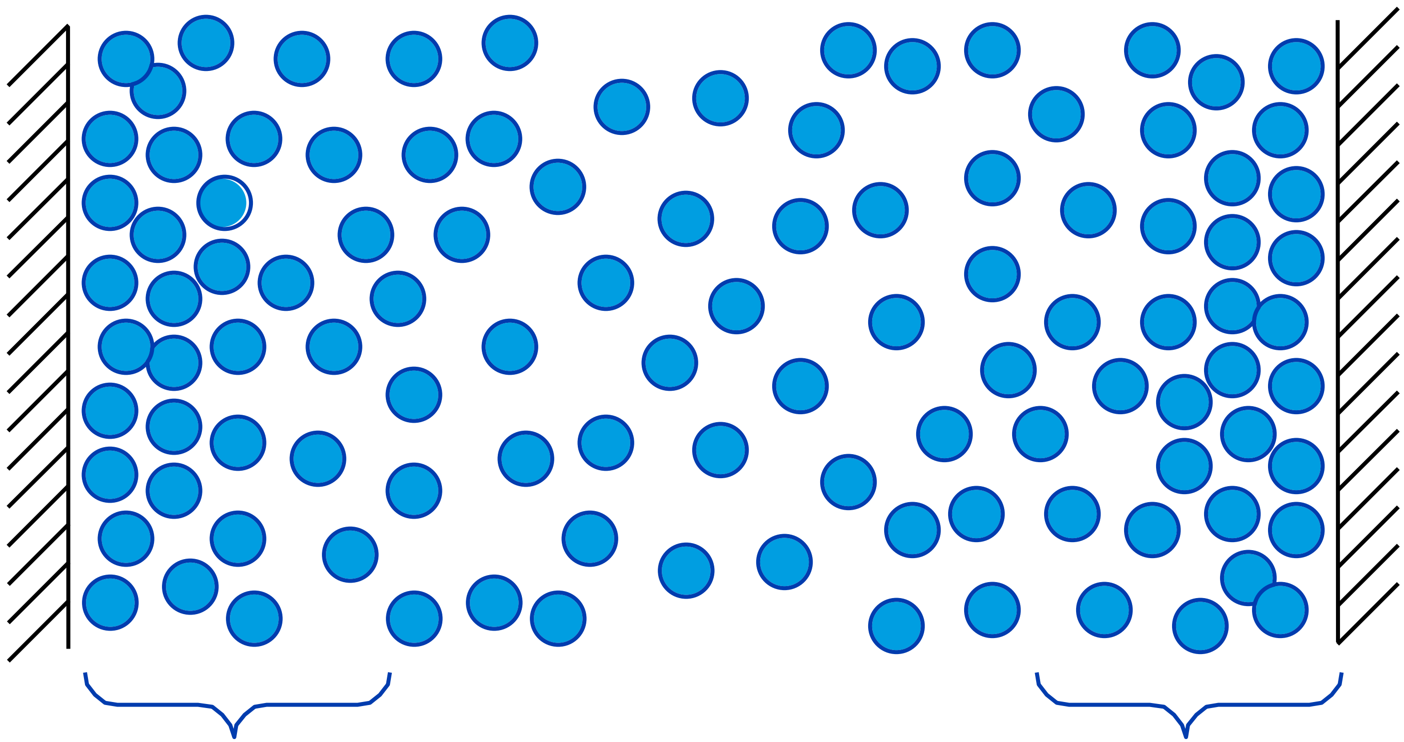
Raviv, Laurat & JK, *Nature* **413**, 51-54 (2001)
Raviv, Perkin, Laurat & JK *Langmuir* **20**, 5322-5332 (2004)
Perkin, Chai, Kampf, JK et al *Langmuir* **22**, 6142-6152, (2006)



For non-associating liquids

Increase in P or ρ
→ solidification

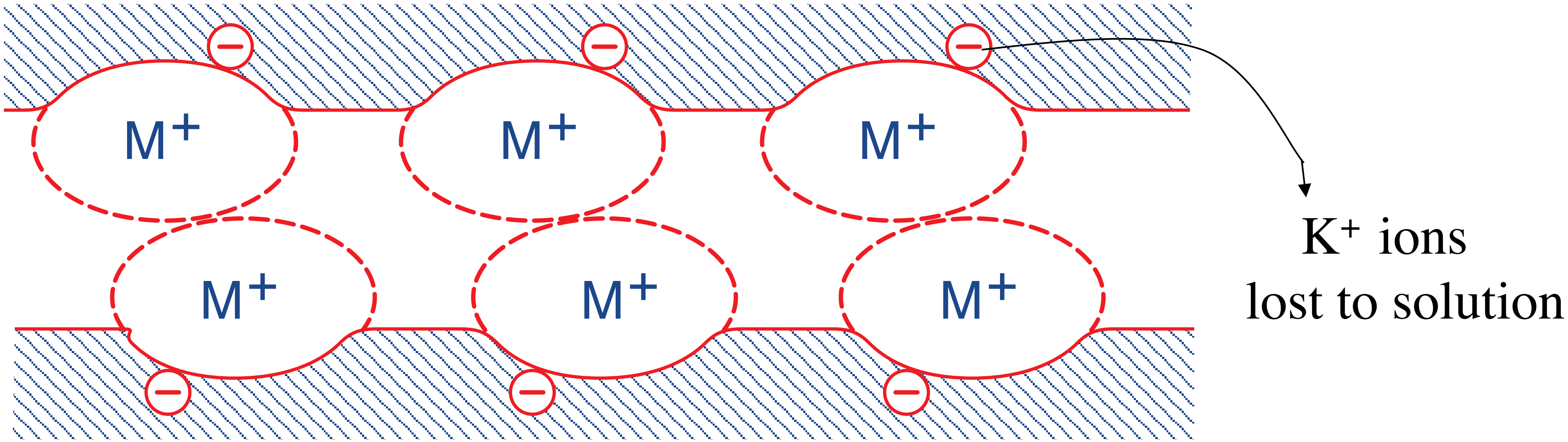
For water
Increase in P or ρ*
→ melting, i.e suppresses tendency for solidification



E.A. Jagla, *Phys. Rev. Lett.* **88**, 245504 (2002); Chandross & Grest 2009
Leng & Cummings, Phys. Rev. Lett., 94, 026101 (2005); JCP 124, 074711 (2006)
K. Gubbins et al. JPCM (2006) [*due to configurational entropy constraints]

Interactions between mica surfaces in aqueous media at high salt concentrations

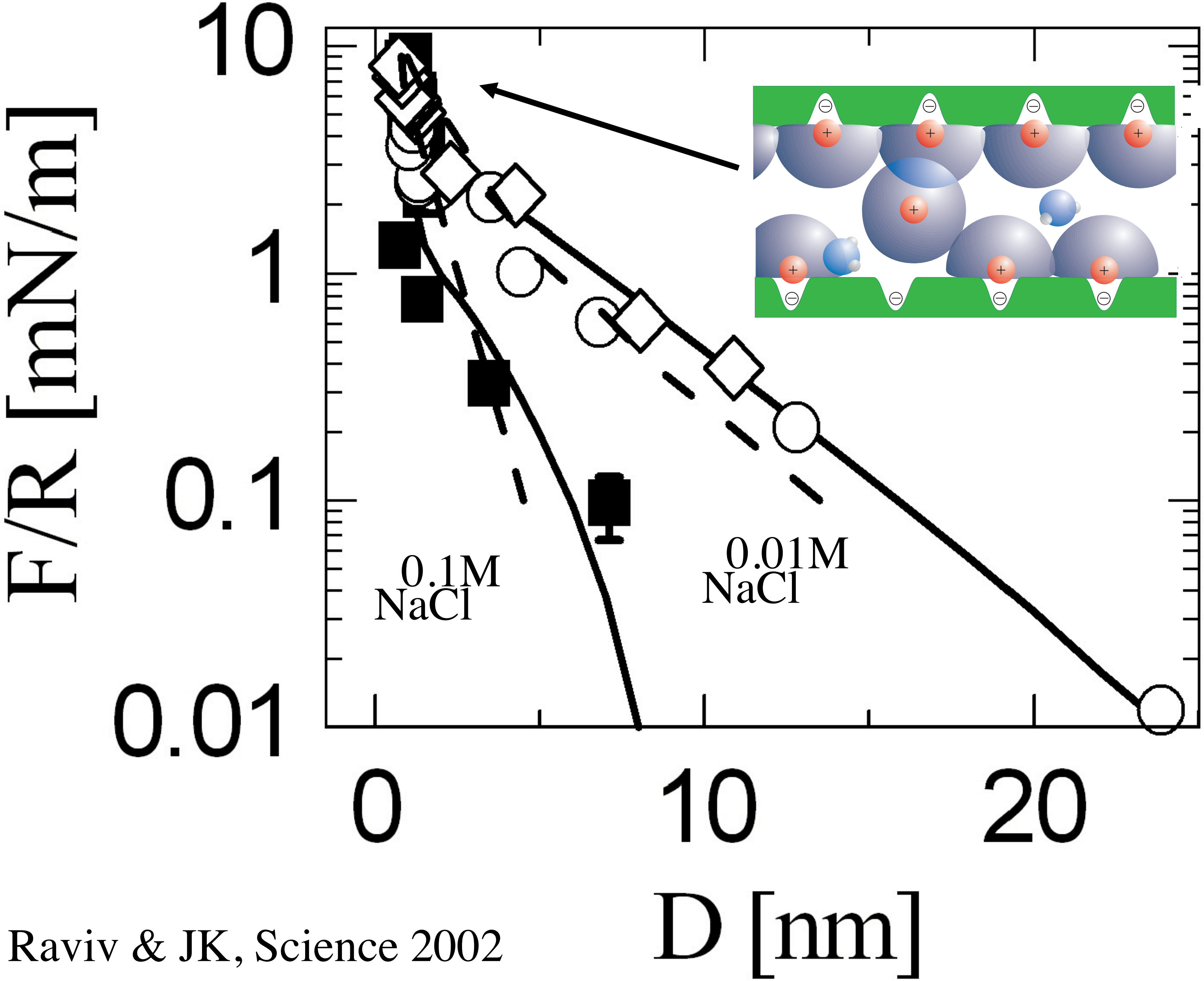
At <u>high salt concentrations</u> negatively-charged mica surface sites are compensated mainly by (trapped) salt ions, M^{+}



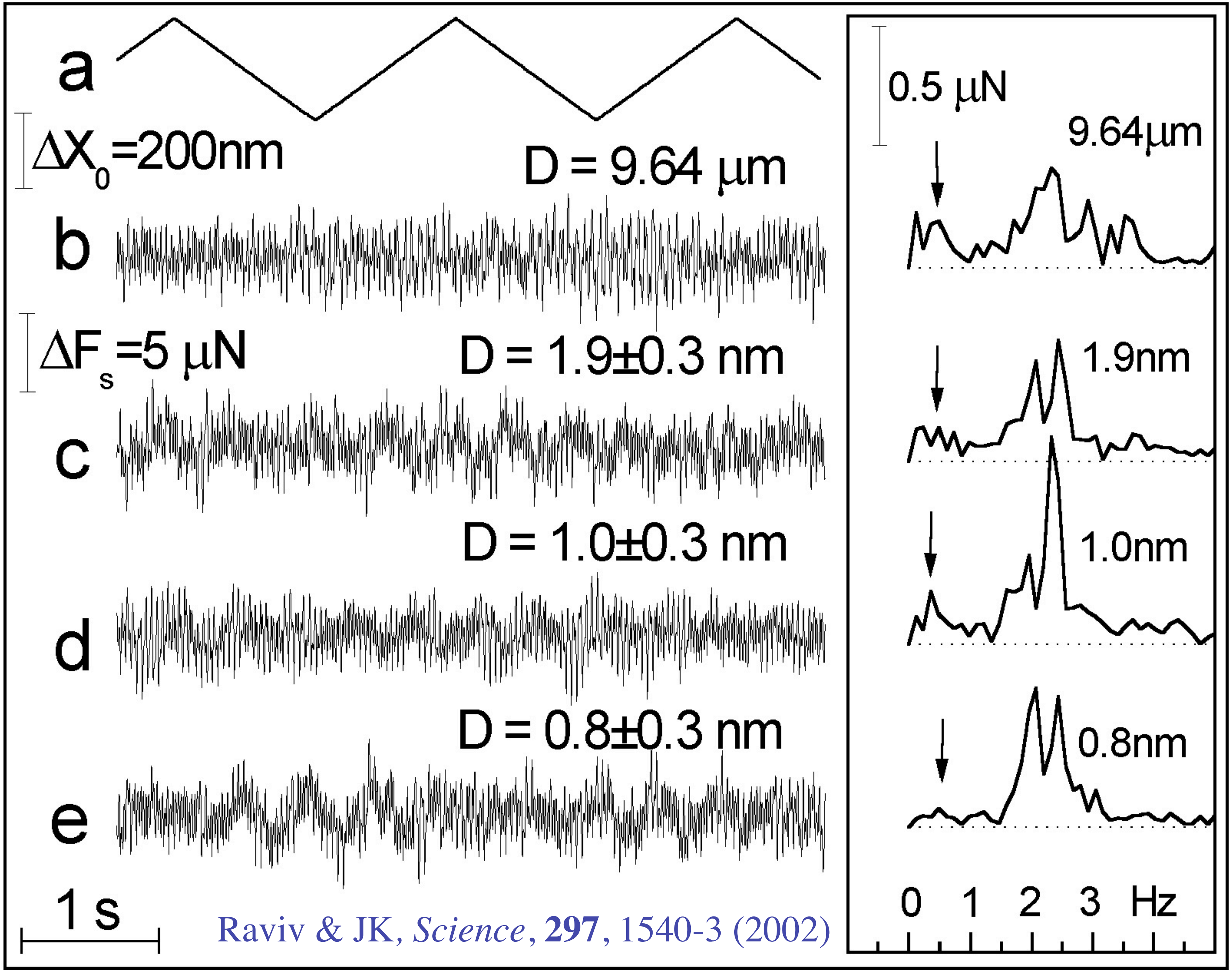
Hydrated M+ **very reluctant to shed their hydration sheaths** - so do not readily condense

