Insight into Polymer Brush-Ionic Liquid mediated Lubrication

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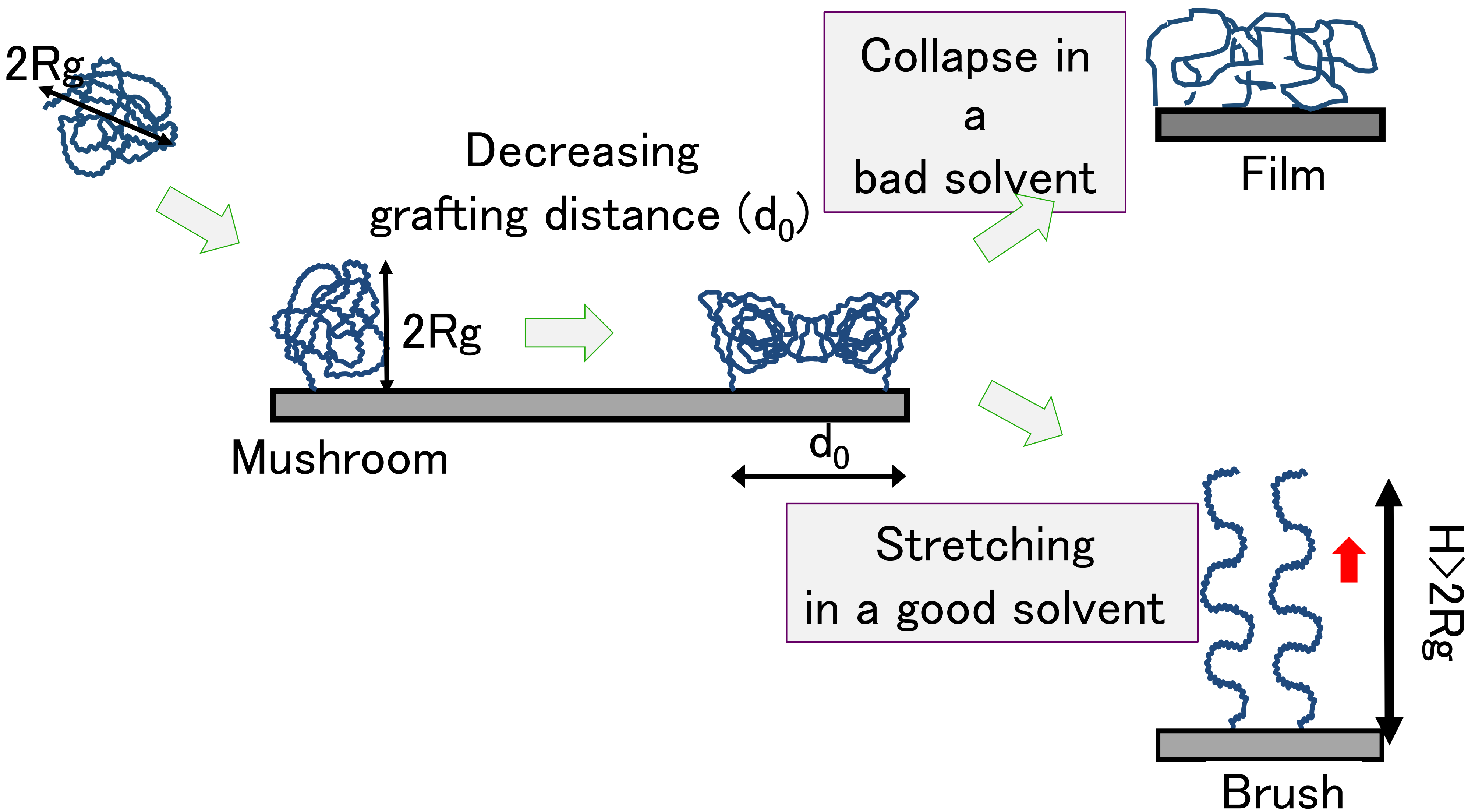
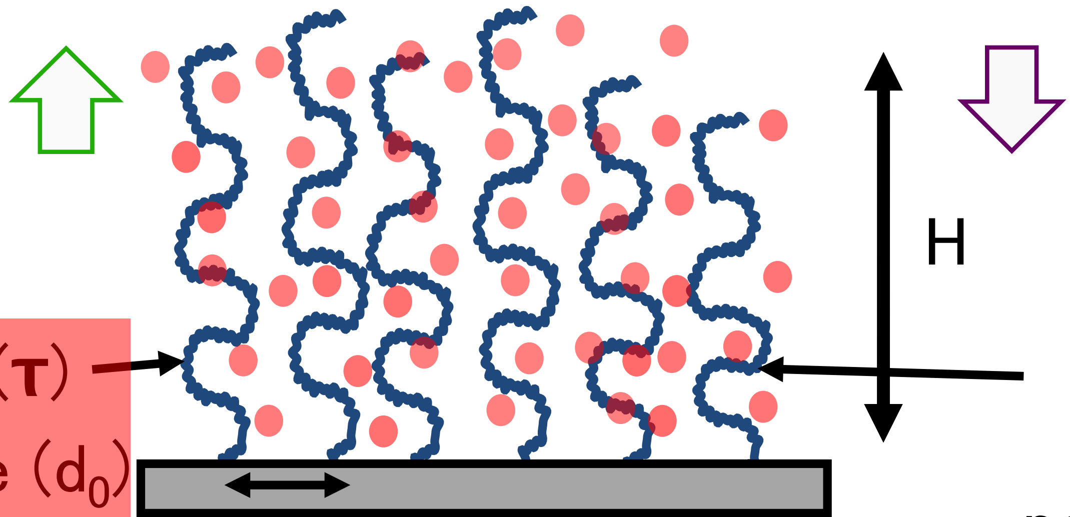
Configuration of Polymers grafted to Surfaces



Polymer Brush Stretching in Good Solvents



$$\Delta f = \Delta f_{\text{int}} + \Delta f_{elast} \xrightarrow[\text{Equilibrium}]{} \left.\frac{\partial \Delta f}{\partial h}\right|_{h=H} = 0$$

$$H \sim \left(8/\pi^2 \right)^{1/3} Na \left(p\tau \frac{a^2}{d_0^2} \right)^{1/3}$$

$$\Delta f_{\text{int}} = \frac{1}{2} k_B T \upsilon \left(\frac{\varphi}{a^3} \right)^2$$

$\upsilon = a^3 (1 - 2\chi) \sim 3/2$ excluded volume parameter

$\varphi =$ monomer volume fraction

$\sigma = a^2 / d_0^2$

$$\Delta f_{elast} = \frac{3}{2} k_B T \frac{h^2}{N(ap)^2}$$

a = monomer size

h =distance to surface

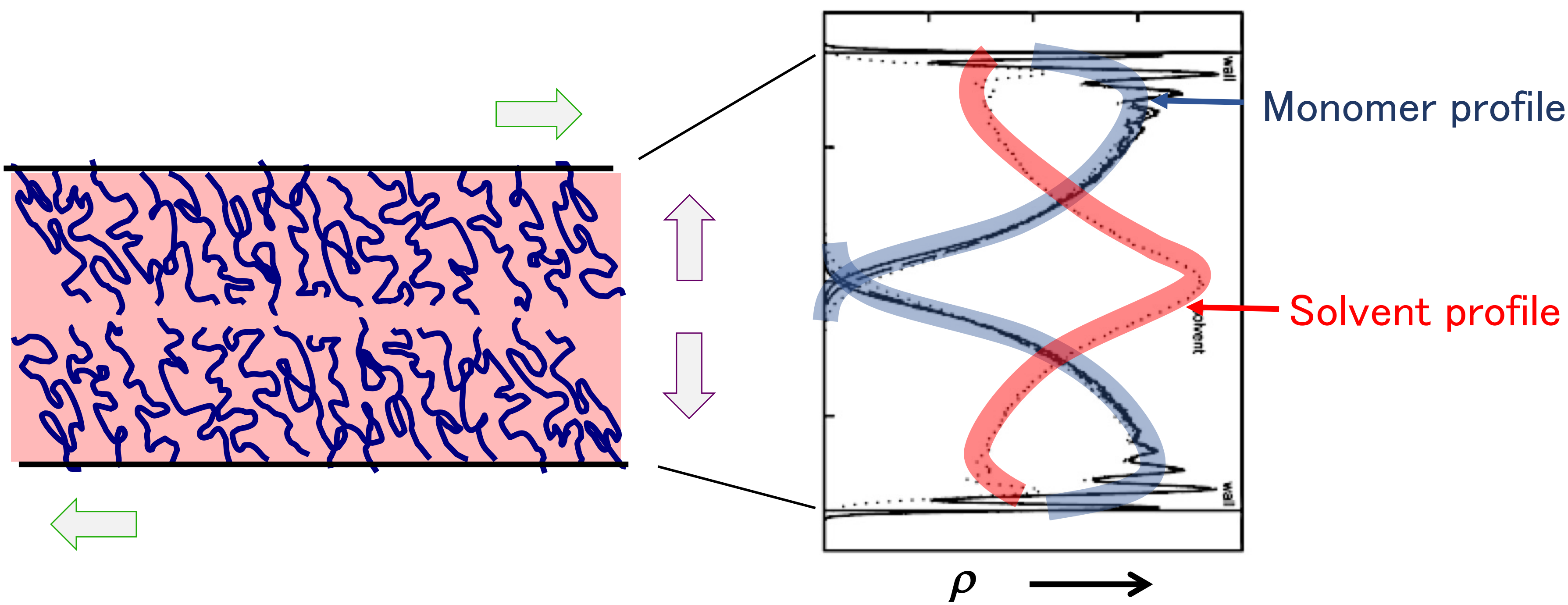
Scaling Concepts in Polymer Physics, de Gennes, 1979

Espinosa-Marzal, Nalam, Bolisetty and Spencer. Soft Matter, 2013

Lubrication mediated by Polymer Brushes

A repulsion (of steric and osmotic origin) hinders interdigitation

A thin film of solvent at the shear plane mediates the reduction of friction

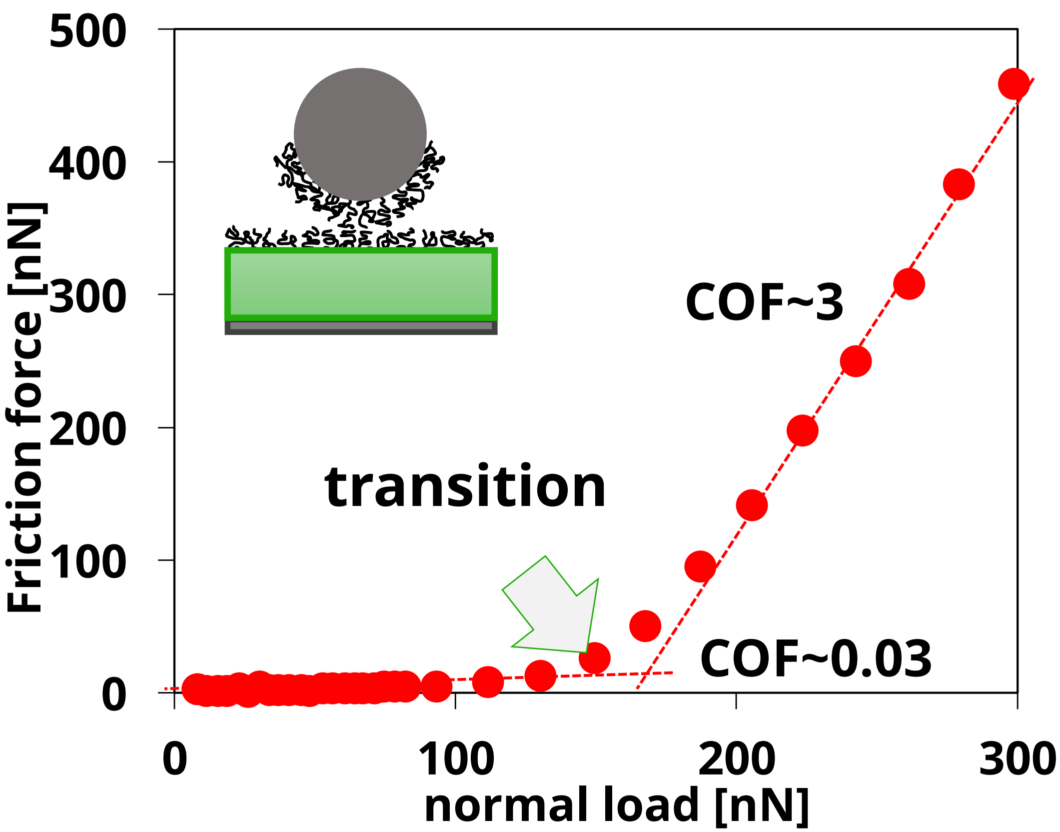


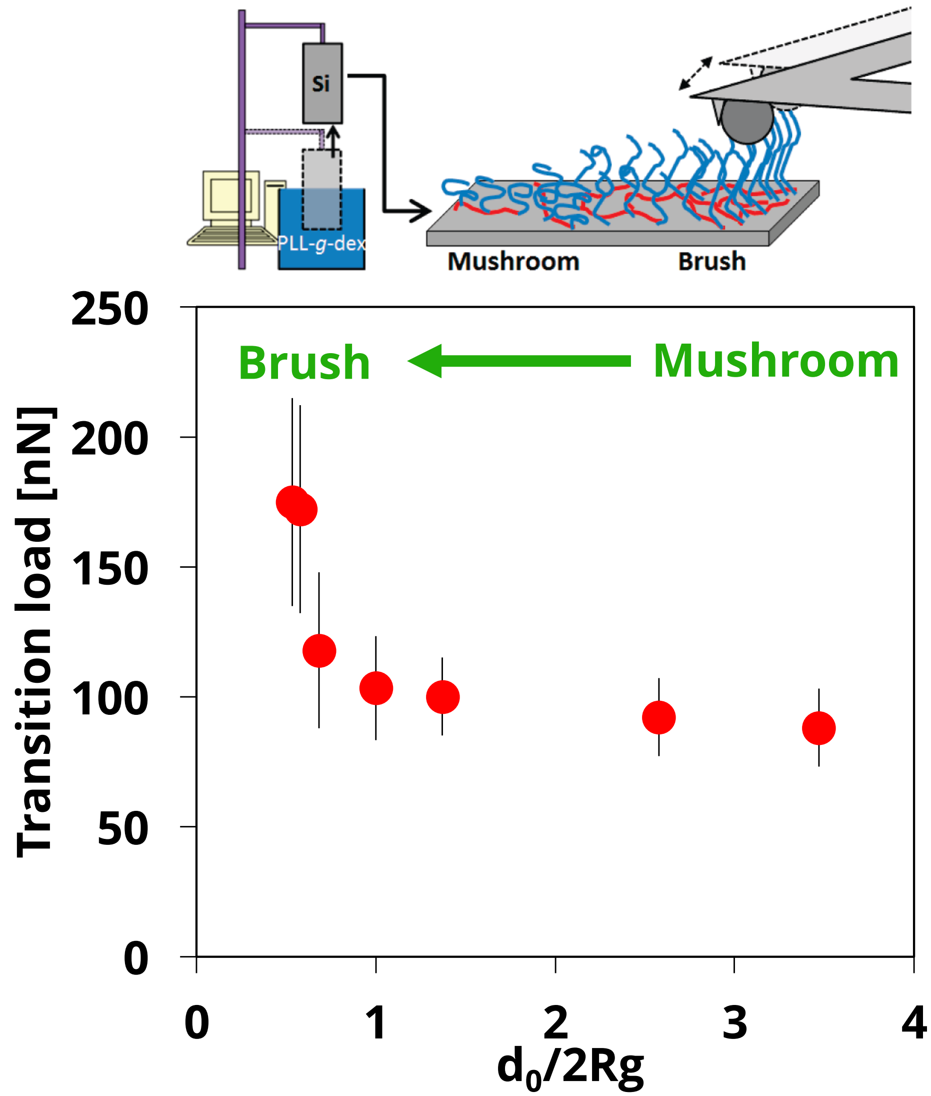
Grest, G. S. Adv Polym Sci 1999.
Klein, J. Annu Rev Mater Sci 1996,

