MD Simulation of sheared Polymer brushes

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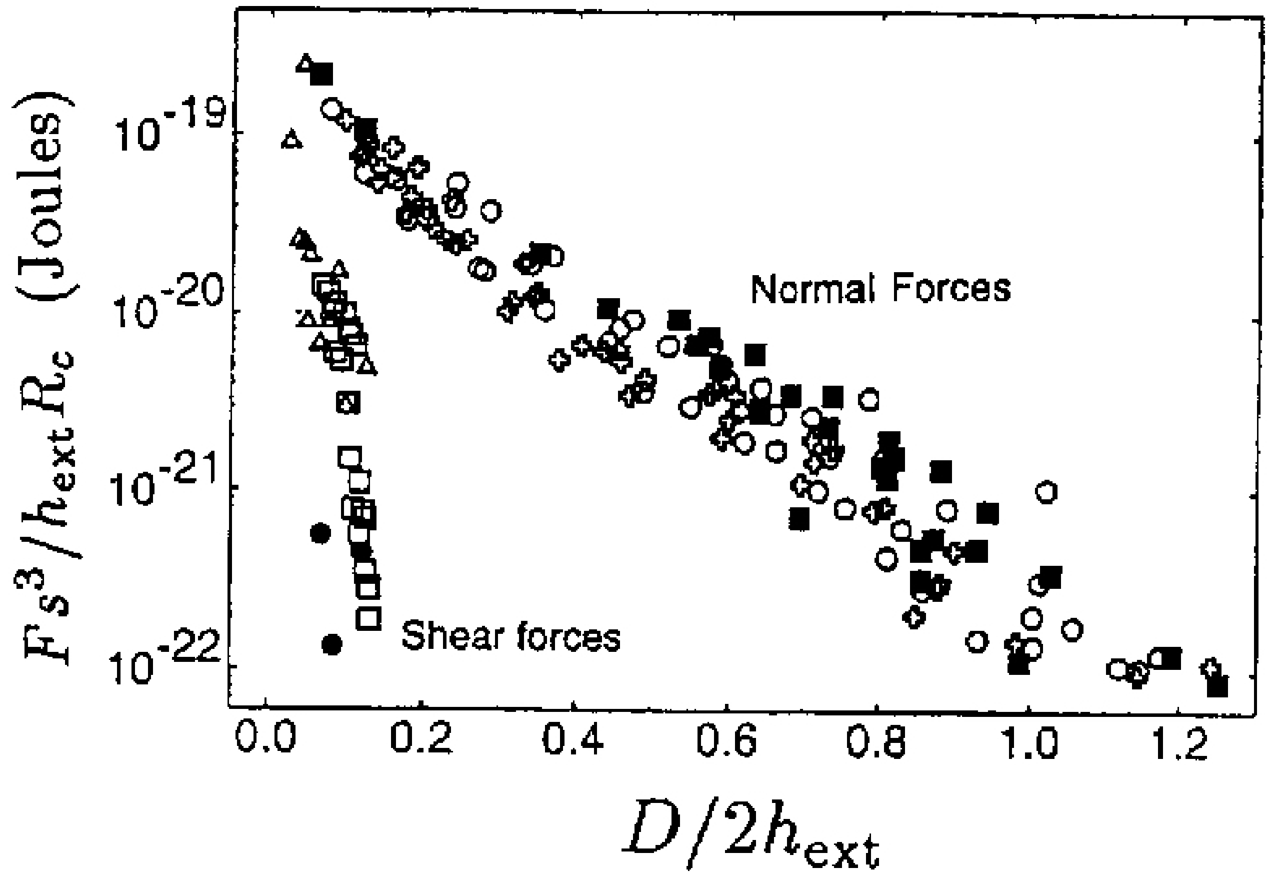
Overview

- Introduction/Motivation
- Simulation Model
    - Potential, Thermostat, Parameters
- Theory
- Simulation
    - Equilibrium, steady state
- Summary/Outlook

