Barcelona September 2013

The Friction between Structured Surfaces

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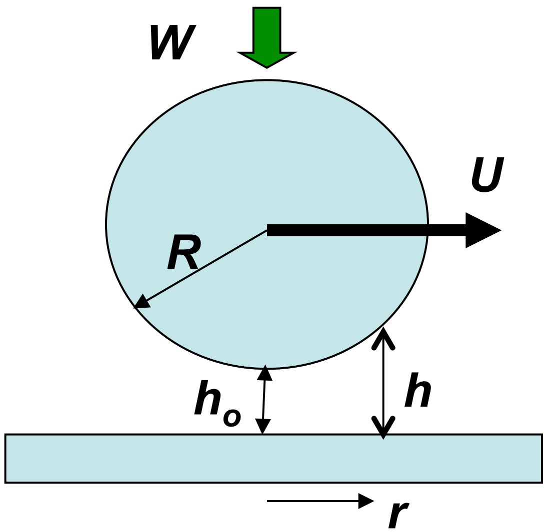
Patrice Malfreyt University of Clermont Ferrand

Origins of hydrodynamic lubrication

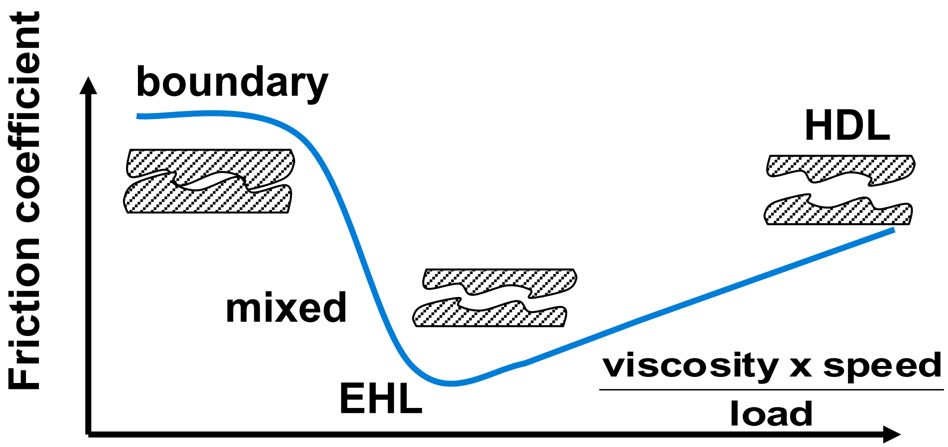


Gap $$h = h_0 + \frac{r^2}{2R}$$

Defines a contact area $$r^2 \approx 2Rh_0$$

Tangential force $$T = \eta\dot{\gamma} \times \pi r^2 \approx \frac{\pi\eta U r^2}{h_0} \quad \left[\dot{\gamma} \approx \frac{U}{h_0}\right]$$

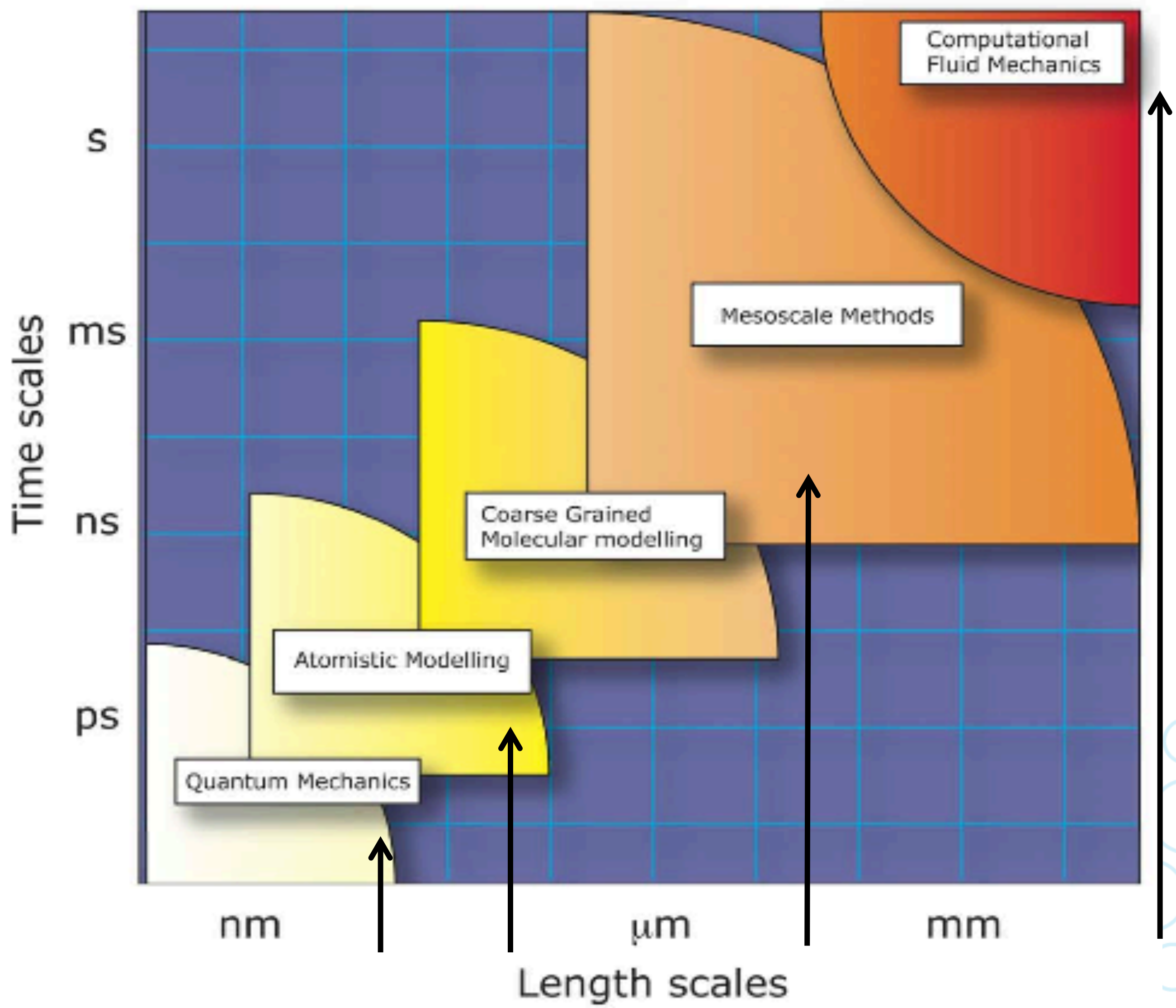
Friction coefficient $$\mu = \frac{T}{W} \approx \frac{\pi\eta U r^2}{W h_0} \approx 2\pi R \times \frac{\eta U}{W}$$



hydrodynamic part of the Stribeck curve

Pyotr Kapitza
J Tech Phys 25, 747 (1955)

Multi-scale Modelling



Navier Stokes equation

DPD
Lattice Boltzmann

Molecular interactions

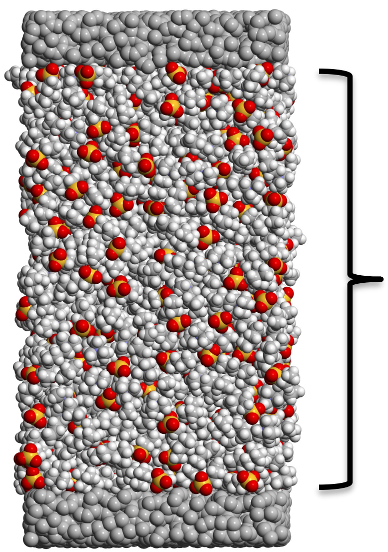
Electronic structure

Atomistic simulations of boundary lubrication

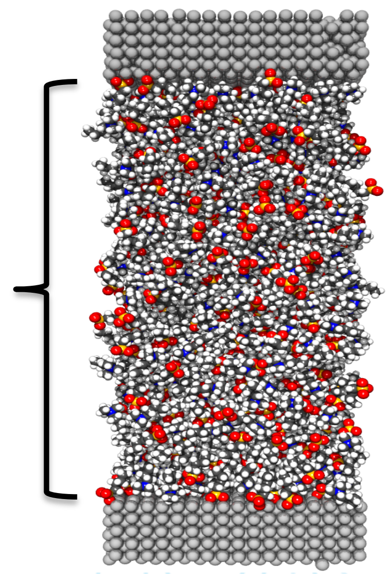
- **Liquids in confinement**

Ionic lubricants

Carbon surfaces

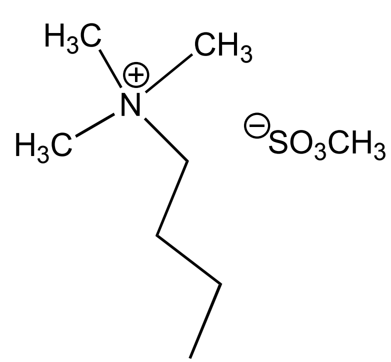


Metallic surfaces



Liquid Lubricant

Ionic liquid



A. Mendonça, P. Malfreyt, Agílio Pádua, *Soft Matter*, **2013**

A. Mendonça, Agílio Pádua, P. Malfreyt, *J. Chem. Theory Comput.*, **2013**

Force field parameterisation

- **Potential function of the system**

$$U = U_{L-L} + U_{S-S} + U_{S-L}$$

Force fields available (all-atoms description)

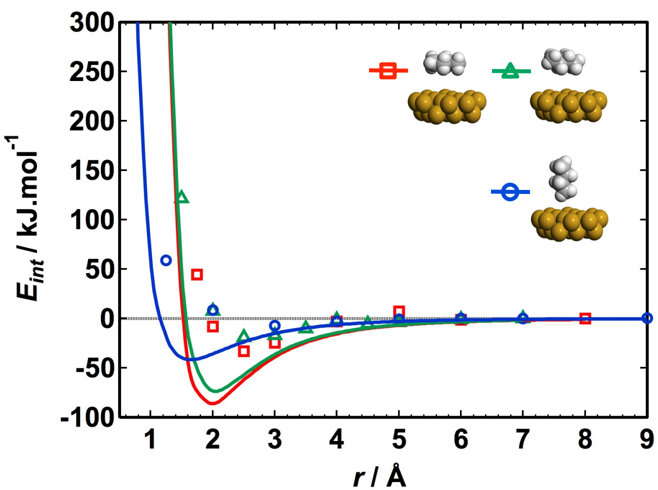
Force field NOT available

- **Surface-Lubricant interactions are complex to describe**
  - Contribution from VDW interactions
  - Coulombic interactions from the polarization of the metal surfaces, in the presence of ions

$$U_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$



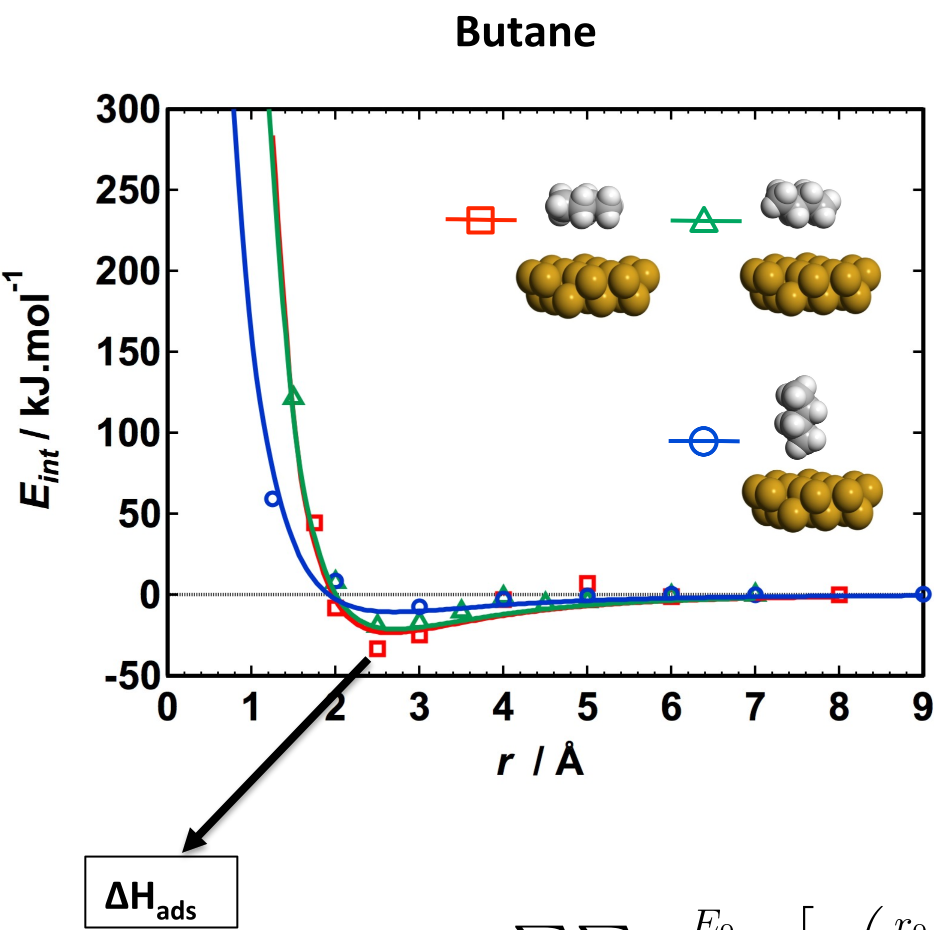
LJ potential is not adequate to describe such interactions