→ Dominance of <u>hydration repulsion</u> at D < nm's

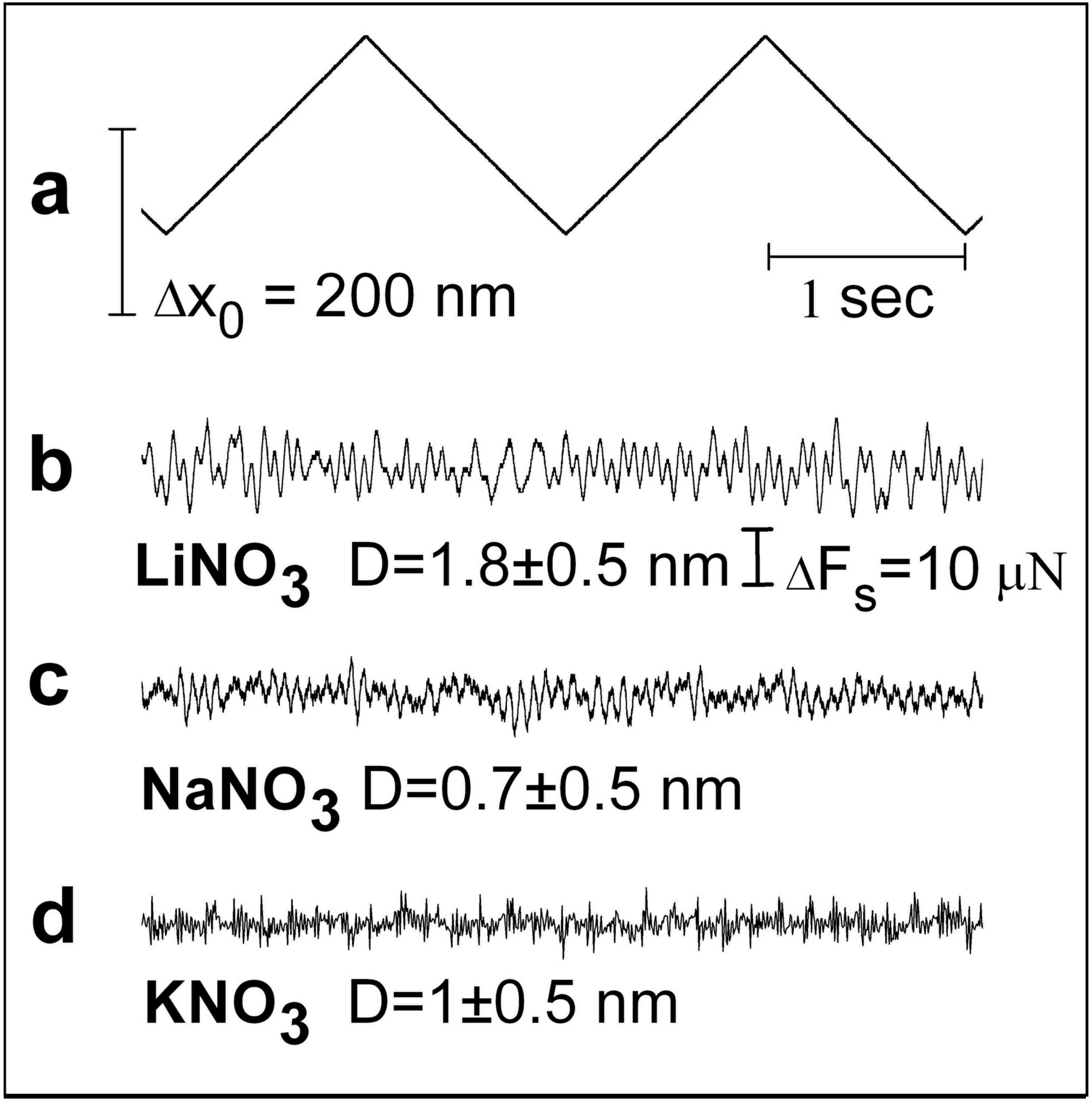
(JK et al., JPCM 16, S5437-S5448, (2004))



Raviv & JK, Science 2002



Raviv & JK, *Science*, **297**, 1540-3 (2002)

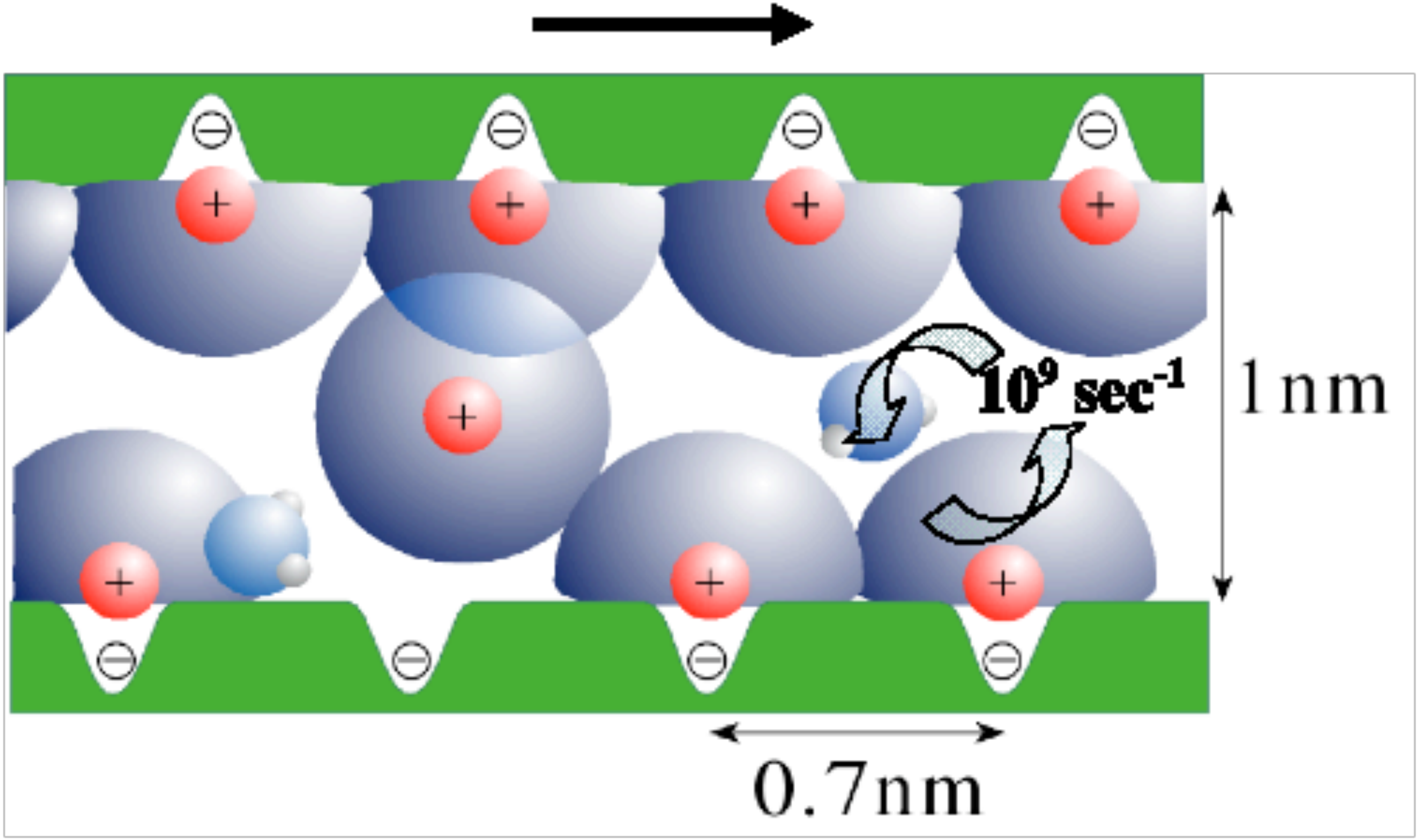


Chai, JK et al., *Langmuir* **24,** 1570-1576 (2008)

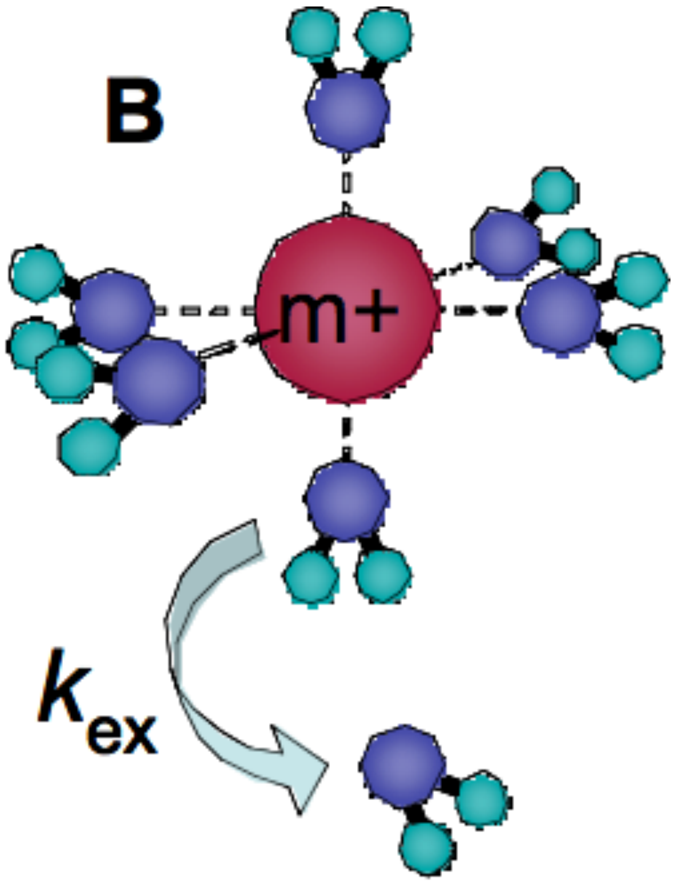
(but note Cs+ behaves very differently, see Goldberg, Kampf, JK et al., *PCCP* **10**, 4939, (2008))

For multivalent ions see Perkin, Goldberg, Kampf, JK et al., *Faraday Discussions* **141**, 399 (2009)

v_s up to 1200 nm/sec, γ up to 1500 sec^{-1} •
ssesec^{-1}

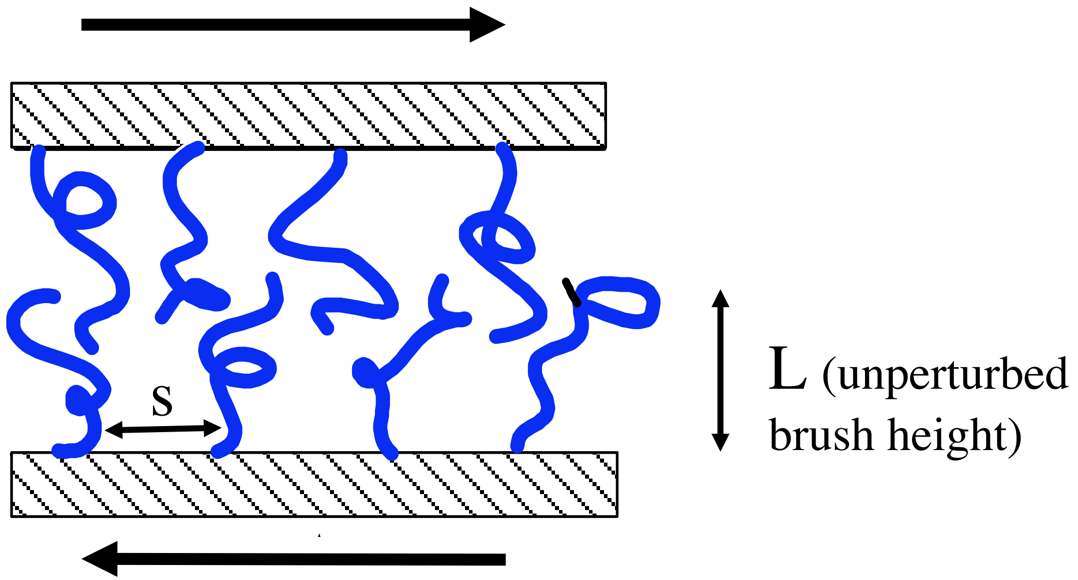


Raviv & JK, *Science*, **297**, 1540-3 (2002)



k_{ex} ranges between ca. 10^9 sec^{-1} (i.e. $\tau \approx 1$ ns) for the alkali metal ions and ca. 10^{-5} sec^{-1} (i.e. $\tau \approx 1$ day) for Cr^{3+}

	Ion	ΔG_{hydr} /crdn. H_2O (kJ/mol)
Large dehydration energies		
	Cs^+	-35
	Na^+	-81
	Ni^{2+}	-345



Polymer brushes can reduce friction 1000-fold

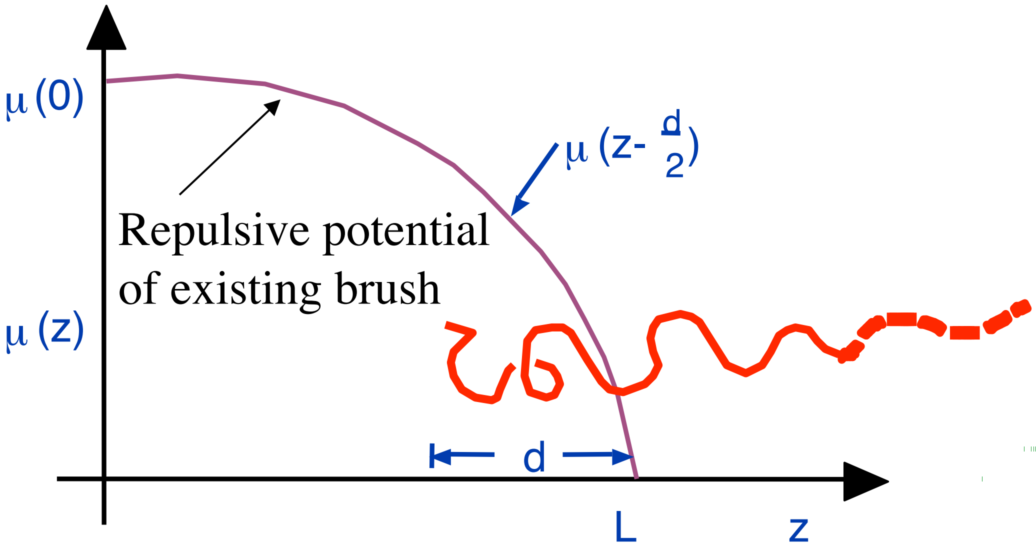
(polystyrene in toluene) $(L/s) \approx 7 - 8$

