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Interfacial Properties of PDMS-Water Systems

Ahmed E. Ismail, Gary S. Grest, David R. Heine,[1]
Mark J. Stevens, and Mesfin Tsige[2]

Sandia National Laboratories
[1]Corning, Inc.
[2]Southern Illinois University

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Motivations

- 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

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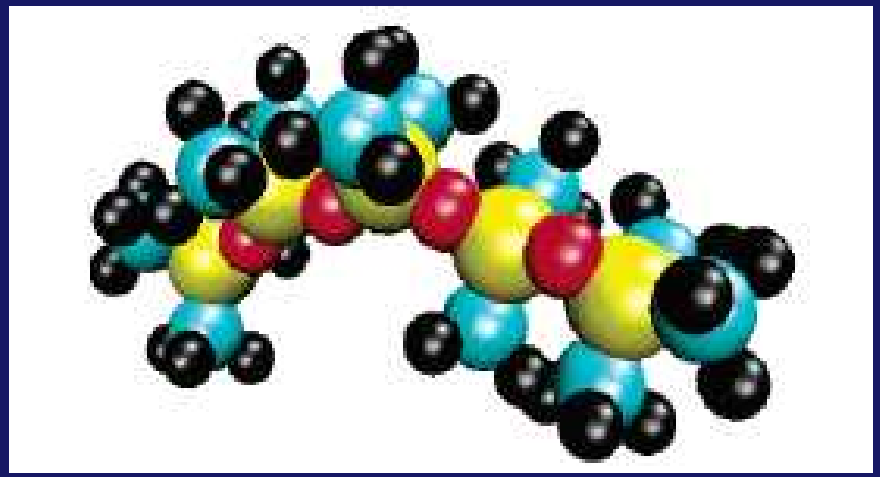
Simulation details

- PDMS
  - 500 20mers (103500 atoms) or 100 100mers (107000 atoms)
  - Box: 100 A x 100 A x 170 A
  - Buckingham (Exp-6) potential Smith et al. (2004)
    - 10 A cutoff
    - P3M-Ewald for electrostatics
  - All-atom NVT simulation at 300 K using RESPA with 10^6 time steps of 2 fs
  - Total time: 2 ns



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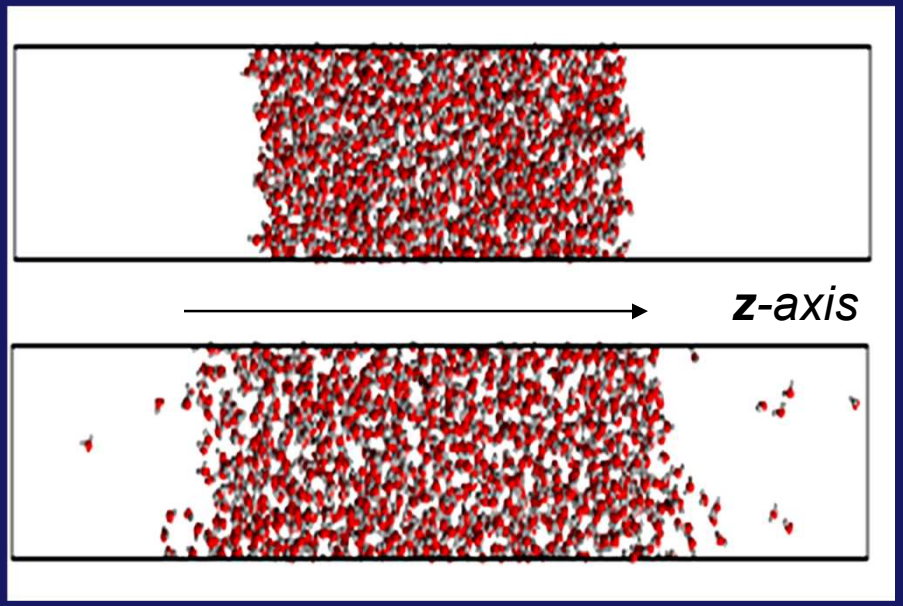
Simulation details