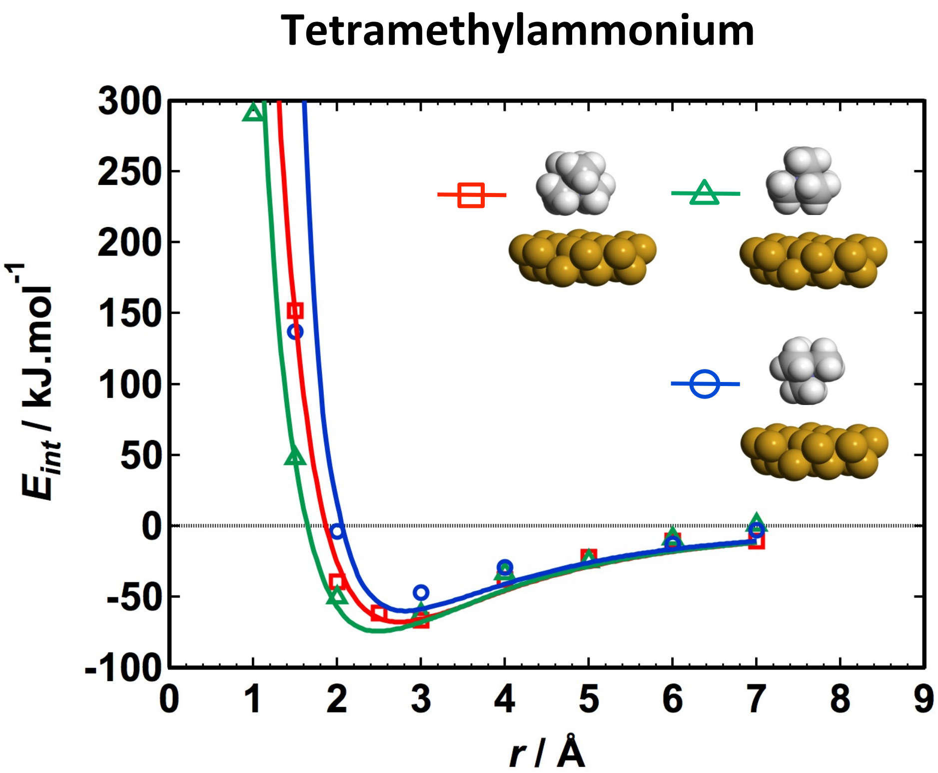
↓

Development of an interaction model based in DFT calculations

Energies of interaction

MO6-L/ TZVP, ECP10MHF





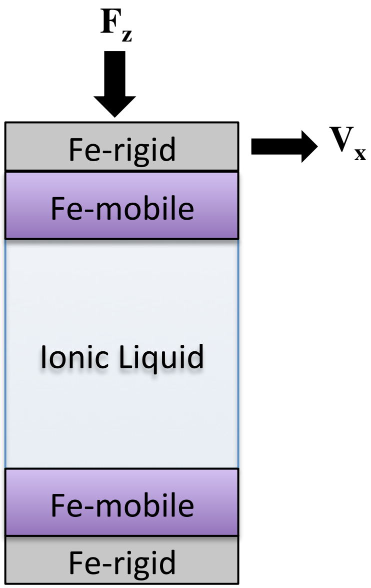
$$U_{ij}(r_{ij}) = \sum_i \sum_j \frac{E_0}{(n-m)} \left[m \left(\frac{r_0}{r_{ij}} \right)^n - n \left(\frac{r_0}{r_{ij}} \right)^m \right]$$

$i =$ Interaction site in the fragment

$j =$ Atom in the metal surface

Non-equilibrium simulations

- **Shear and load conditions**



Experimental conditions:

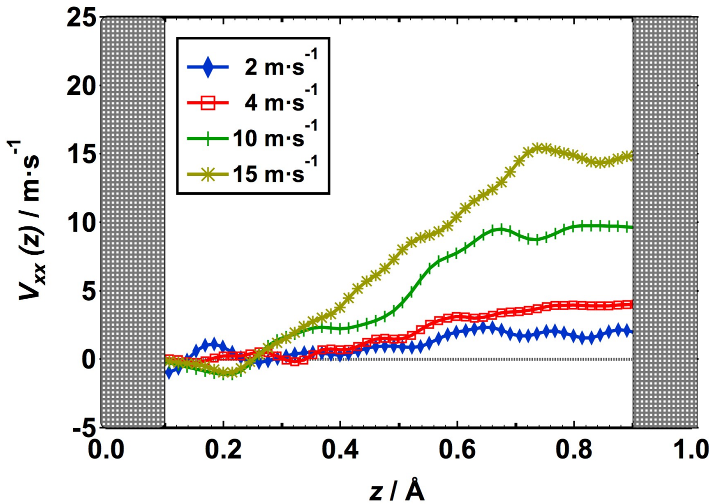
- Normal applied pressure: 1 GPa
- Shear velocity: 0.01 – 0.1 m/s

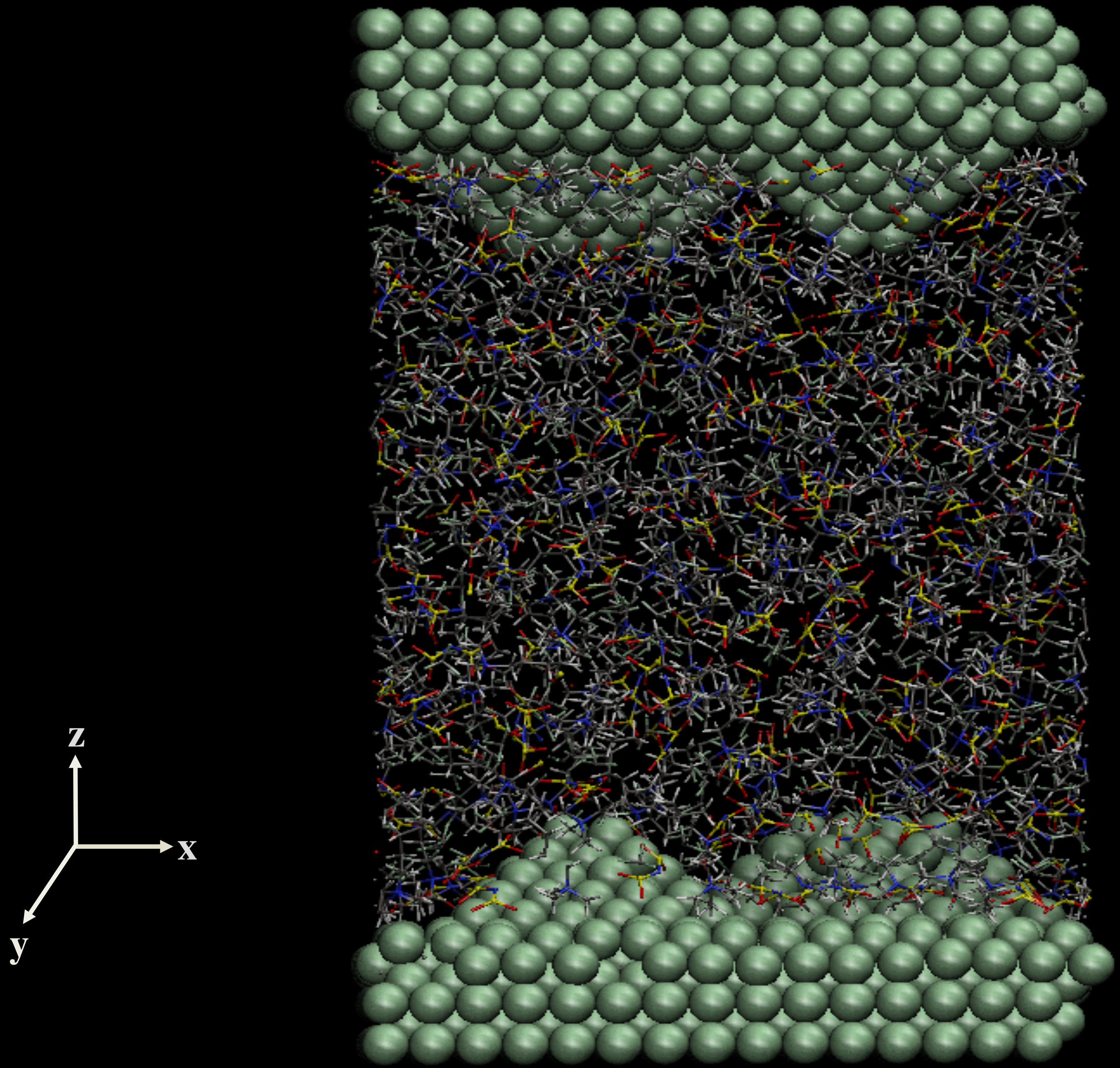
Simulated conditions:

- Normal applied pressure: 90 – 800 Mpa (Experimental value ~ 1 Gpa)
- Shear velocity: 0.01 – 15 m·s^{-1} (Experimental value ~ 0.01 m·s^{-1})

Shear will create a gradient of velocity in the *z*-direction, for the particles in the fluid:

$$v_\alpha(z_k) = \frac{\sum_{i=1}^{N} H_k(z_i)(v_i)_\alpha}{\sum_{i=1}^{N} H_k(z_i)}$$



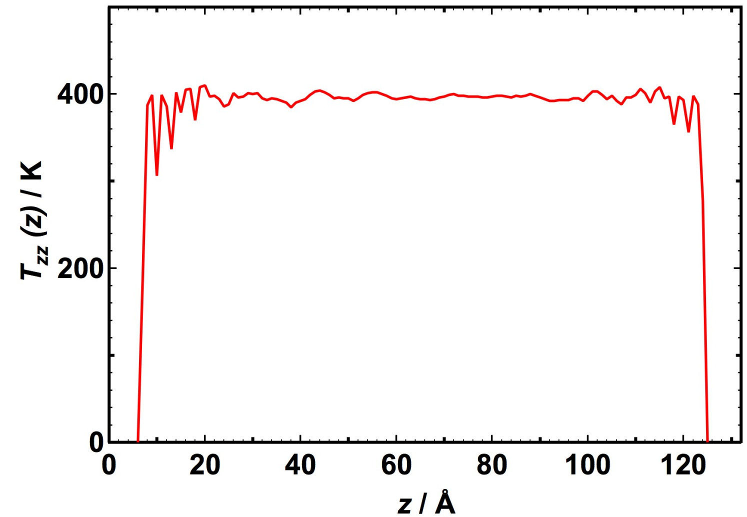


z
x
y

Thermodynamic properties

- **Temperature**

$$k_B T_{\alpha\beta}(z_k) = \left\langle \frac{\sum_{i=1}^{N} H_k(z_i) m_i \left[(v_i)_\alpha - u_\alpha(z_k)\right]\left[(v_i)_\beta - u_\beta(z_k)\right]}{\sum_{i=1}^{N} H_k(z_i)} \right\rangle$$

