Interfacial Properties of Polydim[SAND2007-7383C]/ater Systems

Ahmed E. Ismail, Gary S. Grest, David R. Heine, Mesfin Tsige,* and M. J. Stevens

Sandia National Laboratories, *Department of Physics, Southern Illinois University

AIChE 2007 Annual Meeting

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

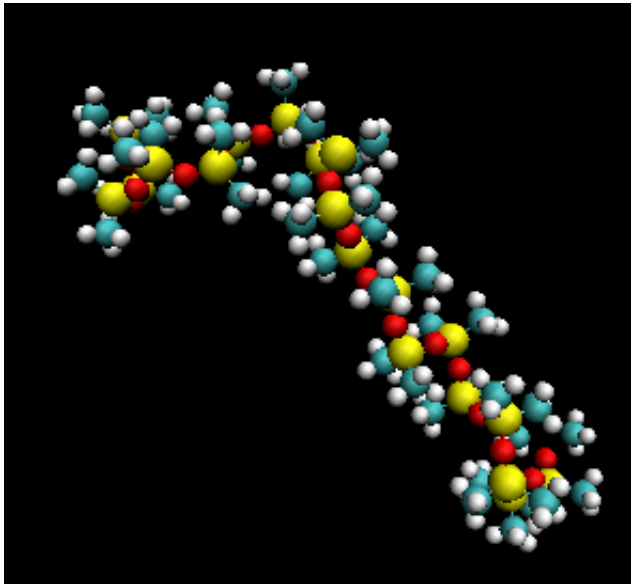
Outline

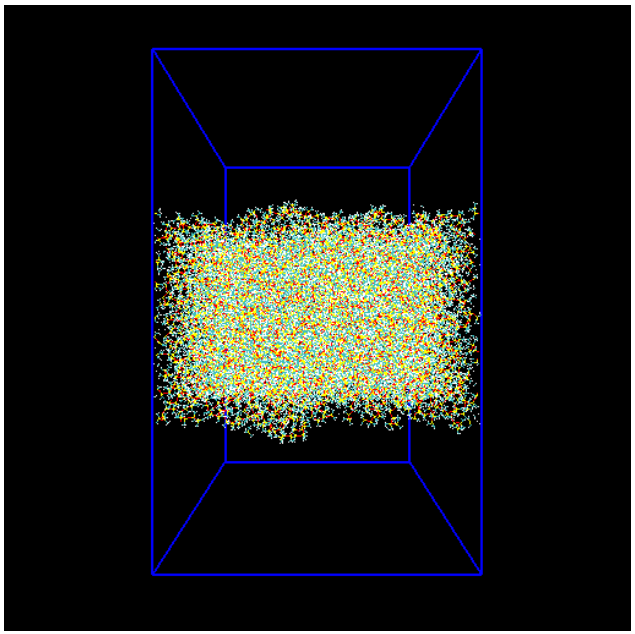
Motivation

- Siloxanes are commercially valuable silicon polymers
  - Adhesives and sealants
  - Lubricants
  - Heat transfer fluids
- Study the interaction of water and siloxanes – in particular polydimethysiloxane (PDMS)
  - Diffusion of water through bulk PDMS
  - Dynamics of wetting a PDMS surface
    - ★ Surface tensions both PDMS and water
    - ★ Not widely available for PDMS; many studies for water