Water slab at 300 K



Water slab at 500 K

- Water
  - 5000+ molecules
  - Box: 100 A x 100 A x 135 A
  - SPC/E model of Berendsen *et al.*
  - Lennard-Jones potential
    - 9.8 A cutoff
    - P3M-Ewald for electrostatic computations
  - NVT simulations between 300 K and 500 K using SHAKE with 2 x 10^6 timesteps of 1 fs
  - Total time: 2-8 ns

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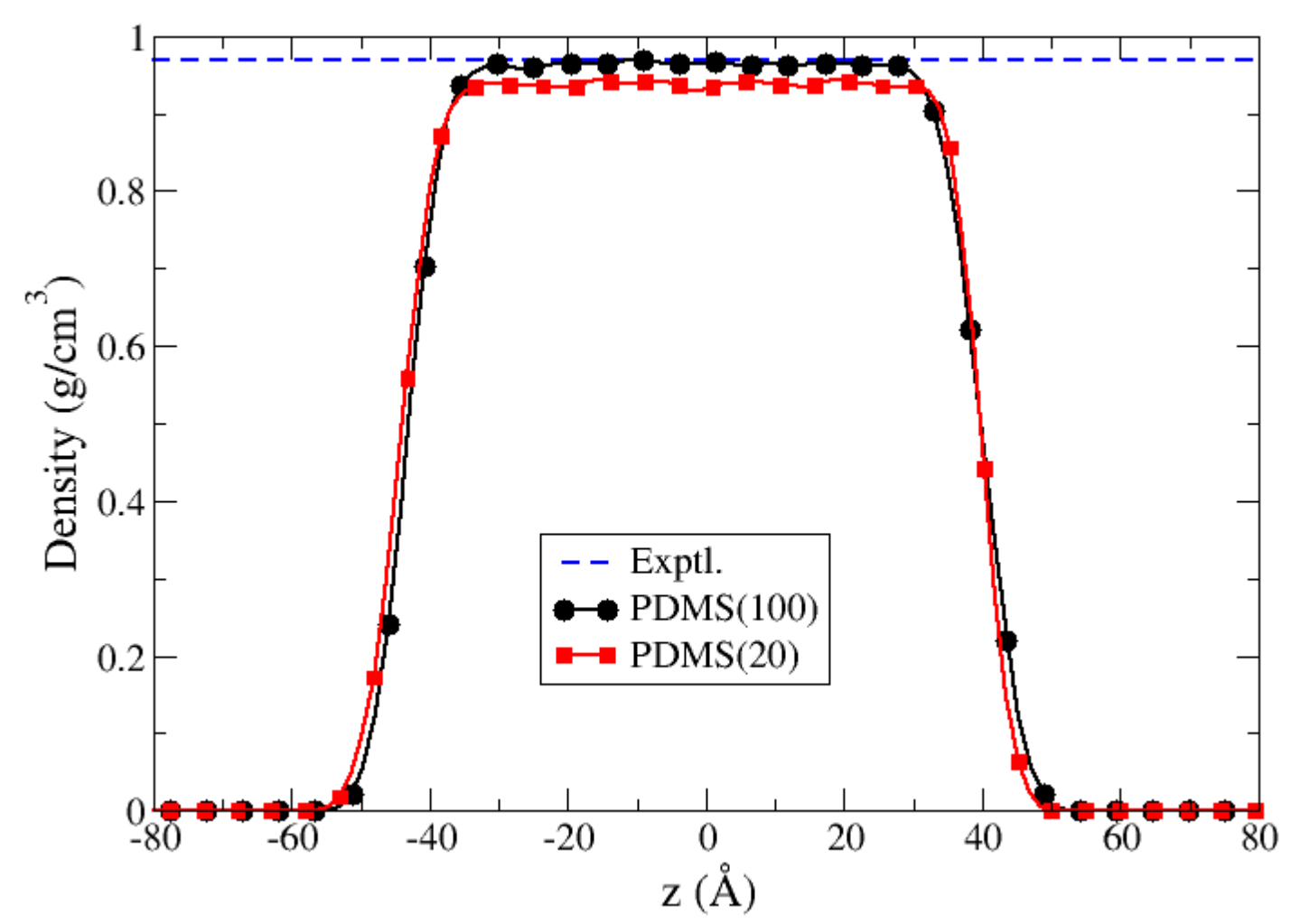
Density of PDMS