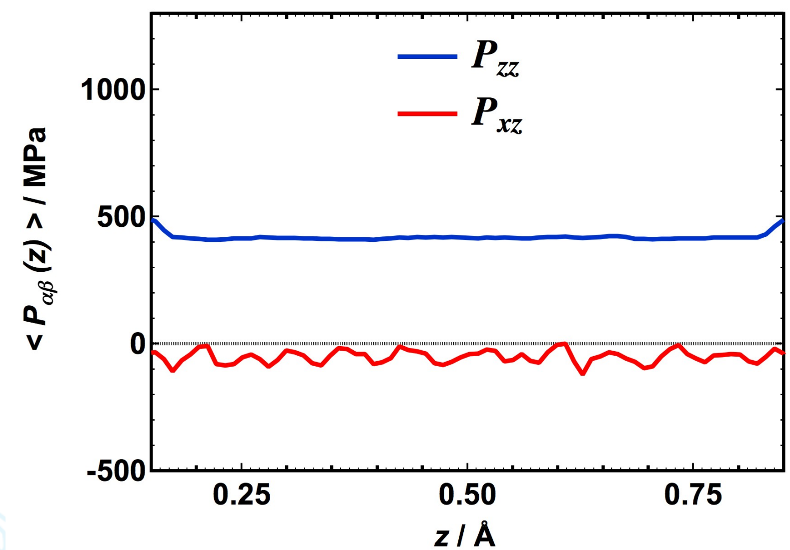


- **Pressure**

$$P_{\alpha\beta}(z_k) = P_{\alpha\beta}^{kin}(z_k) + P_{\alpha\beta}^{conf}(z_k)$$

$$P_{\alpha\beta}(z_k) = \langle \rho(z_k) \rangle k_B T_{\alpha\beta}(z_k)$$

$$+ \frac{1}{L_x L_y} \left\langle \sum_{i=1}^{N-1} \sum_{j>i}^{N} \frac{(\boldsymbol{r_{ij}})_\alpha (\boldsymbol{F_{ij}})_\beta}{|z_{ij}|} \theta\left(\frac{z_k - z_i}{z_{ij}}\right) \theta\left(\frac{z_j - z_k}{z_{ij}}\right) \right\rangle$$

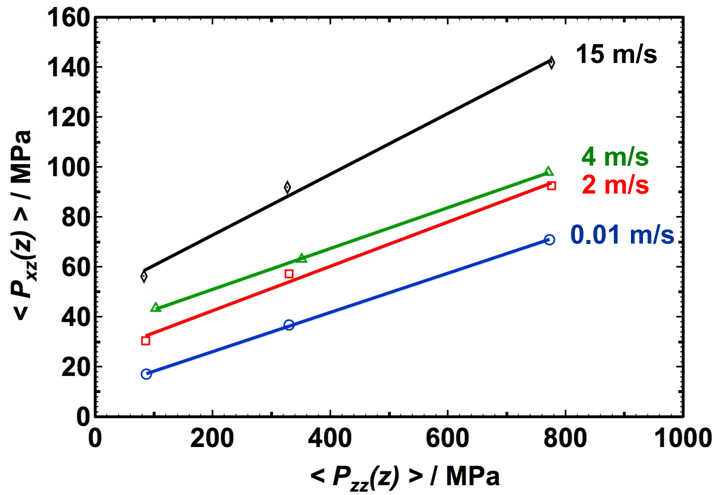


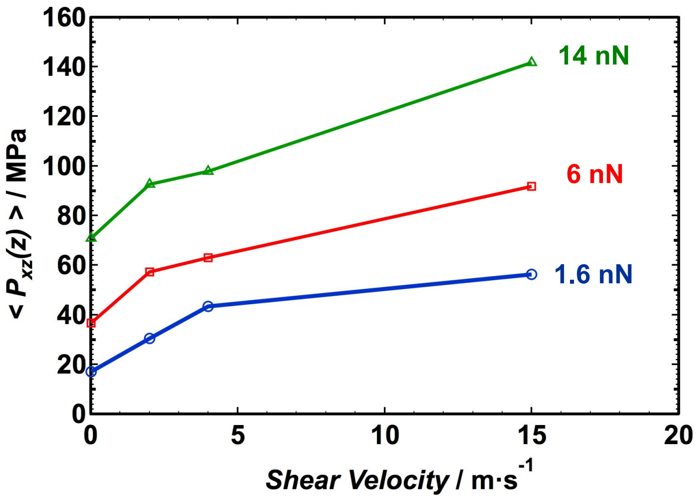
Kinetic friction coefficient calculation

Amontons' 1st Law : $F_x = \mu F_z$

Modified Amontons' 1st Law (for adhering surfaces) : $F_x = F_0 + \mu F_z$

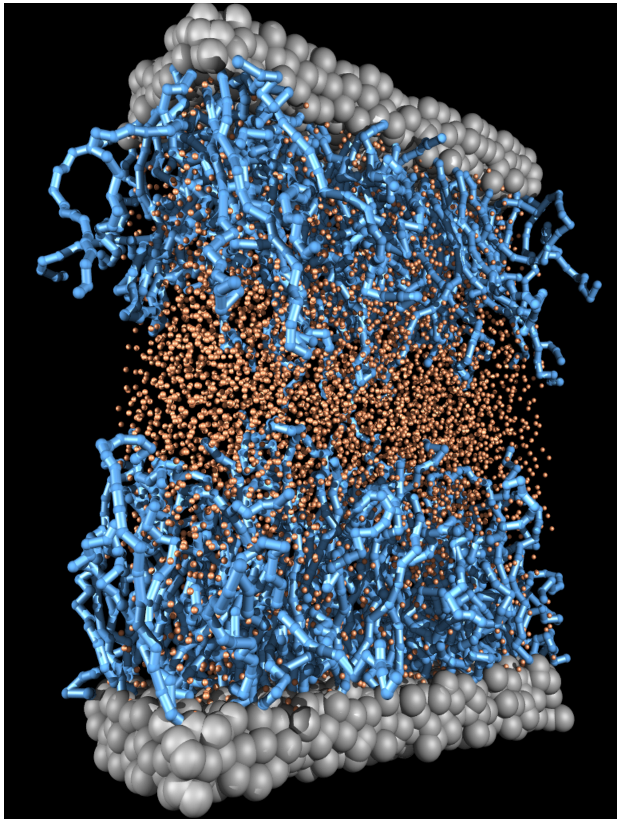
Definition in terms of pressure $\langle P_{xz}(z_k) \rangle = P_0 + \mu \langle P_{zz}(z_k) \rangle$



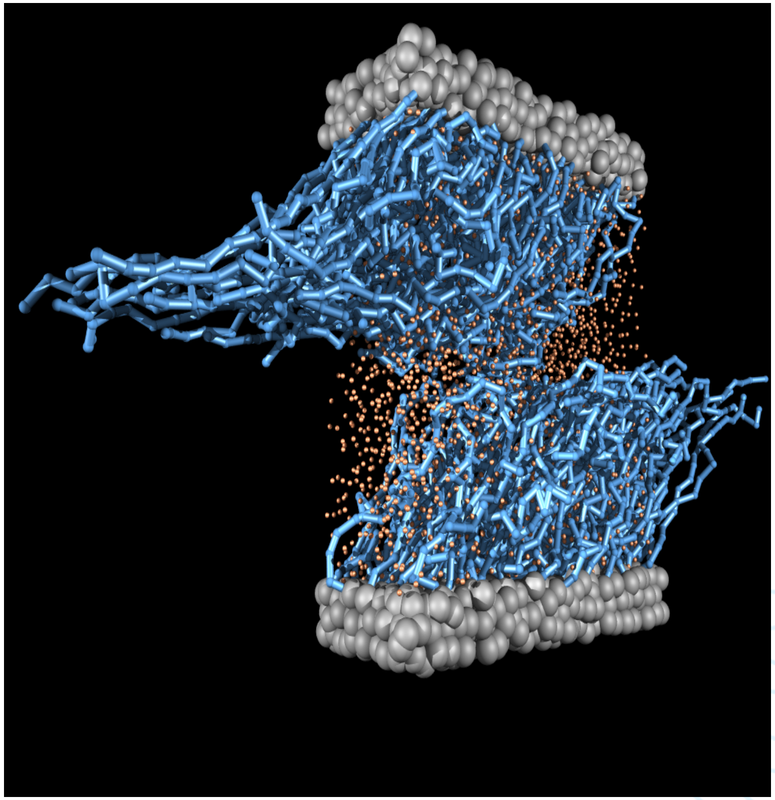


Shear velocity ($m \cdot s^{-1}$)	μ
0.01	0.078
2	0.089
4	0.082
15	0.122

Polymer brushes under shear a structured surface

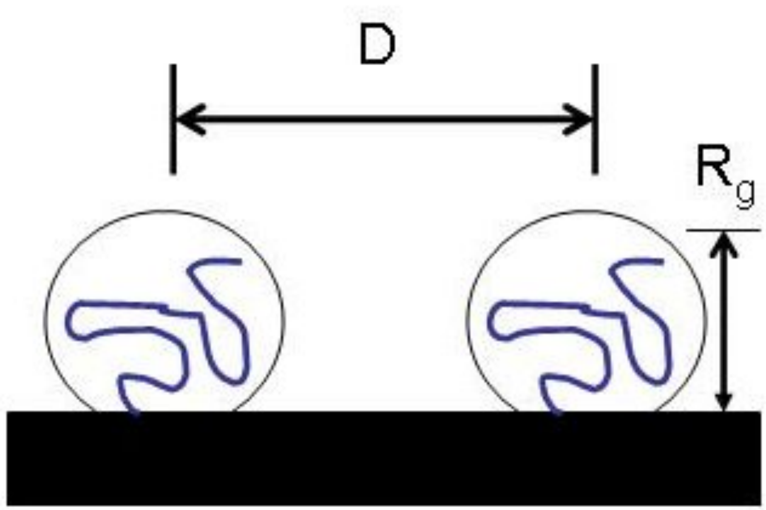


At equilibrium

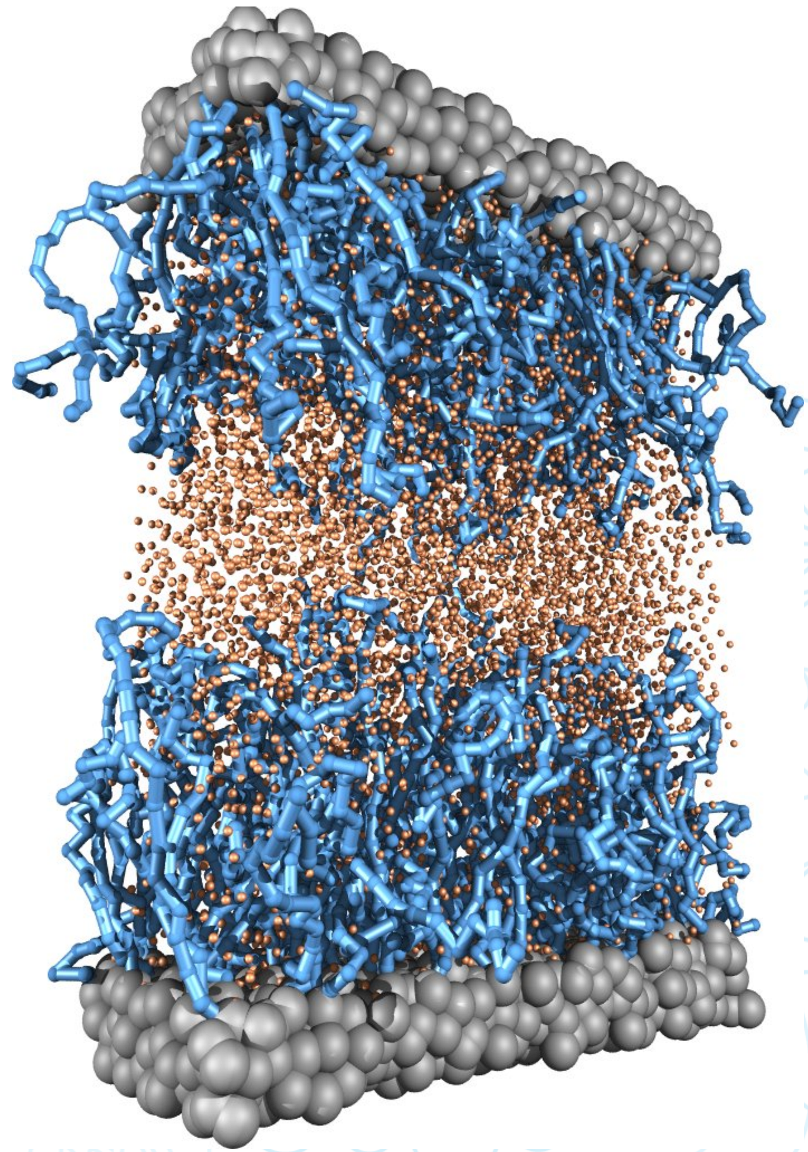


Under shear

Polymer brushes



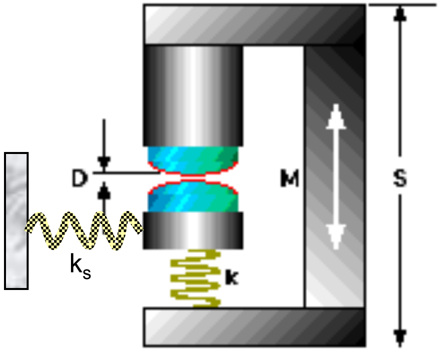
Polymer mushroom



The excluded volume repulsion (in a good solvent) balances the elastic pressure

Alexander, de Gennes 1977

The surface forces apparatus



D. Tabor, R.H.S. Winterton, J.N. Israelachvili in the early 1970s at Cambridge University

SFA of Polyelectrolyte brushes

U. Raviv, S. Giasson, N. Kampf, J. F. Gohy, R. Jerome, J. Klein, Nature 2003, 425, 163. **$(PMMA)_{41}(PSGMA)_{115}$ physisorbed on to mica ε_{exp} = 0.0006-0.001**