(JK et al., *Nature* **370**, 634 (1994))

(Tadmor, JK, et al. *Phys. Rev. Lett.* **91**, 115503 (2003);

Tsarkova, JK et al., *Macromolecules*, **40**, 2539-2547 (2007));
Eiser and JK, *Macromolecules*, **40**, 8455-8463 (December 2007))

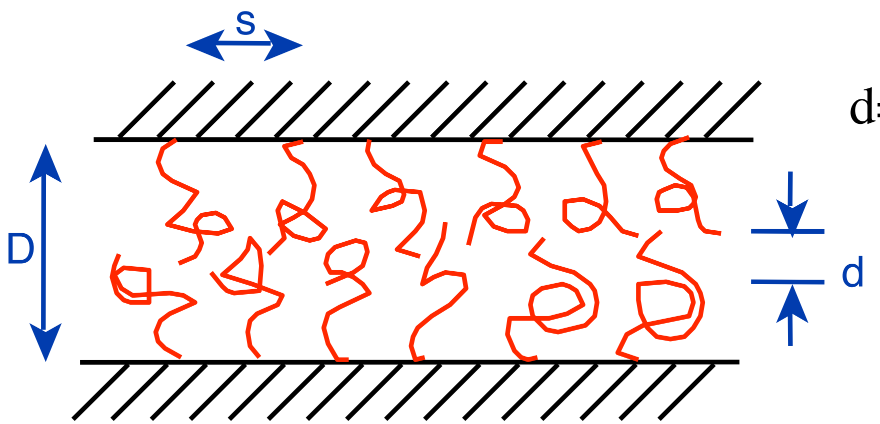
For compressed, overlapping brushes



J.K., Annual Rev. Material Sci <u>26</u>, 581 (1996)
eqs. (17) - (22)

$$\Rightarrow d^3 \cong \frac{R_0^4}{L'}, \quad \text{i.e.} \quad d \propto L'^{-1/3} \propto D^{-1/3}$$

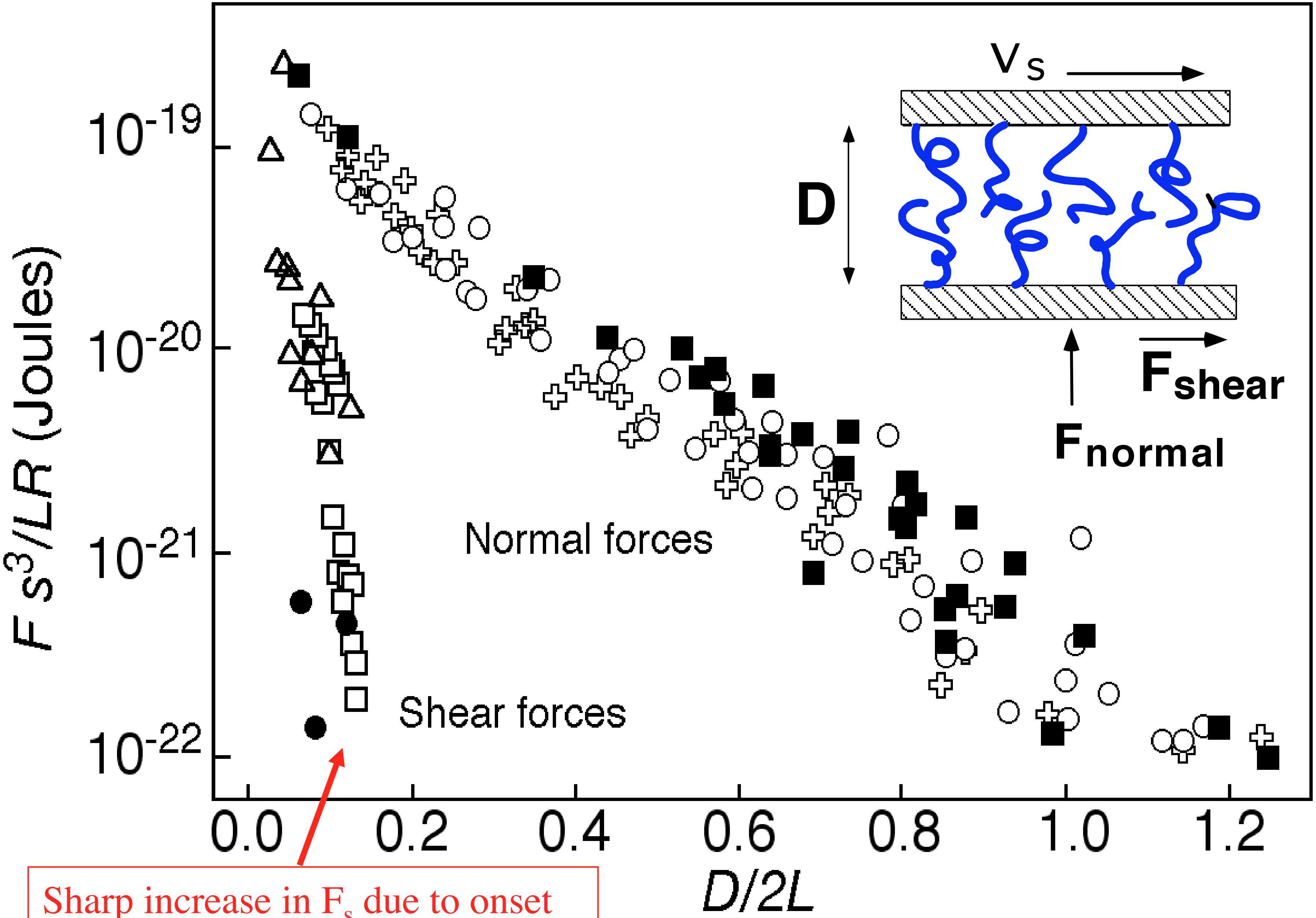
Witten et al, 1990
Wijmans et al, 1994
Grest, 1999
Sokoloff, 2006



d=interpenetration

E. Eiser & JK
Macromolecules, **40**, 8455-8463 (2007)

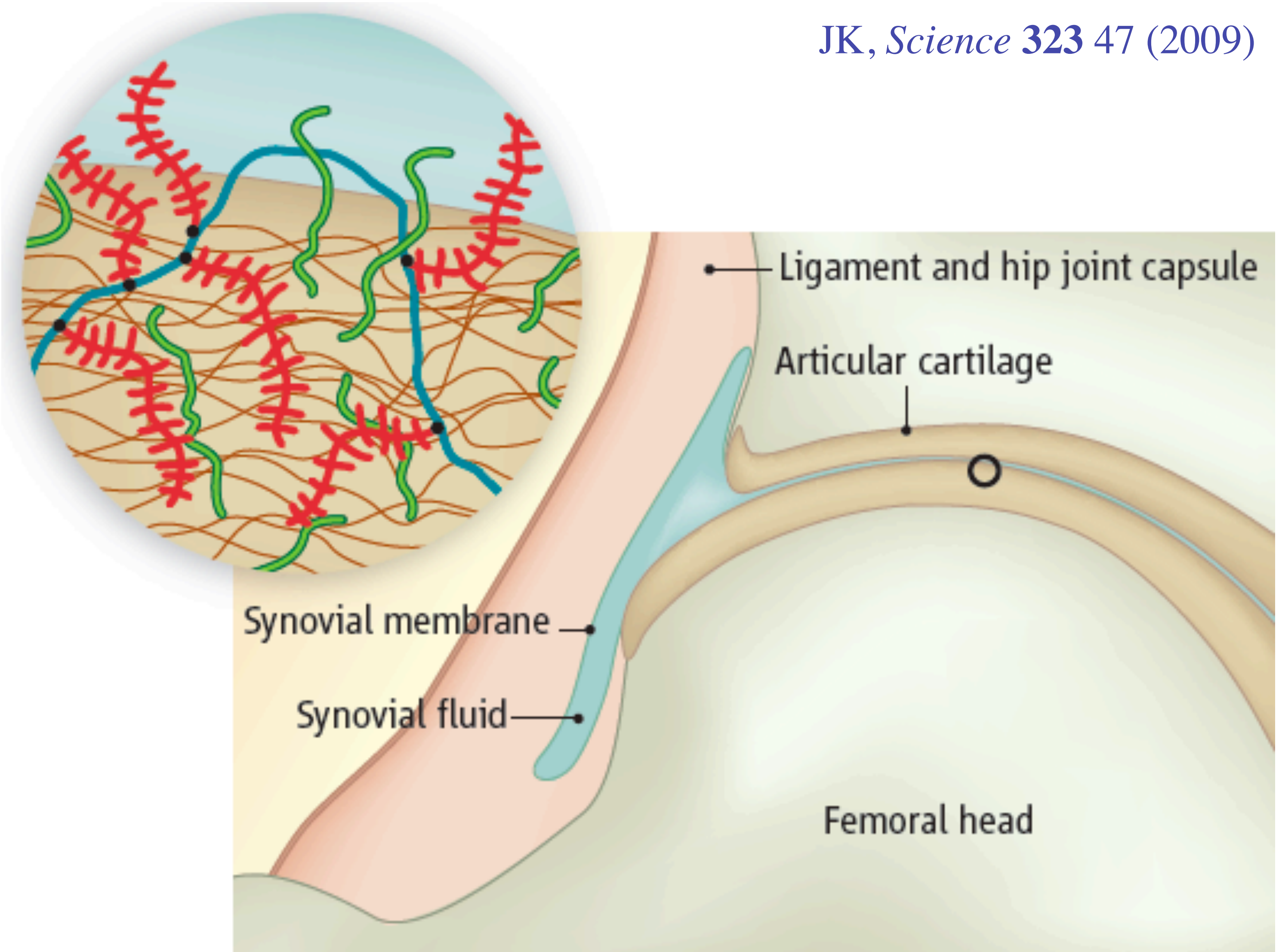
L. Tsarkova &JK
Macromolecules, **40**, 2539-2547 (2007)