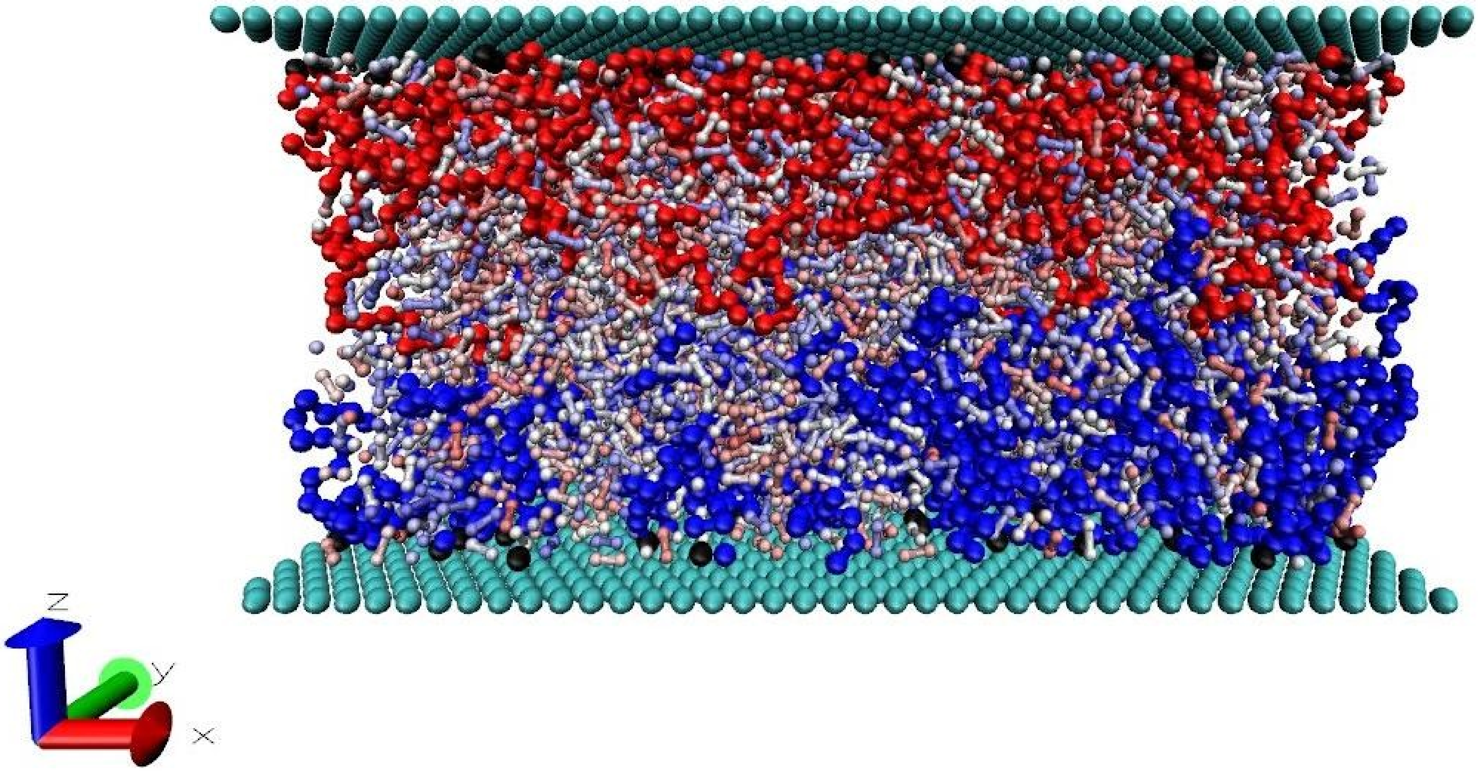
Motivation



Kinetic friction coefficient: $\mu_{kin} = \frac{F_{shear}}{F_{normal}} \sim 10^{-4}$

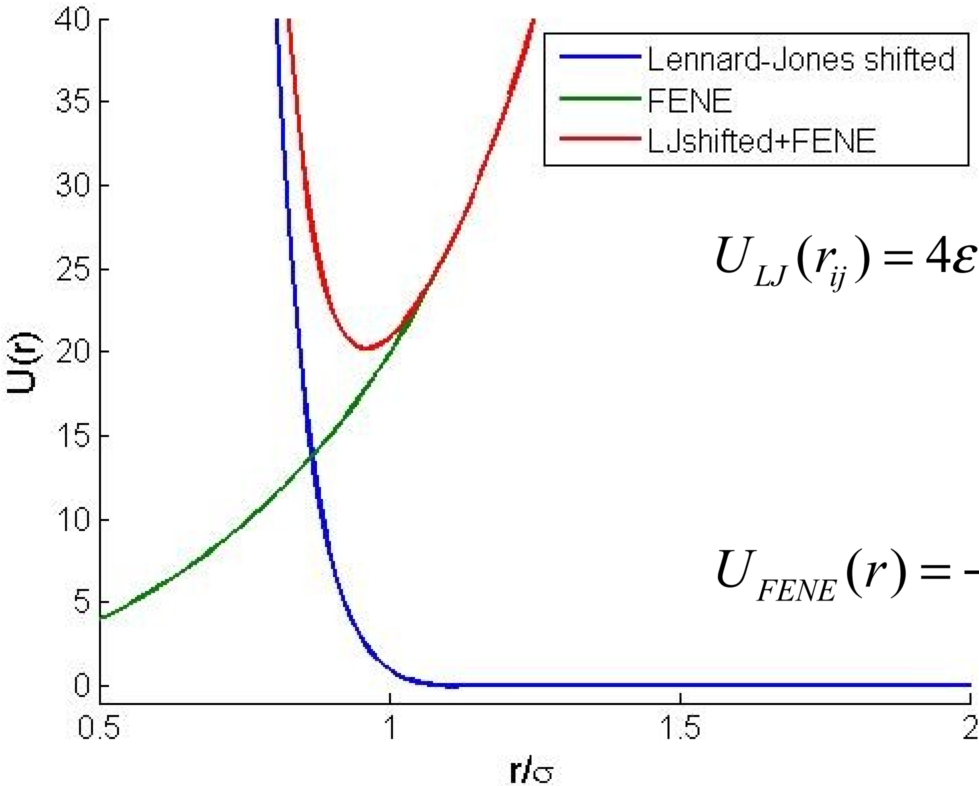
J. Klein, Annu. Rev. Mater. Sci., **26**,581 (1996)
Shear, Friction, and Lubrication Forces Between Polymer-Bearing Surfaces

Scheme of two opposing polymer brushes



1. No solvent / dry brushes
2. Brushes with solvent
3. Brushes with solvent & polymer stars (Leonid Spirin, Mainz)

Interaction Potentials between monomers: bead-spring (Kremer-Grest) model*



$$U_{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right]$$

$$r_c = 2^{1/6}\sigma$$

$$U_{FENE}(r) = -\frac{1}{2}kr_0^2 \ln\left[1-\left(r/r_0\right)^2\right], r \le r_0$$

$$k = 30\varepsilon/\sigma$$

$$r_0 = 1.5\sigma$$

*Grest, Kremer; Phys. Rev. A; 33; 3628 (1986)

Langevin type of Equation of motion: DPD Thermostat*

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i^{\det} + \vec{F}_i^{dissipative} + \vec{F}_i^{random}$$

$$\vec{F}_i^{dissipative} = -\gamma_{DPD} \sum_{j \neq i} \omega^D(r_{ij})(\vec{e}_{ij} \cdot \vec{v}_{ij})\vec{e}_{ij} \qquad \vec{e}_{ij} = (\vec{r}_i - \vec{r}_j)/r_{ij}$$

$$\vec{F}_i^{random} = \lambda \sum_{j \neq i} \omega^R(r_{ij})\theta_{ij}\vec{e}_{ij} \qquad \vec{v}_{ij} = \vec{v}_i - \vec{v}_j$$

Random noise: $\left\langle \theta_{ij}(t)\, \theta_{kl}(t') \right\rangle = \left(\delta_{ij}\delta_{jl} + \delta_{il}\delta_{jk} \right) \delta(t - t')$

Fluctuation-dissipation theorem: $\lambda^2 = 2k_B T \gamma_{DPD} \;\rightarrow\; \left[\omega^R\right]^2 = \omega^D$

$$\omega^D(r_{ij}) = (1 - r_{ij}/r_c)^2 \quad \left(r_{ij} < r_c \right)$$

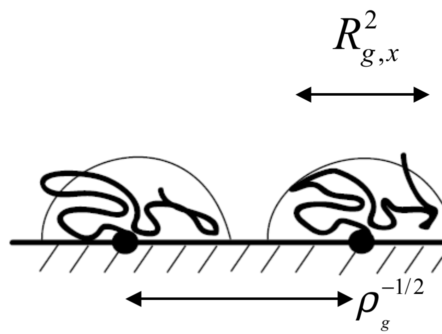
$$\gamma_{DPD} = 5 \qquad T = 1.68\varepsilon / k_B$$

*P. Espanol and P. Warren *Europhys. Lett.* 30, 191 (1995)

Parameter:

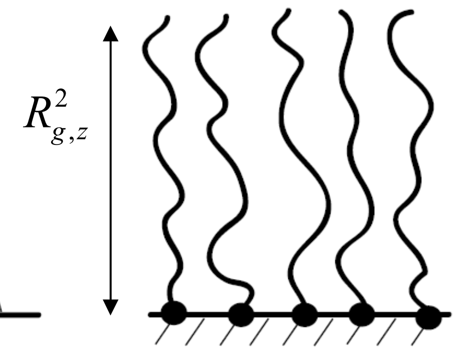
- Chain length: N_{mon}
- Wall distance: D_z
- grafting density: $\rho_g = \frac{N_g}{A}$

mushrooms



$$\rho_g^* = 1/\pi R_g^2$$

brush



$$\rho_g = 2.2\rho_g^*$$

D_z=12
D_z=14.75
D_z=17.5

- ■ 1.1
- □ 1.1 dry
- ● 2.2
- ○ 2.2 dry
- ◆ 4.4
- ◇ 4.4 dry
- ◀ 1.1 N60
- ◁ 1.1 N60 dry
- ▶ 2.2 N60
- ▷ 2.2 N60 dry

Shear rate: $\dot{\gamma} = \frac{v_{wall}}{D_z}$

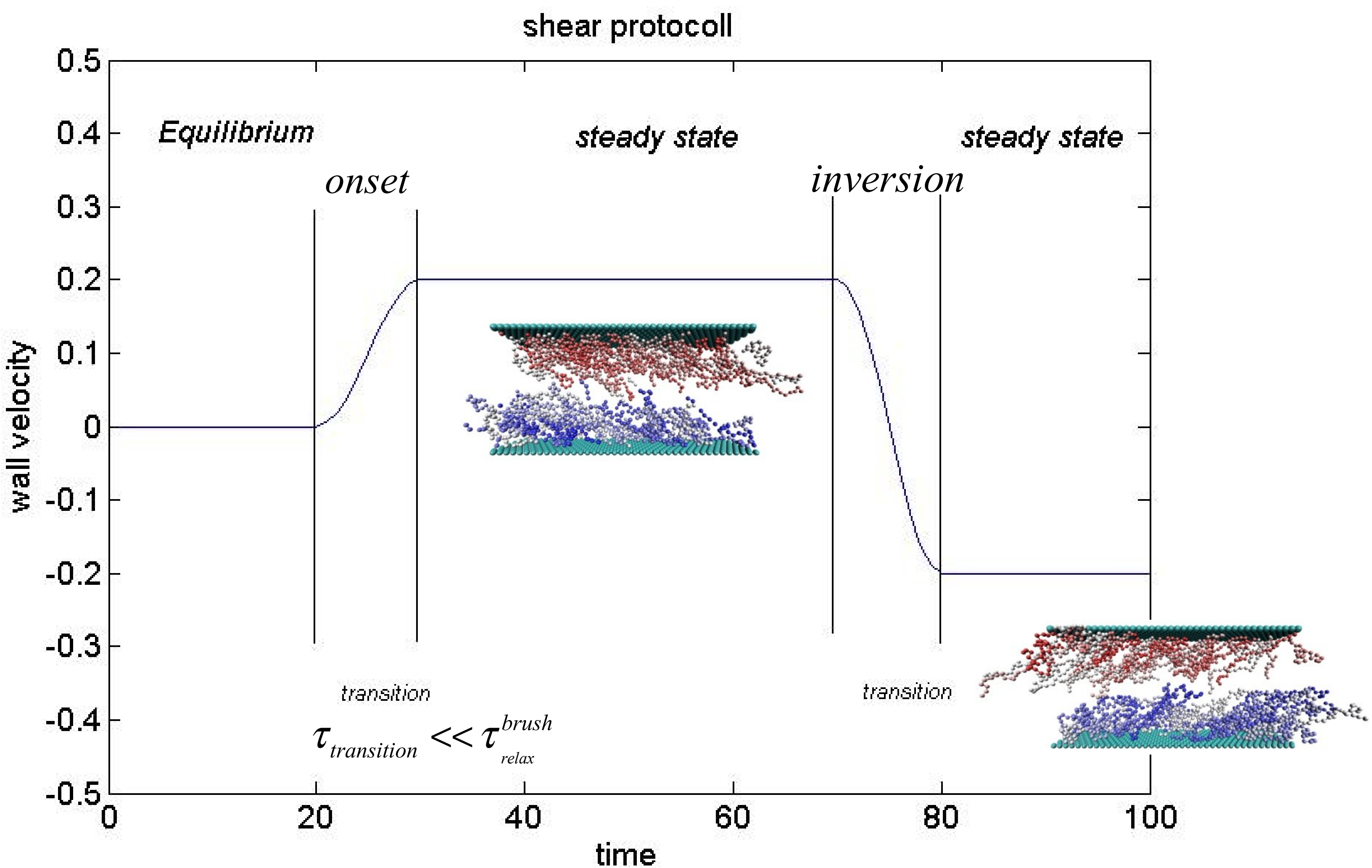
Observables: $R_g^2 \equiv \langle R_g^2 \rangle \equiv \frac{1}{N} \left\langle \sum_i \left(\vec{r}_i - \vec{r}_{cm} \right)^2 \right\rangle$