Simulation details

PDMS surface tension

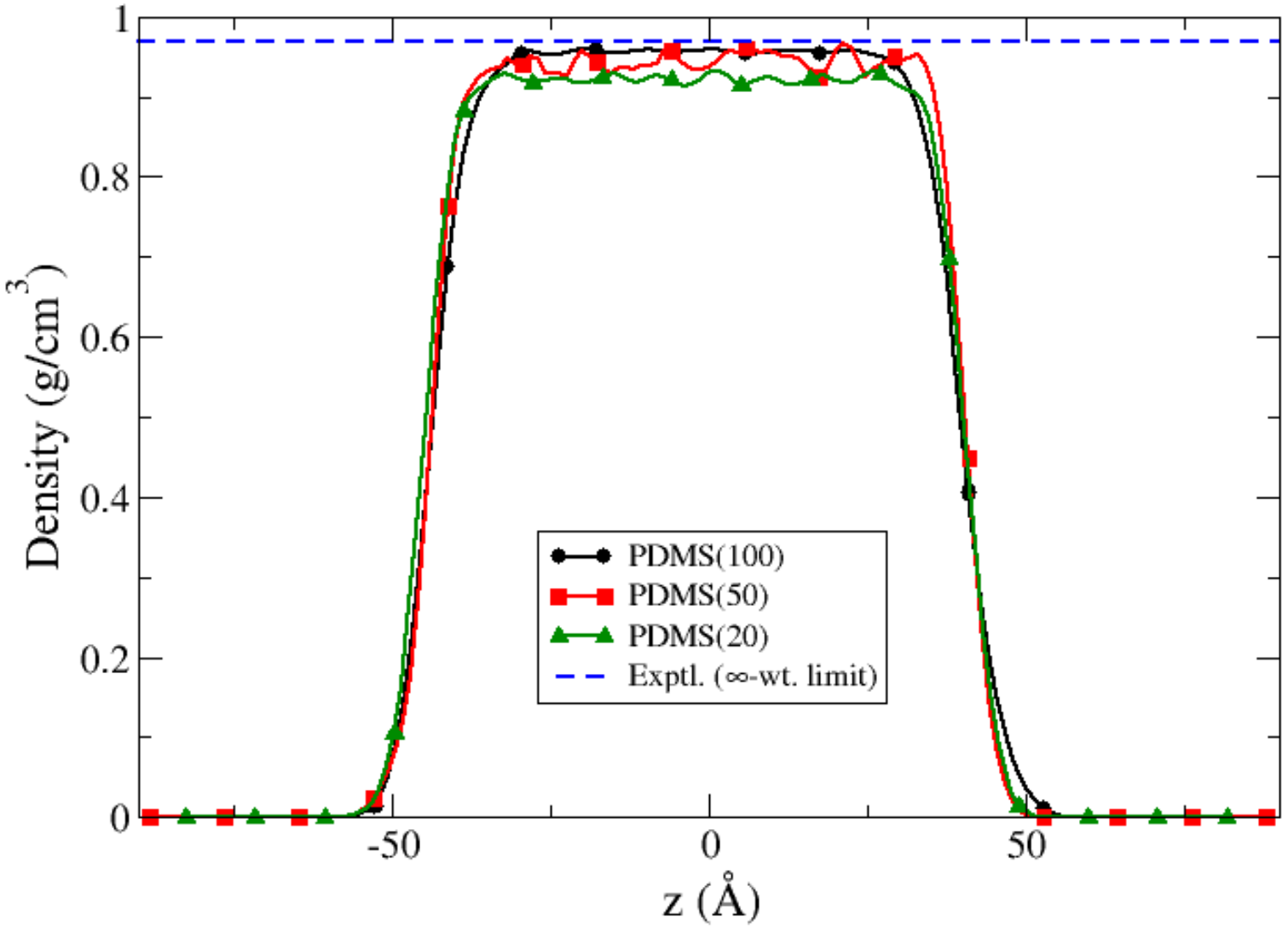




- 500 20-mers (103500 atoms) or 100 100-mers (107000 atoms)
- Simulation box: 100 Å$\times$ 100 Å$\times$ 170 Å
- Buckingham (Exp-6) potential of Smith et al. (2004)
  - 10 A cutoff
  - PPPM Ewald for electrostatics
- All-atom NVT simulation at 300 K using RESPA with 10^6 time steps of 2 fs
- Total time: 2 ns

Simulation results: liquid-vapor density

Density of longer chains rapidly approaches bulk limit



Simulation results: surface tension

Density of longer chains rapidly approaches bulk limit

Surface tension includes results of simulation plus long-range correction:

$$\gamma = \gamma_p + \gamma_{tail}$$

where

$$\gamma_p = \frac{L_z}{2}\left(p_z - \left(\frac{p_x + p_y}{2}\right)\right)$$

$$\gamma_{tail} = \frac{\pi}{2}\int_{-\infty}^{\infty}\int_{-1}^{1}\int_{r_c}^{\infty} r^3 \frac{\mathrm{d}U(r)}{\mathrm{d}r} g(r)\left(1 - 3s^2\right) \times \left(\rho(z)\,\rho(z - sr) - (\rho_G(z))^2\right)\,\mathrm{d}r\,\mathrm{d}s\,\mathrm{d}z$$

Simulation results: surface tension of PDMS

Surface tension increases with molecular weight for -CH_3 PDMS

	Surface tension, mN/m		
Chain type	γ_p	γ_{tail}	$\gamma = \gamma_p + \gamma_{tail}$
20-mer -CH_3	15.0	5.5	20.5
50-mer -CH_3	18.0	5.7	23.7
100-mer -CH_3	18.5	5.4	23.9
20-mer -OH	16.4	5.2	21.6