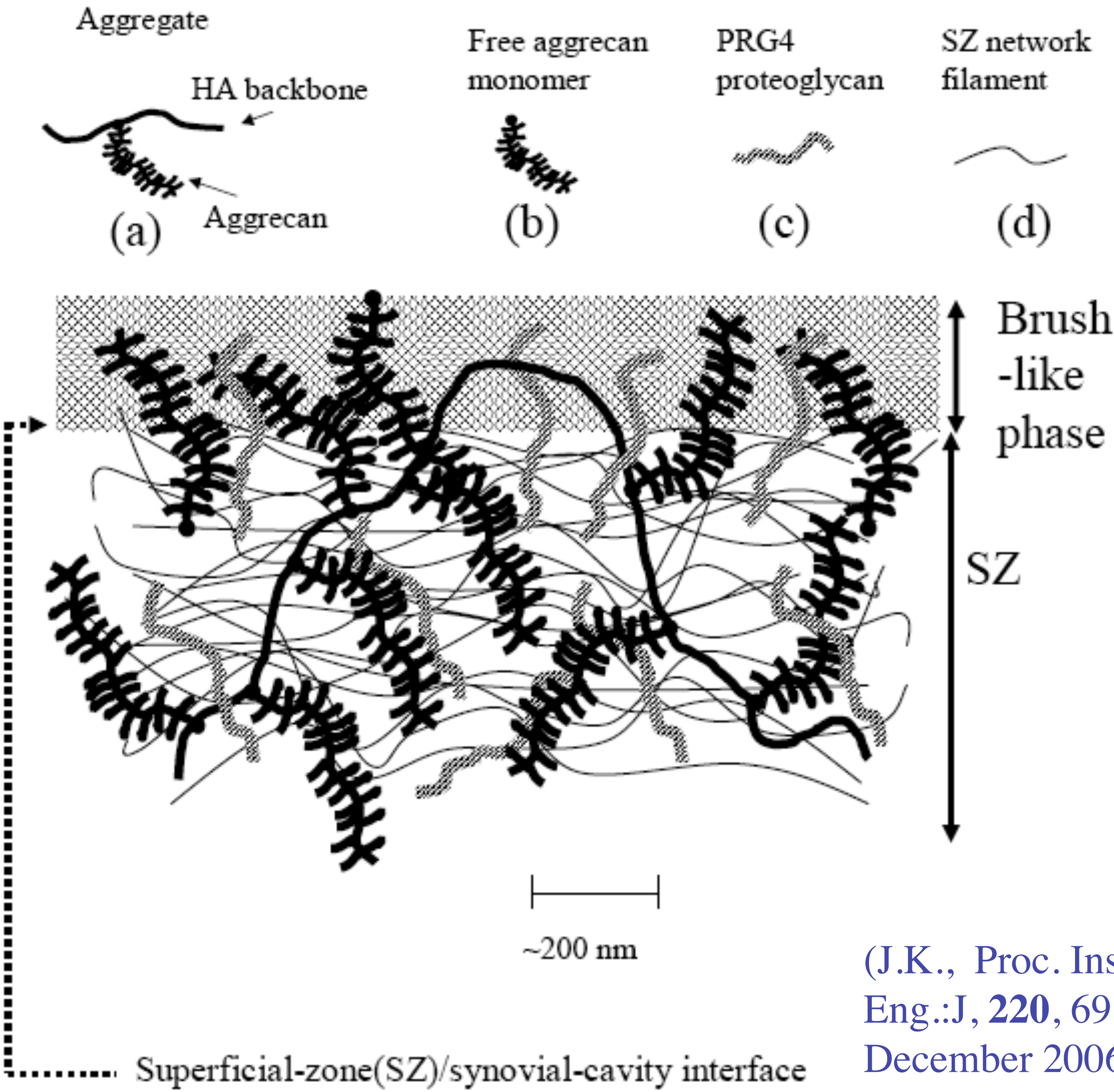


Sharp increase in F_s due to onset of glassy regime at mean pressure ≈ 0.3 MPa

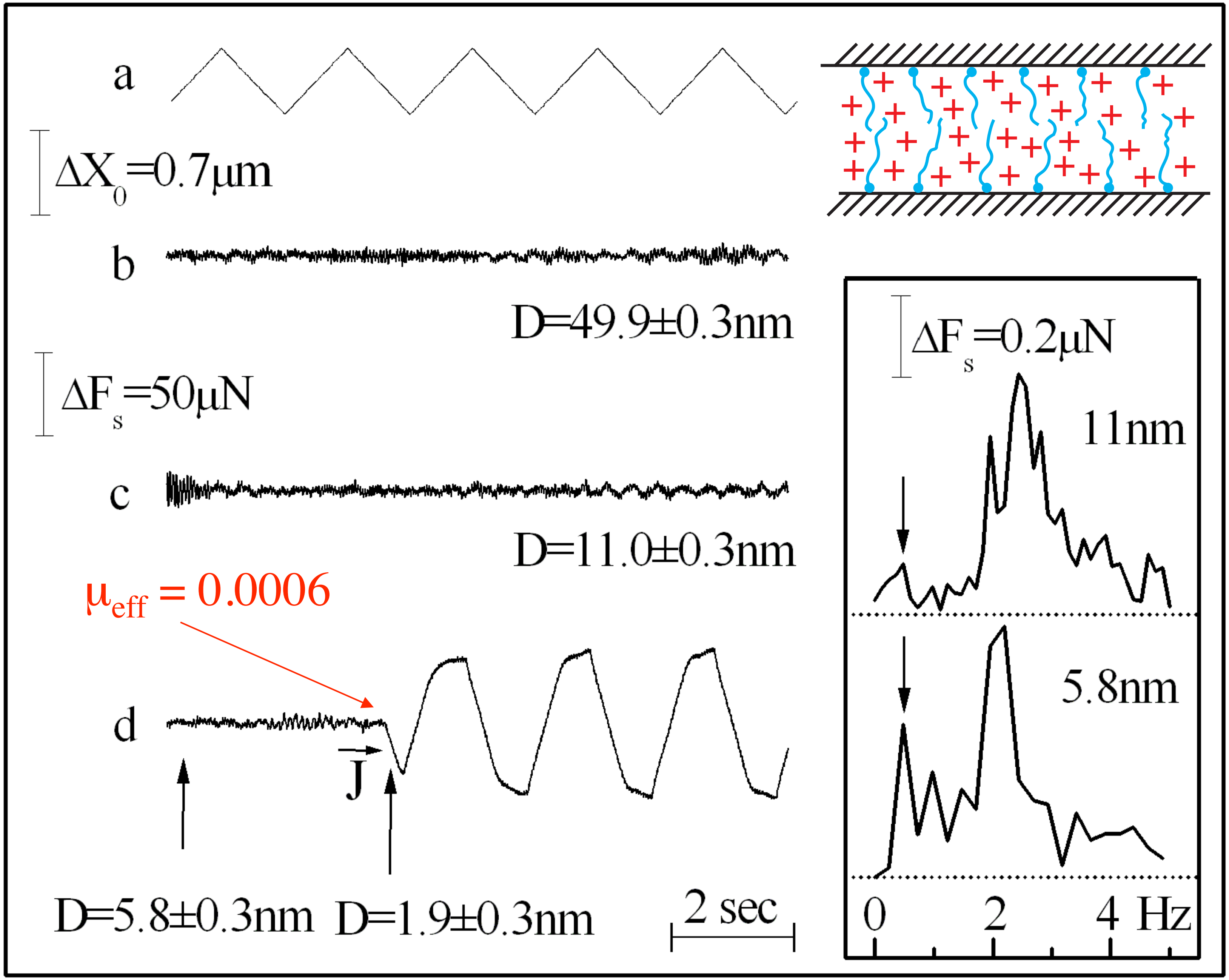
(JK et al., *Nature* **370**, 634 (1994))

JK, *Science* **323** 47 (2009)

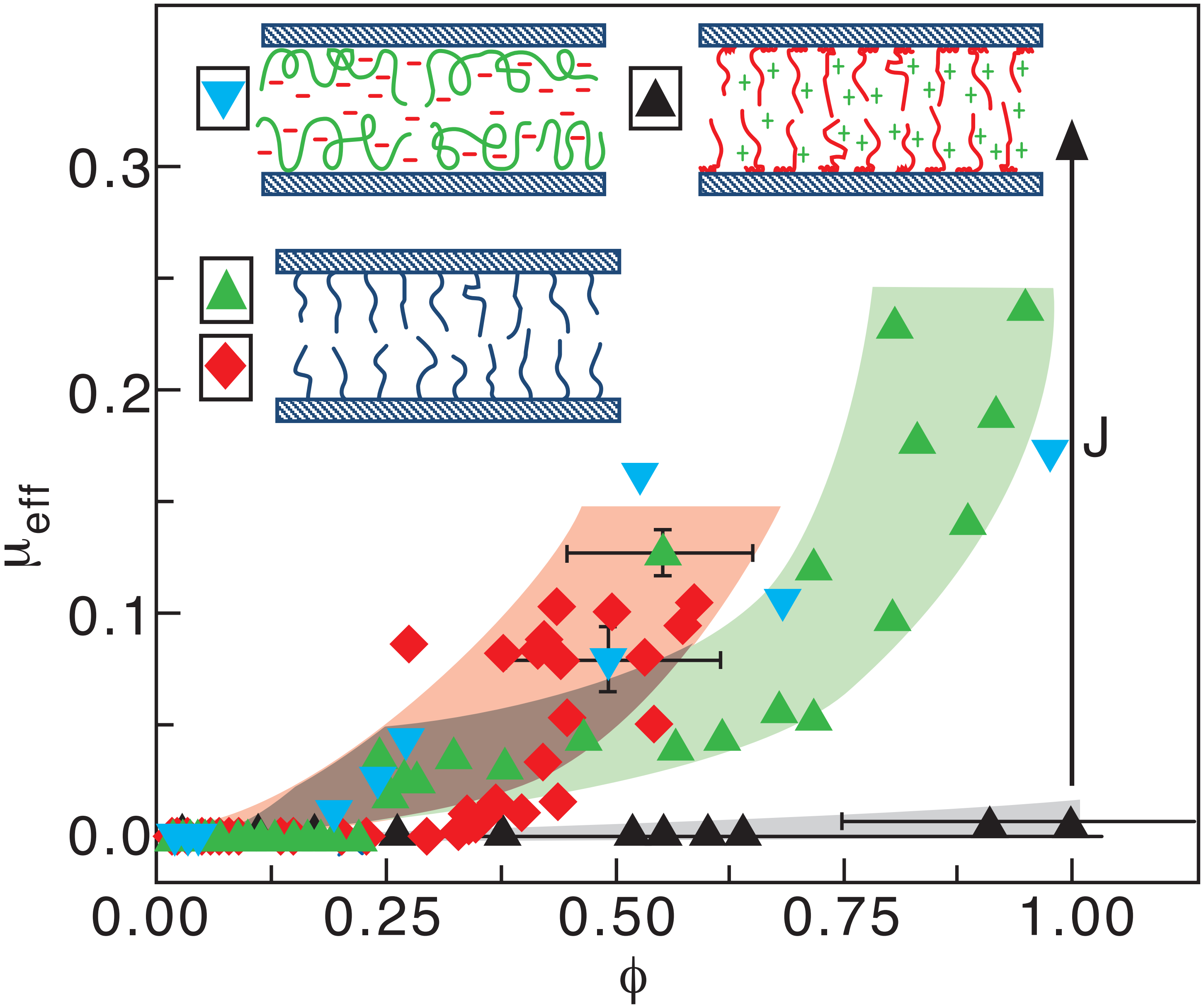




(J.K., Proc. Inst. Mech. Eng.:J, **220**, 691-710, December 2006)



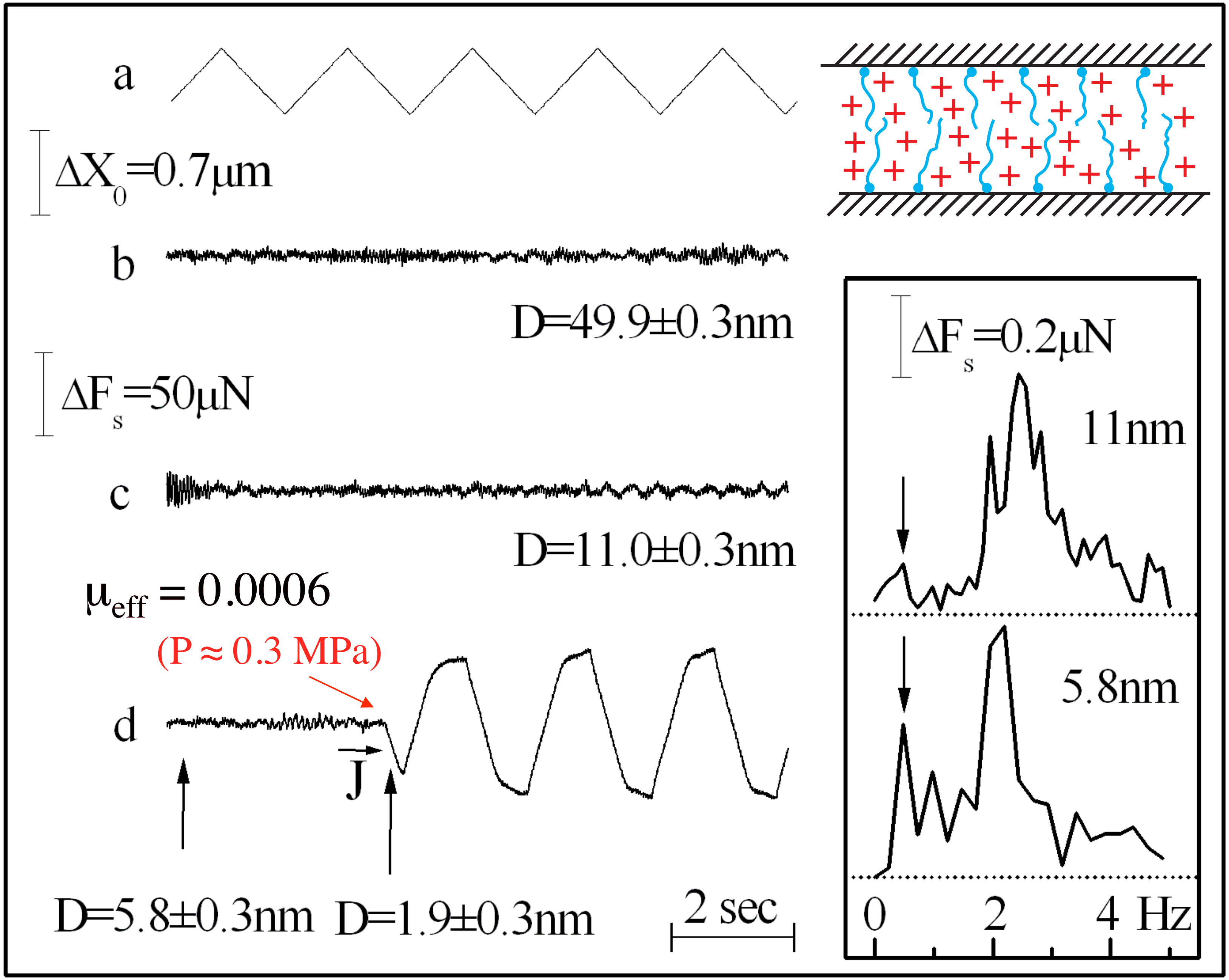
Raviv, JK et al., *Nature*, **425**, 163-165, (2003); *Langmuir* 2008



Nature, **425**, 163-165, (2003)

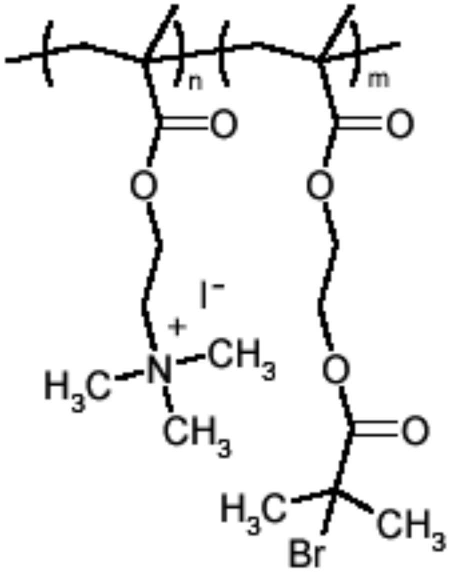
Langmuir, **24,** 8678-8687 (2008)