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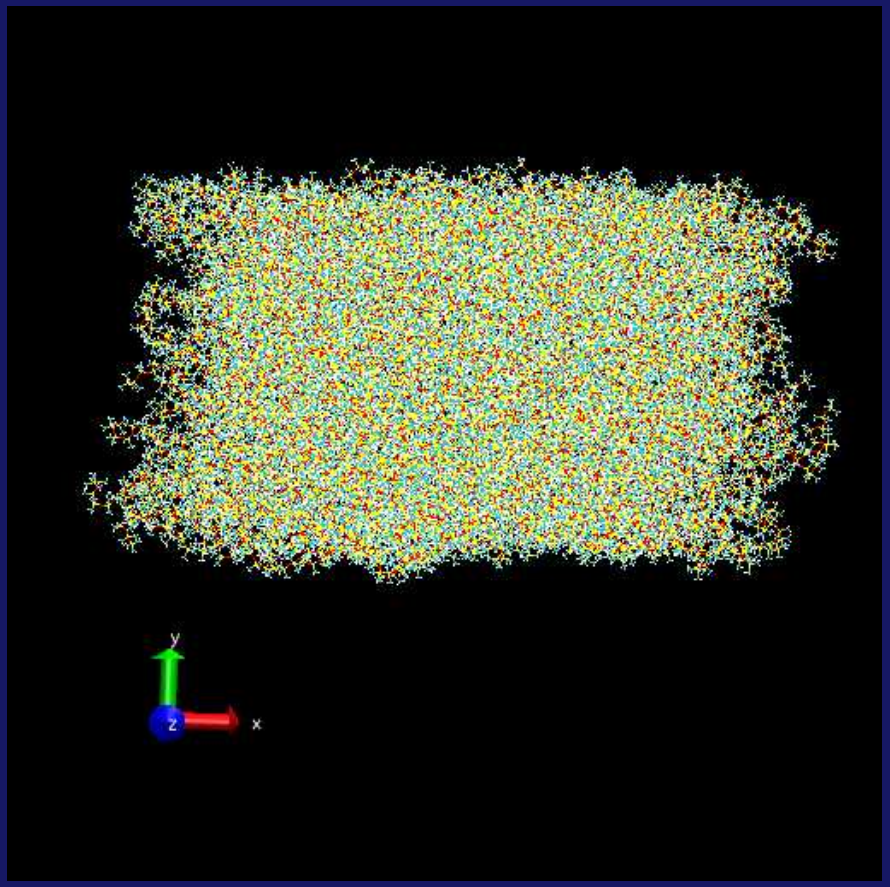
Surface tension of PDMS

- PDMS(20):
  16.8 ± 1.7 mN/m
  (with tail: 22.0 mN/m)
- PDMS(100):
  17.6 ± 1.5 mN/m
  (with tail: 22.9 mN/m)