Influence of grafting Density on Hydration Lubrication

Smaller grafting distance (d_0) increases the transition load

Dextran brushes, water as solvent

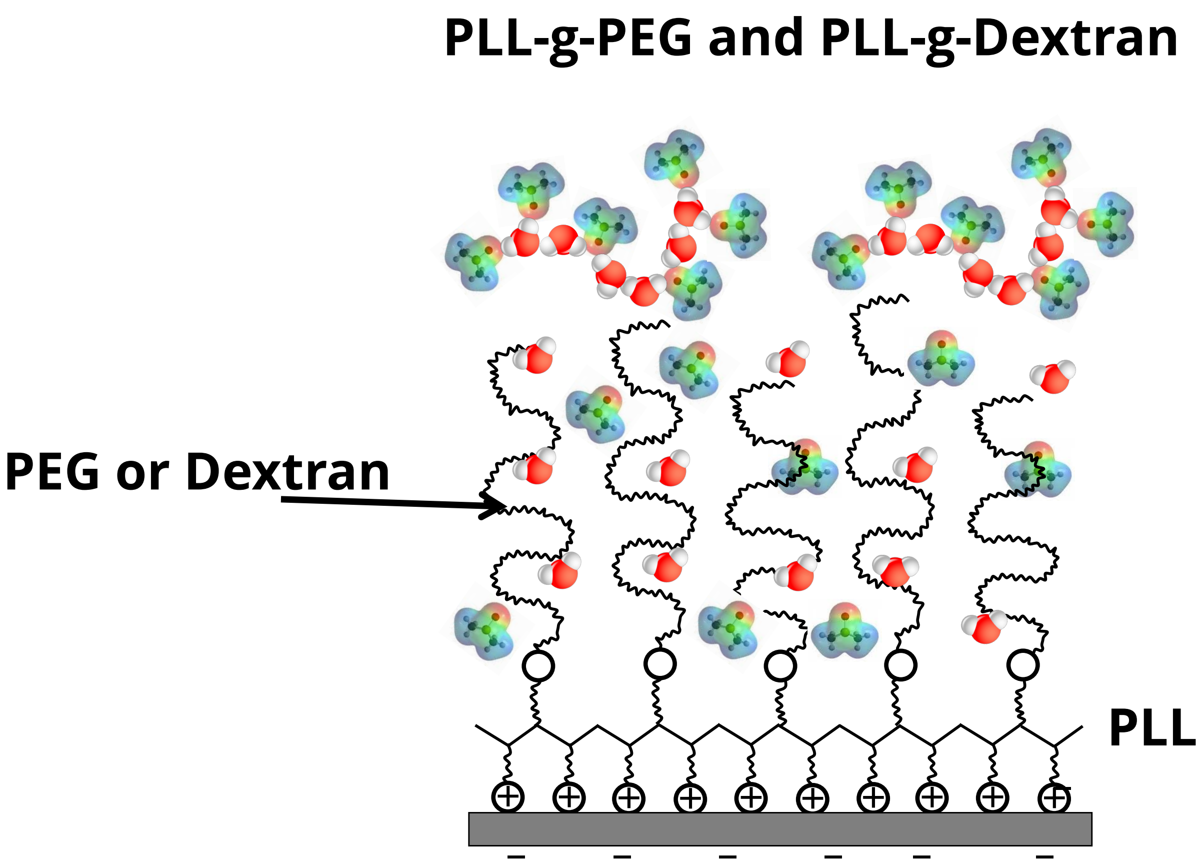




Adapted from Rosenberg, Goren, Crockett, and Spencer, et al. Applied Mat & Interf, 2011

Influence of Solvent Quality on Polymer-Brush Lubrication

Aqueous mixtures with viscous co-solvents



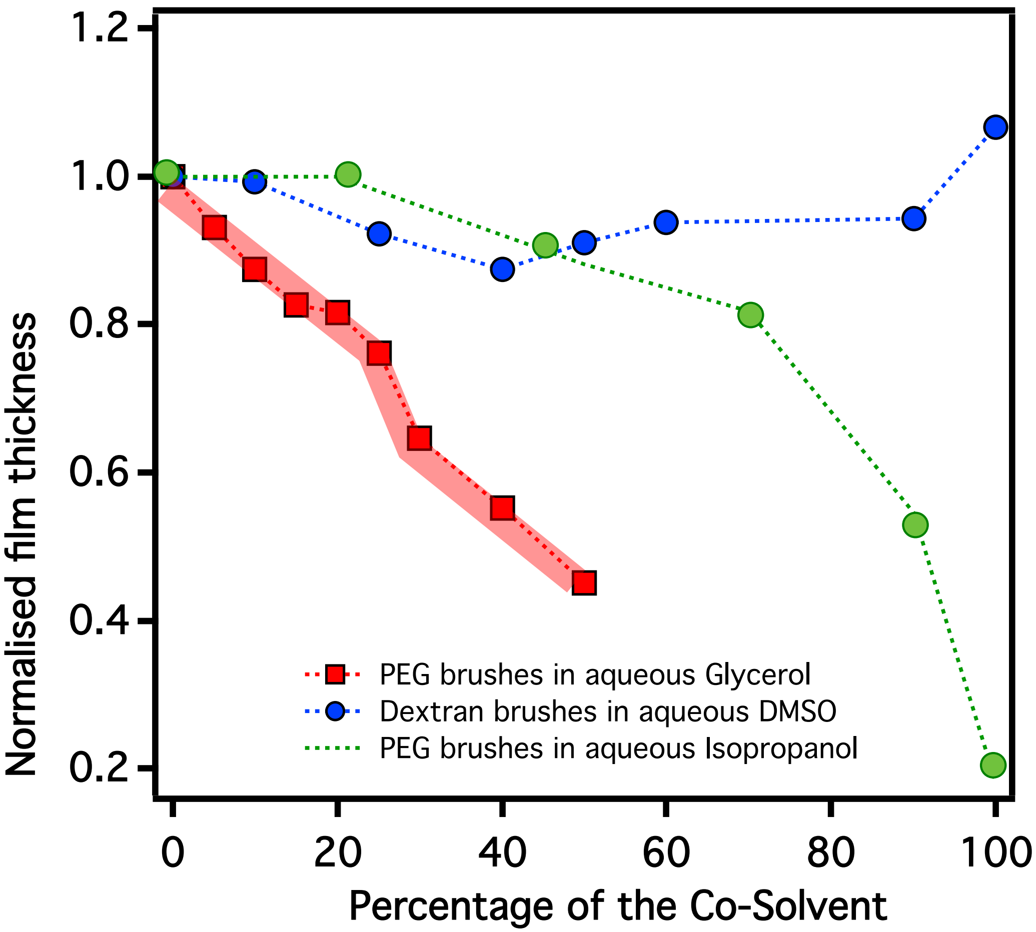
<u>Co-solvents in water</u>
Isopropanol~4.5 mPas
Glycerol ~1413 mPas
DMSO ~2 mPas

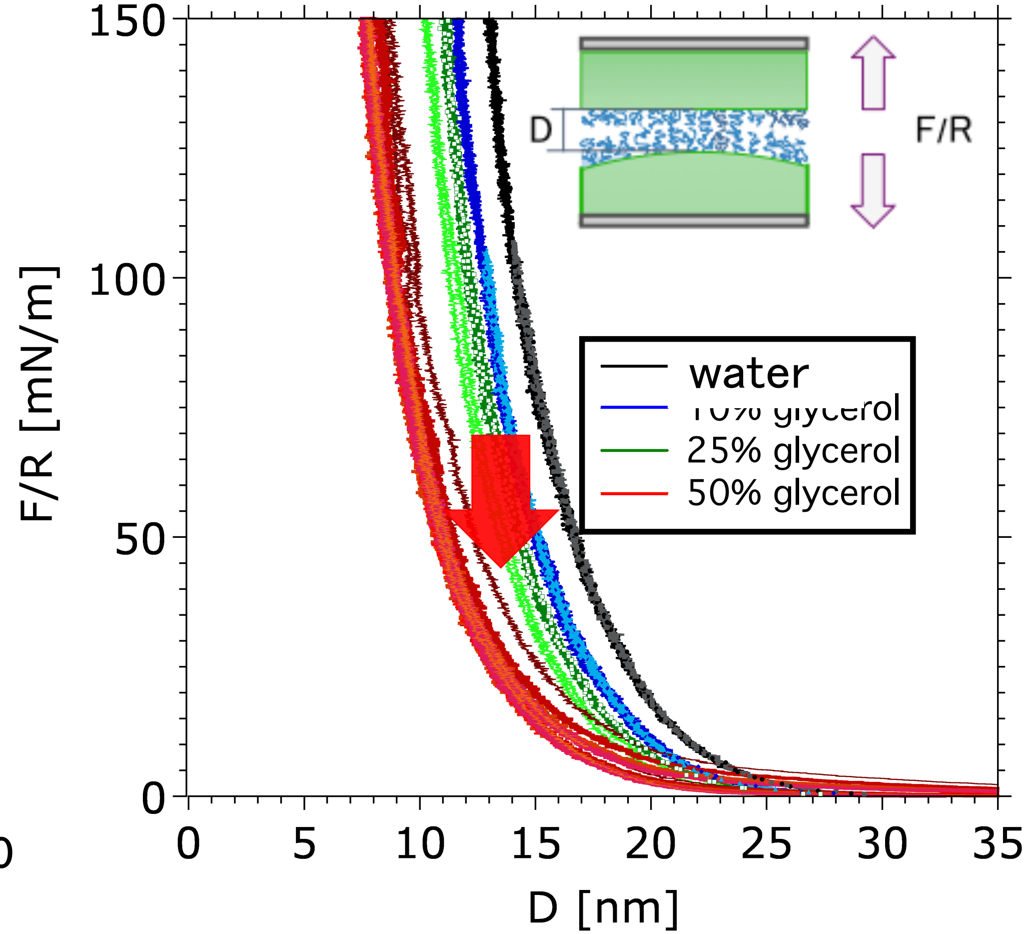
Nalam, Daikhin, Espinosa-Marzal, Clasohm, Urbakh, Spencer, Journal of Physical Chemistry C 2013
Espinosa-Marzal, Nalam, Bolisetty, Spencer. Soft Matter 2013
Nalam, P. C.; Ramakrishna, S. N.; Espinosa-Marzal, R. M.; Spencer, N. D. Langmuir 2013

Influence of solvent quality on repulsion

Significant collapse and decrease in repulsion with increasing glycerol concentration (bad solvent for PEG)