B. Liberelle, S. Giasson, Langmuir 2008, 24, 1550. PS-b-PAA covalent bound to mica ε_{exp} = 0.05-0.25

Fully charged polyelectrolyte brushes show friction coefficient ca. 40% lower Than neutral brushes (shear rate 10^4 s^{-1})

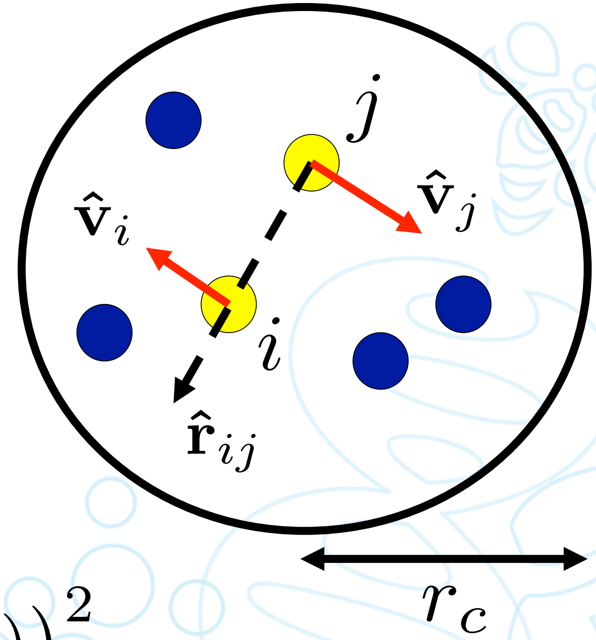
Dissipative particle dynamics (DPD)

$$\mathbf{f}_{ij}^{C} = \begin{cases} a_{ij}\,\omega_C(r_{ij})\,\hat{\mathbf{r}}_{ij} & (r_{ij} < r_c) \\ 0 & (r_{ij} \geq r_c) \end{cases}$$

$$\omega_c(r_{ij}) = (1 - r_{ij}/r_c) \qquad (r_{ij} < r_c)$$

$$\mathbf{f}_{ij}^{D} = -\gamma\omega^{D}(r_{ij})\,(\hat{\mathbf{r}}_{ij}.\mathbf{v}_{ij})\,\hat{\mathbf{r}}_{ij}$$

$$\mathbf{f}_{ij}^{R} = \sigma\omega^{R}(r_{ij})\theta_{ij}\frac{1}{\sqrt{\delta t}}\hat{\mathbf{r}}_{ij}$$



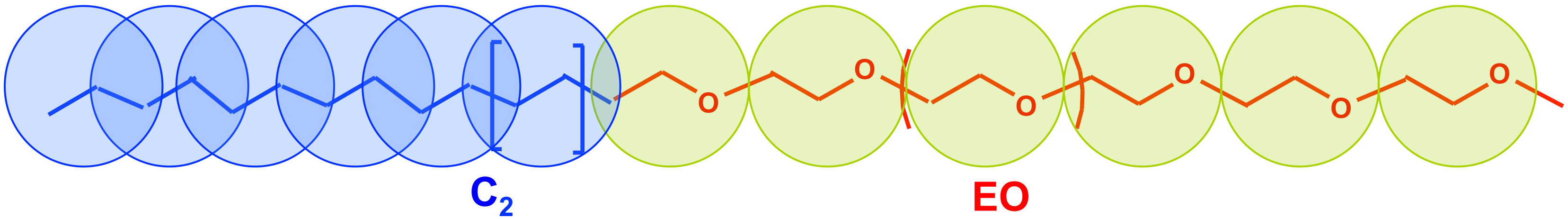
Fluctuation-dissipation theorem:

$$\gamma = \frac{\sigma^2}{2k_BT} \quad \text{et} \quad \omega^{D}(r_{ij}) = \left(\omega^{R}(r_{ij})\right)^2$$

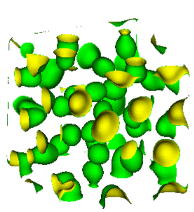
Can we use a longer timestep?

- By fitting to the water diffusion coefficient, we obtain timesteps of ca. 10ps. We are routinely performing runs of 10μs on 20,000 dpd particles.
- The lowest shear rates that we can study are between 10^5 and 10^6 s^{-1} (perhaps one order of magnitude higher that the experimental oscillatory shear rates)
- The ratio of the Flory of the radius of the polymer to interpolymer spacing is the same in experiment and the dpd model. 1 dpd unit of pressure corresponds to 10 MPa
- A water bead contain 3-4 molecules, the polymer dpd 6-8 momomers.

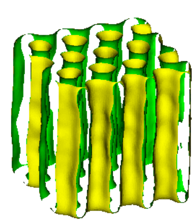
DPD parameter fitting: the mixing of water and a surfactant