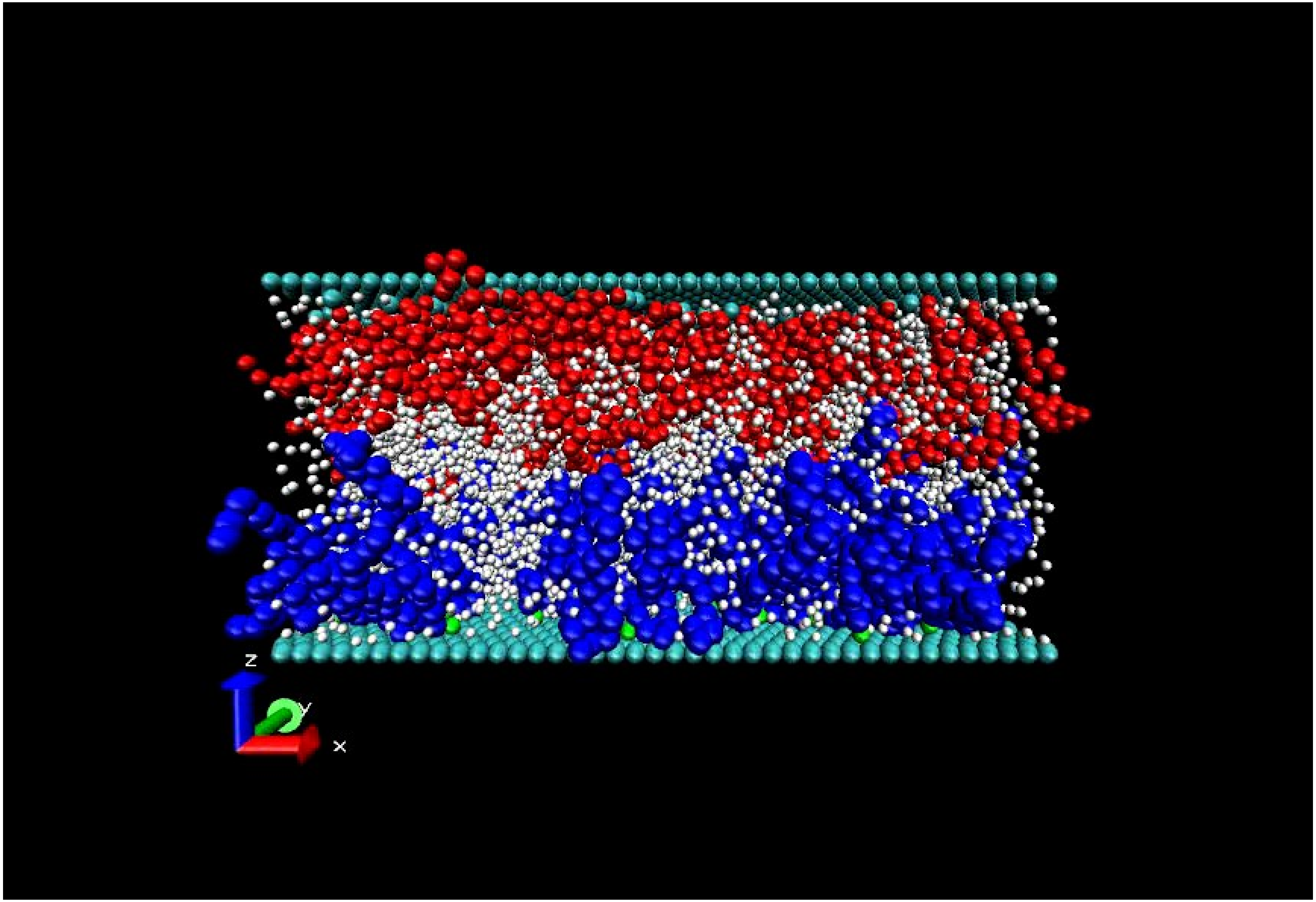
Stress tensor: $\sigma_{ij},\ i, j = x, y, z$