- Experimental results:
  20.9 mN/m



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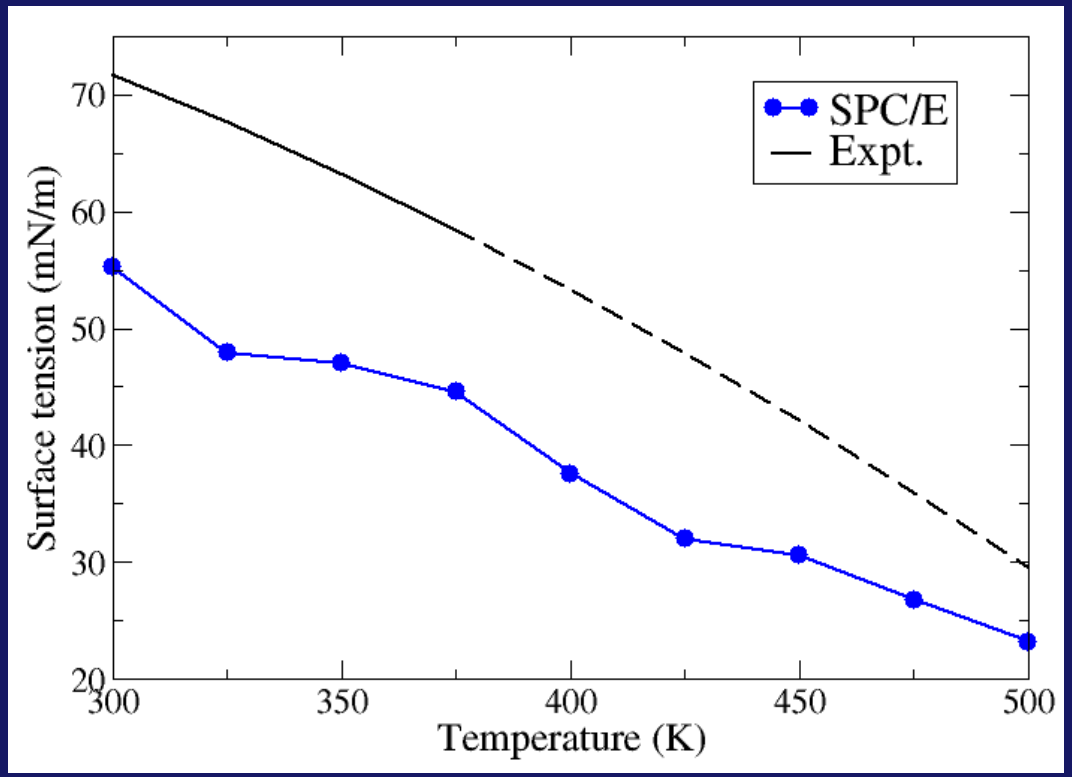
Surface tension of water

- Uncorrected surface tension approximately 25% too low.
- Other non-polarizable potentials show similar (or worse) underestimations of surface tension.



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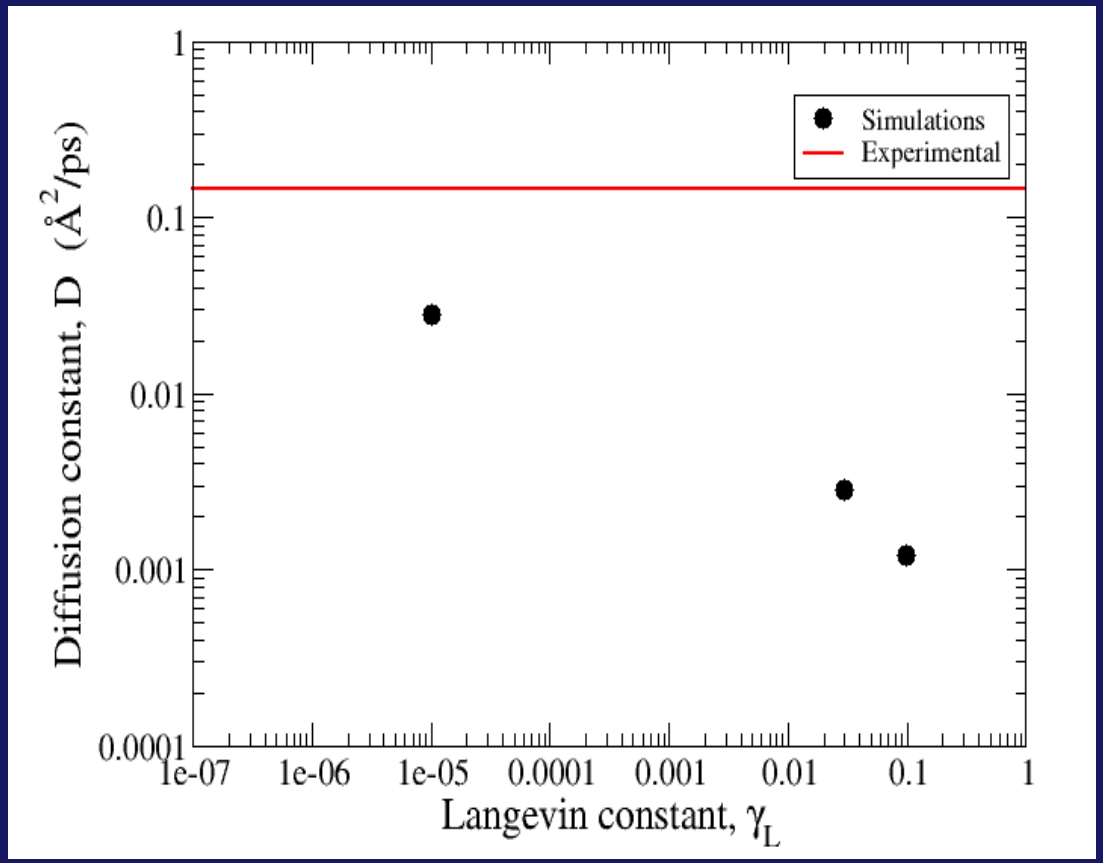
Diffusion of water through bulk PDMS