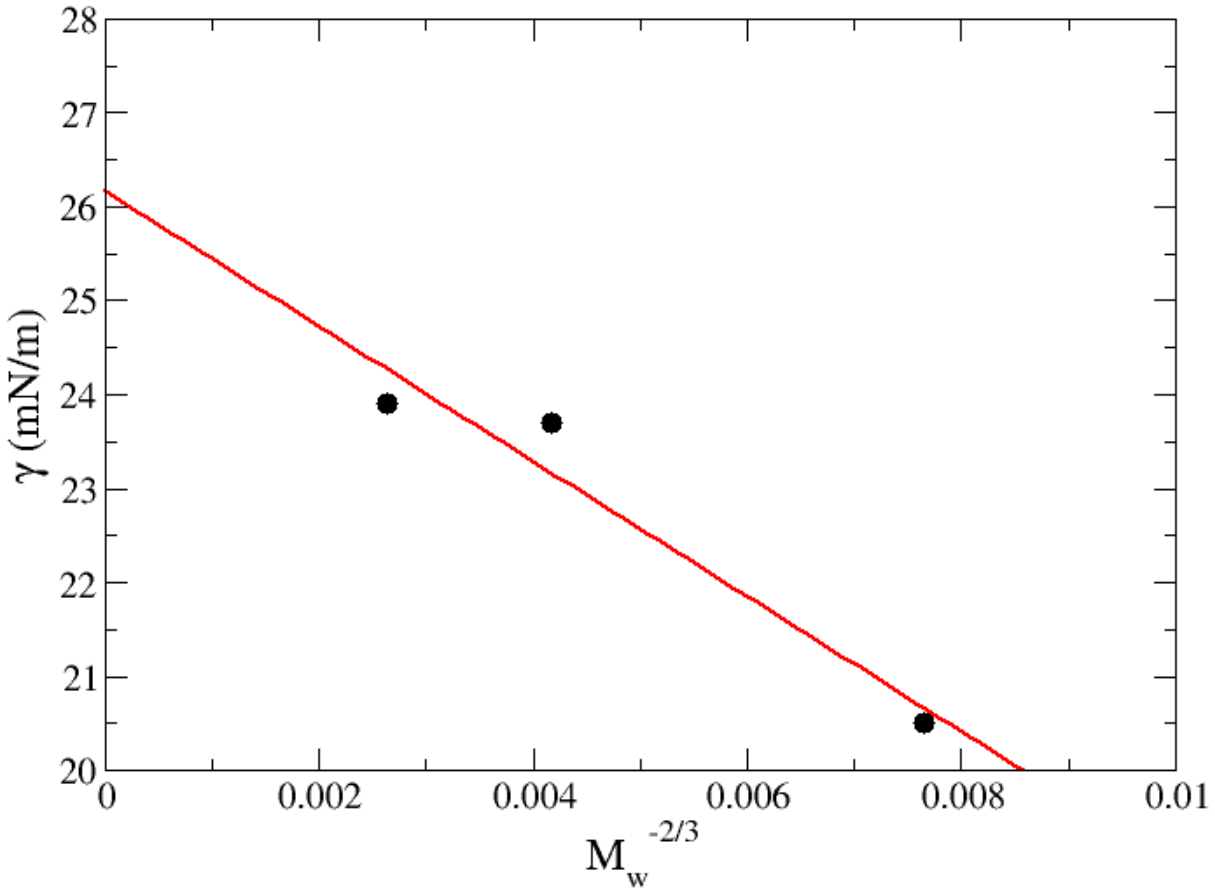
Exptl. value, infinite molecular weight:

γ = 21.0 mN/m.

[Dee and Sauer, *Macromolecules*, **26**, 2771 (1993).]