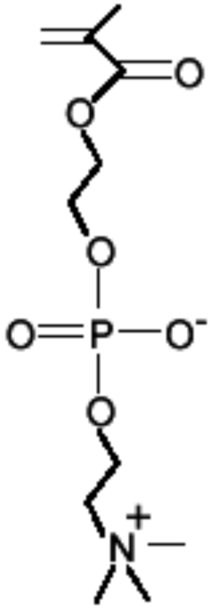
But there is a small problem…

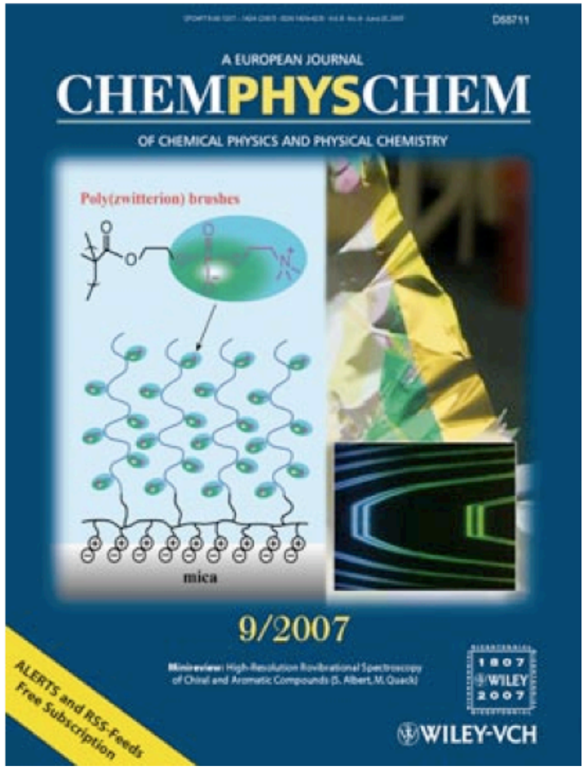


Raviv, JK et al., *Nature*, **425**, 163-165, (2003); *Langmuir*, 2008

Meng Chen, Hagai Cohen, Wuge Briscoe,
Steven Armes (Sheffield), JK







Macro-initiator

MPC

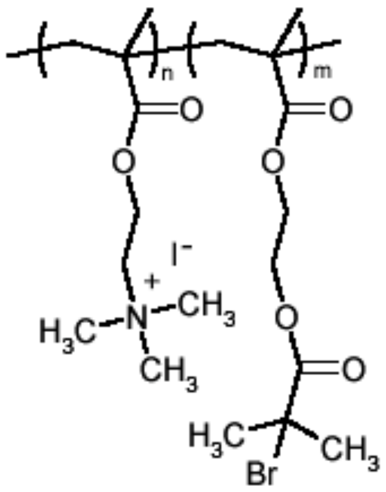
Emulating phospholipid headgroups at cell-membrane surface (Ishihara)

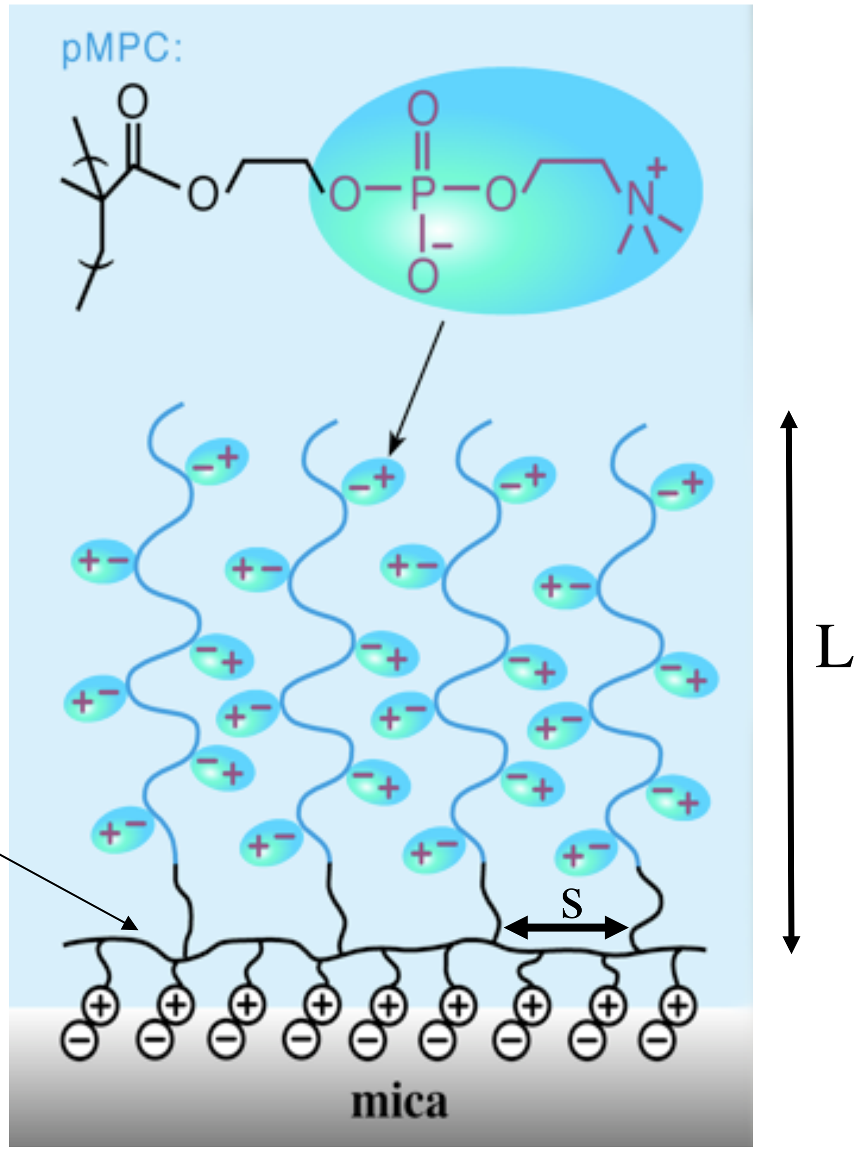
Chen, JK et al, *ChemPhysChem*, **8**, 1303-1306 (2007)

2-**M**ethacryloyloxyethyl **p**hosphoryl**c**holine

Meng Chen, Hagai Cohen
Wuge Briscoe
Steven Armes (Sheffield)

Very highly hydrated - ca. 17 - 21 water molecules/ monomer (Ishihara)



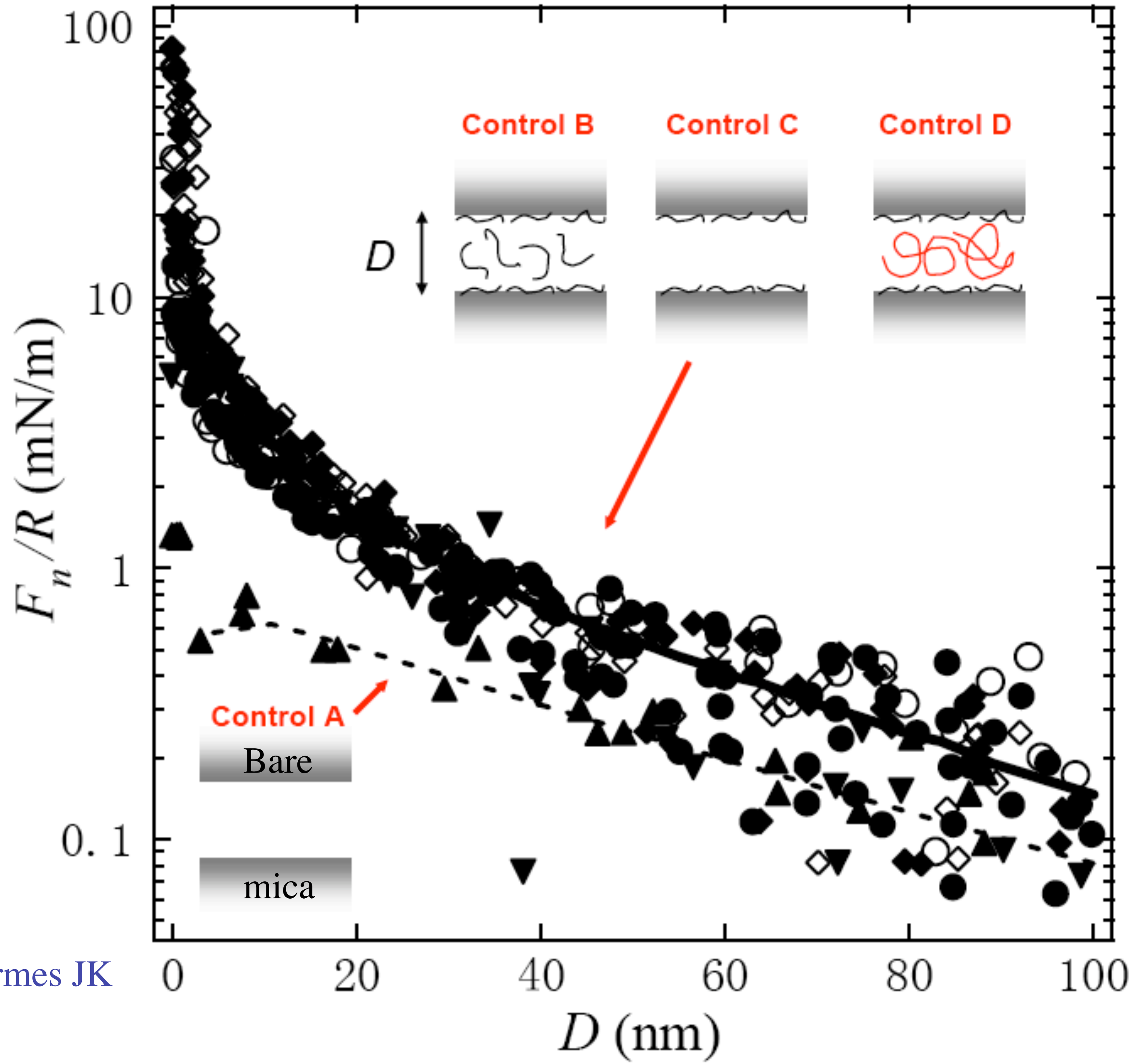


High brush density

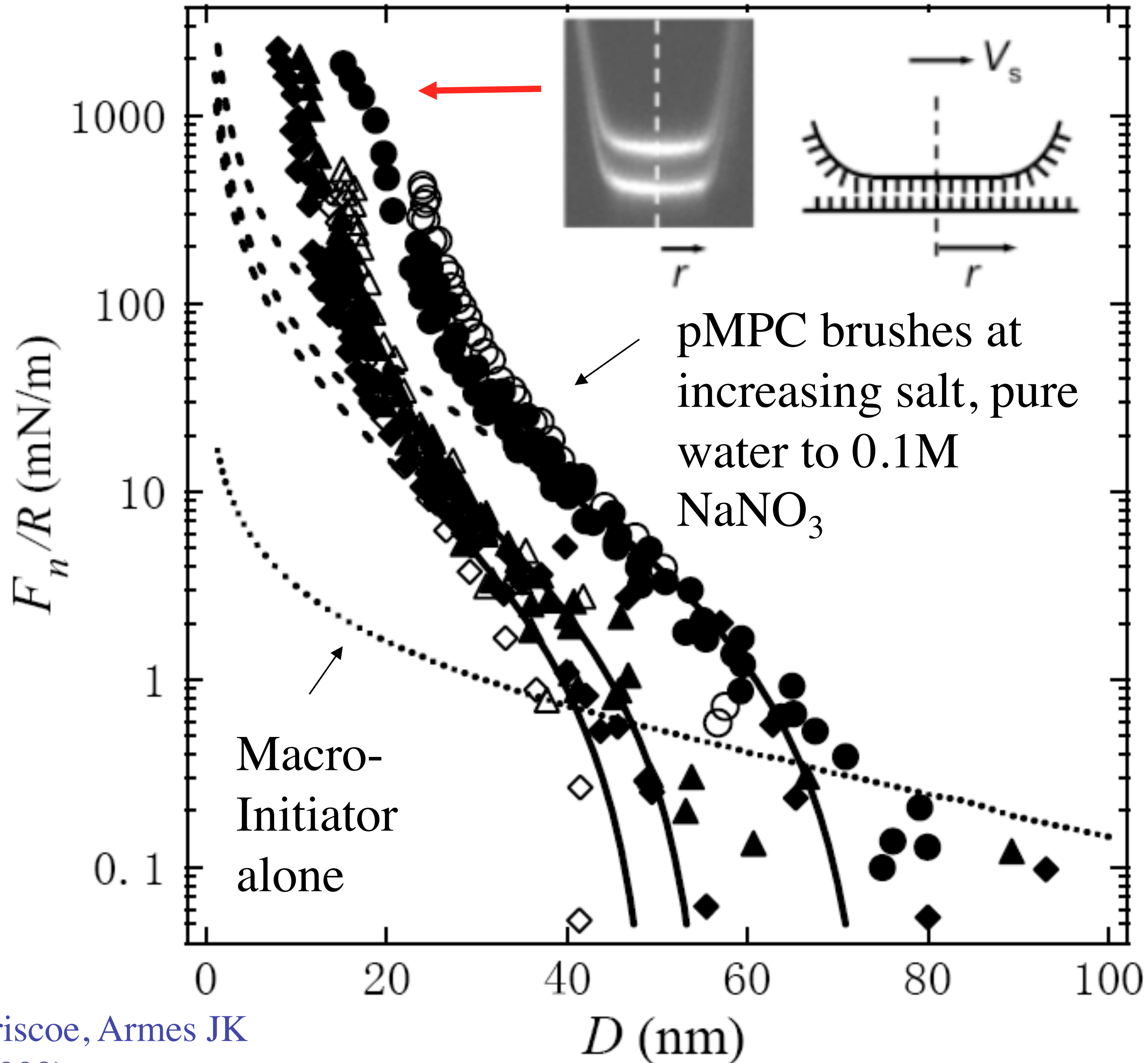
$(L/s) \approx 15$

Chen, JK et al, *ChemPhysChem*, **8**, 1303-1306 (2007)