- Langevin diffusion
- 10 water molecules through bulk PDMS
- Goal: find Langevin constant γ_L for which calculated diffusion matches experimental data



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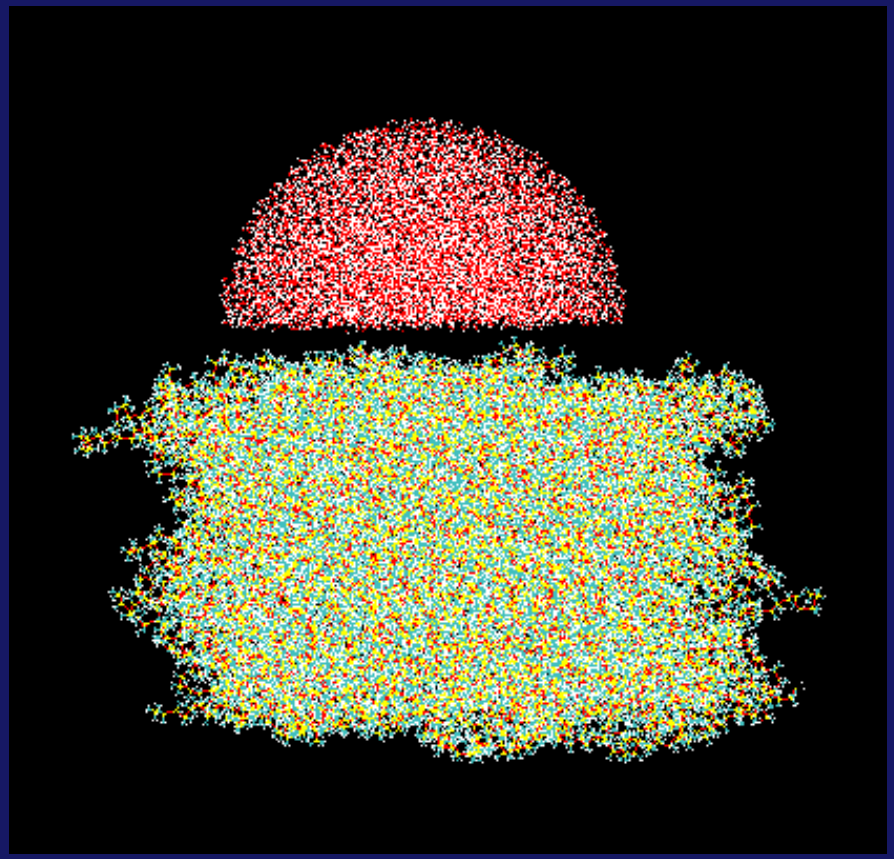
PDMS-water interface systems

- Hemispherical water drop (~10000 molecules) placed 7 A above PDMS slab
- MD simulation for 1.0 ns