Simulation results: surface tension of PDMS

−2/3-power law dependence

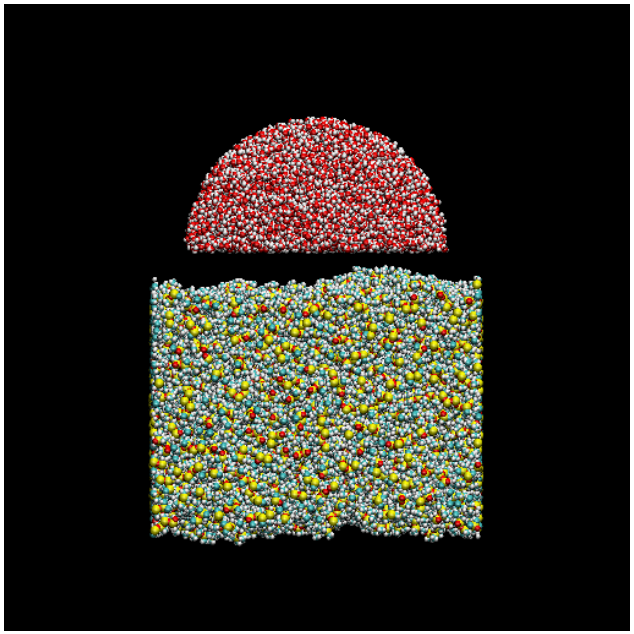


$\gamma(M_w = \infty) = 26.2$ mN/m (simulation)

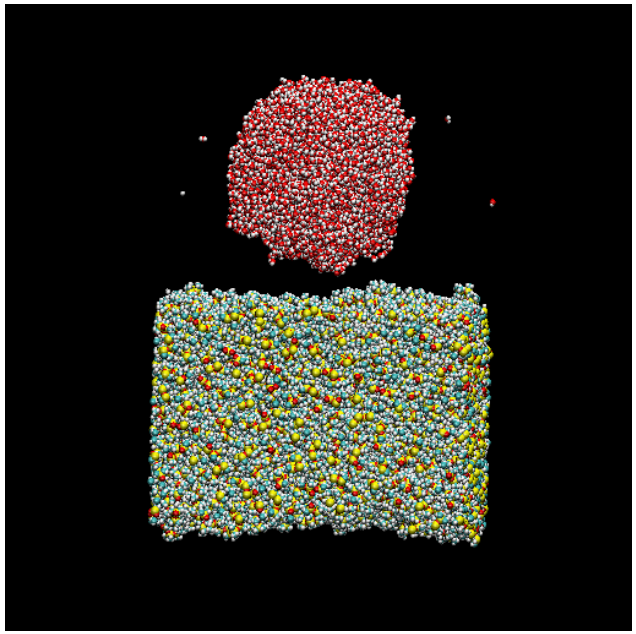
$\gamma(M_w = \infty) = 21.0$ mN/m (experimental)