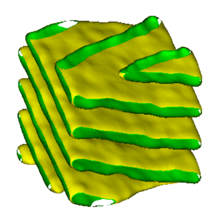
Water	Surfactant



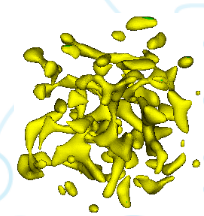
micellar



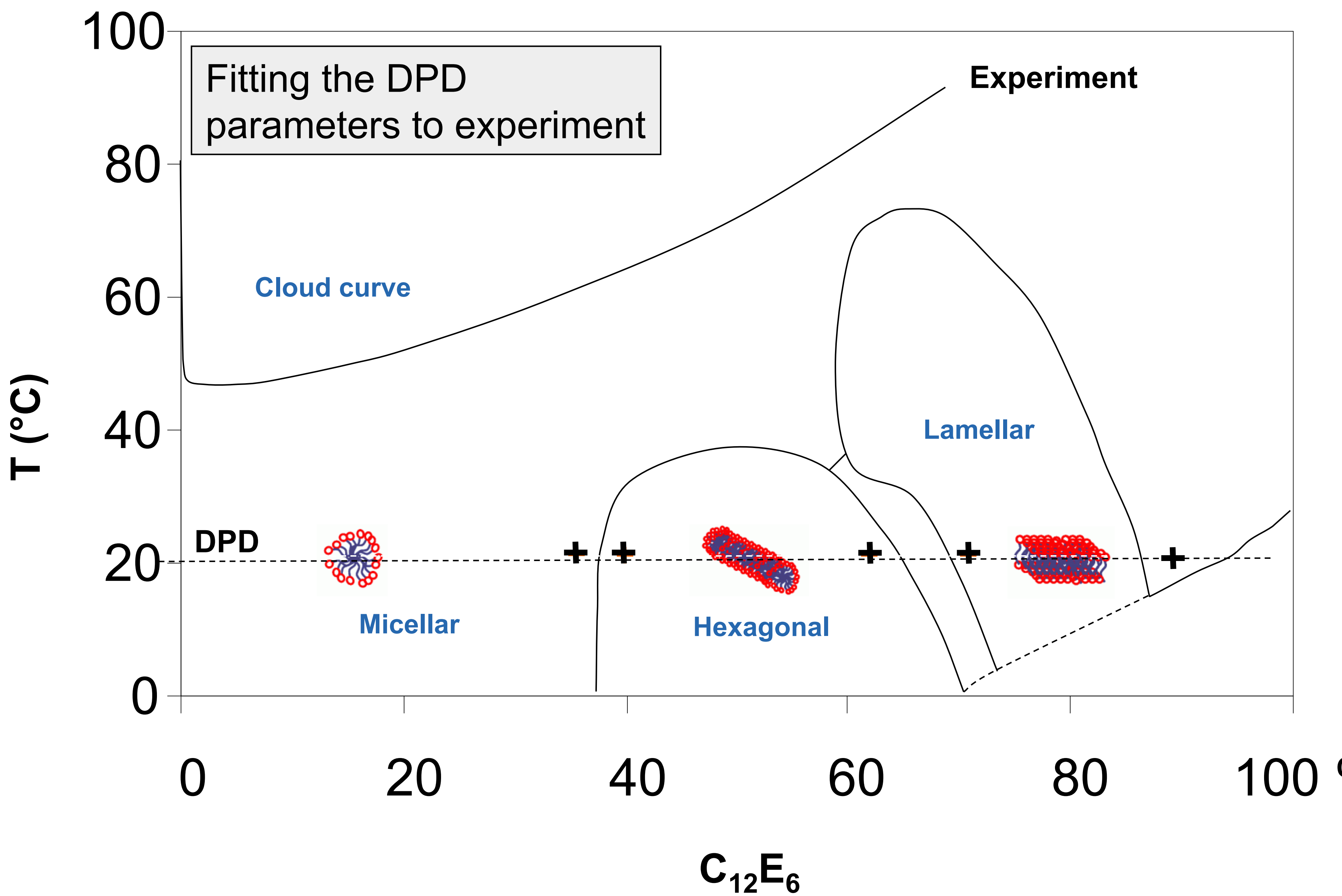
hexagonal



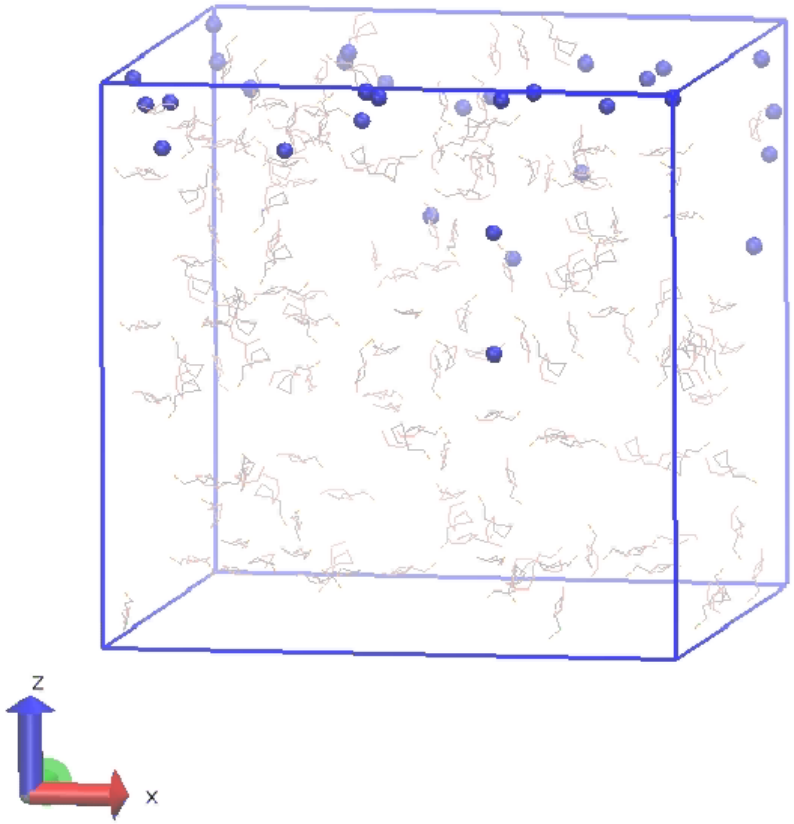
lamellar



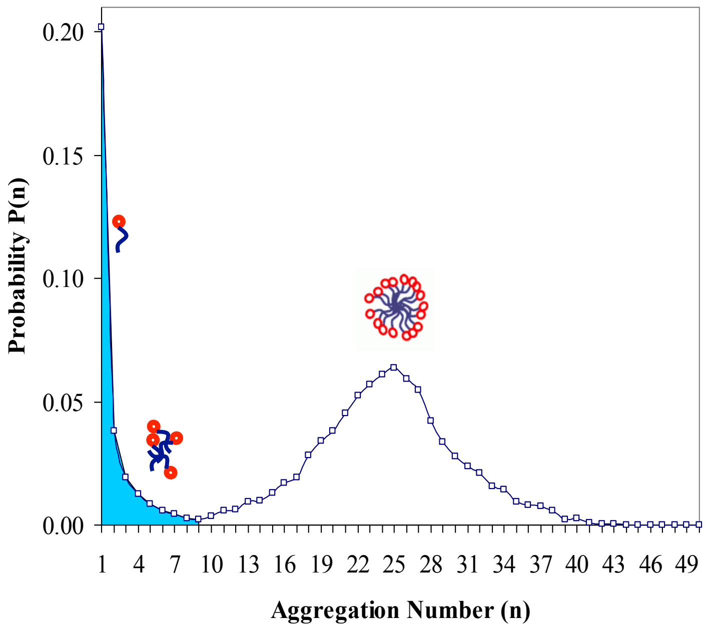
Inverse micellar


Fitting the DPD
parameters to experiment
Experiment
Cloud curve
Lamellar
DPD
Micellar
Hexagonal
T (°C)
$C_{12}E_6$
100
80
60
40
20
0
0
20
40
60
80
100

Micellisation



Massimo Noro
And Patrick Warren
Unilever Port Sunlight

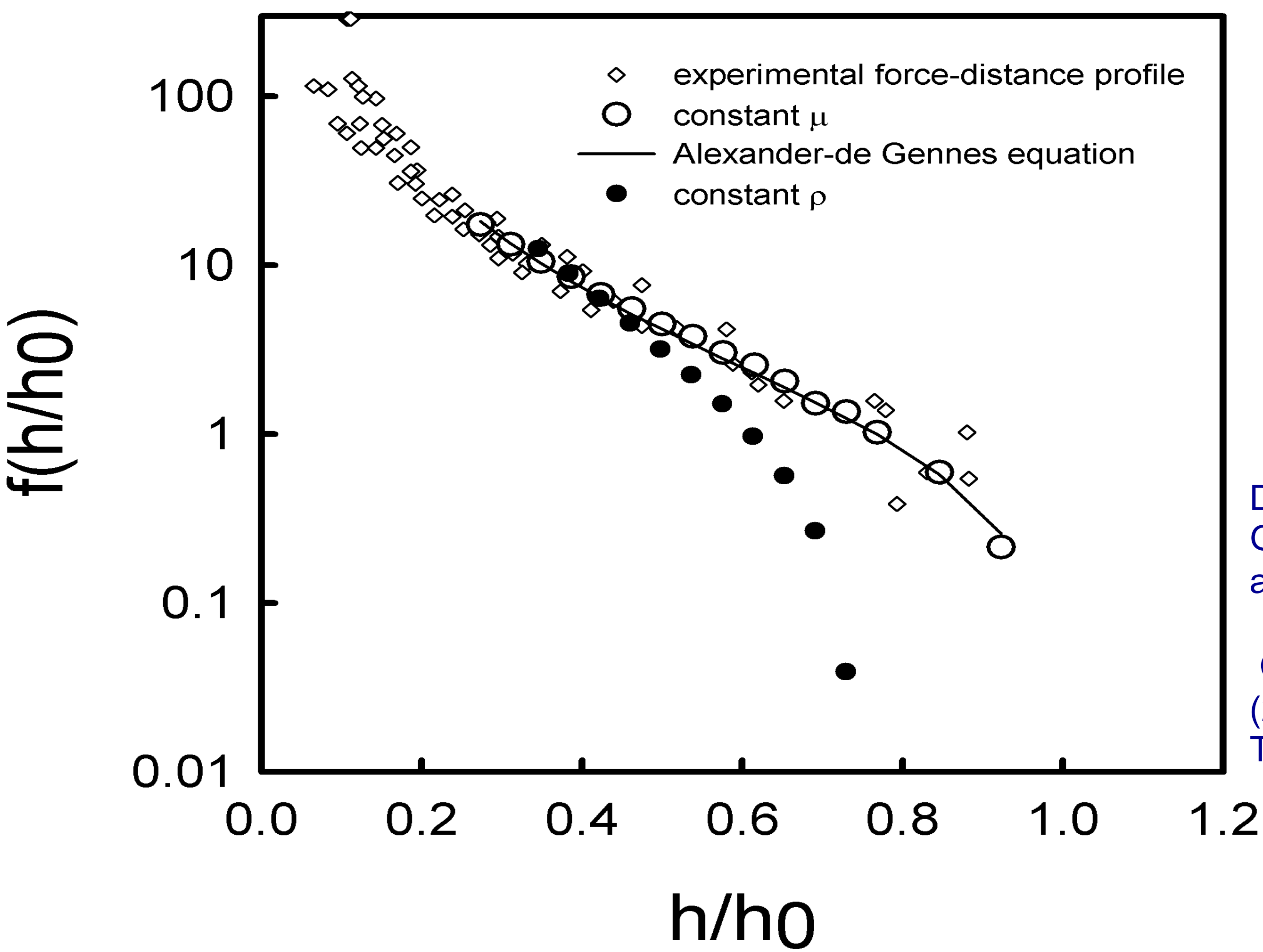


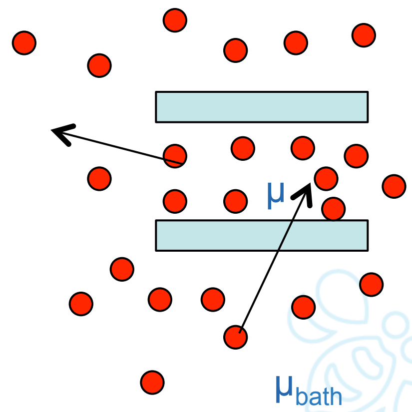
CH3(CH2)11PO6EO2OSO3- Na+

calculated cmc 0.000082 wt

experimental cmc 0.0001 wt.

Force-distance curve for neutral polymer brushes





Dissipative dynamics in the Grand Canonical Ensemble: application to polymer brushes,

ChemPhysChem, **5**, 457-464 (2004) Gujon, Malfreyt and Tildesley

Electrostatic potential

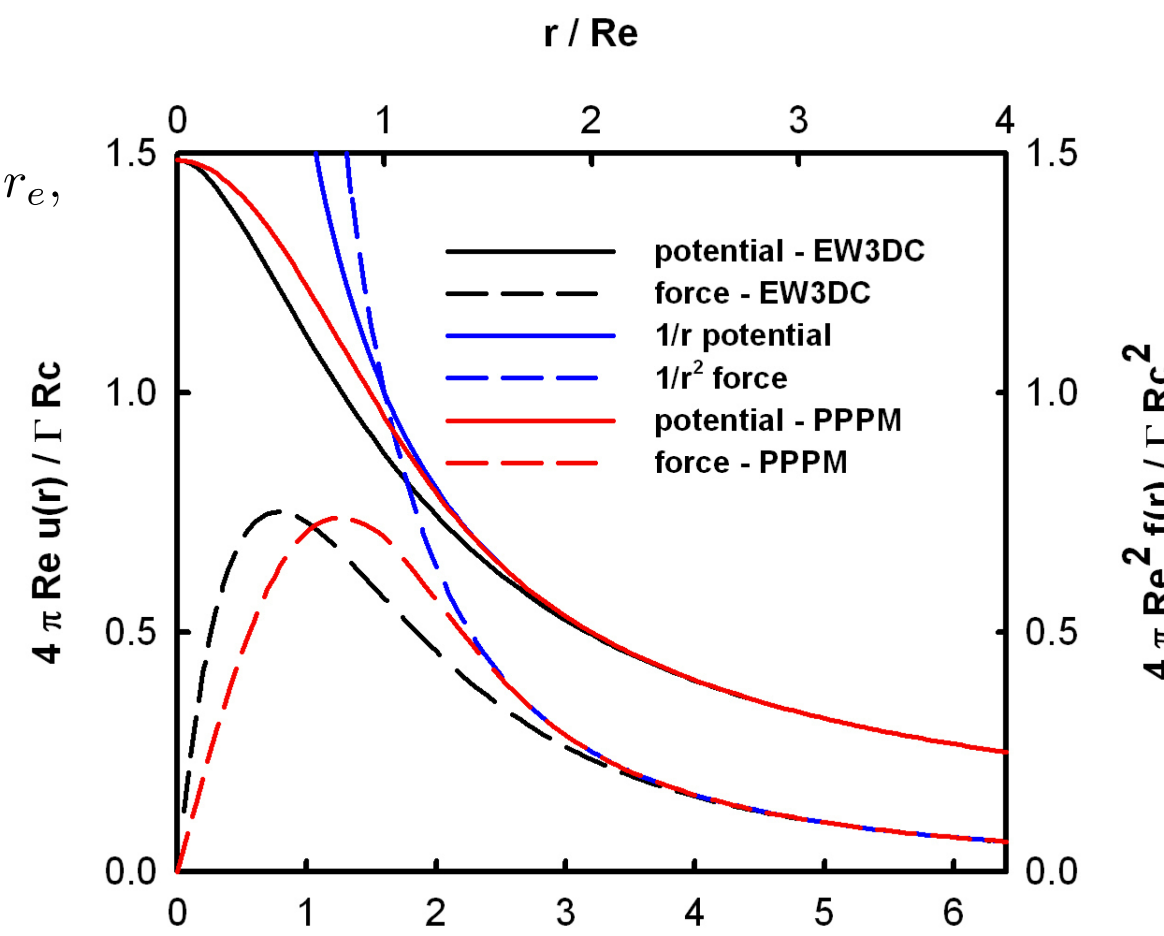
PPPM method:

$$f(r) = \frac{3}{\pi r_e^3}(1 - r/r_e) \text{ for } r < r_e,$$

Ewald method:

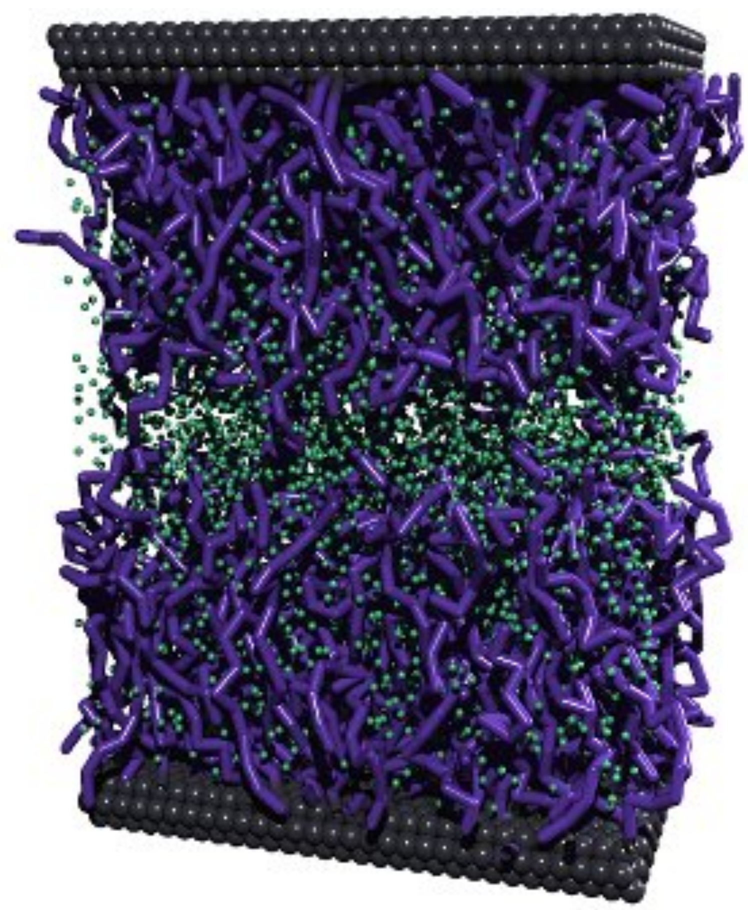
$$\rho(r) = \frac{q}{\pi \lambda^3} \exp(-2r/\lambda)$$