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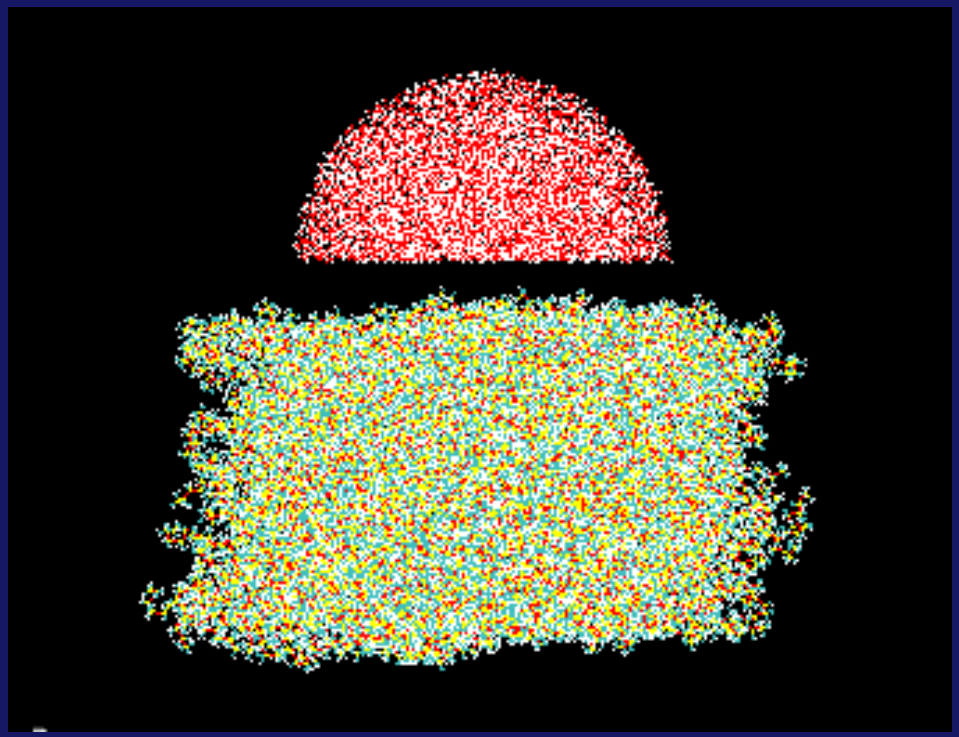
PDMS-water interface

- Drop quickly forms spheroid
  - Less than 0.03 ns required
- Contact angle can be measured from interfacial profile



0 ps

PDMS-water interface

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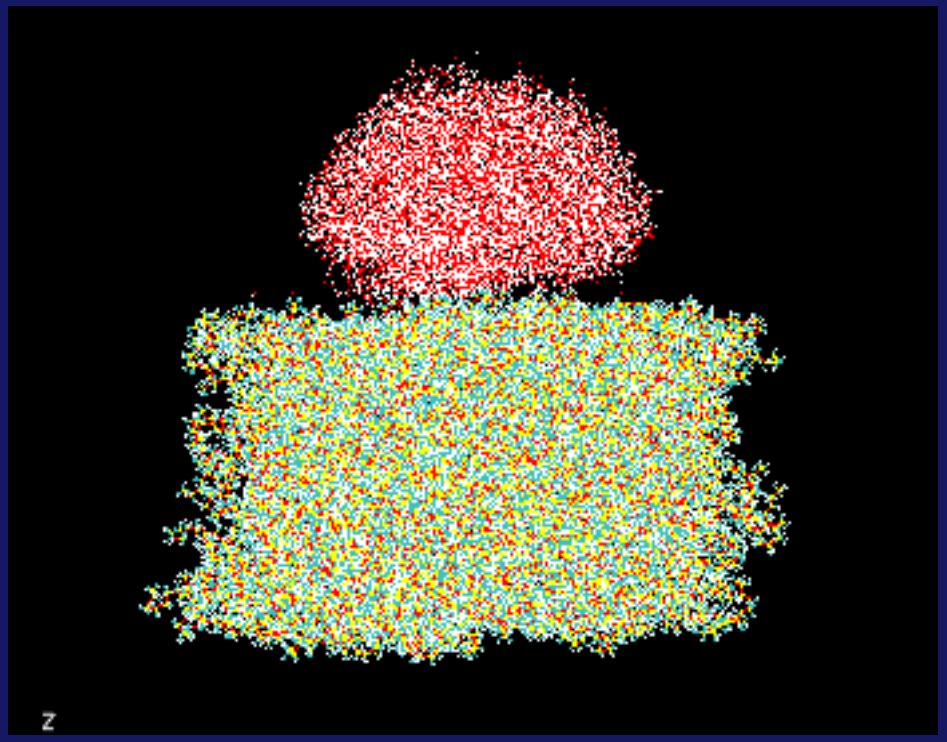