Surface tension of PDMS-water interface

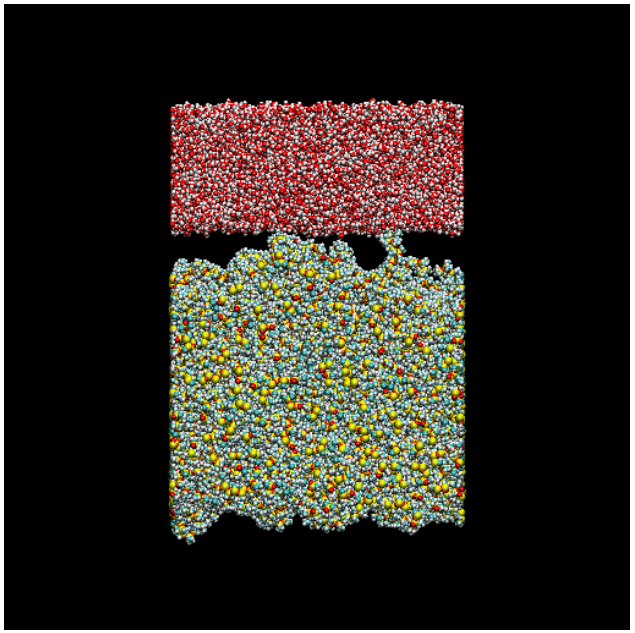
Three different geometries tested



Hemispherical drop



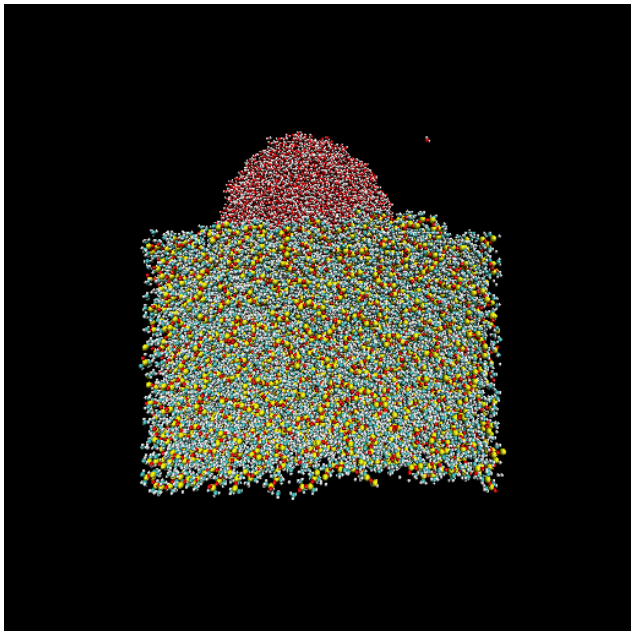
Spherical drop



Slab

Surface tension of PDMS-water interface

Three different geometries tested



Hemispherical drop

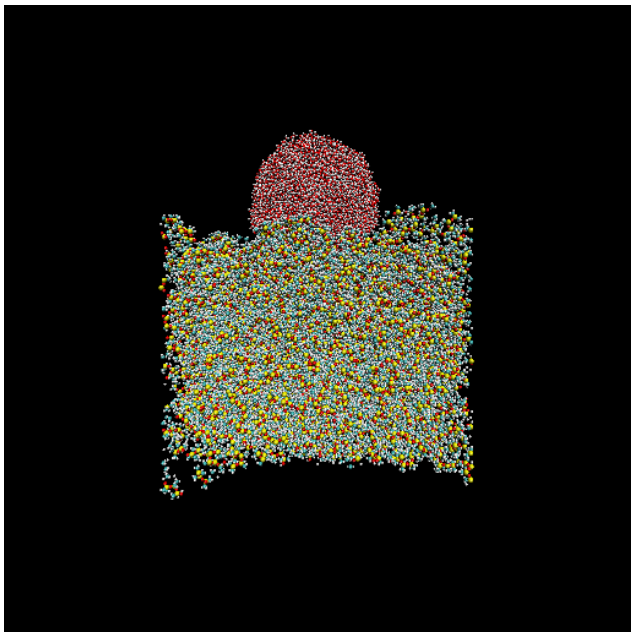
- 60 Å radius hemispherical drop ($\sim$ 10000 molecules) placed on top of PDMS slab
- 2 ns simulation in *NVT* ensemble at 300 K
- Measure contact angle as a function of PDMS chain length

Chain length	Contact angle (deg.)
20-mer -CH_3	108 ± 10
50-mer -CH_3	108 ± 10
100-mer -CH_3	108 ± 10

- Exptl. contact angle: 105-120 degrees

Surface tension of PDMS-water interface

Three different geometries tested



Spherical drop

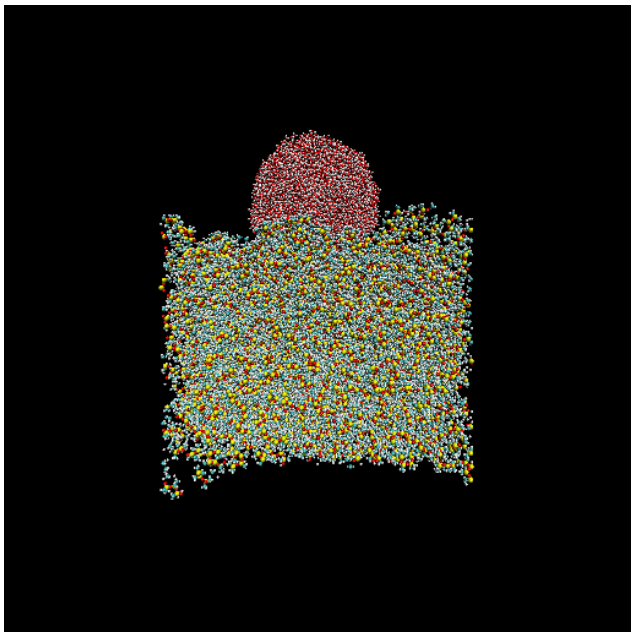
- 50 Å radius spherical drop ($\sim$ 10000 molecules) placed on top of PDMS slab
- 2 ns simulation in *NVT* ensemble at 300 K
- Measure contact angle as a function of PDMS chain length
- Use Young's equation to determine surface tension of PDMS-water interface:

$$\gamma_{PW} = \gamma_P + \gamma_W \cos\theta$$

where $\gamma_W = 61$ mN/m is the surface tension of SPC/E water

Surface tension of PDMS-water interface

Three different geometries tested



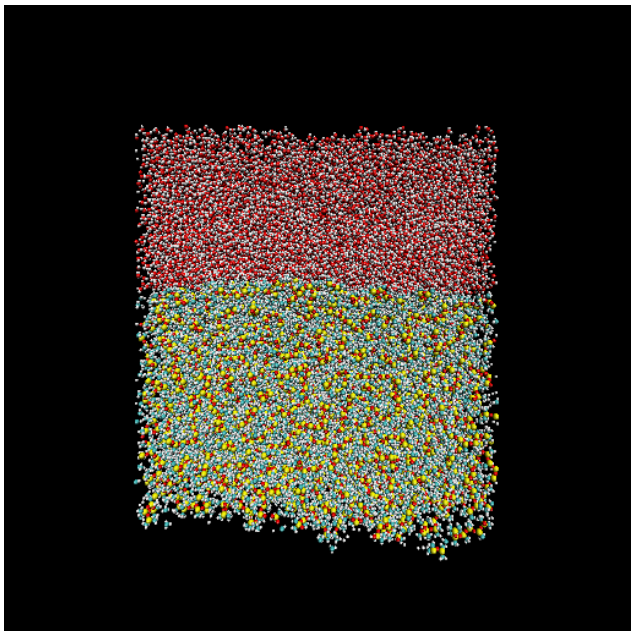
Spherical drop

Chain length	Contact angle (deg.)
20-mer -CH_3	108 ± 10
50-mer -CH_3	108 ± 10
100-mer -CH_3	108 ± 10

- Using Young's equation, we find $\gamma_{PW} = 39 \pm 8$ mN/m.
- Exptl. value ~ 40 mN/m

Surface tension of PDMS-water interface

Three different geometries tested



Slab

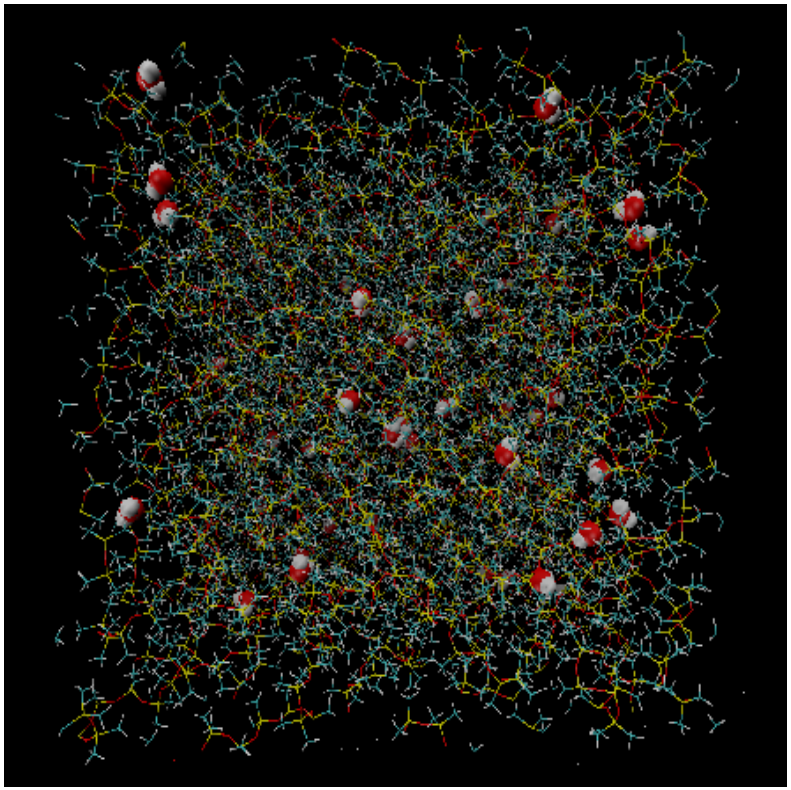
- 50-Å thick slab of water ($\sim$ 20000 molecules) placed on top of PDMS slab
- 2 ns simulation in *NVT* ensemble at 300 K
- Measure total surface tension
- γ for PDMS-water surface tension given by overall γ, less water-vapor, PDMS-vapor interfaces:

$$\gamma_{PW} = \gamma_{tot} - (\gamma_P + \gamma_W)$$

- For 100-mer -CH_3 PDMS, $\gamma_{PW} = 127 - (24 + 61) = 42 \mathrm{mN/m}$

Diffusion of water through PDMS

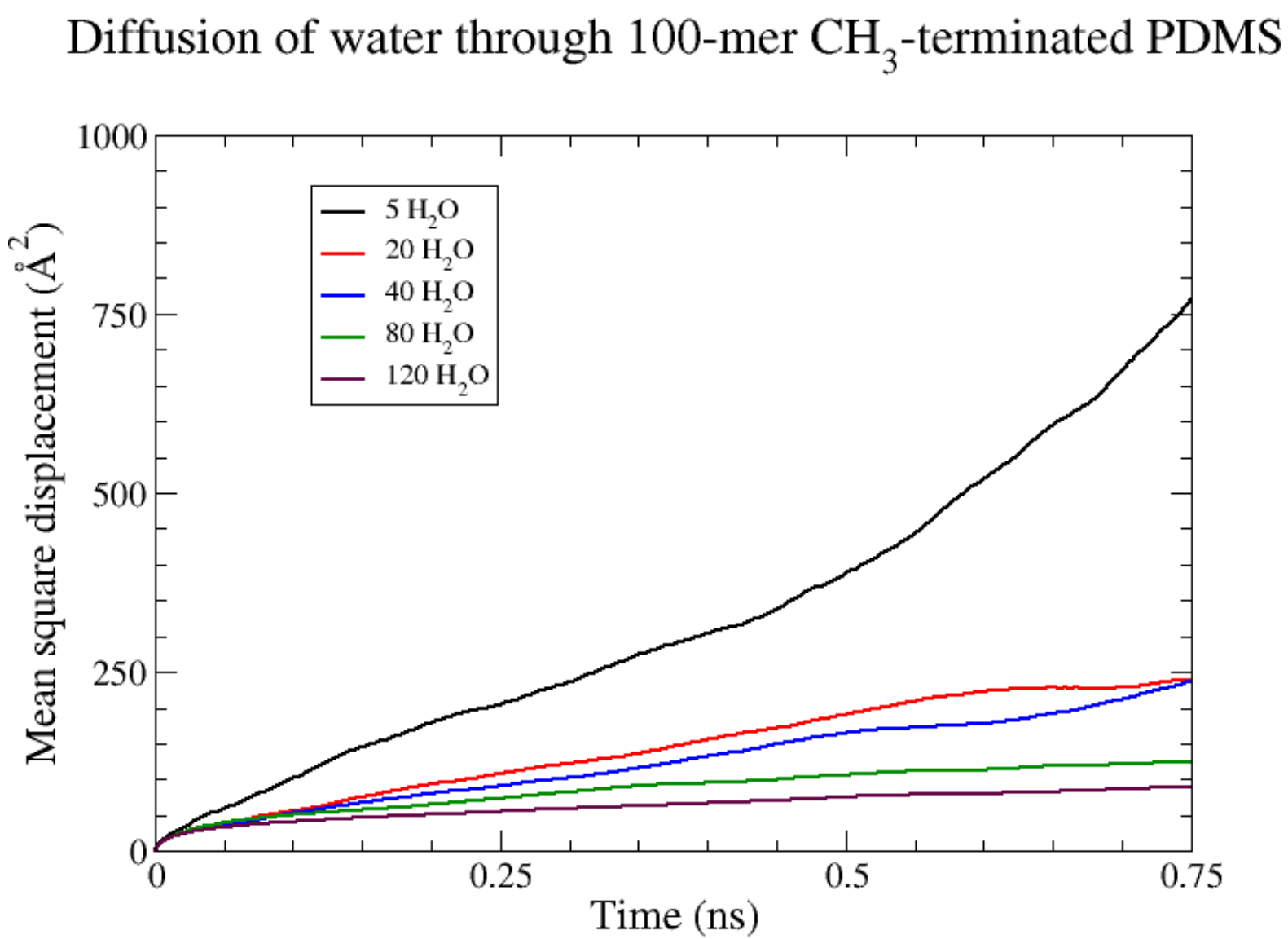
Simulation methodology



- 5-120 water molecules placed in bulk sample of 100 20-mers or 20 100-mers (-CH_3 and -OH terminated)
- > 2 ns MD simulations in the *NVT* at $T = 300$ K.
- Measure rms displacement of waters as a function of time
- Goals:
  - Determine diffusion constant
  - Observe phase separation