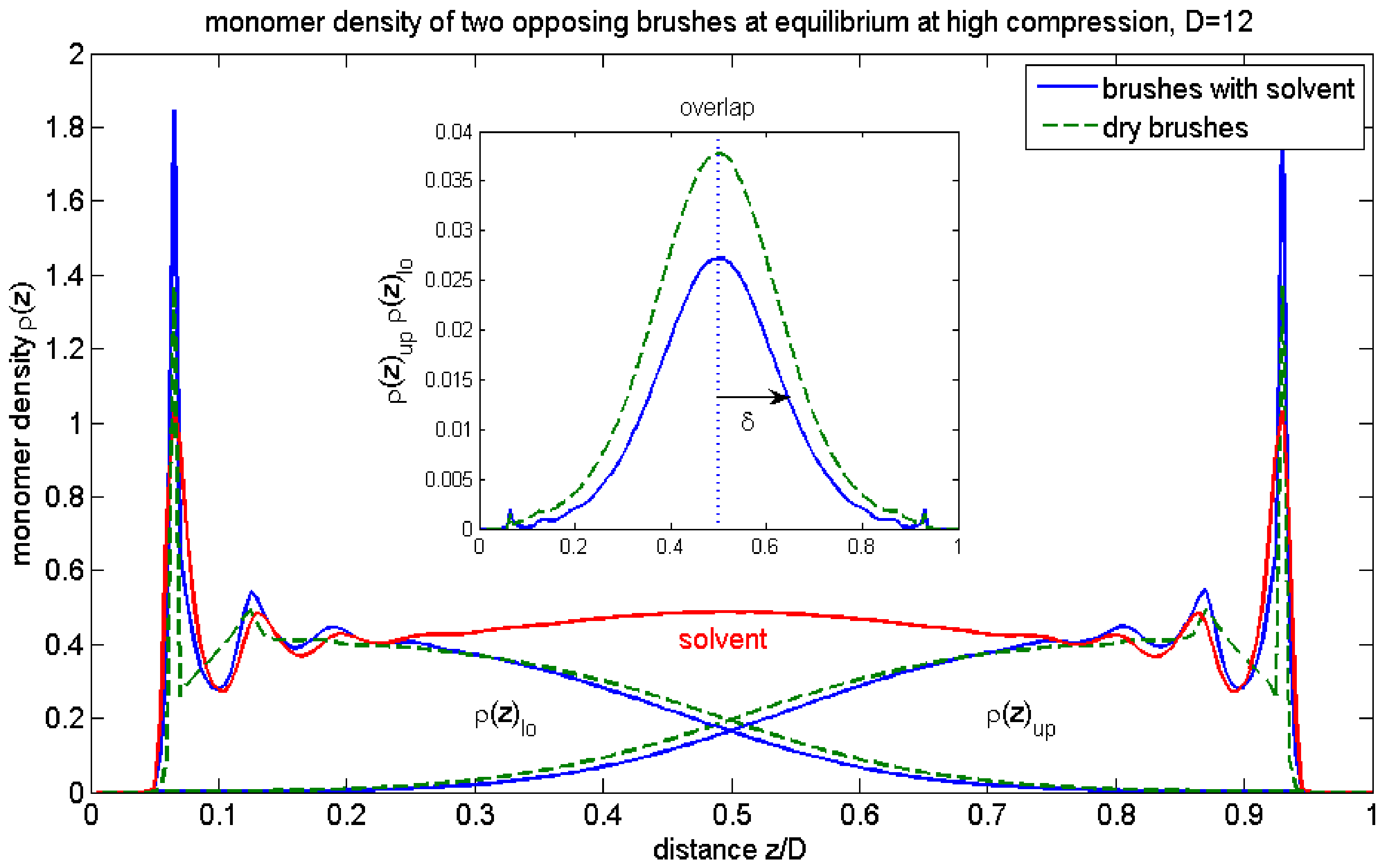
Monomer density…

all units in LJ-units

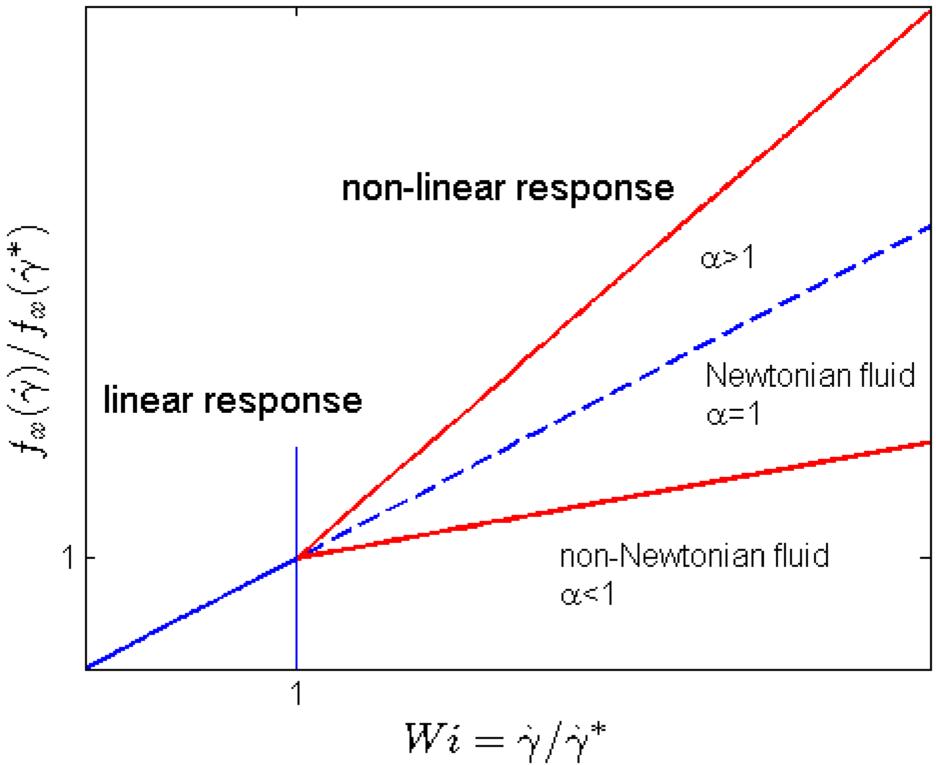
$$t = \sqrt{\frac{\sigma^2 m}{\varepsilon}}$$


shear protocoll
Equilibrium
onset
steady state
inversion
steady state
transition
transition
$\tau_{transition} << \tau^{brush}_{relax}$
wall velocity
time
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
20
40
60
80
100


z
y
x


monomer density of two opposing brushes at equilibrium at high compression, D=12
monomer density ρ(z)
distance z/D
brushes with solvent
dry brushes
solvent
ρ(z)lo
ρ(z)up
overlap
ρ(z)up ρ(z)lo
δ
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0.1
0.3
0.5
0.7
0.9
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04

shear force vs. shear rate of fluids



1. Newtonian fluid:

$$f_x(\dot\gamma) \sim Wi$$

2. Non-Newtonian response:

$$f_x(\dot\gamma) \sim Wi^{\alpha}$$

$$\frac{1}{\dot\gamma^*} = \tau_{\mathrm{Relaxation}}$$

$$Wi = 0 \qquad Wi < 1 \qquad Wi = 1 \qquad Wi > 1$$

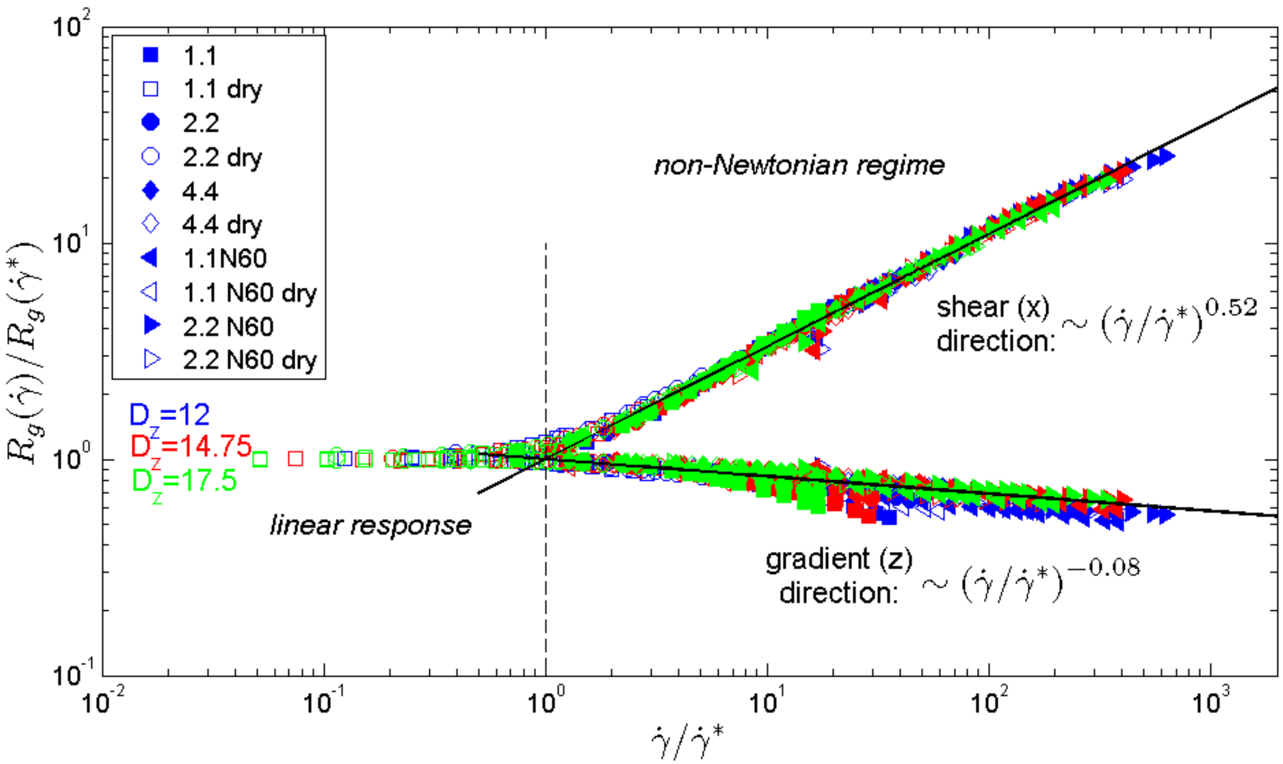
$Wi = 0$: δ, $R^2_{g,x}(0)$

$Wi < 1$: $f_x^{lin}(\dot\gamma)$

$Wi = 1$: $\dot\gamma^*$, $f_x(\dot\gamma^*)$

$Wi > 1$:

$$\frac{f_x(\dot\gamma)}{f_x(\dot\gamma^*)} \sim \left(\frac{\dot\gamma}{\dot\gamma^*}\right)^{\alpha} \qquad \frac{R^2_{g,x}(\dot\gamma)}{R^2_{g,x}(0)} \sim \left(\frac{\dot\gamma}{\dot\gamma^*}\right)^{\beta}$$