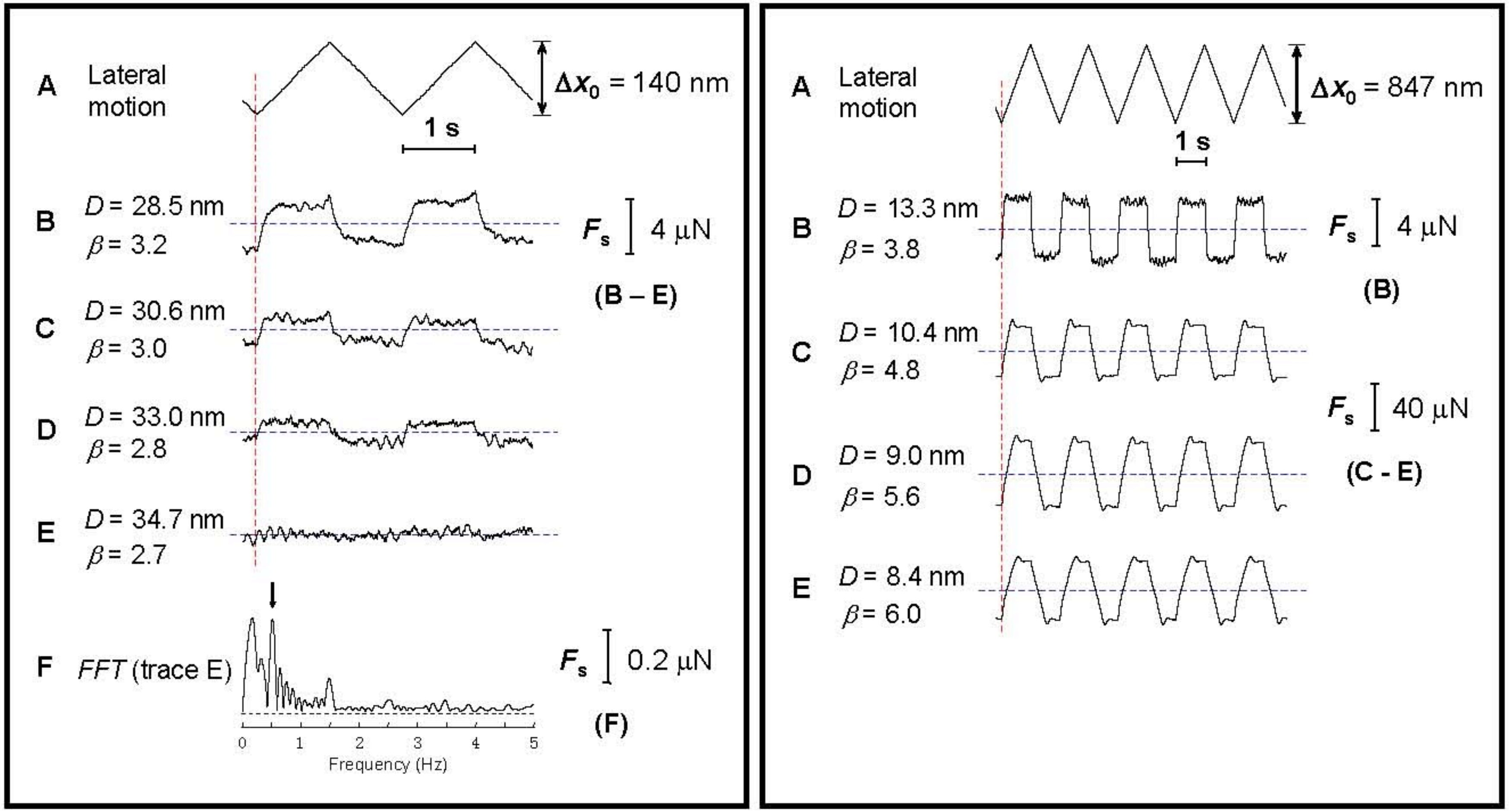
Interactions between macroinitiator coated mica surfaces



(Chen, Briscoe, Armes JK *Science* 2009)

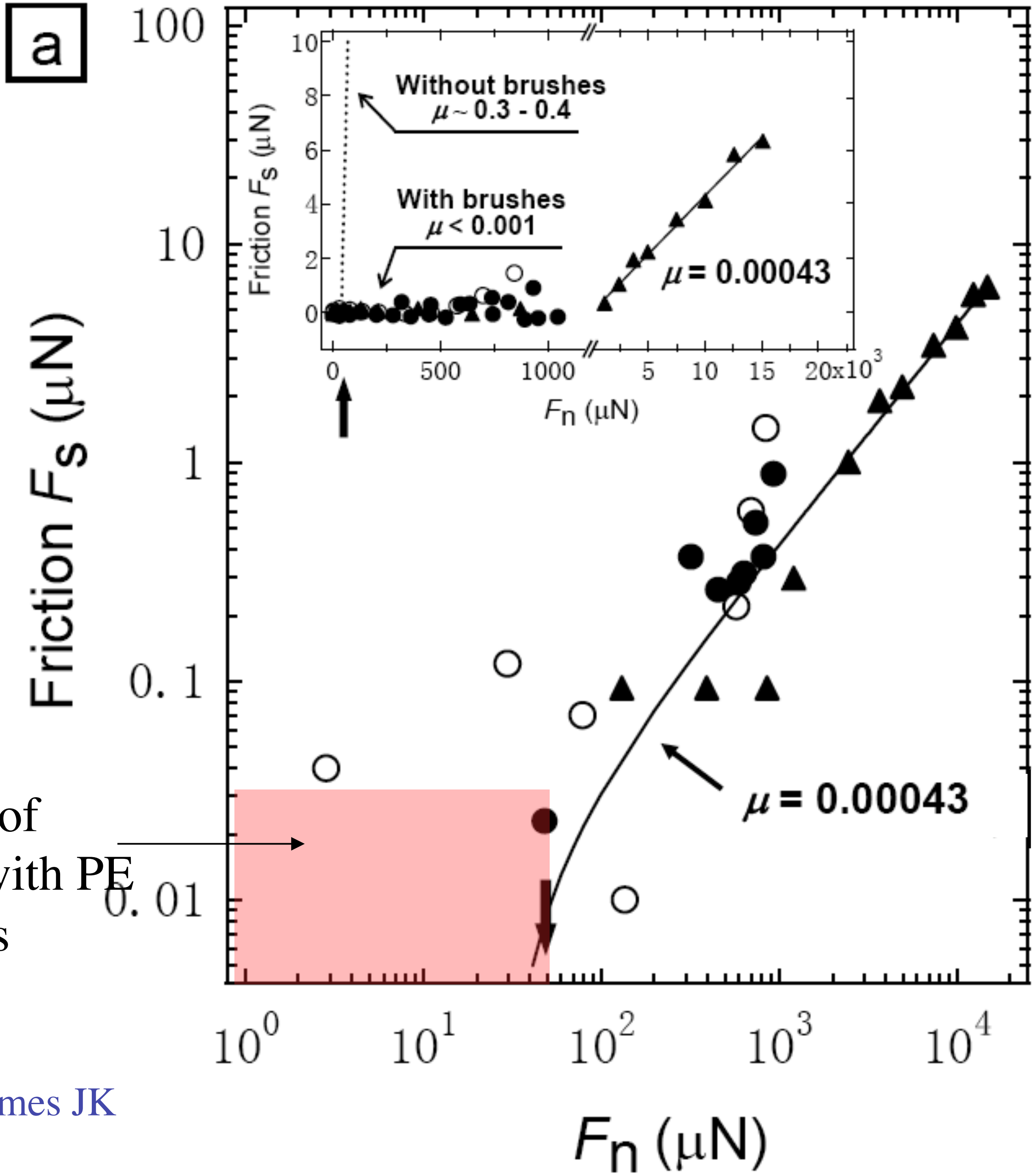


(Chen, Briscoe, Armes JK *Science* 2009)

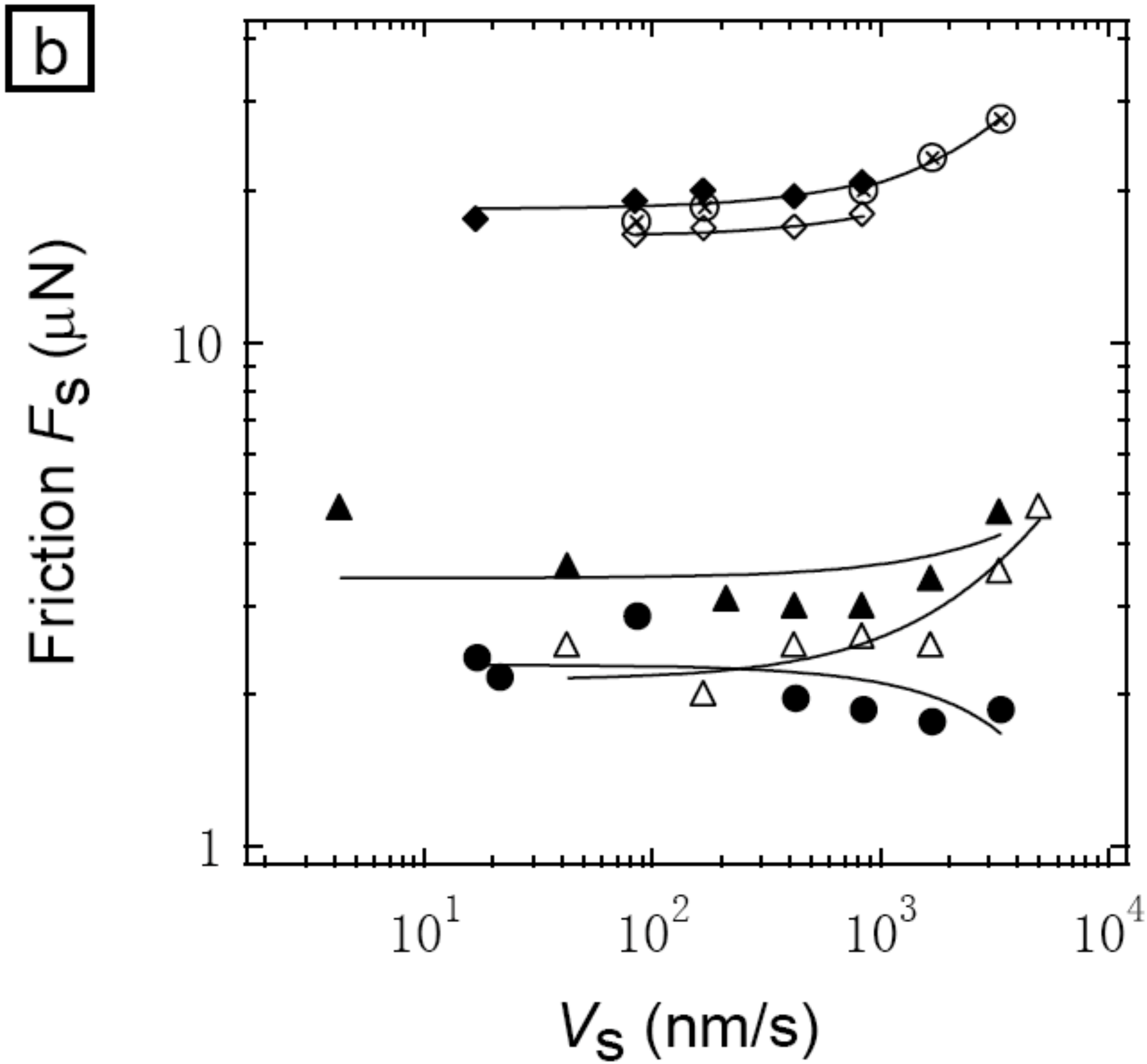


Frictional response with compressed pMPC brushes

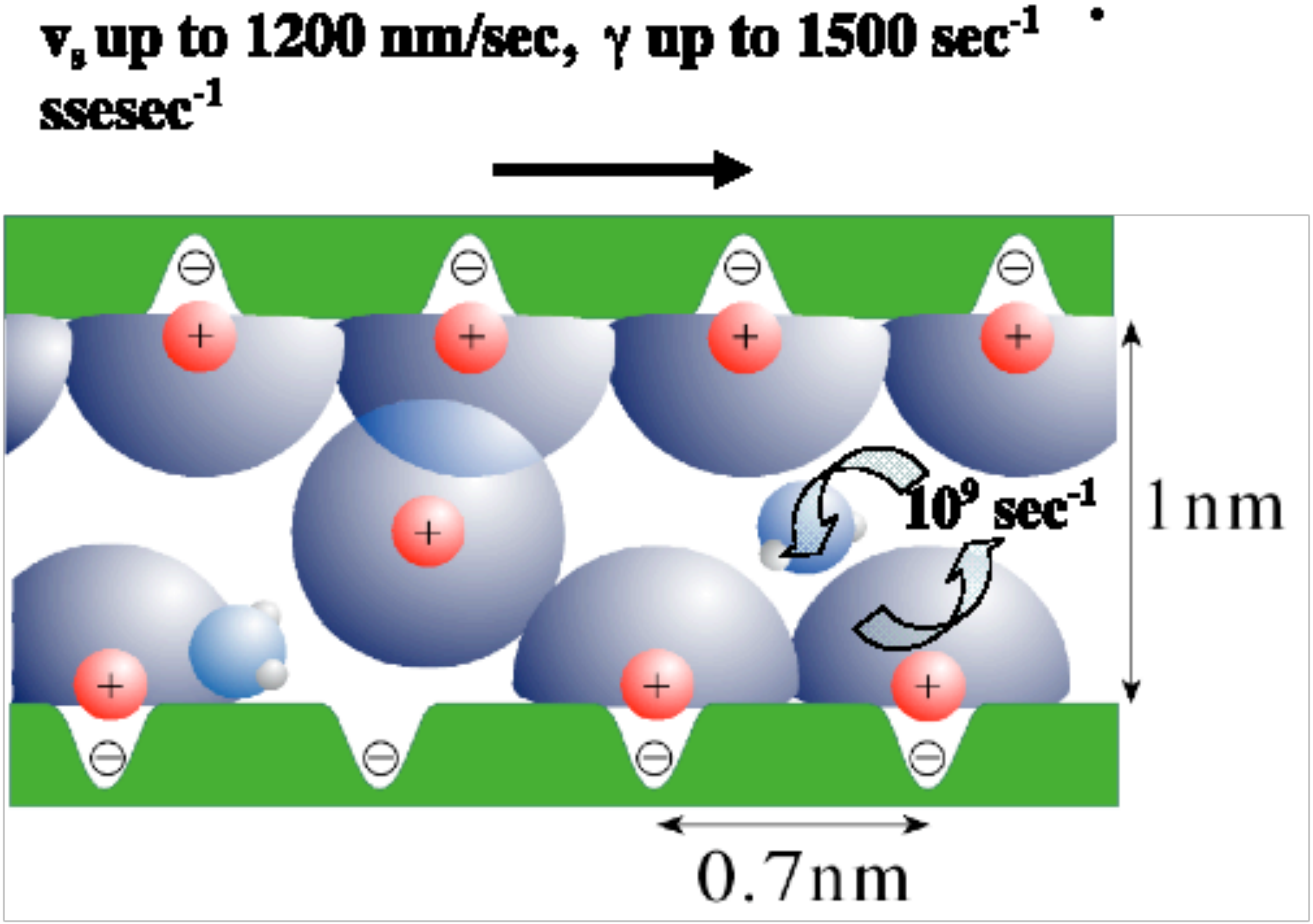
Range of loads with PE brushes



(Chen, Briscoe, Armes JK *Science* 2009)