PEG brushes in mixtures of glycerol and water

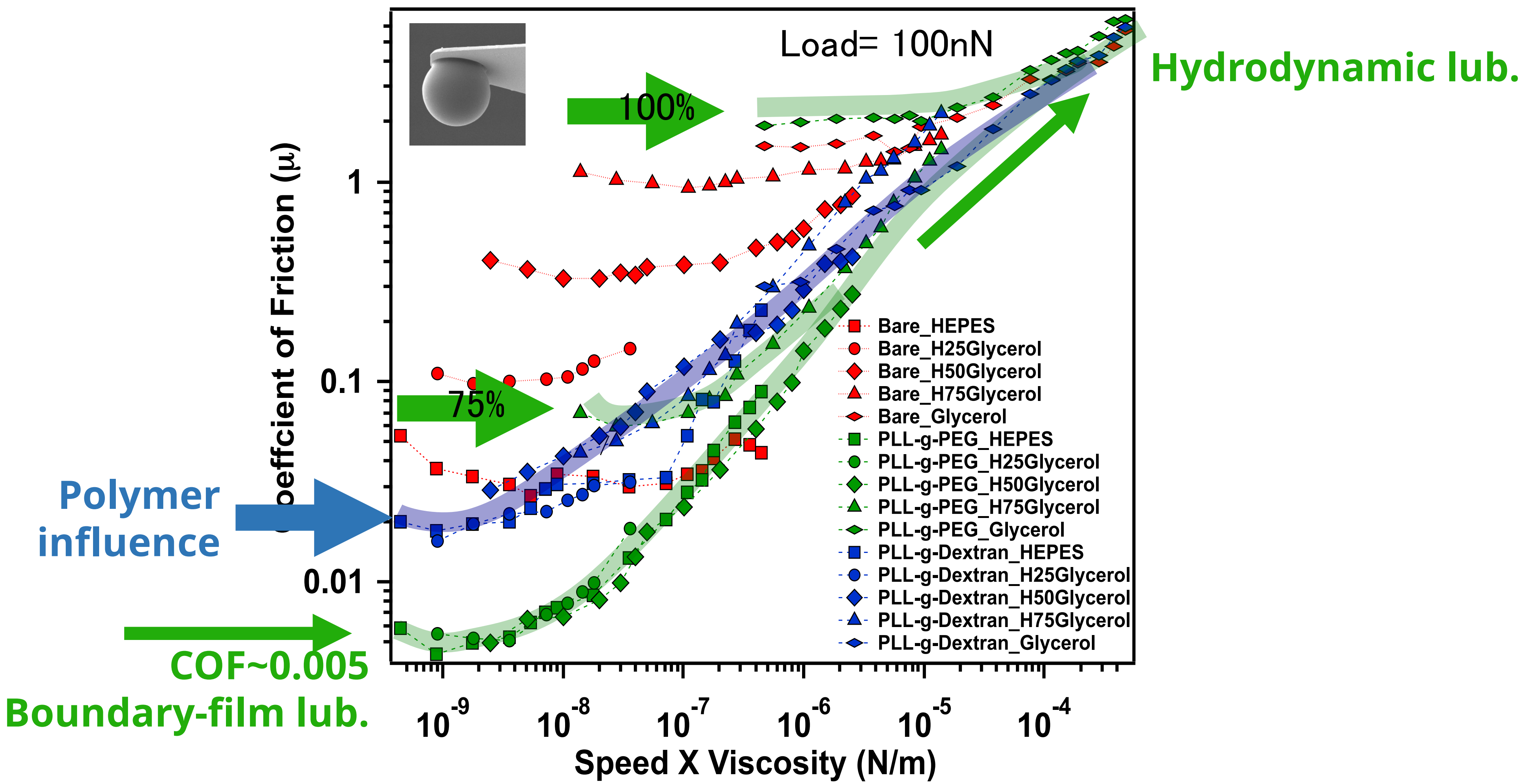




Nalam, Daikhin, Espinosa-Marzal, Clasohm, Urbakh, Spencer, Journal of Physical Chemistry C 2013

Nano–Stribeck curves for aqueous glycerol mixtures

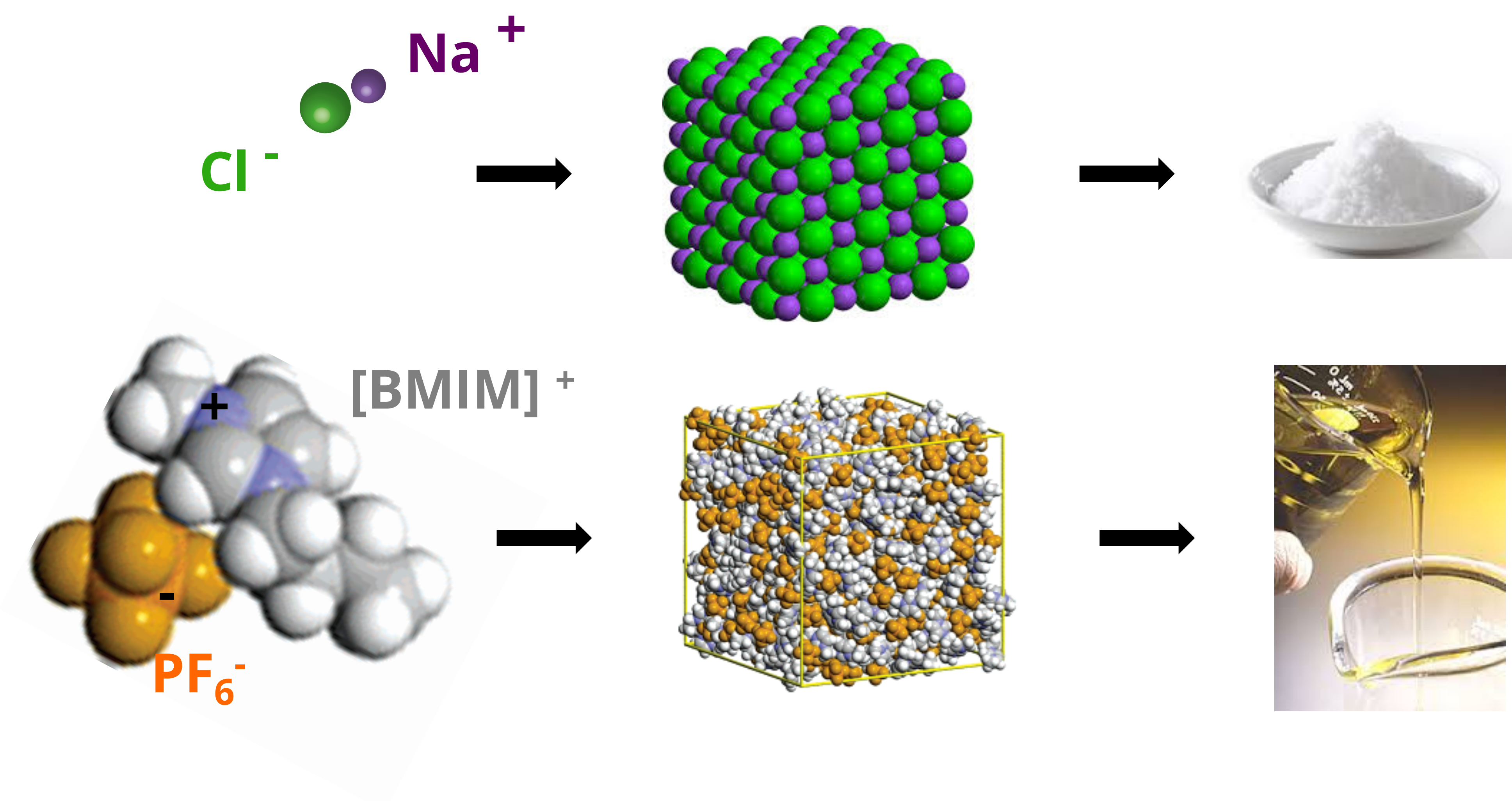
Friction decreases with increasing solvent quality
Influence of polymer chemistry on friction as well



Nalam, P. C.; Ramakrishna, S. N.; Espinosa-Marzal, R. M.; Spencer, N. D. Langmuir 2013

Ionic liquids (ILs)

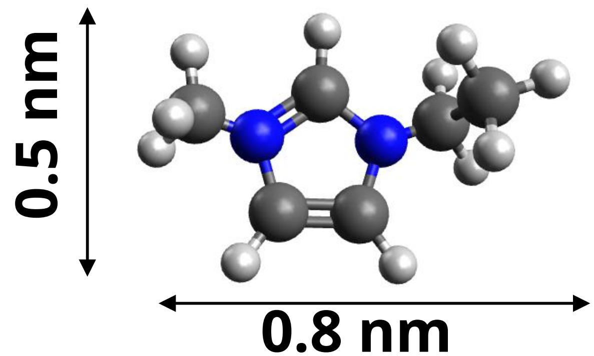
Ionic liquids are salts, whose melting point is below 100°C



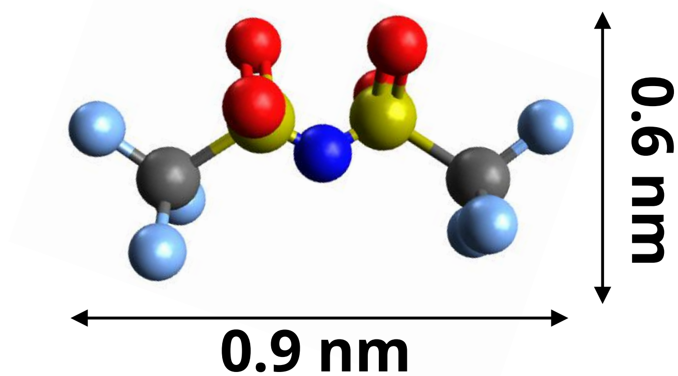
Canongia Lopes, J. N., & Pádua, A. A. (2006). The Journal of Physical Chemistry B, 110.
Courtesy of Andrea Arcifa, ETH Zurich.

ILs are “ionic” solvents

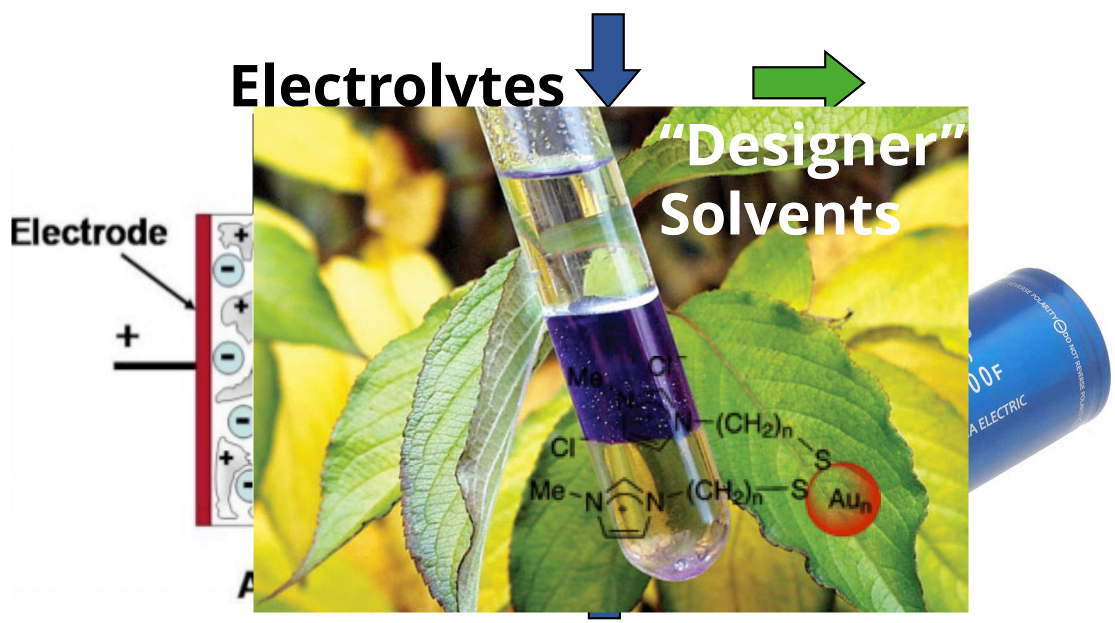
[EMIM]$^+$



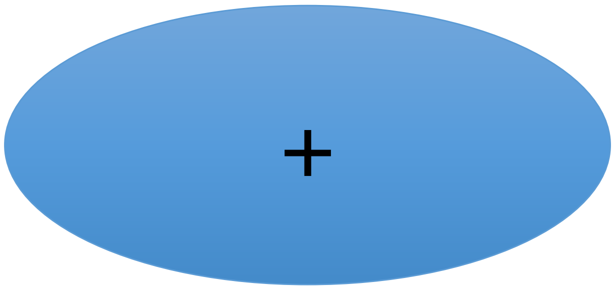
[TFSI]$^-$



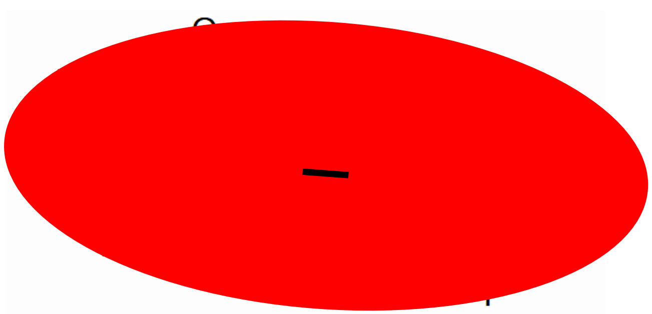
- Wide electrochemical window
- Negligible vapor pressure
- Thermal stability
- Non–flammability
- Surface–active
- High viscosity
- Ionic solvents with high charge density



Model System



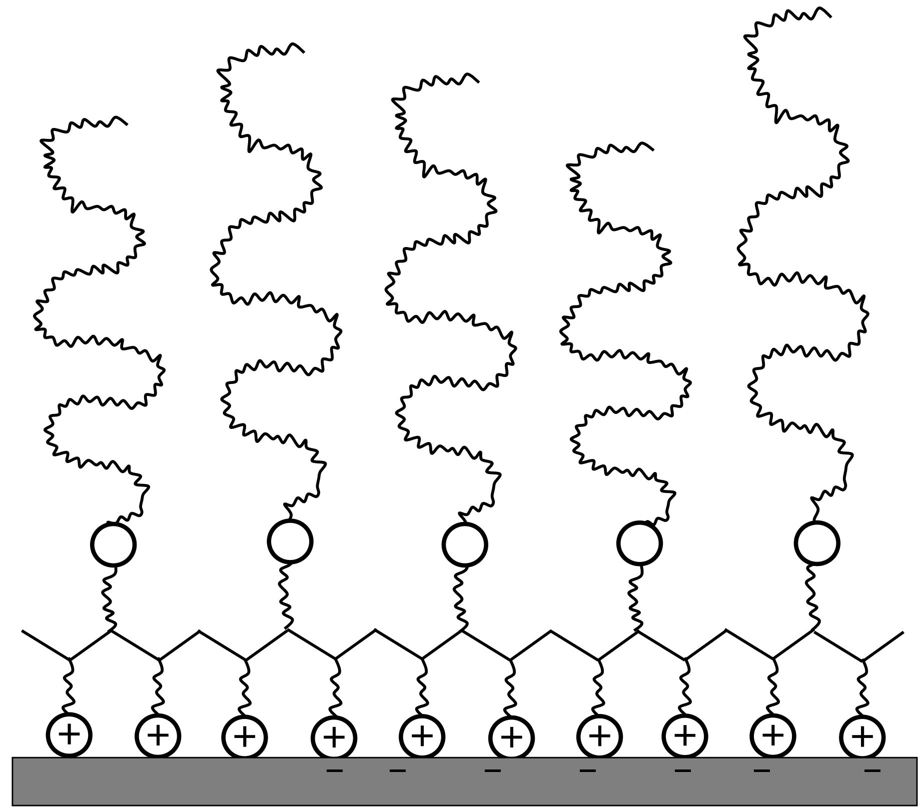
[EMIM]+, [HMIM]+



[TFSI]-

Neutral brush

PLL(20kDa)-g[3.5]-PEG(5kDa)