Comparison of PPM and Ewald for slab geometries



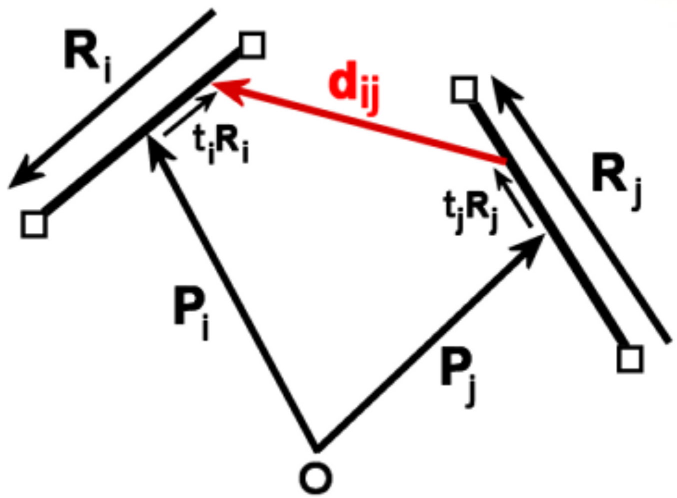
Electrostatic interactions in dissipative particle dynamics: toward a mesoscale modeling of the polyelectrolyte brushes. Journal of Chemical Theory and Computation, **5**, 3245-3259, (2009) Ibergay, Malfreyt and Tildesley

Entanglement of DPD Polymers



Bilayer simulations

Calculate the minimum separation



Additional Entanglement Force

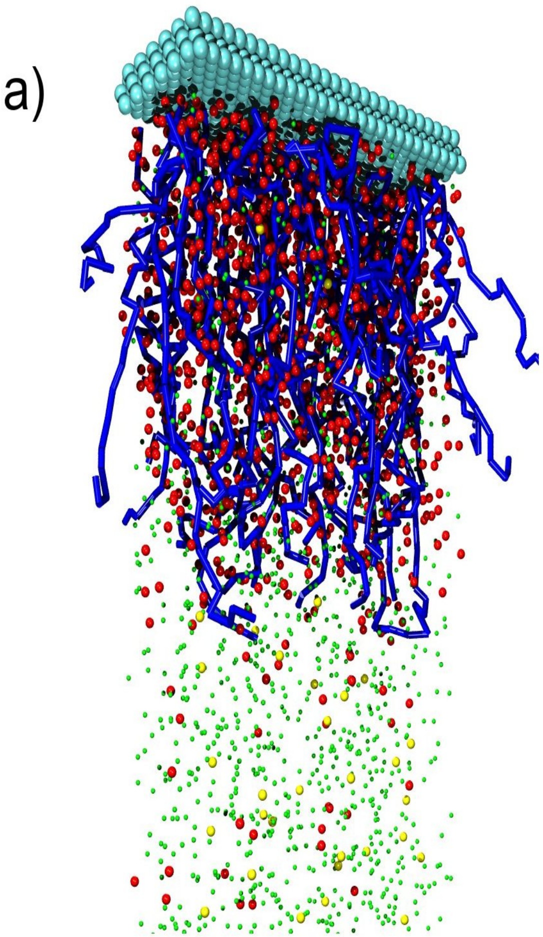
$$\mathbf{f}_{ij}^{E} = a_{ij}^{E}\left(1 - \frac{d_{ij}}{r_c^{E}}\right)\hat{\mathbf{d}}_{ij} \qquad d_{ij} \prec r_c^{E}$$

Mesoscopic simulation of entangled polymer brushes under shear: compression and rheological properties, Macromolecules, **42**, 4310–4318 (2009) (Goujon, Malfreyt and Tildesley)

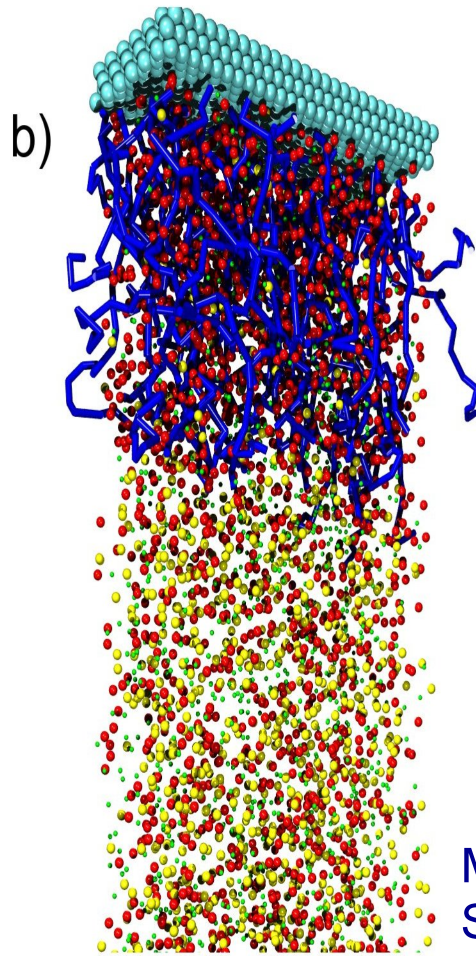
The interaction of polyelectrolyte brushes

- Simulation in the grand canonical ensemble
  - Do not destroy the dynamics or hydrodynamics
- Modelling of chain crossing
  - Do not lose the speed advantage of DPD
- Electrostatics through distributed charge
  - Use modified Ewald over PPM
- Explicit modelling of counterions and solvent

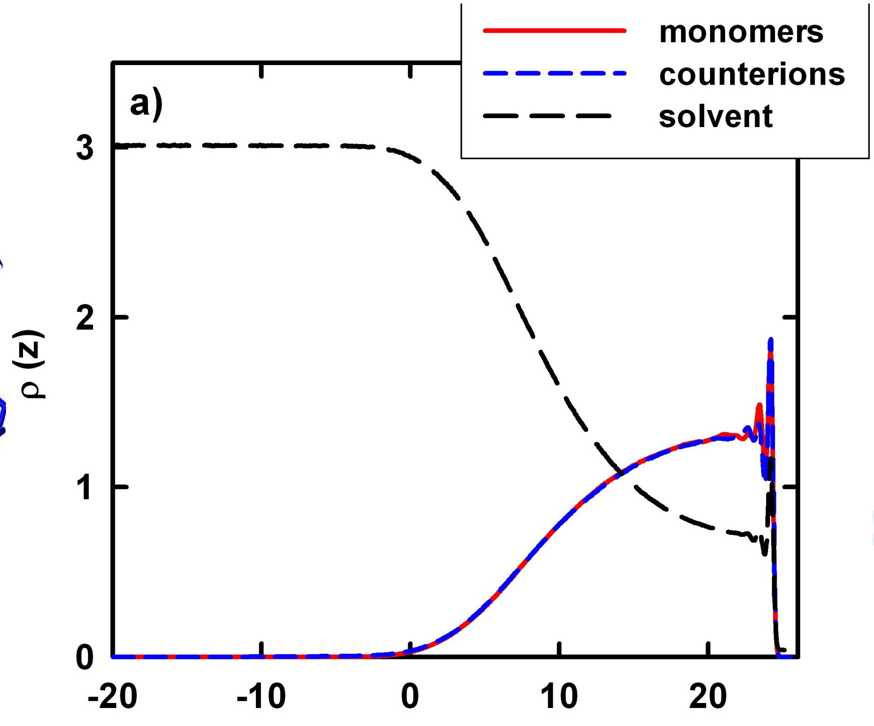
Modelling of polyelectrolytes single brush



$c_s = 0.012$



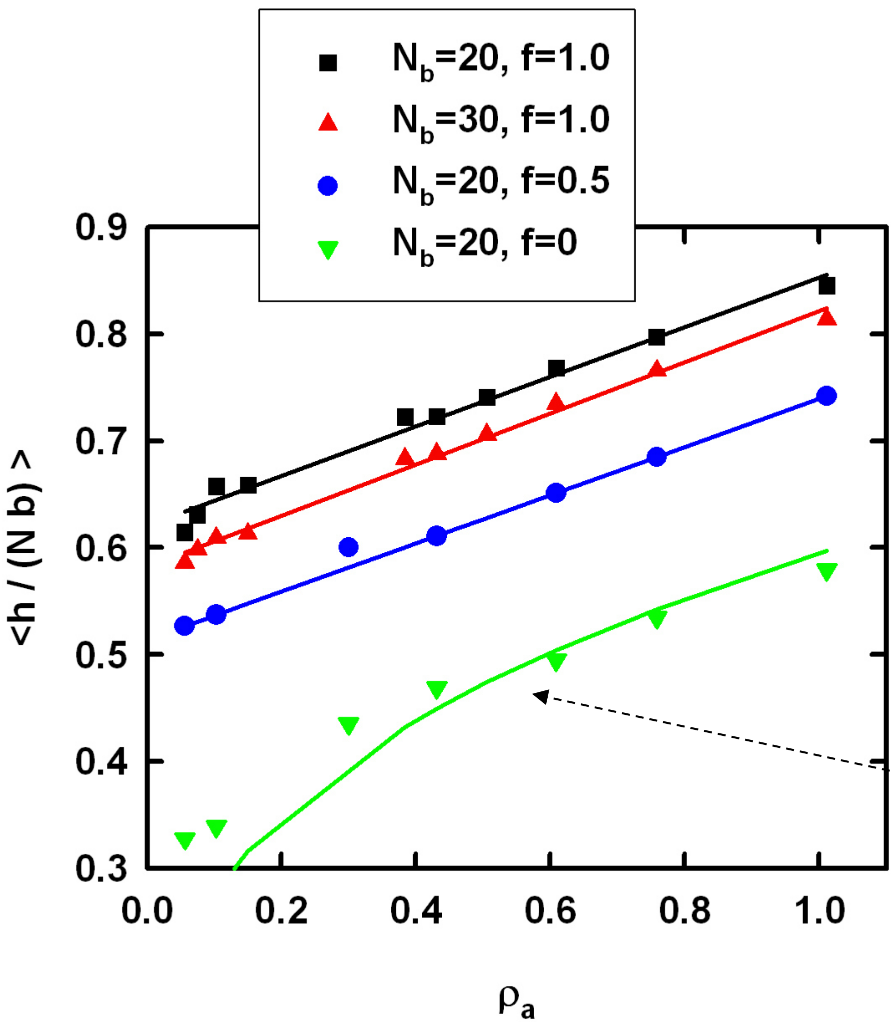
$c_s = 0.239$



$c_s = 0.0$

Modeling of Polyelectrolyte Brushes with Salt Journal of Physical Chemistry B, **114**, 7274-7285, (2010) (with Cyrille Ibergay and Patrice Malfreyt)