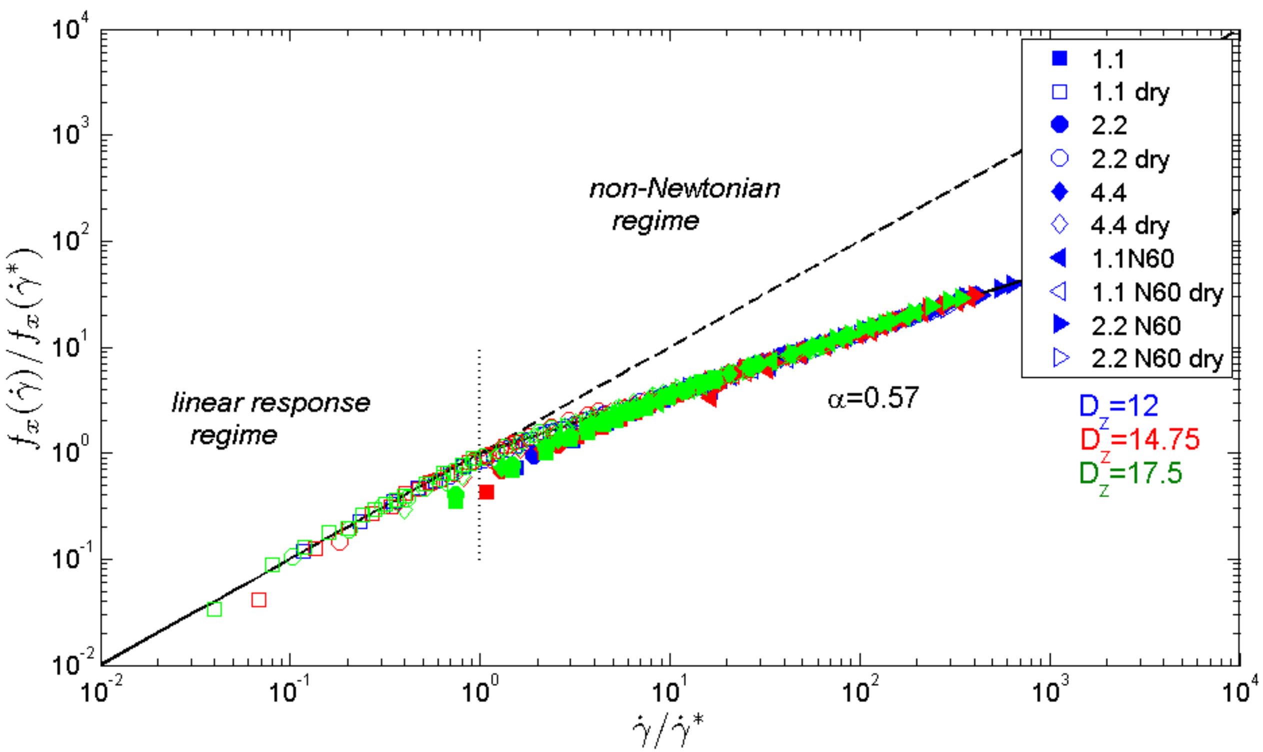


$$R_{g,x}(\dot\gamma) \sim N$$

$$\frac{R_{g,x}^2(\dot\gamma)}{R_{g,x}^2(0)} \sim \left(\frac{\dot\gamma}{\dot\gamma^*}\right)^{\frac{6(5\upsilon-2)}{19\upsilon}}$$