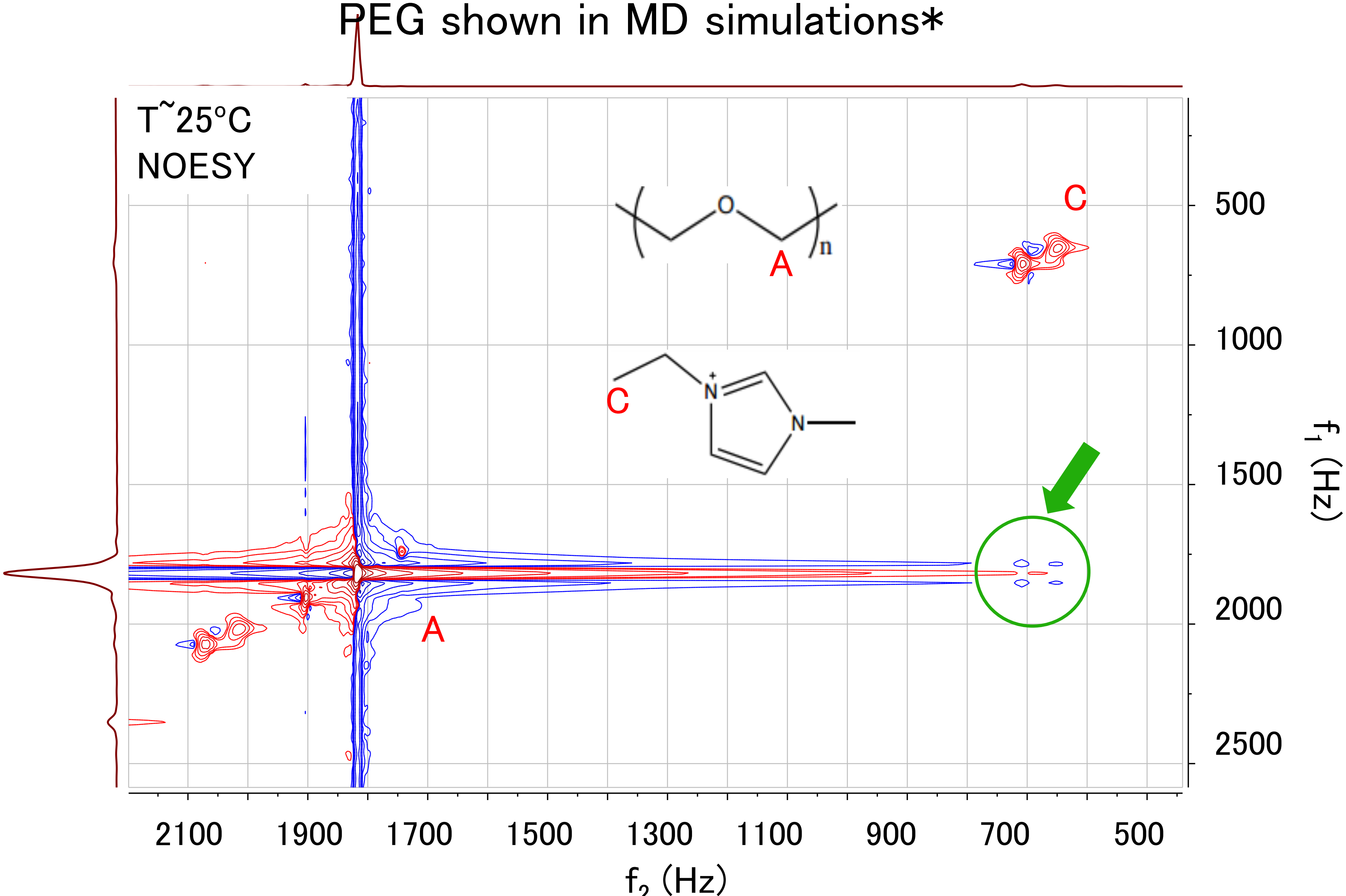


Kenausis, Voros, Elbert, Huang, Hofer, Ruiz-Taylor, Textor, Hubbell, Spencer. Journal of Physical Chemistry B 2000, 104
Drobek, Spencer, Heuberger. Macromolecules 2005, 38

Affinity between PEG and [EMIM][TFSI] by 2-D ^{1}H NMR

Spatial proximity of cation and PEG (4–5 Å) indicated by the cross-peak

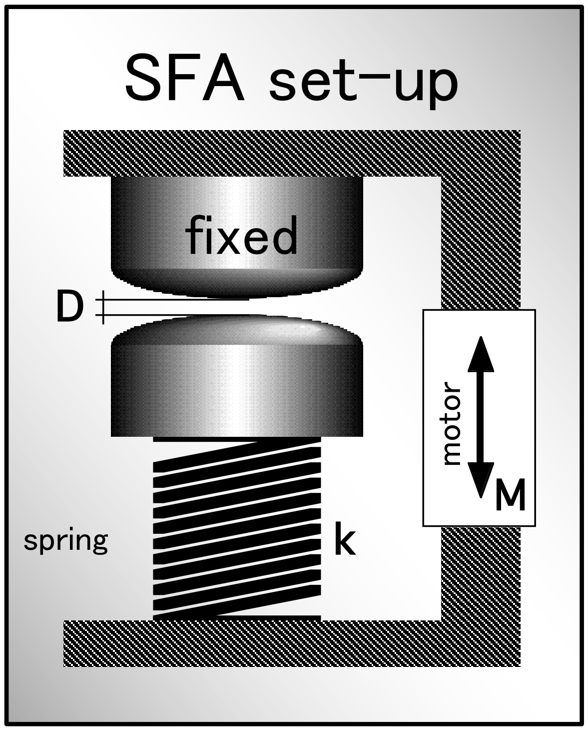
Consistent with hydrogen bond between imidazolium cations and hydroxyl in PEG shown in MD simulations*



*Costa& Ribeiro, The Journal of Chemical Physics, 2006

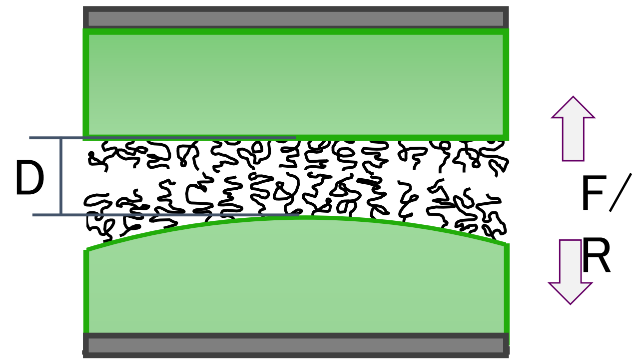
Extended Surface Forces Apparatus

Measurement of surface separation D (±30 pm) between mica surfaces and of the refractive index by multiple beam interferometry



$$F = k(\Delta D - \Delta M)$$

D=film thickness

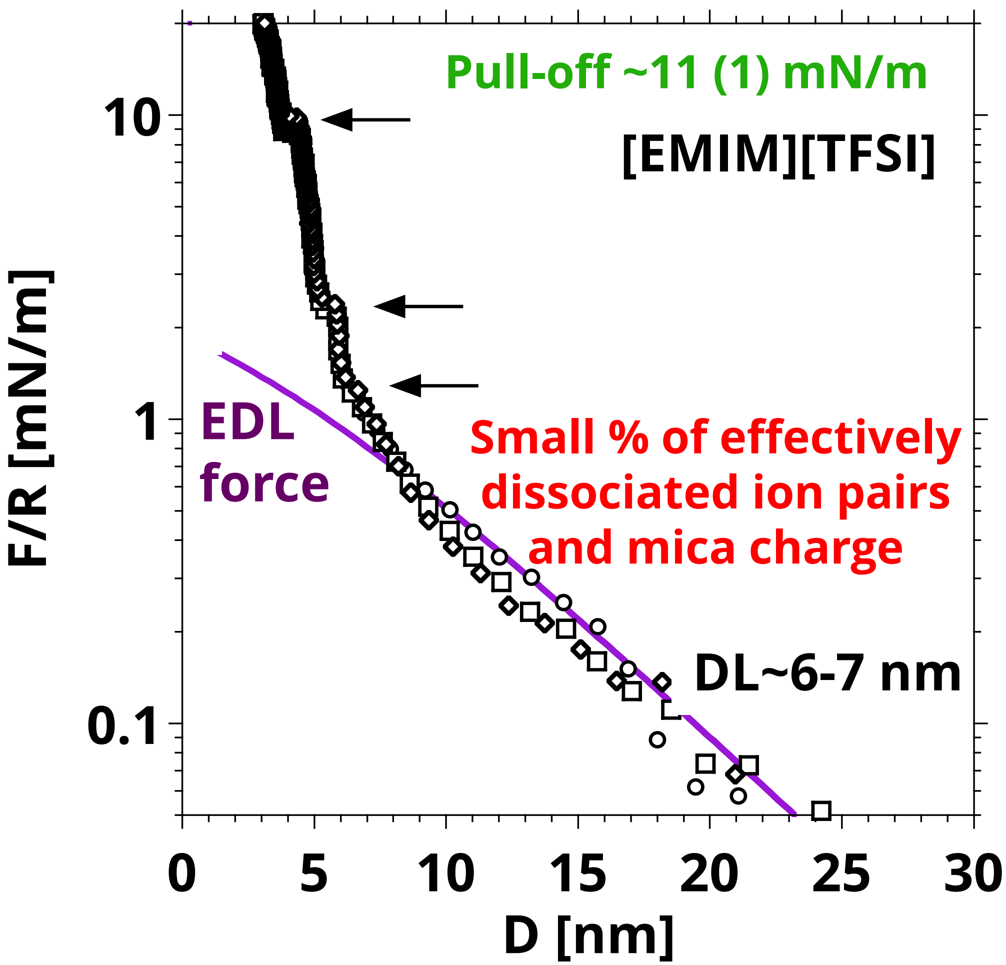


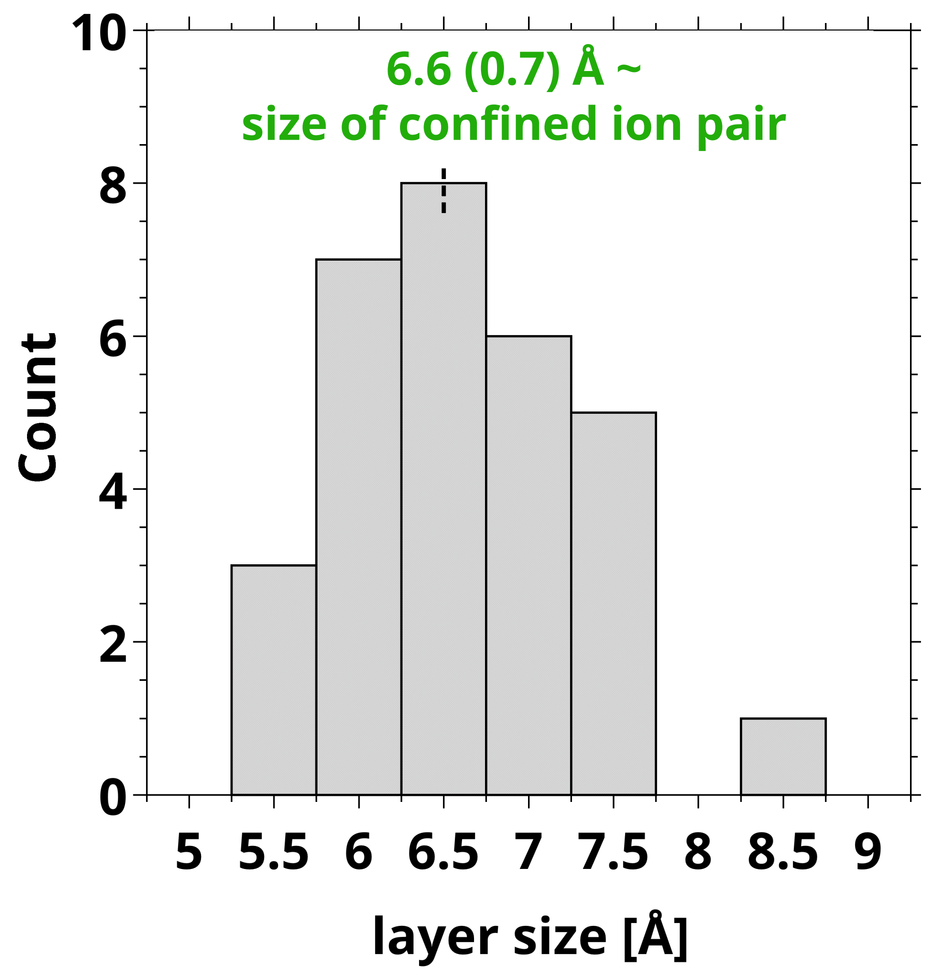
- Vacuum dry ILs; polymer solutions prepared under continuous dry N2-flow
- IL droplet (200 μL) with PLL-g-PEG, c=0.3 mg/ml
- Adsorption under a dry N_2 atmosphere ("dry") Surface approach speed = 5 Å/s (to exclude hydrodynamic effects)
- All force measurements in dry N_2 atmosphere (0% RH) and 25°C

Heuberger & Heuberger et al. Review of Scientific Instruments, 2001
Tobias Balmber, PhD thesis, 2007

Surface forces before copolymer adsorption

EDL force and steps in structural forces characteristic of the confinement of ILs