Diffusion of water through PDMS

Strong concentration effects on diffusion



Diffusion of water through PDMS

Concentration, terminal-group effects on diffusion

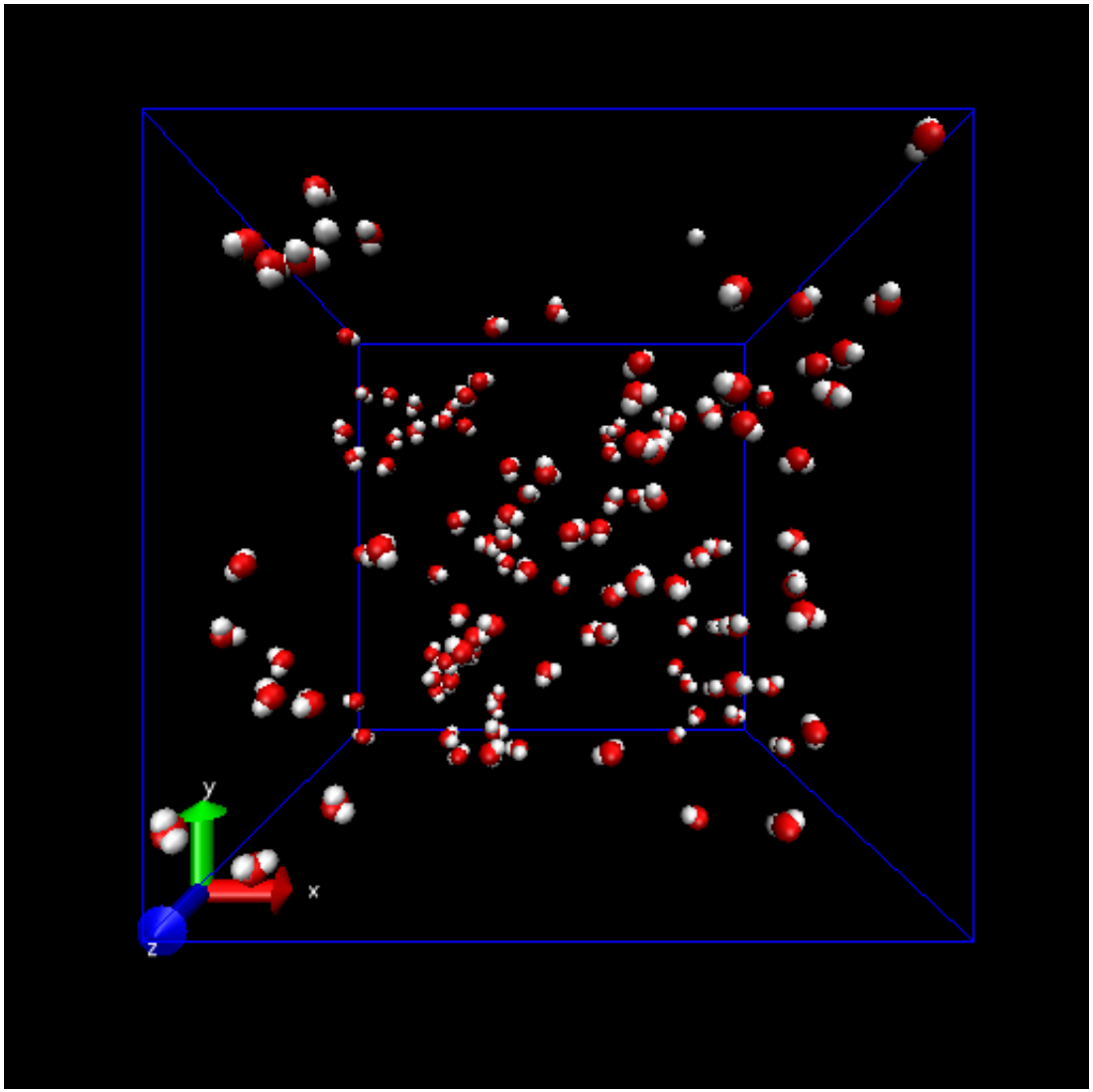
Chain type	Diffusion constant, D (Å^2 ps^{-1}) 5 H_2O	20 H_2O
20-mer -CH_3	0.2742	0.0531
20-mer -OH	0.1524	0.0513
100-mer -CH_3	0.1490	0.0518
100-mer -OH	0.1197	0.0808

Exptl. value, bulk H_2O: 0.2272 Å^2 ps^{-1}

Phase separation observed for concentrations $>$ 20 water molecules

Diffusion of water through PDMS

Water molecules quickly form clusters



Conclusions

- PDMS, water surface tensions underestimated by surface tension
- Diffusion constants reasonable
  - Some termination-group effects
  - Phase separation occurs for intermediate to high concentrations of water
- Contact angle of PDMS-water interface
  - Different geometries yield almost identical contact angles
  - Results in reasonable agreement with experimental data
- PDMS-water interfacial tension
  - Different approaches to calculating PDMS-water interfacial tension yield comparable results
  - Also in good agreement with experimental observations

Acknowledgments

- Scott W. Sides (prior PDMS studies)
- Steven J. Plimpton (LAMMPS)