10 ps

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PDMS-water interface

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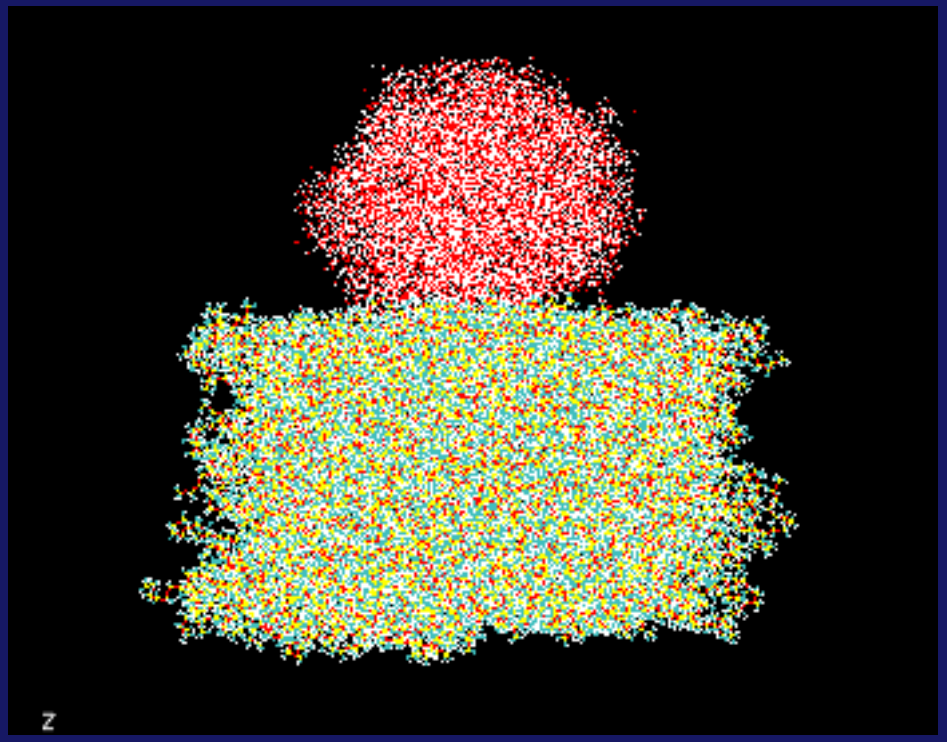

20 ps

PDMS-water interface

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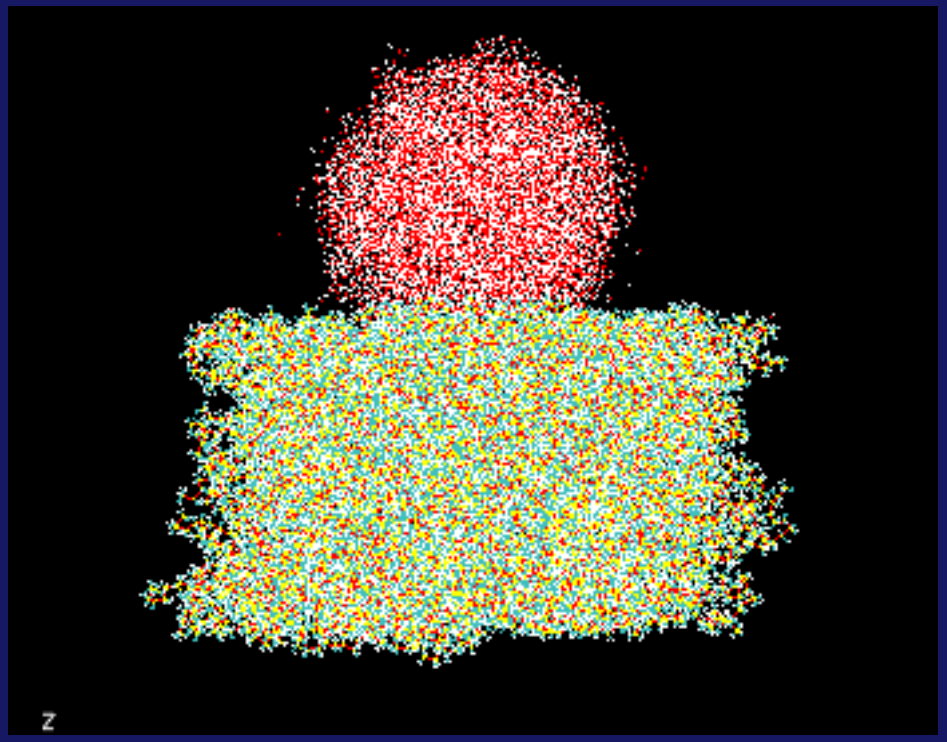