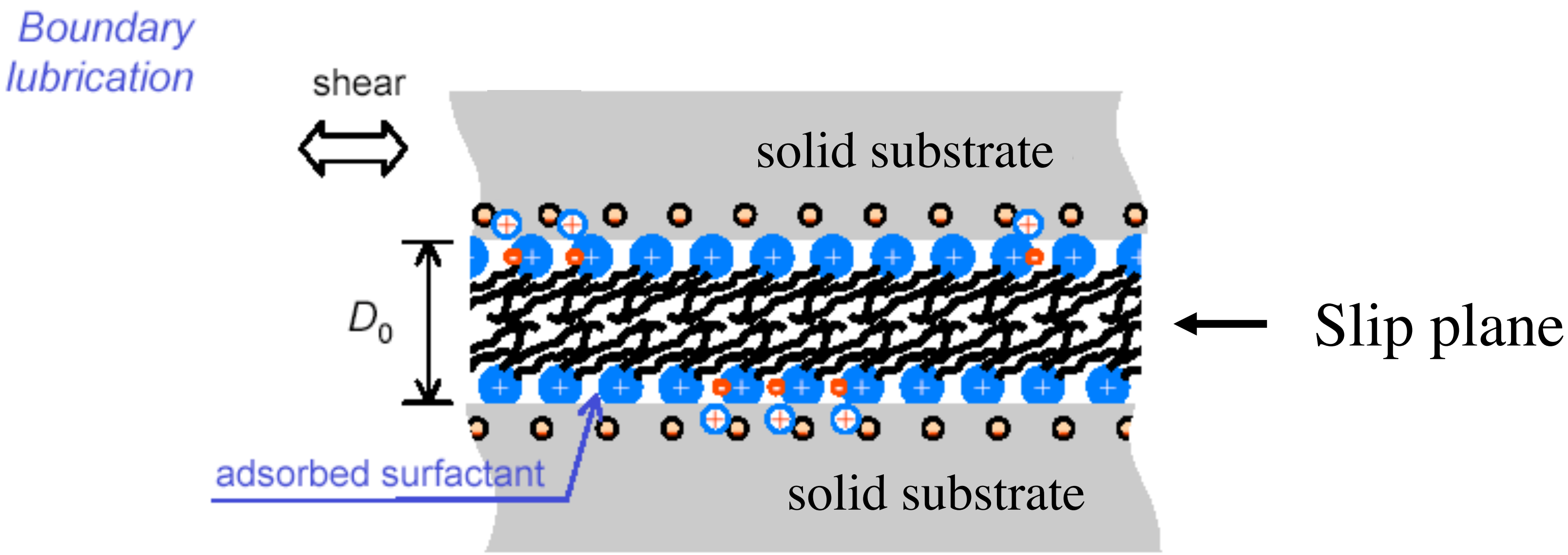
b
Friction F_S (μN)
10
1
10^1
10^2
10^3
10^4
V_S (nm/s)



v_s up to 1200 nm/sec, γ up to 1500 sec^{-1}
ssesec^{-1}
10^9 sec^{-1}
1 nm
0.7nm

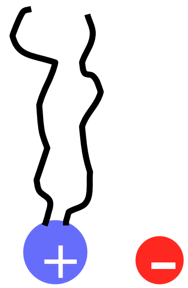
In **air** or oil, boundary lubrication provided classically (engineering tribology) by surfactants coating the rubbing surface, so that friction takes place between surfactant tails, preventing wear of substrate (Hardy 1922, Bowden & Tabor. 1954)

Characteristic friction rather large: μ = ca. 0.05 - 0.1
2 orders of magnitude larger than in mammalian joints

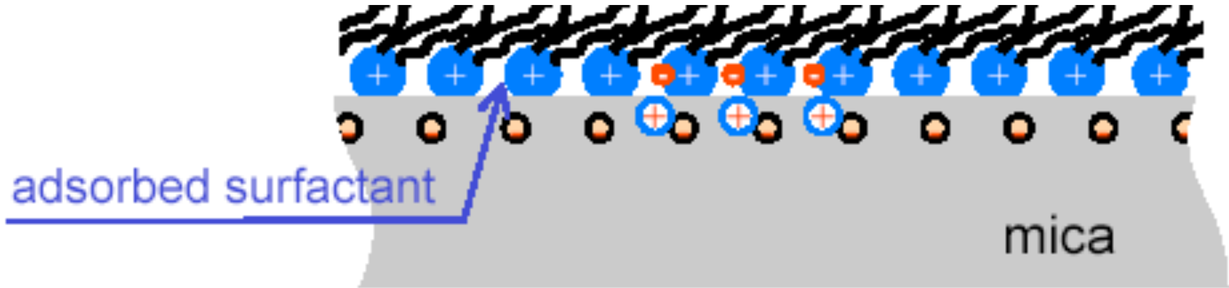


Wuge Briscoe, JK et al., *Nature* **444**, 191-194 (2006)

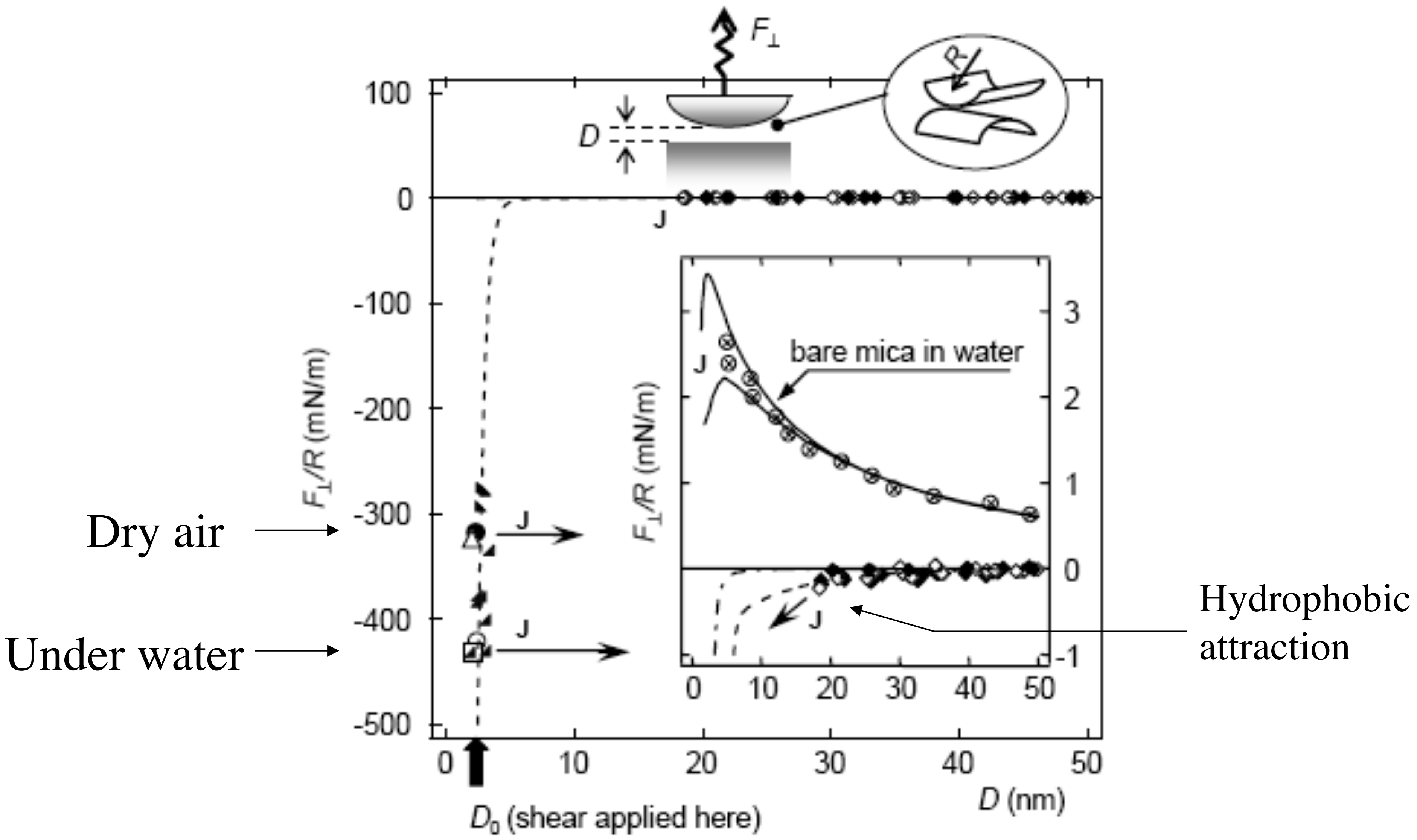
Incubate mica surfaces in DDunAB
(DimethyDi-undecaneAmmonium Bromide
$(C_{11}H_{12})_2N^+(CH_3)_2Br^-$ (Bob Thomas)



Then rinse to remove excess surfactant.



Wuge Briscoe, JK et al., *Nature* **444**, 191-194 (2006)



Wuge Briscoe, JK et al., *Nature* **444**, 191-194 (2006)

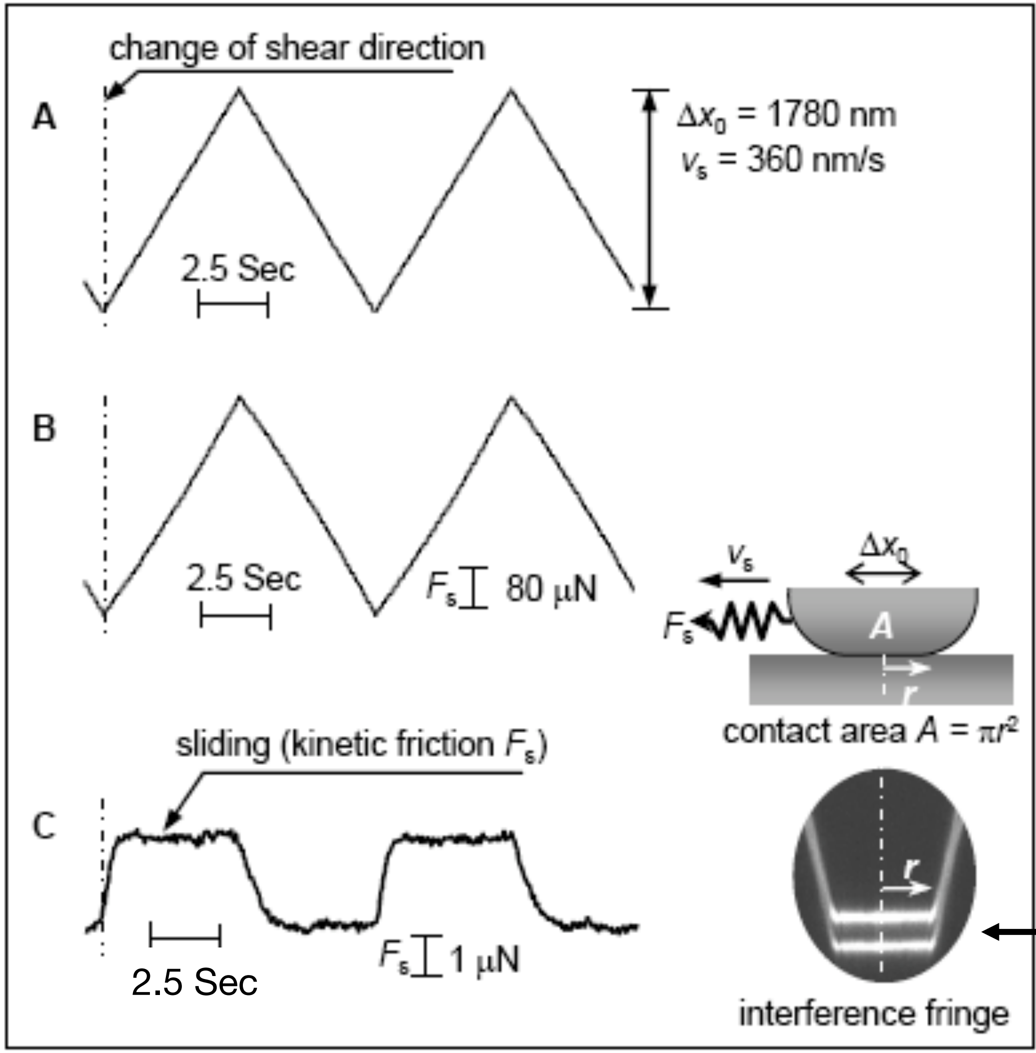
Wuge Briscoe, JK et al., *Nature* **444**, 191-194 (2006)