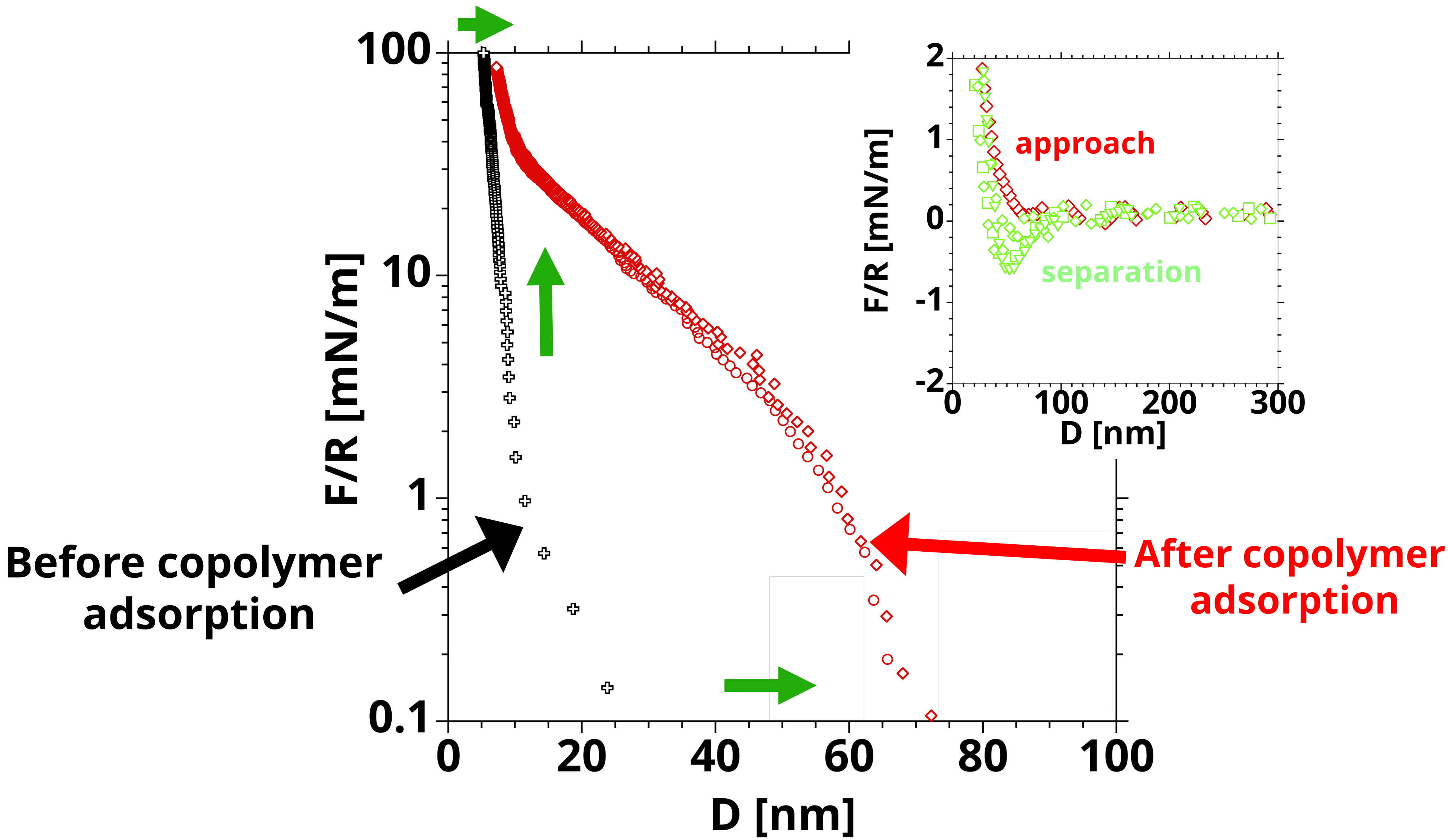


Gebbie, M. A.; Smith, A.; Dobbs, H. A.; Warr, G.; Banquy, X.; Valtiner, M.; Rutland, M. W.; Israelachvili, J.; Perkin, S.; Atkin, R. Long range electrostatic forces in ionic liquids. Chem Commun ***2016****.*

Surface Forces between adsorbed PLL-g-PEG films

Slow adsorption in dry N_2 atmosphere (~30 h)

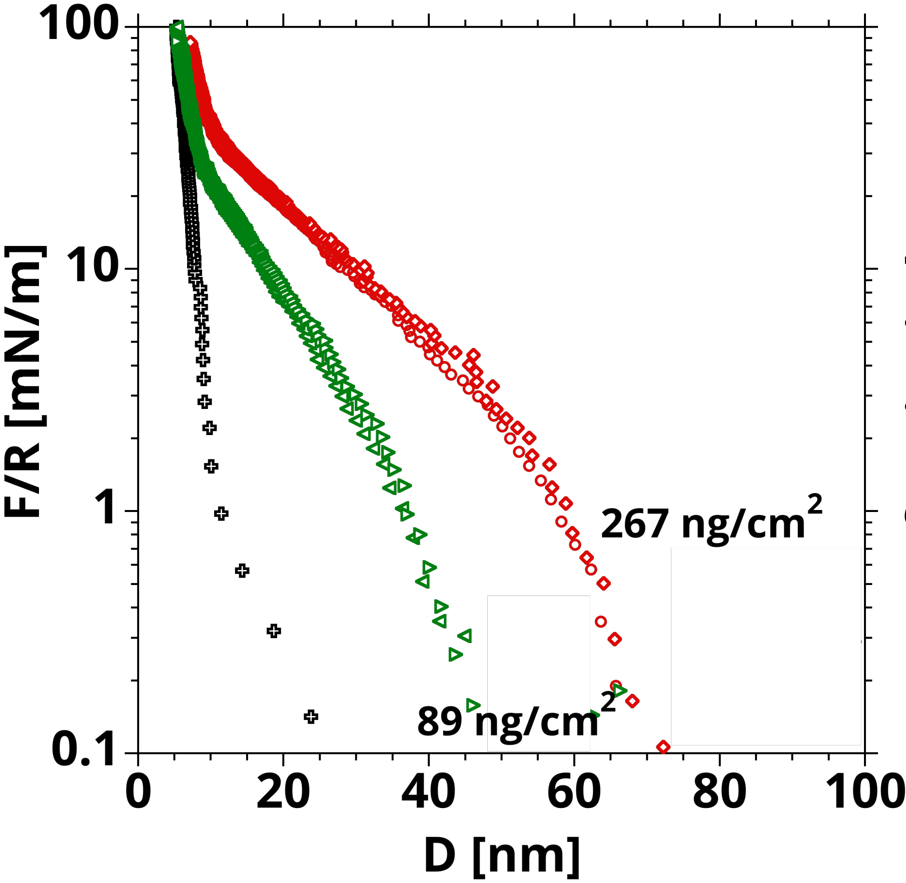
Significant reduction of pull-off force and small adhesion-induced hysteresis

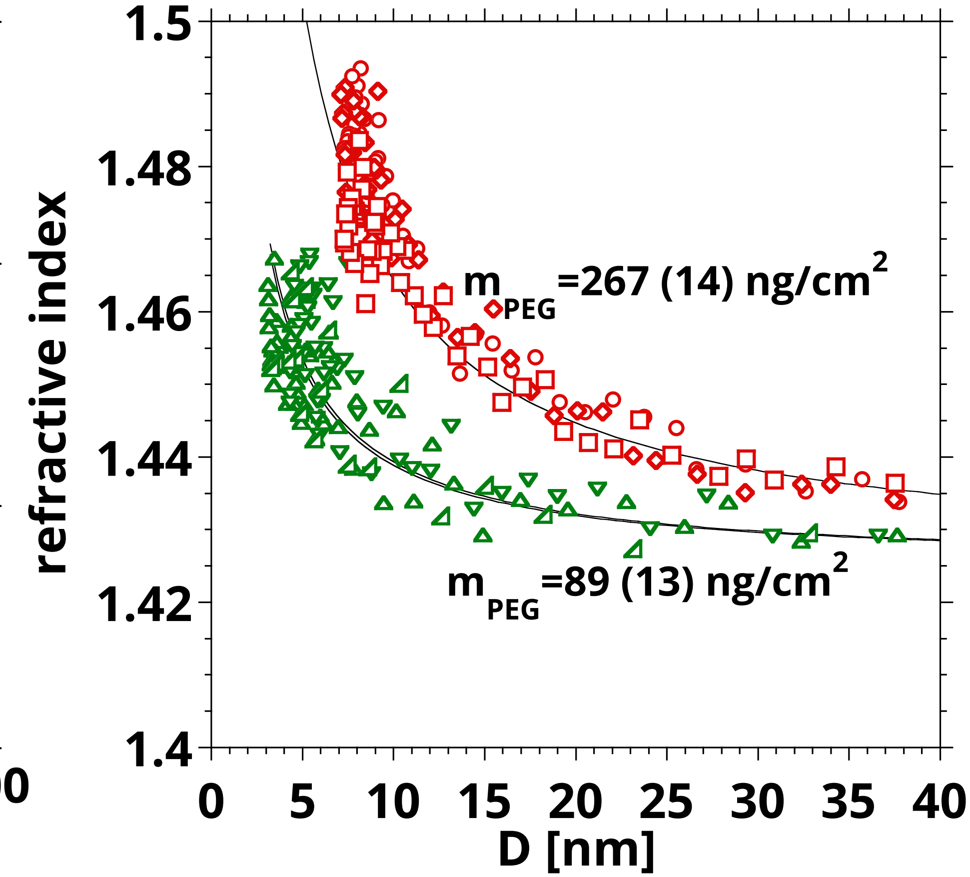


Variable grafting density

Refractive index: $$n(D) = n_{IL} + \frac{2\Gamma}{\rho D}(n_{PEG} - n_{IL})$$

n_{IL}=1.425
n_{PEG}=1.53
ρ =1.12 g/cm^3





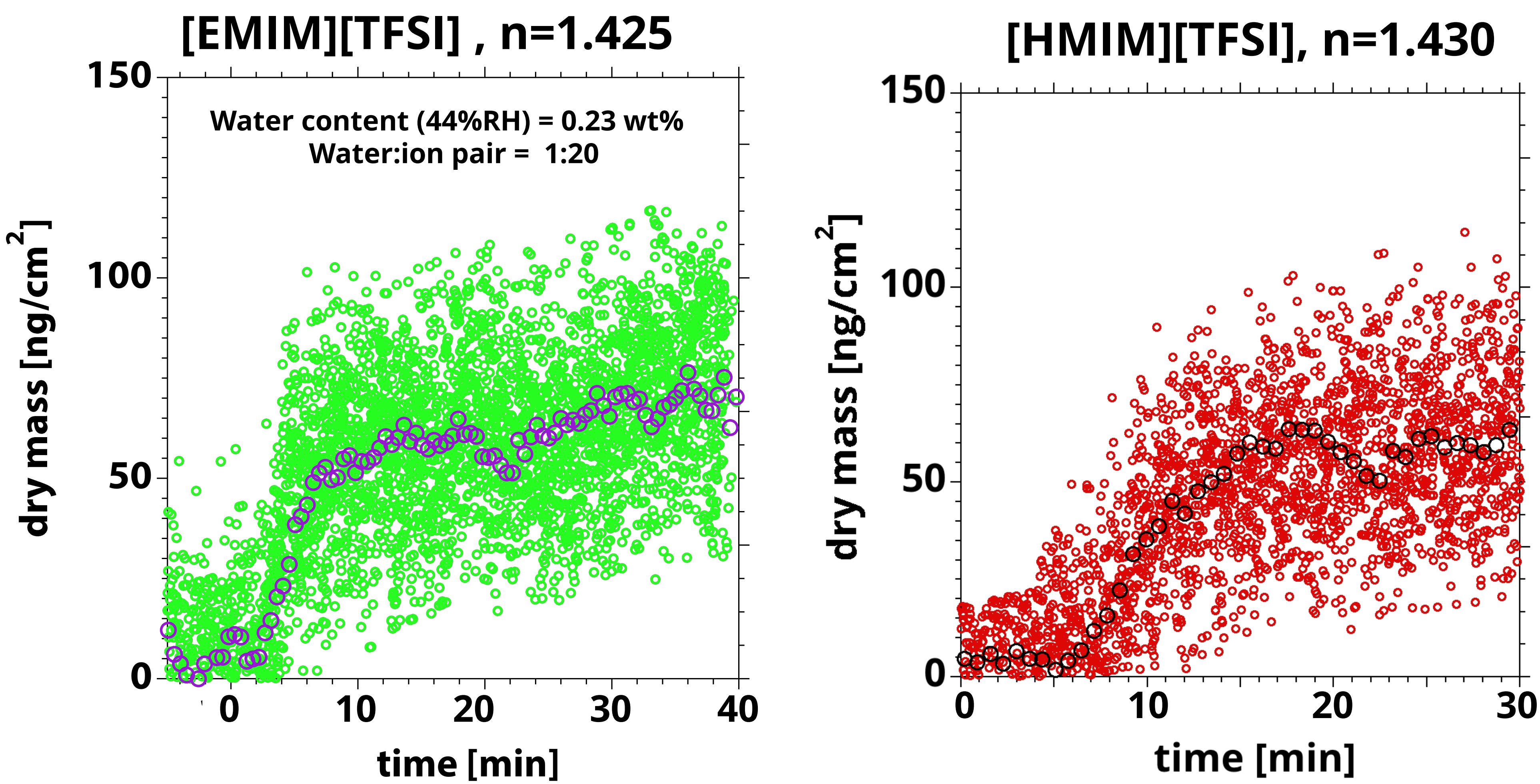
$$A_{PEG} = M_{PEG} M_{copol} / (N_A M_{PEG} \Gamma)$$

$$d_0 = \sqrt{A_{PEG}/(1.5 * \sqrt{3})}$$

*Raviv Frey, Sak, Laurat, Tadmor& Klein. Langmuir 2002

Adsorption of PLL–g–PEG in IL on mica

Multiple beam interferometric measurements (TInAS)*
Exposure to ambient air (30–40%RH)
Fast adsorption