30 ps

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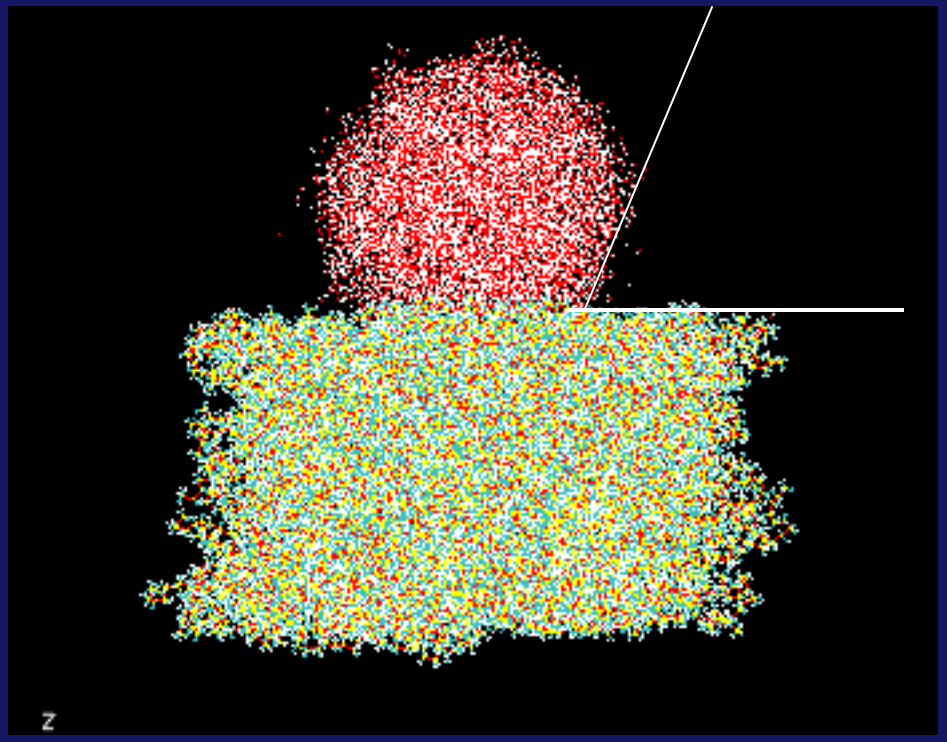
PDMS-water contact angle

- PDMS(20) simulations:
  120 degrees
- PDMS(100) simulations:
  116 degrees
- Experimental data:
  105-120 degrees



30 ps

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PDMS-water surface tension

- PDMS-water surface tension γ_{PW} can be calculated as:

$$\gamma_{PW} = \gamma_{WV} - \gamma_{PV}\cos\left(\theta - \frac{\pi}{2}\right)$$

- Using simu

$$\gamma_{PW} = (50.2) - (17.2)\cos\left(\frac{62\pi}{180}\right)$$

$$= 42.1\text{mN m}^{-1}$$

which is in good agreement with experimental measurements of interfacial tension (~40 mN/m)

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Conclusions

- PDMS, water surface tensions underestimated by surface tension
- Contact angle of PDMS-water interface in good agreement with experimental data
- PDMS-water interfacial tension also in good agreement with experimental observations
  - Role of cutoff effects?
  - System-size effects (chain length, number of chains)

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Acknowledgments

- Scott Sides
- Steve Plimpton

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