$$\frac{6(5\upsilon-2)}{19\upsilon} \approx 0.52$$

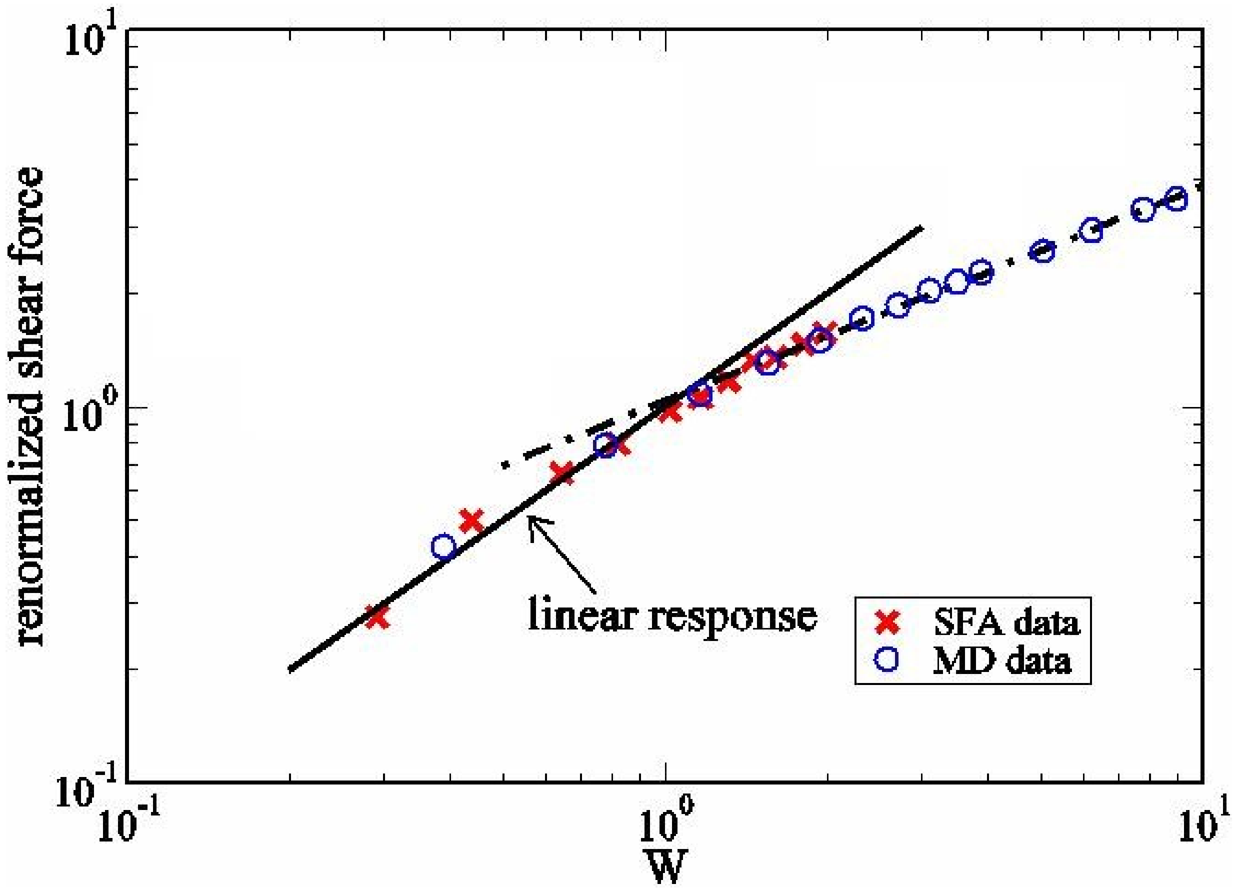
$$\upsilon = 3/5$$



$$f_x(\dot{\gamma}) \sim N$$

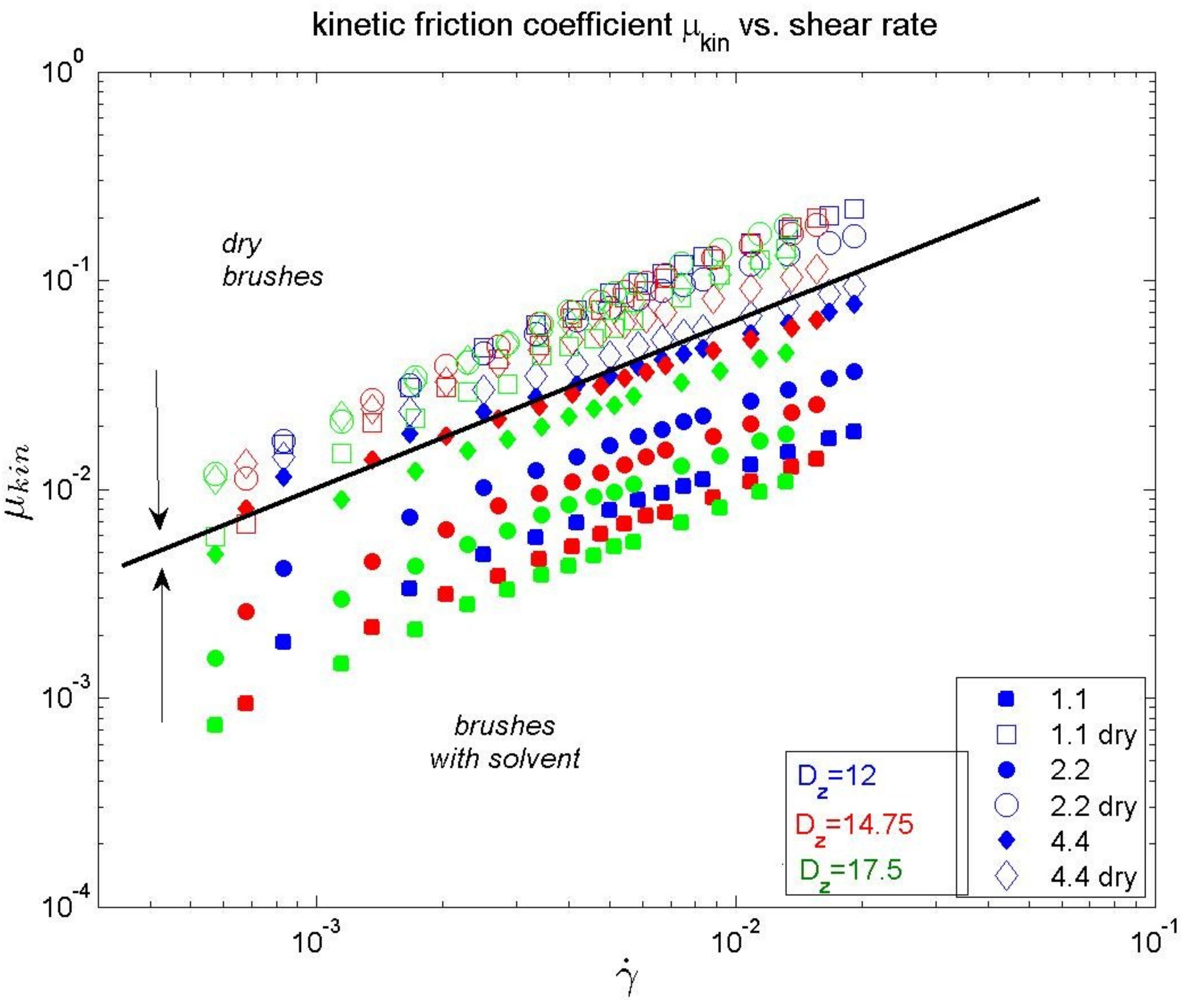
$$\frac{f_x(\dot{\gamma})}{f_x(\dot{\gamma}^*)} \sim \left(\frac{\dot{\gamma}}{\dot{\gamma}^*}\right)^{\frac{3(7\nu-2)}{19\upsilon}}$$

$$\alpha = \frac{3(7\nu-2)}{19\upsilon} \approx 0.57$$



$$\alpha = 0.57$$

P.A. Schorr, et. al. , *Macromolecules, 36*, 389 (2003).



$$\mu_{kin} = \frac{F_x^{wall}}{F_z^{wall}} \quad \begin{array}{ll} \sim 10^{-2} & \text{dry brushes} \\ \sim 10^{-3} & \text{brushes with solvent} \end{array}$$