Height of brush with grafting density



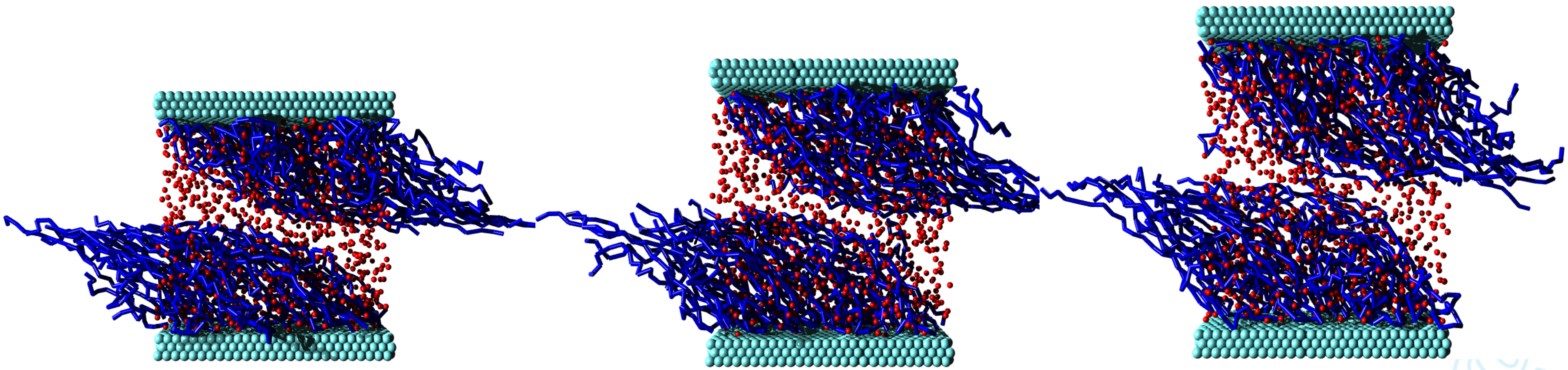
Charged brush

$$\frac{h}{N_\mathrm{b} b} \simeq \frac{f + d^2 \ \rho_a}{1+f}$$

Neutral brush

$$\frac{h}{(N_b b)} \approx \rho_a^{1/3}$$

Configurations of charged bilayers under shear

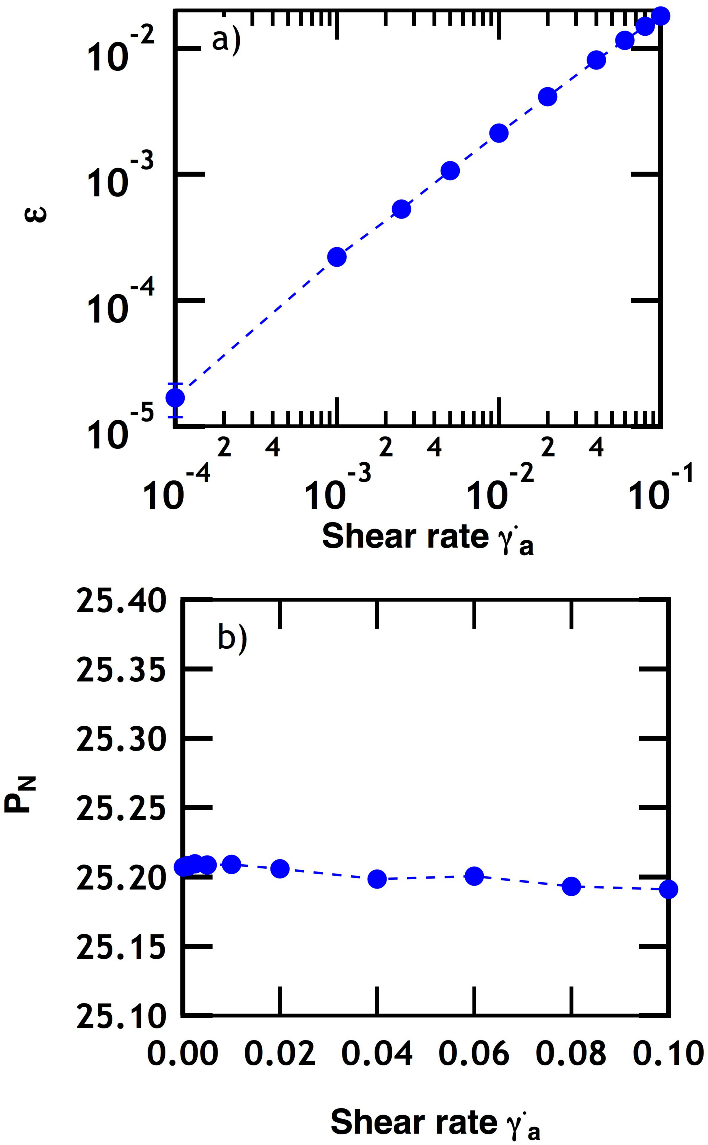


D = 13	D = 17	D = 21
f=0.5	f=0.5	f=0.5
$\dot{\gamma}_a = 0.6$	$\dot{\gamma}_a = 0.6$	$\dot{\gamma}_a = 0.6$

The kinetic friction coefficient of neutral and charged polymer brushes
Soft Matter **9** 2966-2972, 2013 (Goujon, Malfreyt, Ghoufi and Tildesley)

What has the lower friction coefficient, a neutral or fully charged polymer?

The effect of shear rate on friction coefficient



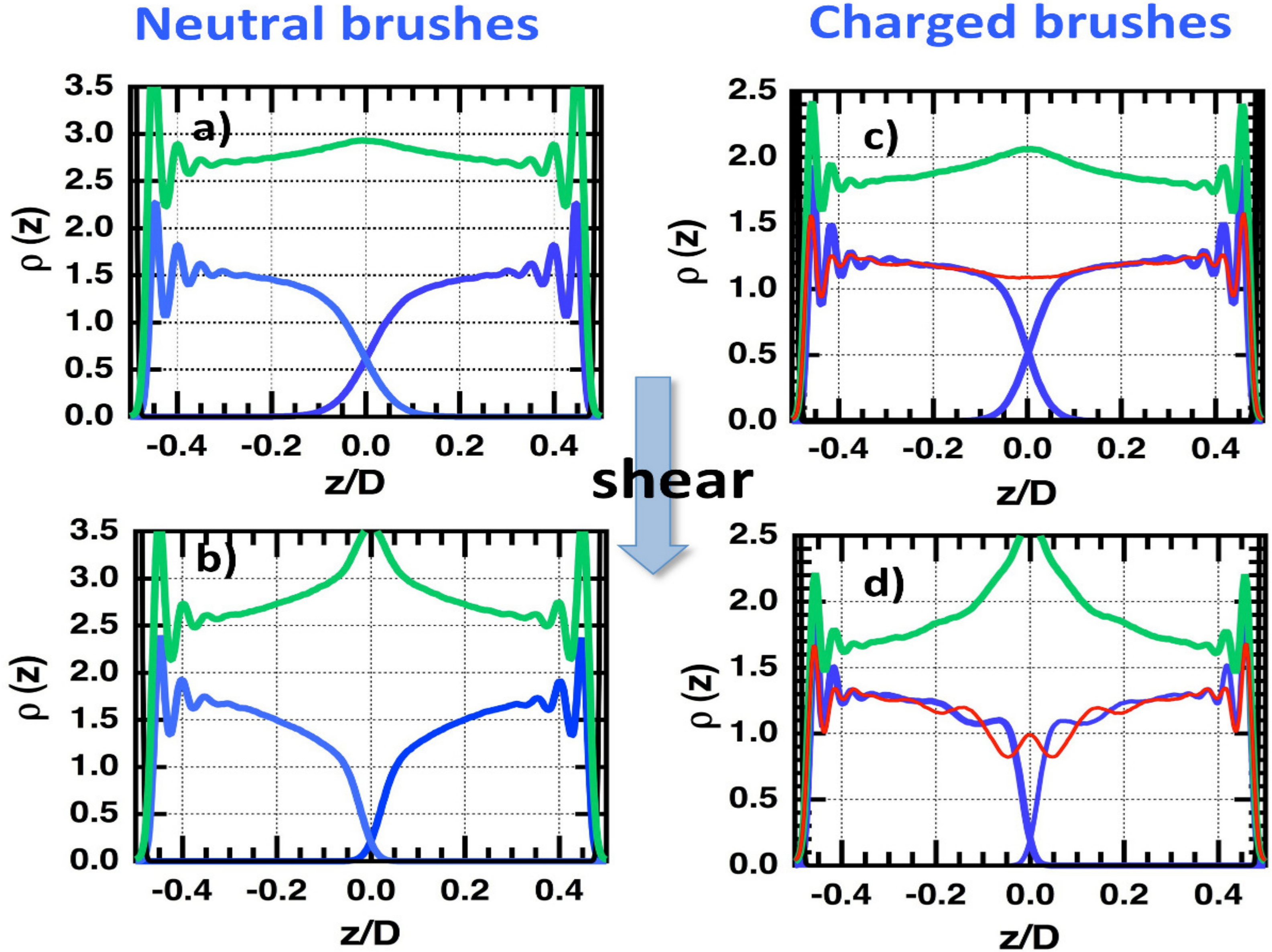
$$\varepsilon = -P_{xz} / P_{zz}$$

The friction coefficient decreases to be within the observed experimental range for low shear (a shear rate of 10^{-4} in DPD units corresponds to ca. 10^6 s^{-1})

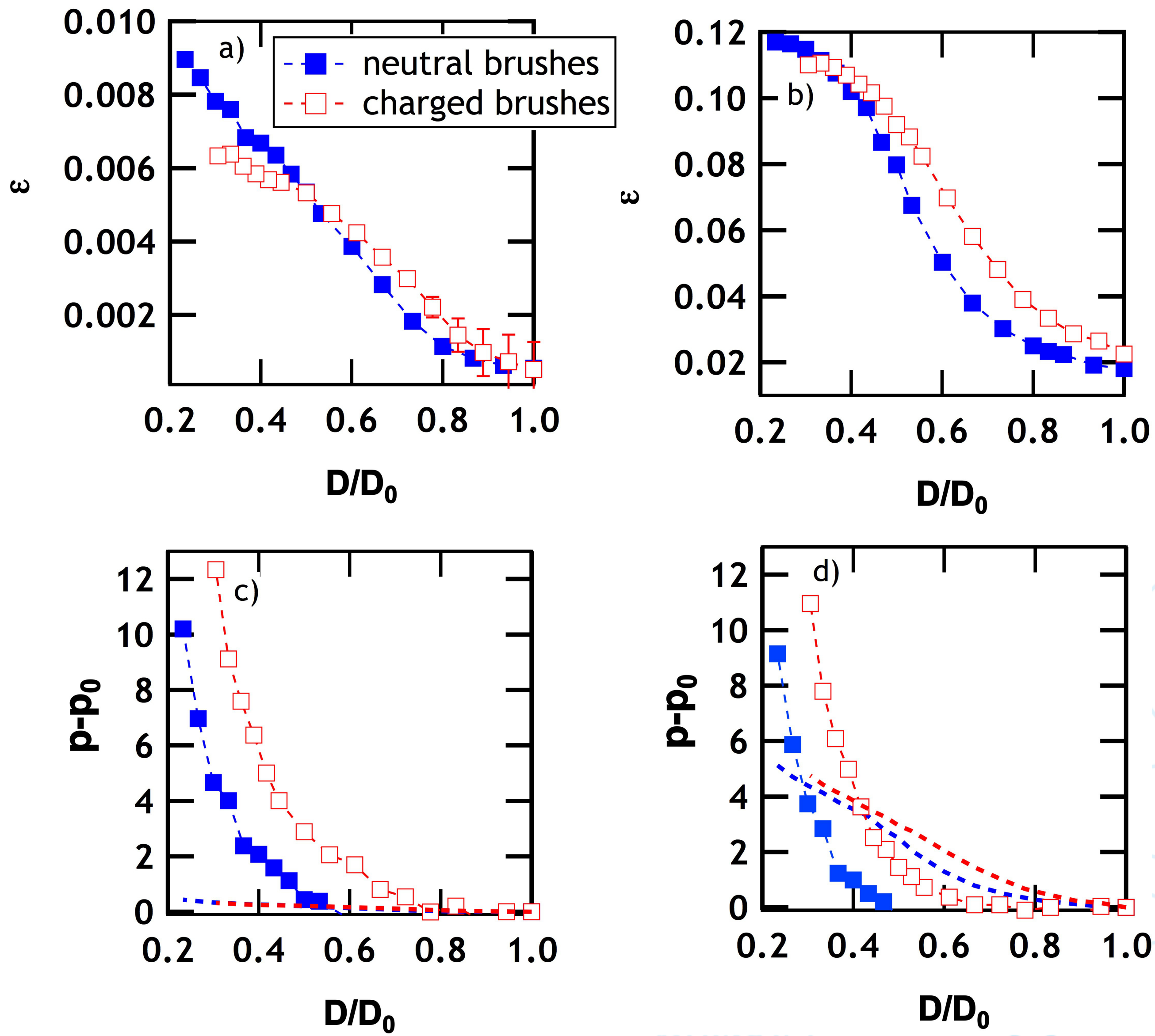
ε_{exp} = 0.0006-0.001 298K
ε_{dpd} = 0.00002-0.0003 298K