Back and forth lateral motion →

Response in air →

Response under water →

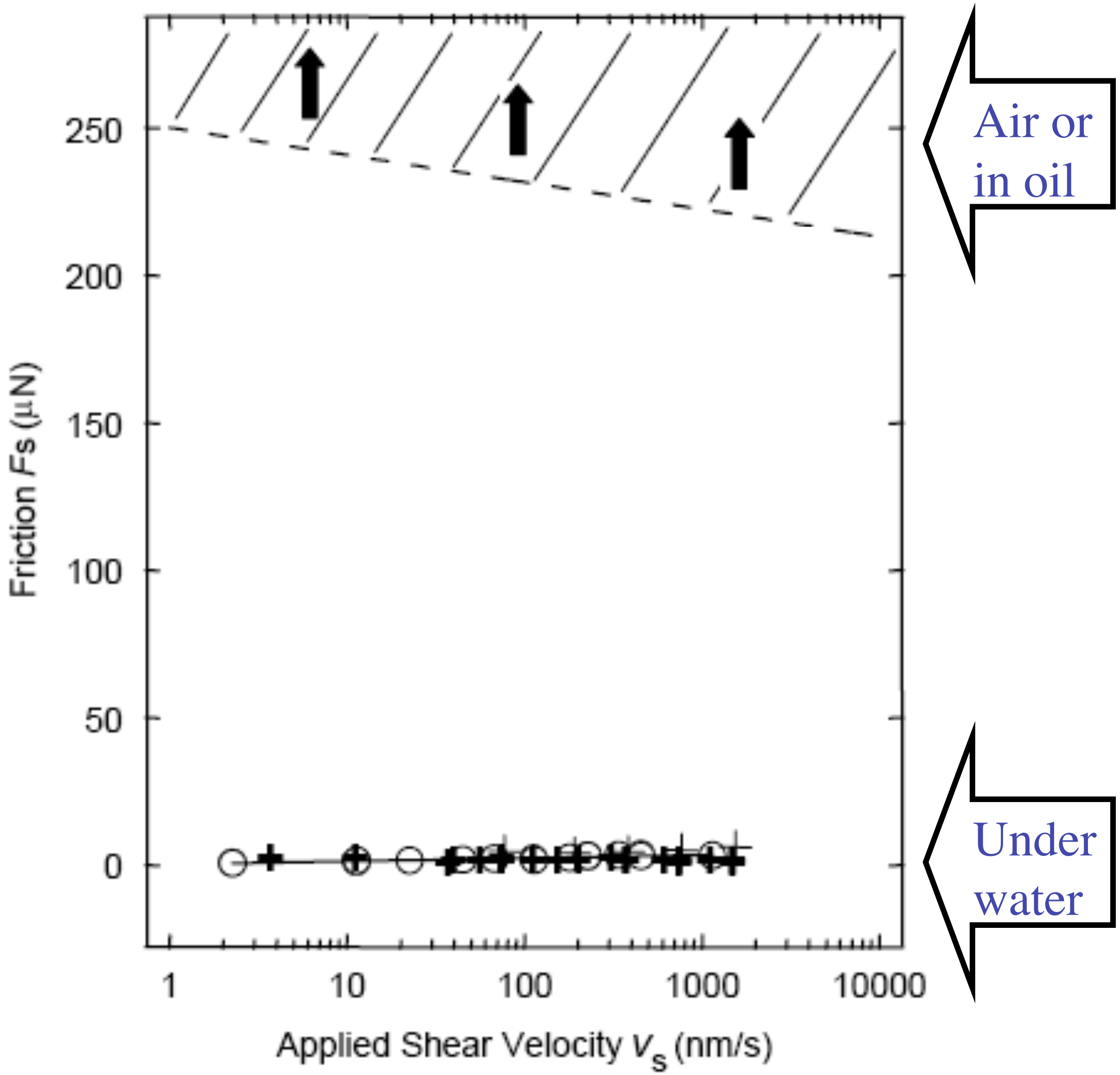
(note factor of x80 in shear force scale)



(No applied load, but 'equivalent' mean normal stress $P \approx 4\text{x}10^6$ N/m^2 = 40 atm)

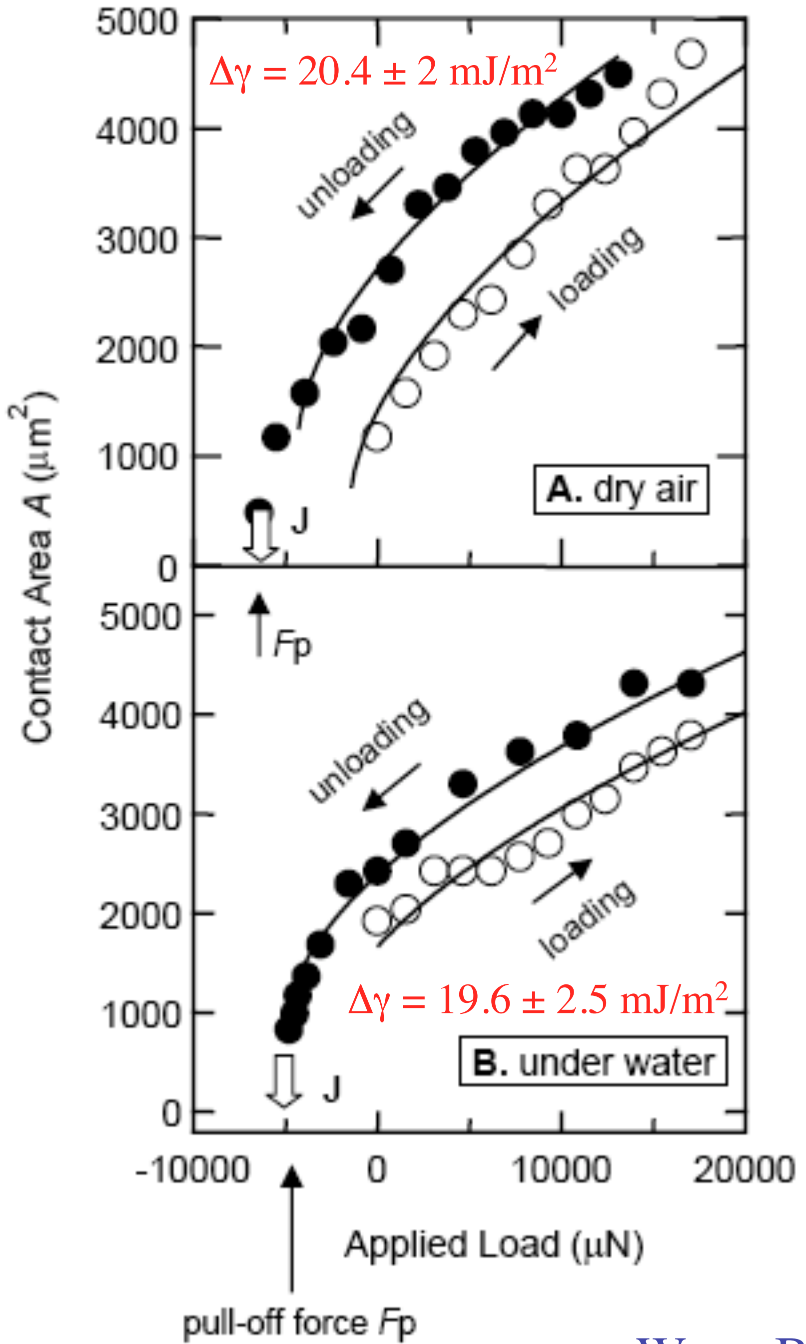
Fringe shift shows swelling of 2.6±2Å per layer on adding water

Briscoe, Klein et al.
Nature, **444**, 191 (2006)



Friction under water drops to ca. 1% of its air/oil values

Why is boundary lubrication under water so much more efficient than in air?



From Johnson-Kendall-Roberts (JKR):

interference fringe

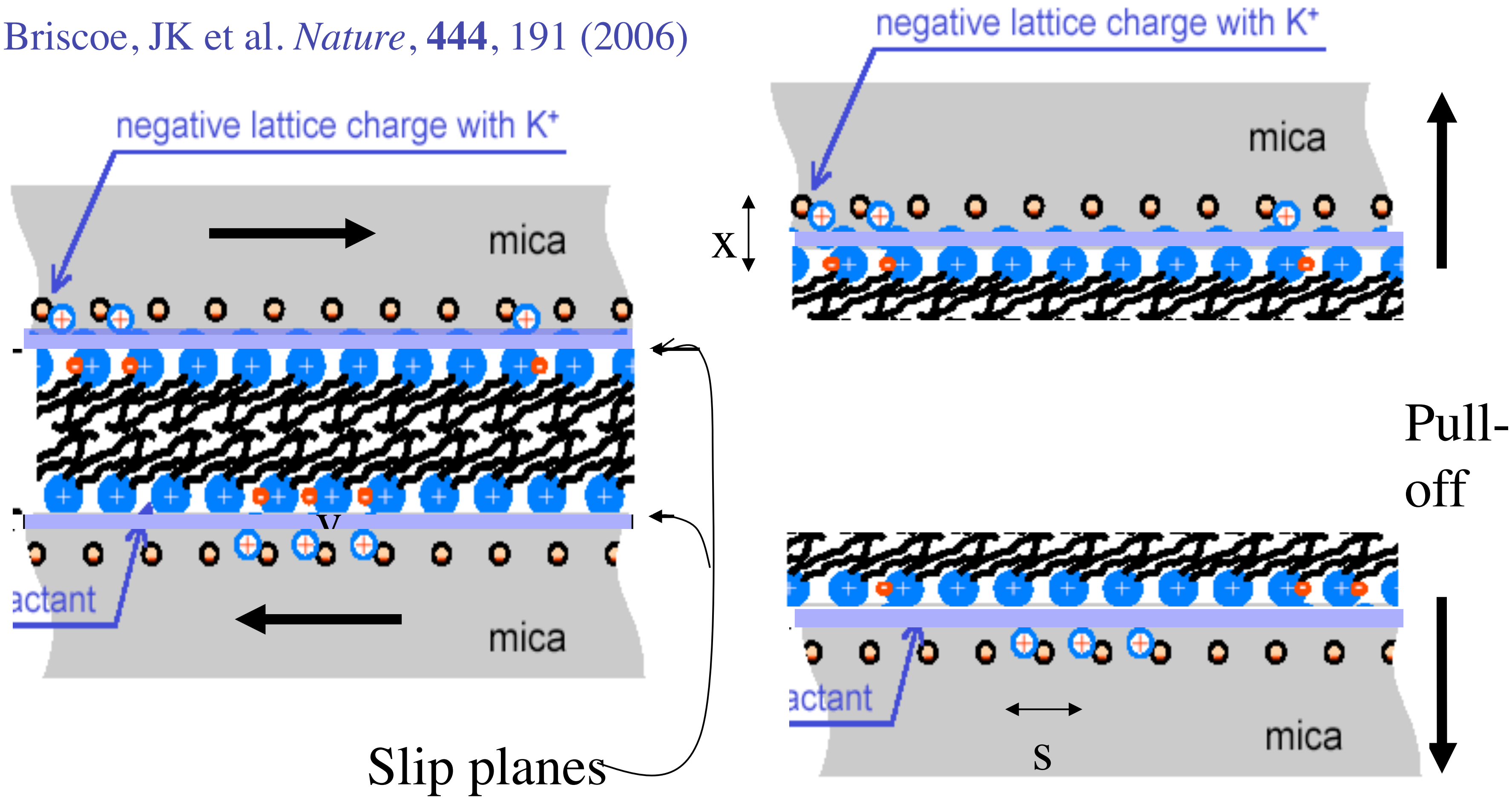
Contact area = $\pi r^2 = \pi\{(R/K)[L + 6\pi R\gamma + (12\pi R\gamma L + (6\pi R\gamma)^2)^{1/2}]\}^{2/3}$

Fit gives γ.

Adhesion hysteresis is $\Delta\gamma = (\gamma_{unloading} - \gamma_{loading}) \approx 20\pm2$ mJ/m² BOTH in dry air and under water

Wuge Briscoe, JK et al., *Nature* **444**, 191-194 (2006)

Briscoe, JK et al. *Nature*, **444**, 191 (2006)



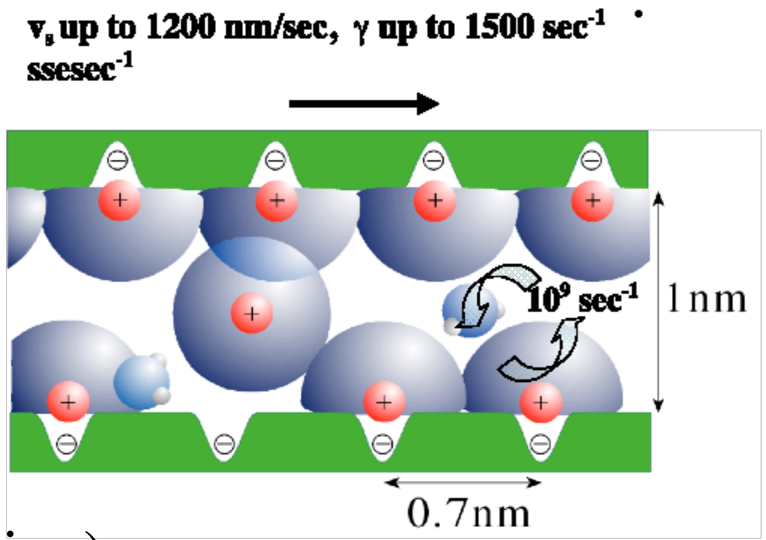
Under water, indication is that **slip plane shifts to substrate, while adhesive interface remains at midplane**

This is consistent with adhesive forces:

$$F_{substrate}/\text{molecule} = e^2/4\pi\varepsilon\varepsilon_0 x^2 > s^2\gamma/h \approx F_{midplane}/\text{molecule}$$

Evidence for shift of slip plane for surfactant lubrication under water from midplane to substrate:

a) Magnitude of frictional stress reduced by > 1 - 2 orders of magnitude relative to air: suggests hydration-sheath lubrication in analogy with hydrated ions (recall ~2.5Å swelling)



b) Adhesion hysteresis is 3-4 orders of magnitude too large to account for frictional stress: suggests midplane adhesion

d) Immersing in water while adhered - results in similar or lower frictional stress (and similar ~2.5Å swelling)

e) Analogous surfactants with less hydrated interface lead to much higher frictional stress

Nature, **444**, 191 (2006)
J. Adhesion, **83**, 705 (2007)

Summary

- Water - by virtue of rapid relaxations and strong dipolar interactions - can act as remarkable lubricant, via a very different mechanism to classical systems
- Hydrated ions can act as molecular ball-bearings
- Charged or poly(zwitterionic) macromolecules: steric (+counterions) + fluid hydration layers
- Boundary lubricants under water slide at hydrated-headgroup/substrate interface

- **Nature** 413, 51-54 (2001).
- **Science** 297, 1540 (2002).
- **Nature** 425, 163 (2003).
- **Nature** 444, 191 (2006).
- **Science,** 323, 47 (2009)
- **Science,** 323, 1698 (2009).