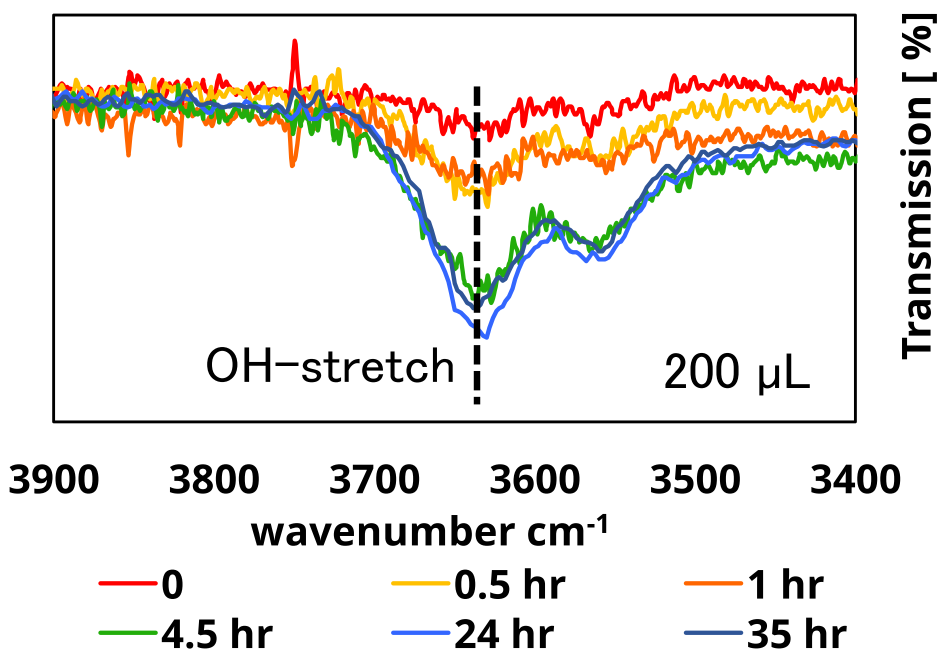


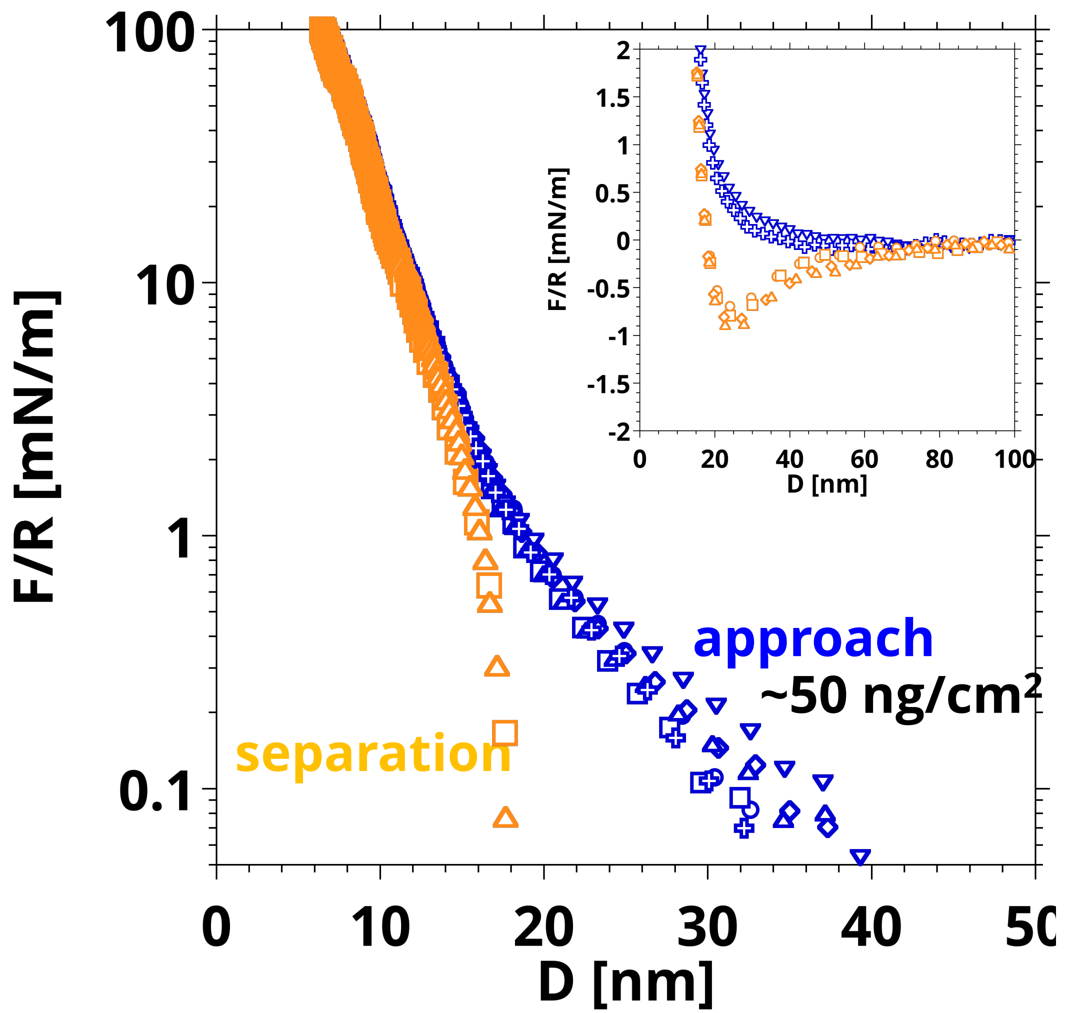
Heuberger, M.; Balmer, T. E. Journal of Physics D: Applied Physics 2007

Adsorption under exposure to 40% RH

Adsorption is rapid but smaller adsorbed mass (~25–50 ng/cm^2)

Water uptake/drying takes ~5 hr
Water content (40%RH) = 0.23 wt%
Water:ion pair = 1:20

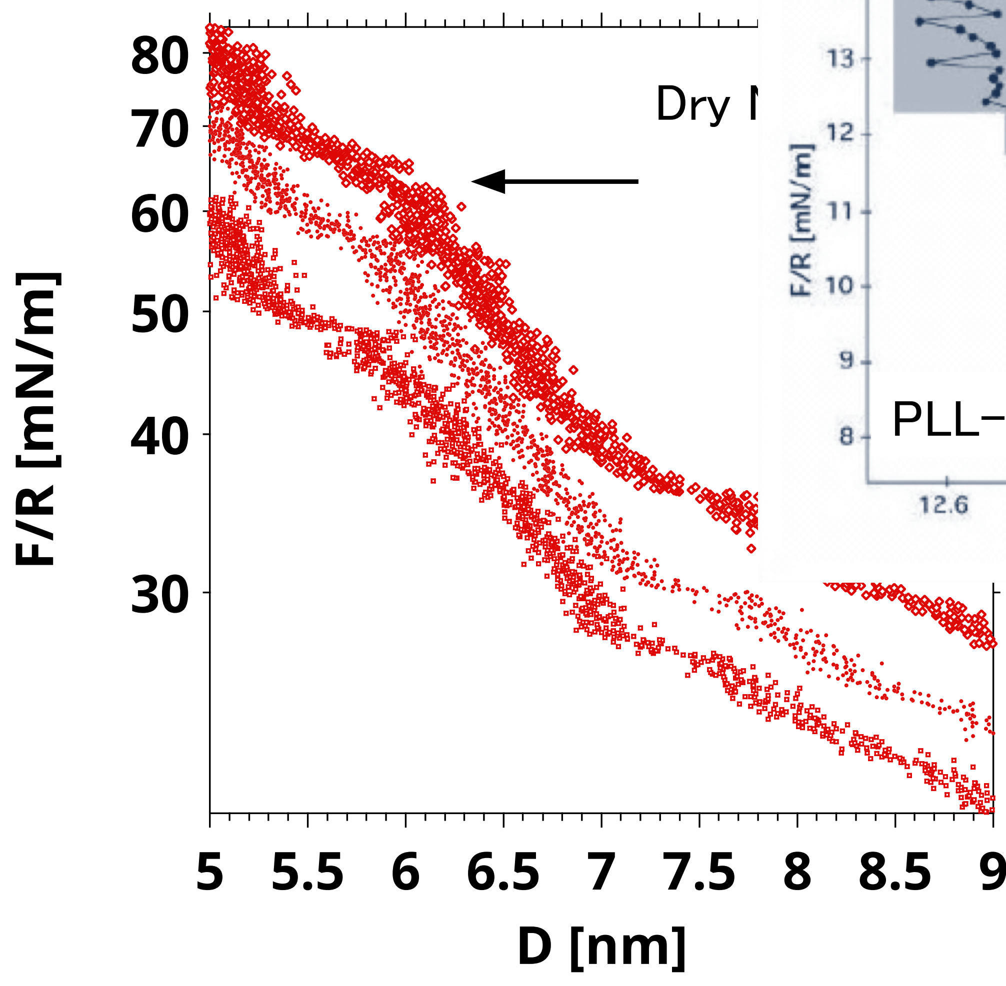


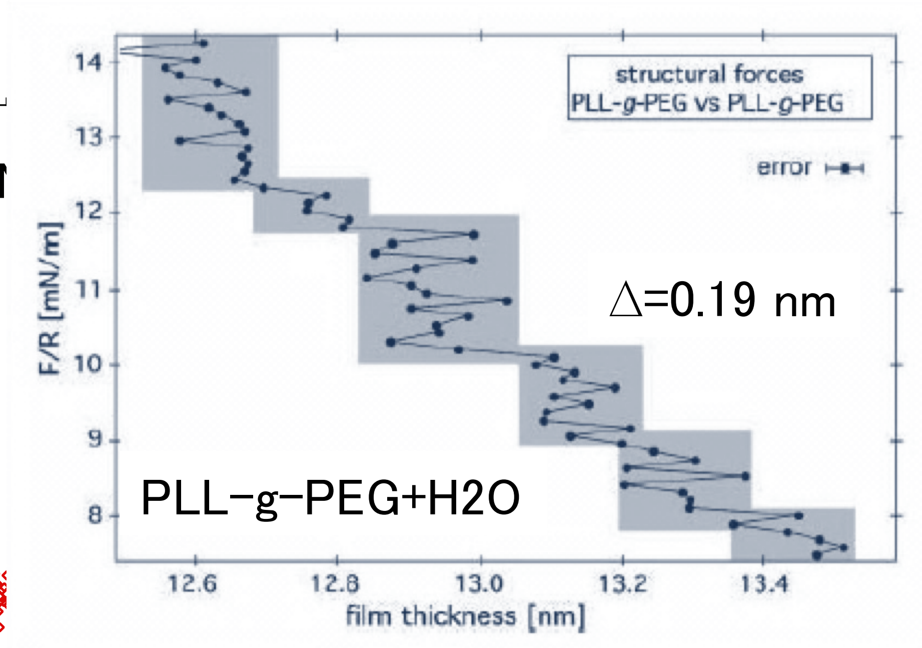


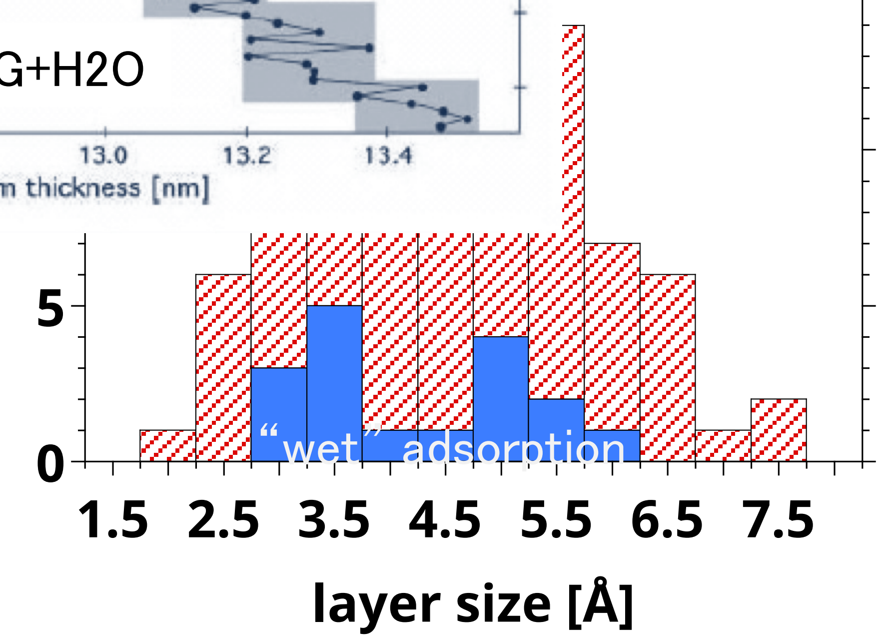
Solvation structure of polymer films at high compression

Layers of IL are squee… …er size
compared to the … ?