Summary

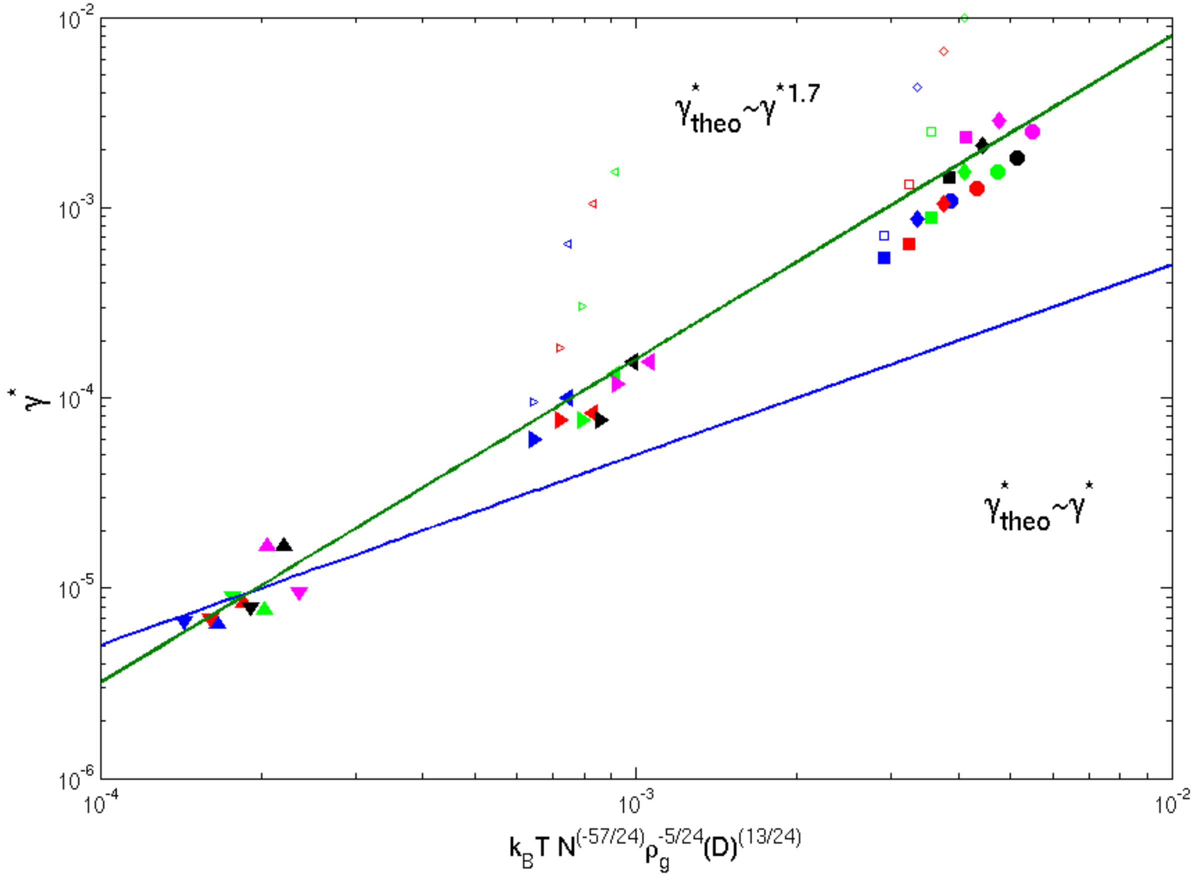
- 2 stationary regimes: Equilibirum, steady state
- Exponent: $\alpha = 0.52$ chain extension
  $\delta = 0.57$ shear thinning
- Friction coefficient: $\mu \sim 10^{-3}$ with solvent

- Outlook: oscillatory shear
- Polydispersity of brushes
- Charged brushes + salt

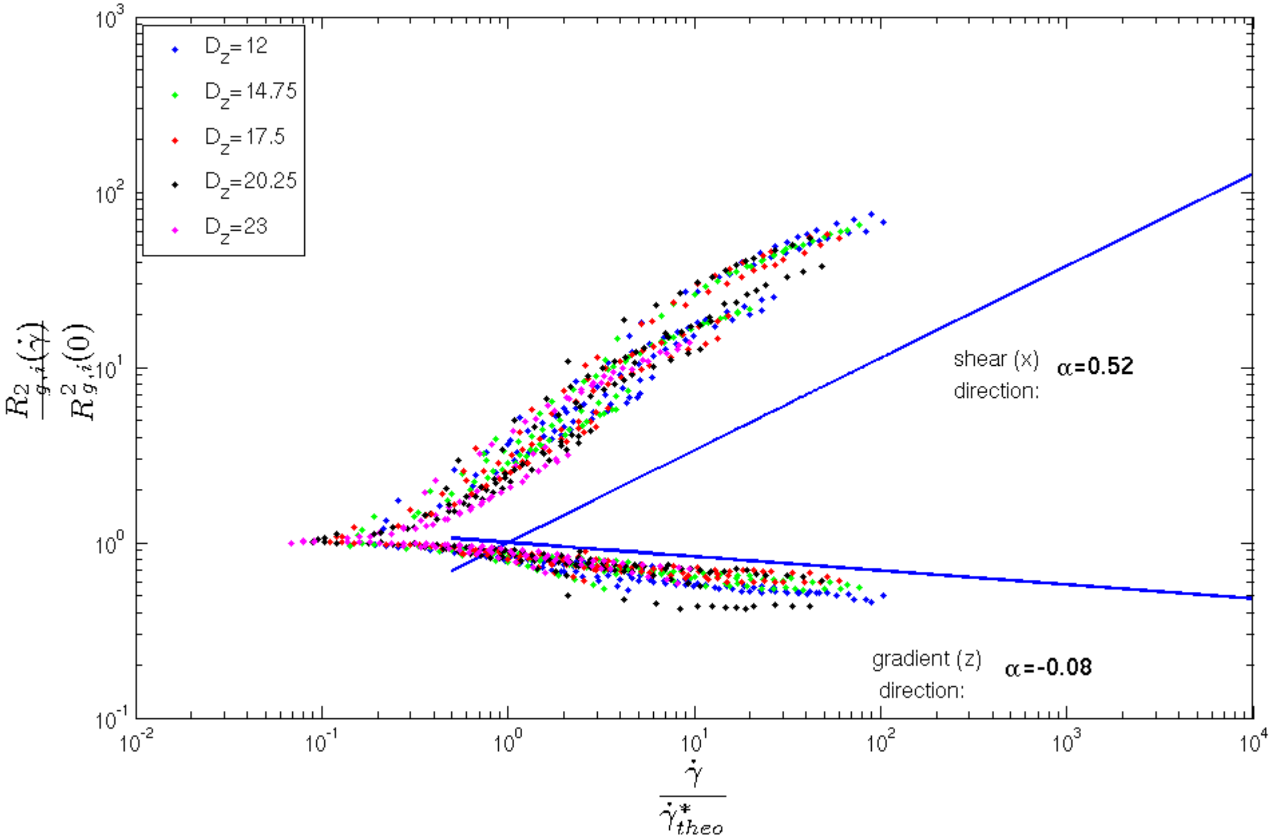
The End

Thank you for listening

Appendix


10^-2
10^-3
10^-4
10^-5
10^-6
γ*
γ*theo~γ*1.7
γ*theo~γ*
10^-4
10^-3
10^-2
kBT N(-57/24)ρg-5/24(D)(13/24)

Appendix


D_z=12
D_z=14.75
D_z=17.5
D_z=20.25
D_z=23
shear (x) direction: α=0.52
gradient (z) direction: α=-0.08
$\frac{R^2_{g,i}(\dot\gamma)}{R^2_{g,i}(0)}$
$\frac{\dot\gamma}{\dot\gamma^*_{theo}}$