The higher value are for the higher compressions with D/D_0=0.2. This behaviour requires a more detailed consideration at even lower shear rates

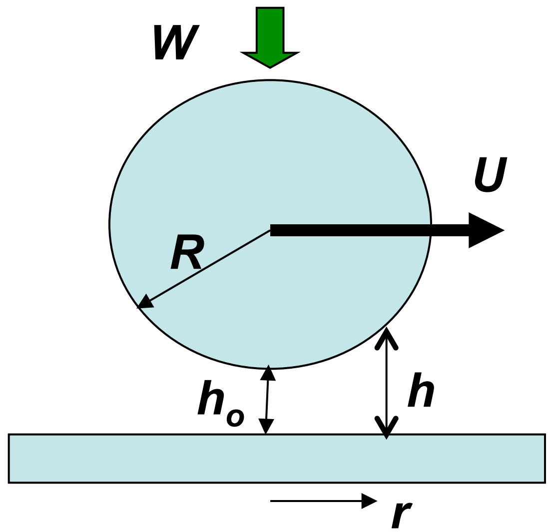
The effect of charge



Charged and neutral brushes



Reminder

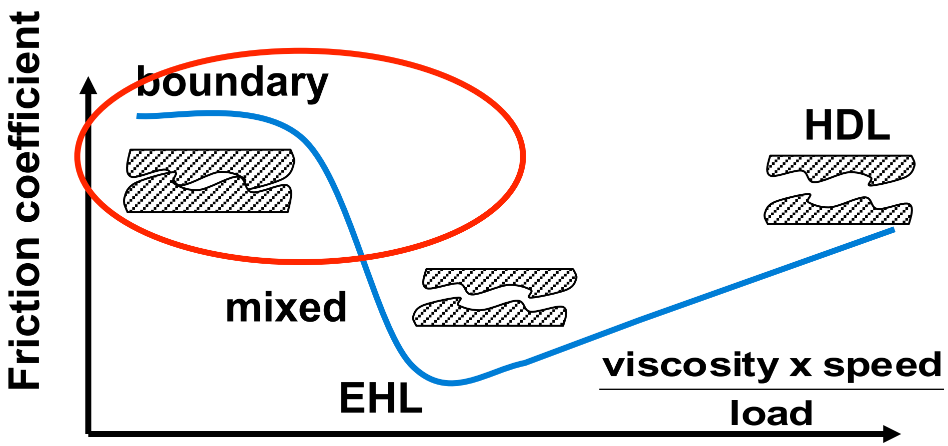


Gap $$h = h_0 + \frac{r^2}{2R}$$

Defines a contact area $$r^2 \approx 2Rh_0$$

Tangential force $$T = \eta\dot{\gamma} \times \pi r^2 \approx \frac{\pi\eta U r^2}{h_0} \qquad \left[\dot{\gamma} \approx \frac{U}{h_0}\right]$$

Friction coefficient $$\mu = \frac{T}{W} \approx \frac{\pi\eta U r^2}{W h_0} \approx 2\pi R \times \frac{\eta U}{W}$$

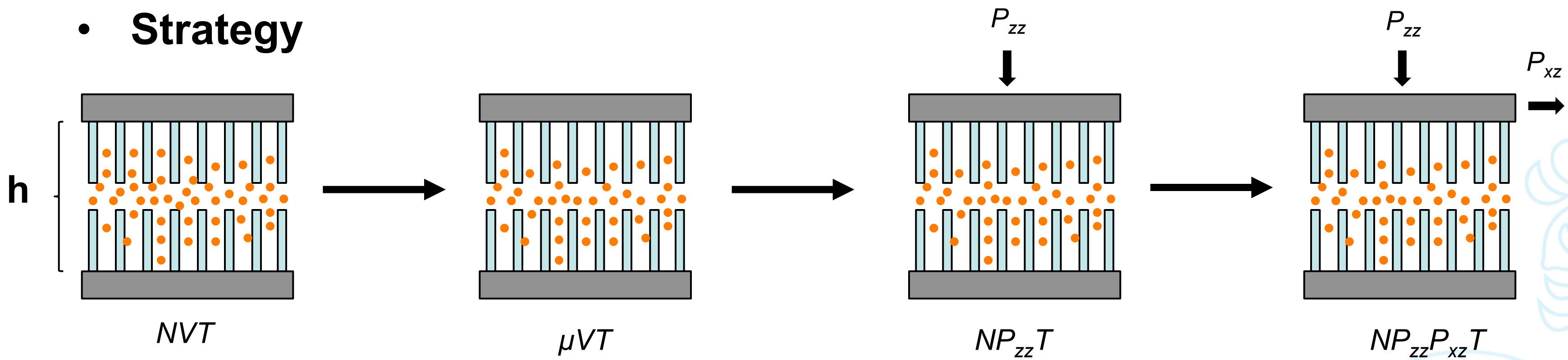


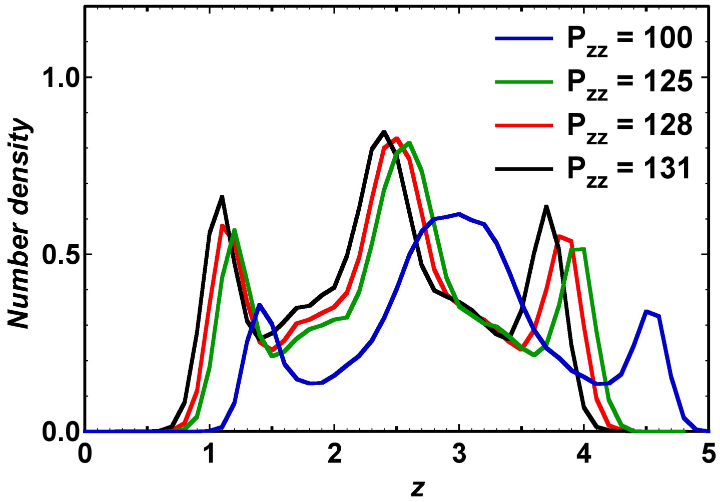
hydrodynamic part of the Stribeck curve

Pyotr Kapitza
J Tech Phys 25, 747 (1955)

Static friction of using Monte Carlo Methods

- **Isostress-Isostrain** ensemble with **configurational bias** methods
  - **Fixed variables: P_{zz}, P_{xz}, N, T**
  - **DPD soft potential**
- **Strategy**

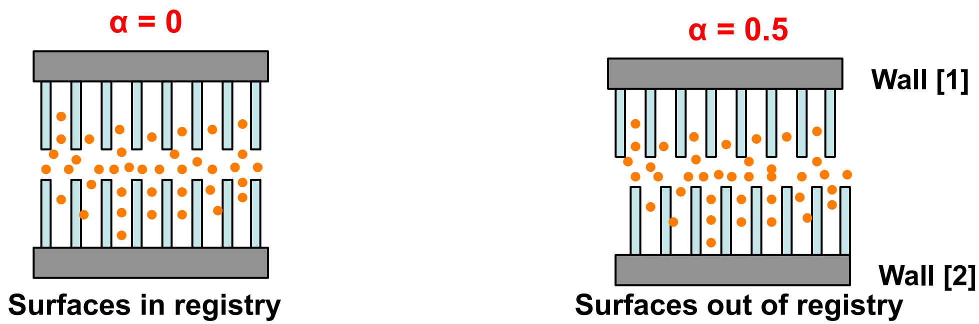




Calculating Static friction of polymer brushes

- **Quasi-static approach for shear** (Chusman *et al*, *Phys. Rev. B*, **1993**; Fuchs *et al*, *Phys. Rev. E*, **1998**)

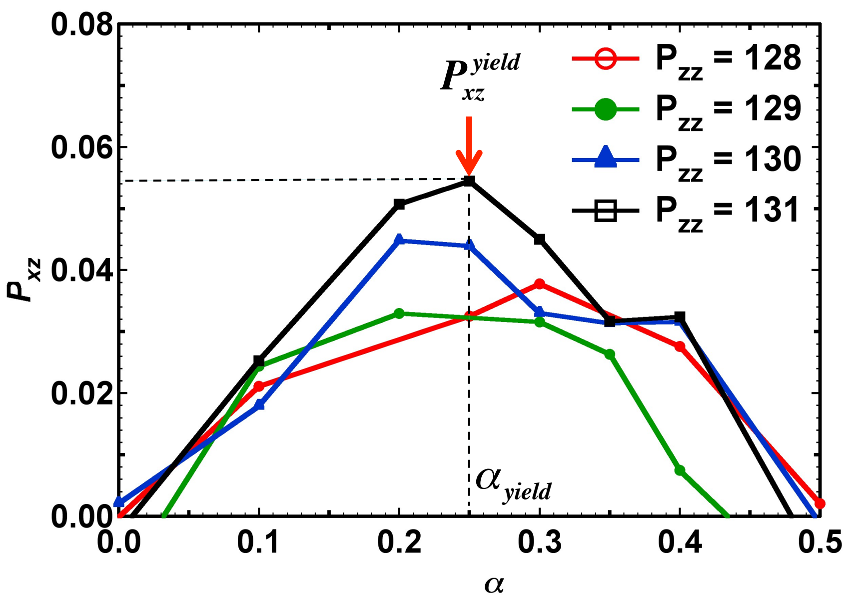
  The thermodynamic state of the film passes trough a succession of equilibrium states, each having a different average alignment of the walls (α)

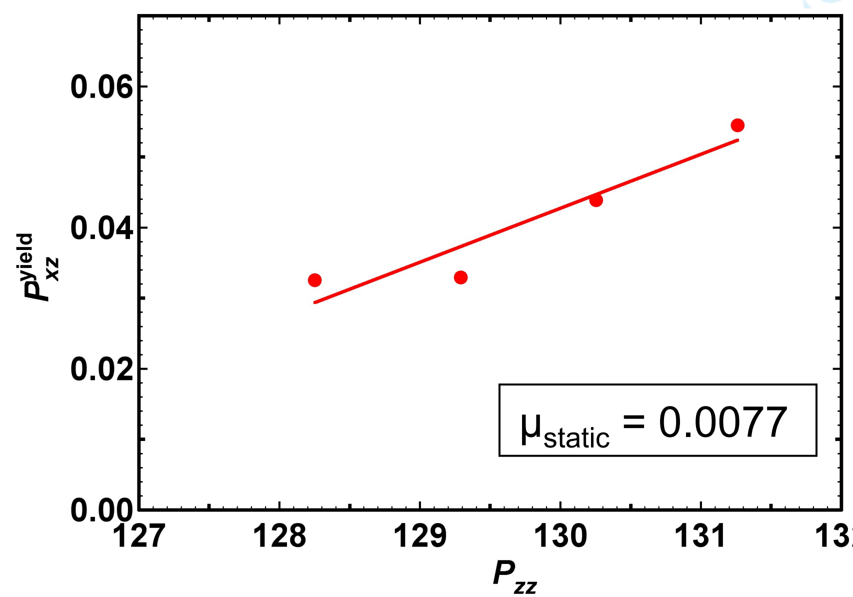


Relative position of the wall atoms in both walls

$$x_i^{[2]} = x_i^{[1]} + \alpha \times l$$
$$y_i^{[2]} = y_i^{[1]}$$
$$z_i^{[2]} = z_i^{[1]} + \delta h$$

***l* = lattice constant**





Conclusion

- DPD simulation of neutral polymer brushes reproduce the experimental force-distance curves
- Simulation of polyelectrolytes show that the brush height depends on charge and grafting density and the behaviour is in the non-linear osmotic brush regime .In excess salt, small dipoles are created at the upper limit of the brush. Scaling of brush height with salt concentration is observed (index -1/3)
- The simulated frictions coefficients from dpd are of the same order of magnitude as the experimental estimates, but no better than this - strongly shear rate dependent.
- Friction decreases with increasing charge fraction at fixed surface separation at high compressions in the model and in experiment

Opportunities

- Static friction coefficients could be calculated using iso-stress Monte Carlo simulations?
- Much more work needs to be done on finding the force field correspondence between the atomistic and dpd levels. This may be case by case dependent
- We need to include surface irregularities in a controlled way
- We need to find a mapping that accommodates lower shear rates
- We need to developed polarizable models for dpd

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DFT calculations