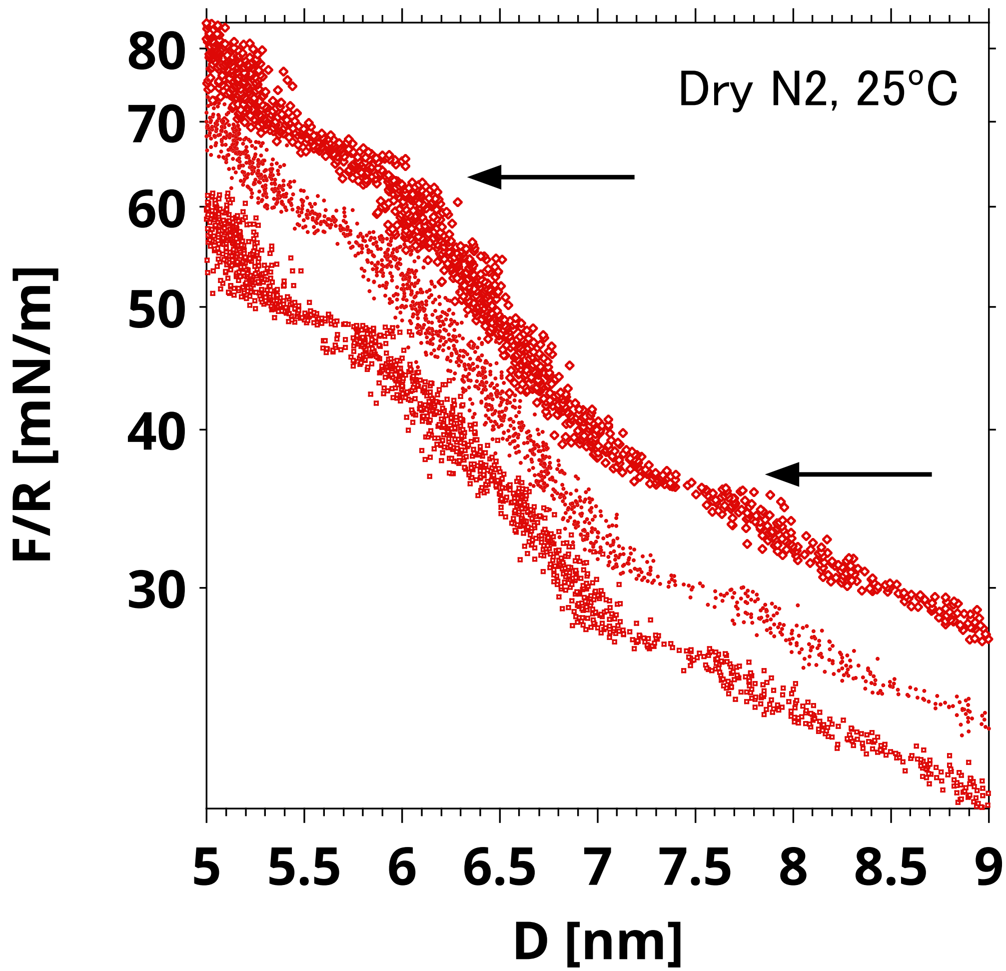
Heuberger, Drobeck&Spencer,
Biophysical Journal 2005







Free energy of solvation



ΔE~5-25 mJ/m²

Area per PEG chain:

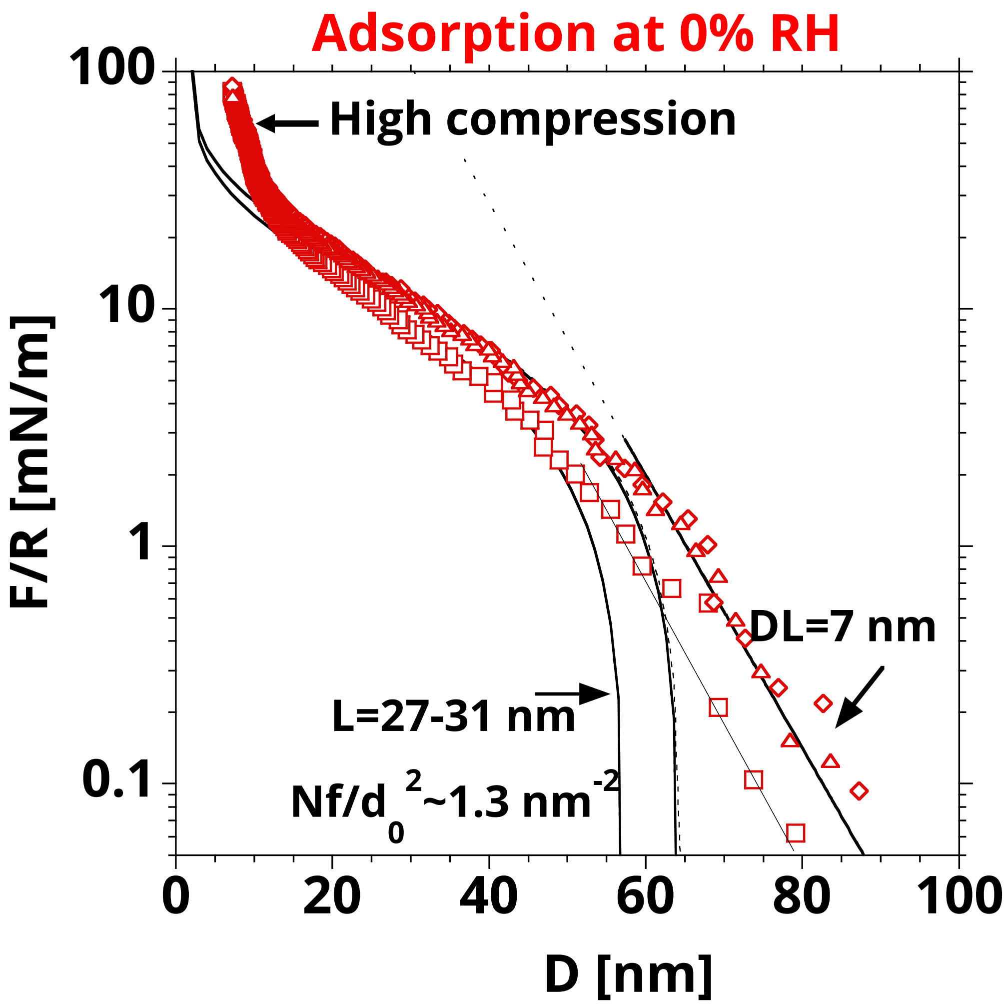
$$A_{PEG} = M_{PEG}M_{copol}/(N_A M_{PEG}\Gamma)$$

ΔG_{IL}~0.04-0.18kT
ΔG_{H2O} ~0.013kT < ΔG_{IL} Per EG

Preferential solvation of PEG by this IL compared to water

Modeling repulsion for polyelectrolyte brushes

Charging of PEG through hydrogen bonding to the cation(*) and $[TFSI]^{-}$ as counterions



Electrical Double Layer force

$$\frac{F}{R} \sim \exp(-\kappa D) \text{ at D>2H}$$

Osmotic repulsion

$$\frac{F}{R} = 4\pi kT \frac{Nf}{d_0^2} \log \frac{2H}{D-2D_0} \text{ at D<2H}$$

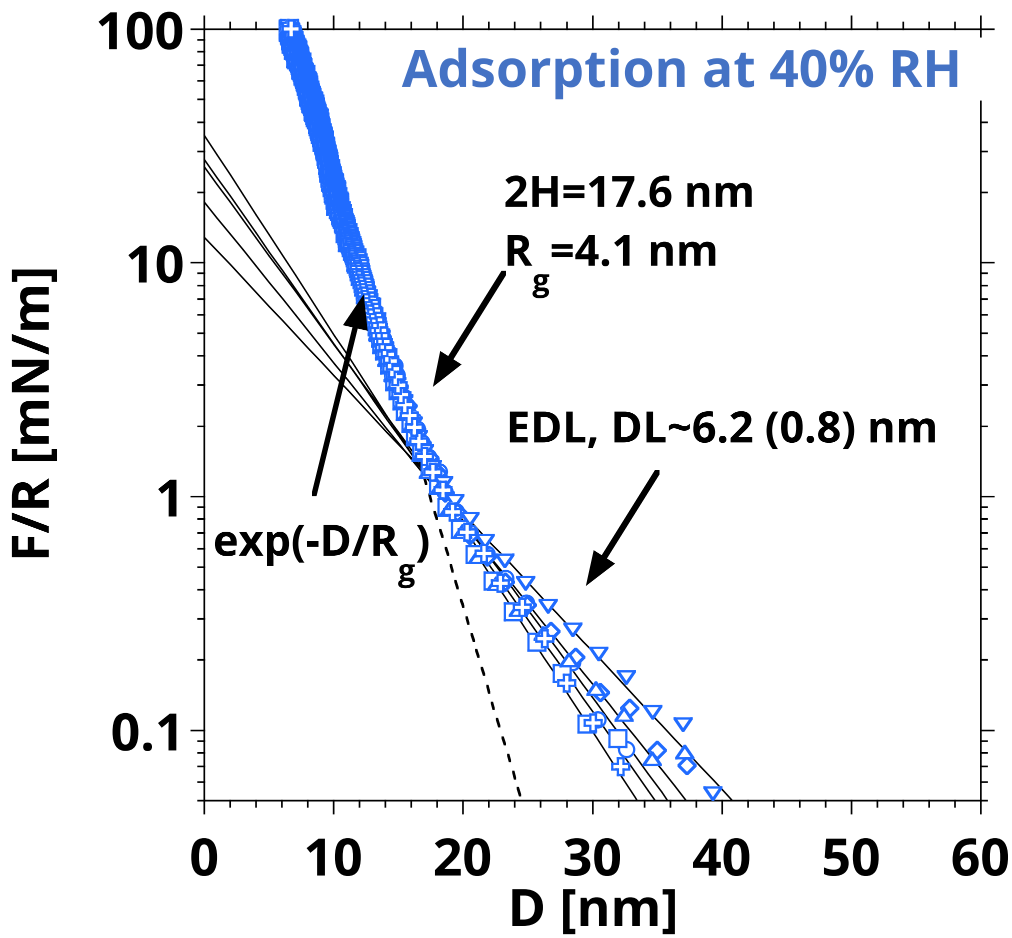
D_0=1 nm (backbone)
f=faction of charged monomers
Fitting parameters: H and charge density $\frac{Nf}{d_0^2}$

Scaling theory fits as well but d_0 is nonsense!

Pincus, P. Macromolecules, 1991
*Lutter, J. Phys. Chem. B, 2013

Modeling repulsion for mushroom films

Exponentially decaying force with two decay lengths



Electrical Double Layer force

$$\frac{F}{R} \sim \exp(-\kappa D) \text{ at } D>4R_g$$

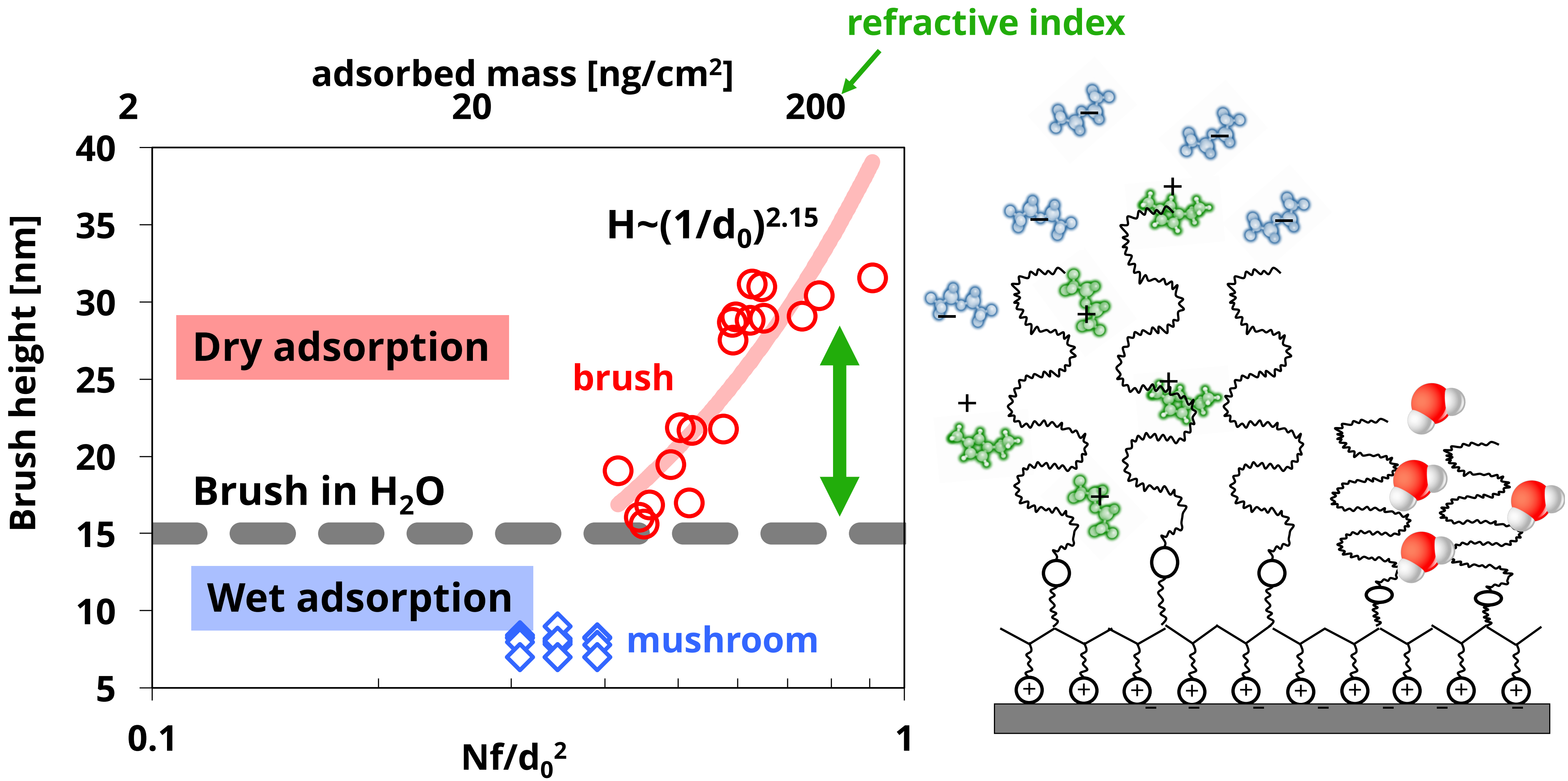
Osmotic repulsion

$$\frac{F}{R} \sim \exp\left(-\frac{D}{R_g}\right)$$

D_0=1 nm (backbone), f=faction of charged monomers

Fitting parameter: $2R_g$ =8 nm

PEG brushes stretch more in IL than in water



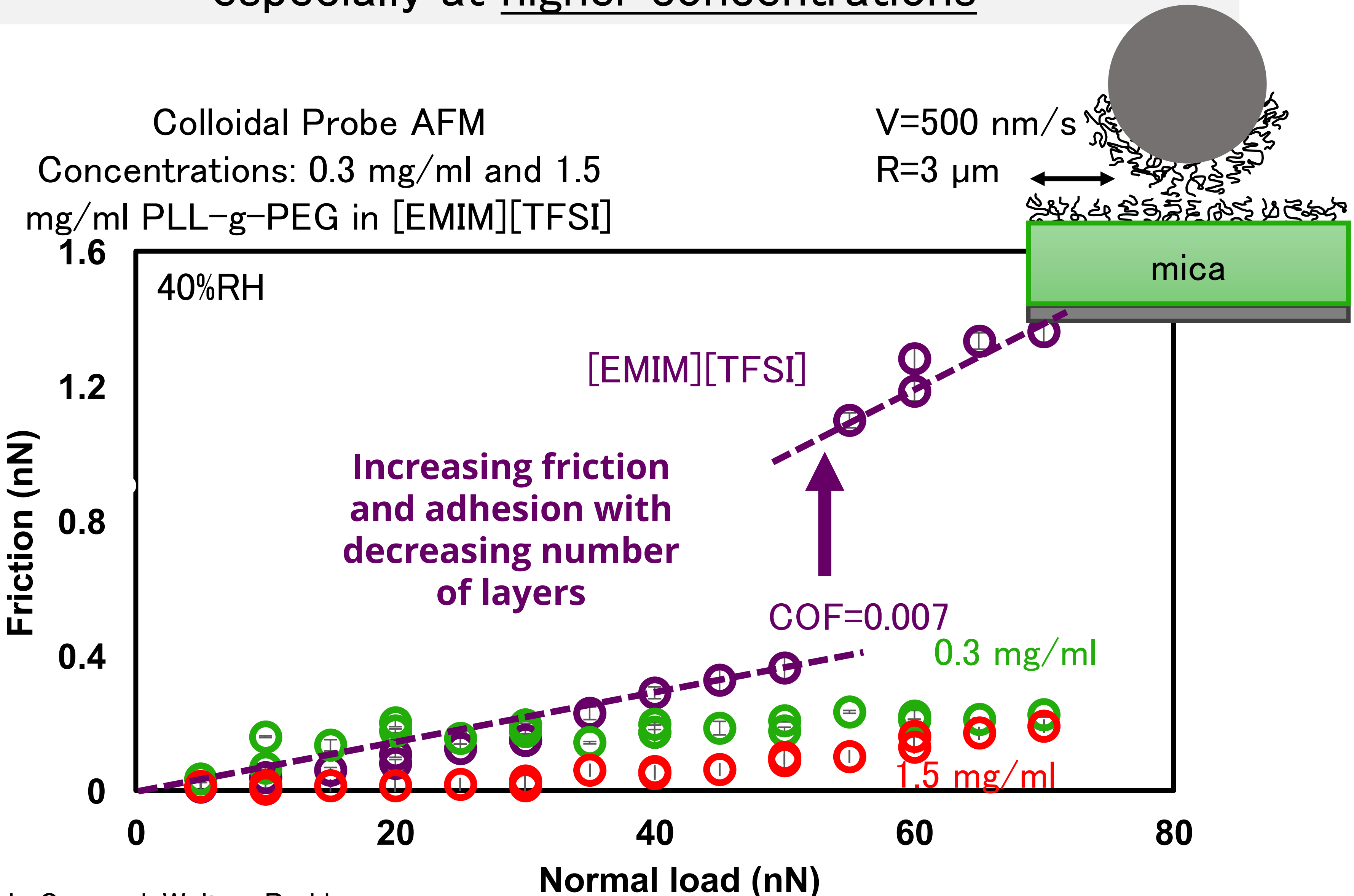
Han & Espinosa-Marzal, JPC Letters, accepted, 2017

Friction force measurements with [EMIM][TFSI]

PLL-g-PEG reduces friction compared to [EMIM][TFSI], especially at <u>higher concentrations</u>

Colloidal Probe AFM
Concentrations: 0.3 mg/ml and 1.5 mg/ml PLL-g-PEG in [EMIM][TFSI]

V=500 nm/s
R=3 µm



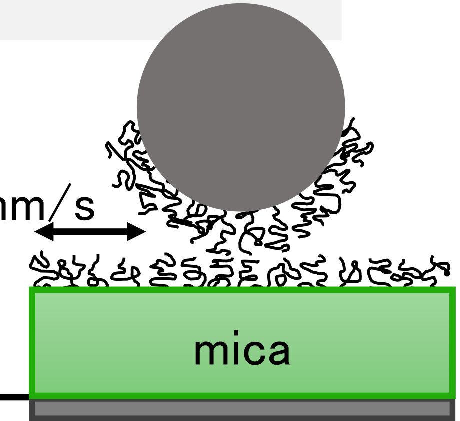
Smith; Lovelock; Gosvami; Welton; Perkin. Phys Chem Phys 2013, 15 (37), 15317–20.

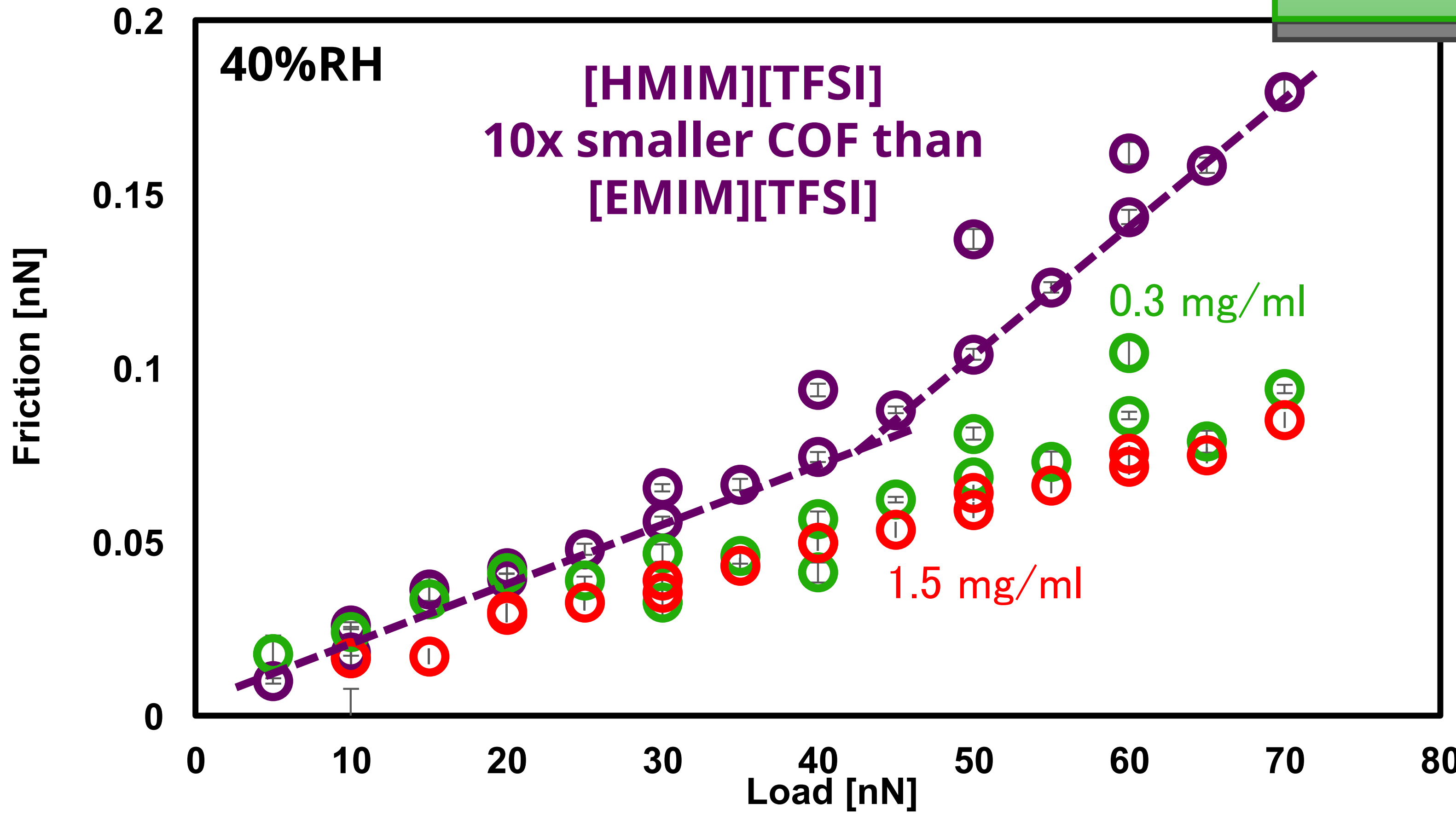
Kramer, G.; Hausen, F.; Bennewitz, R. Faraday Discuss 2017.

Friction force measurements with [HMIM][TFSI]

PLL-g-PEG reduces friction compared to [HMIM][TFSI], especially at <u>higher concentrations</u>

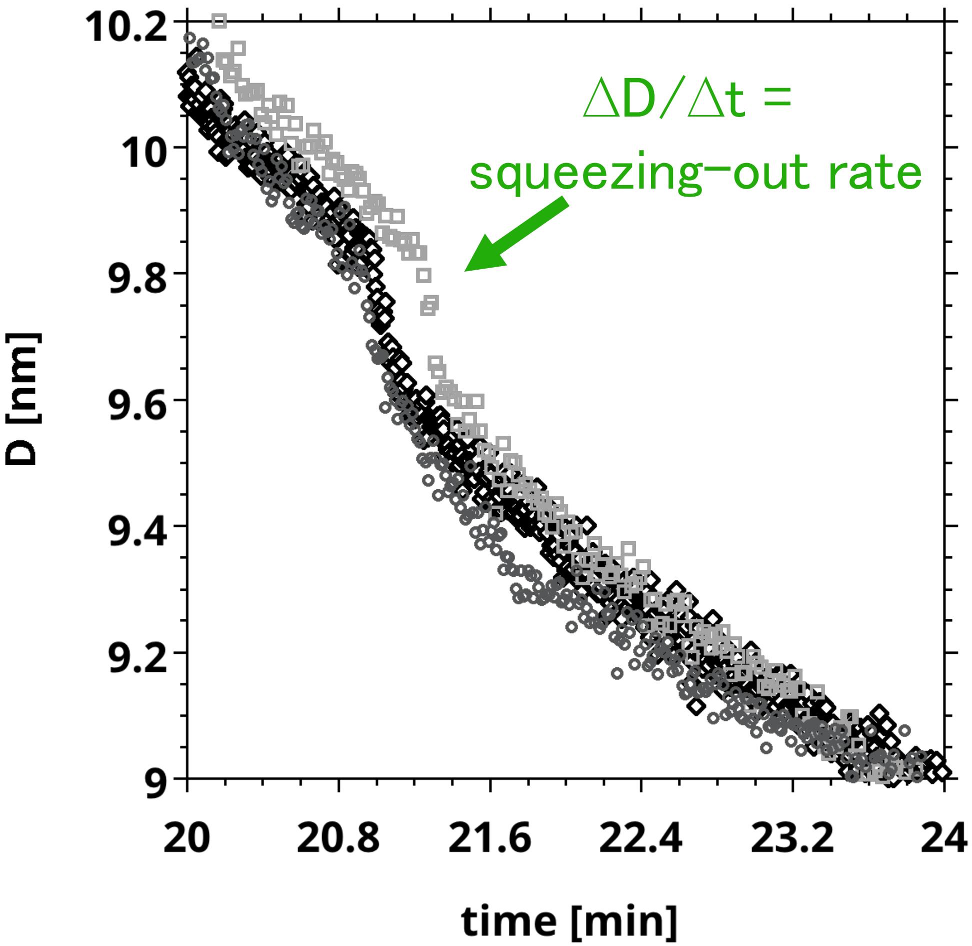
Colloidal Probe AFM
Concentrations: 0.3 mg/ml and 1.5 mg/ml PLL-g-PEG in [HMIM][TFSI]

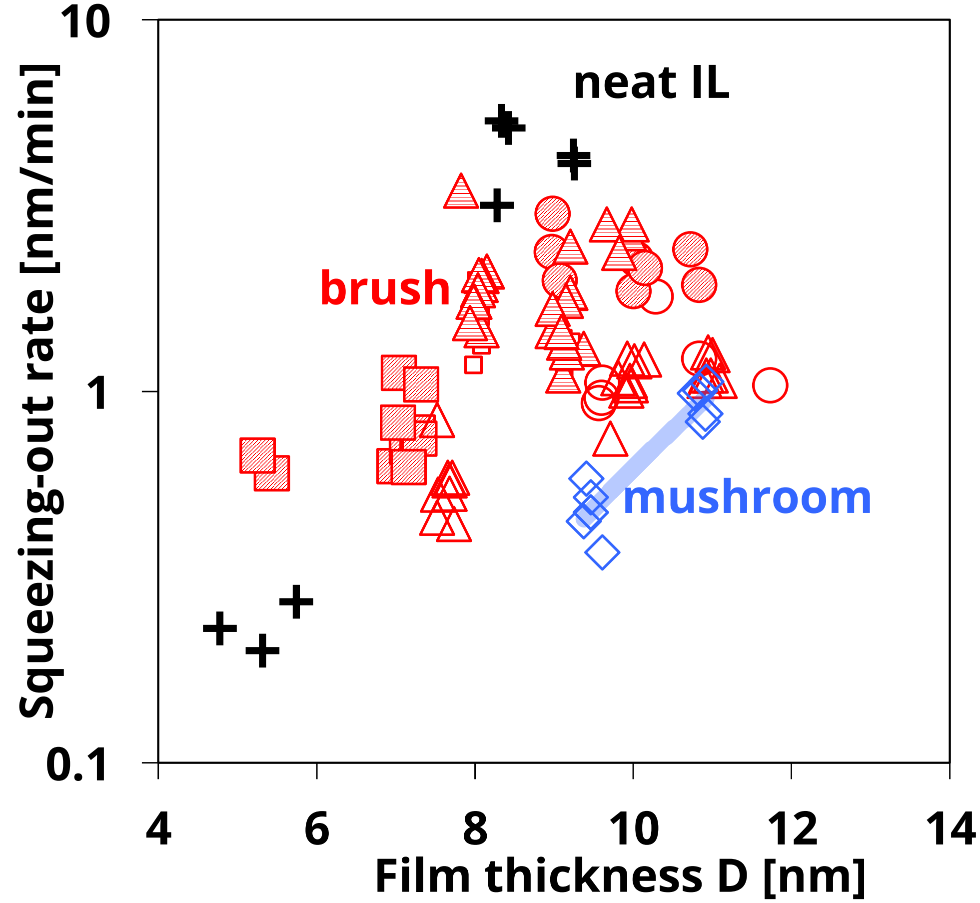




Dynamic behavior of the IL in the confined polymer film

Smaller decrease of squeezing-out rate for the IL in the polymer films than in the neat IL at the same loads





Polymer helps to maintain liquid-like behavior of the IL, which aids to reduce friction force

Conclusions

- Surface forces reveal strong stretching and solvation structure
  - Charging mechanism of PEG through hydrogen bonding to the imidazolium cation
- Reduction of friction compared to the neat ILs
  - Related to the less solid-like behavior of the IL compared to the neat IL
- Influence of water content on polymer adsorption
  - Other grafting methods

Acknowledgments

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(Tel Avid Univ.)

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