SAND2006-6898C

# Capillary Waves at the Liquid-Vapor Interface and the Surface Tension of Water

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# Motivations

- Study the interfacial behavior of composite water-polymer systems
  - Contact angle of water on polydimethylsiloxanes (PDMS)
  - Structure of water near interface with polyethylene oxide (PEO)
- Requires characterization of surface tension of water models
- Most previous simulation studies show large variance in calculated surface tension
  - Insufficient simulation length
  - Electrostatic mesh too coarse

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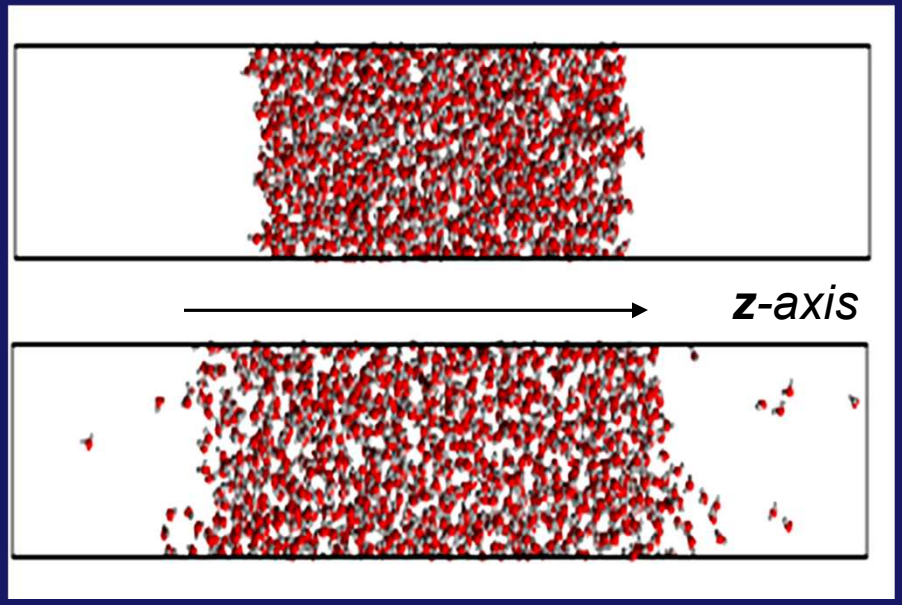
# Pressure-integration simulation details

Water slab at 300 K




Water slab at 500 K

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

$$\gamma_{sim} = \frac{L_z}{2}\left\langle p_\perp - p_\parallel \right\rangle = \frac{L_z}{2}\left\langle p_z - \left(\frac{p_x + p_y}{2}\right)\right\rangle$$

*Pressure-integration form of surface tension*

- Water models tested: SPC/E, TIP3P, TIP3P-C, TIP3P-Ew, TIP4P, TIP4P-Ew
- 1000 molecules
- 23 Å x 23 Å x 135 Å box (interfacial area: 5.3 $nm^2$)
- 10 Å cutoff for LJ, PPPM for Ewald summation
- 2 ns NVT MD simulations at 300 K-500 K with 1 fs timesteps

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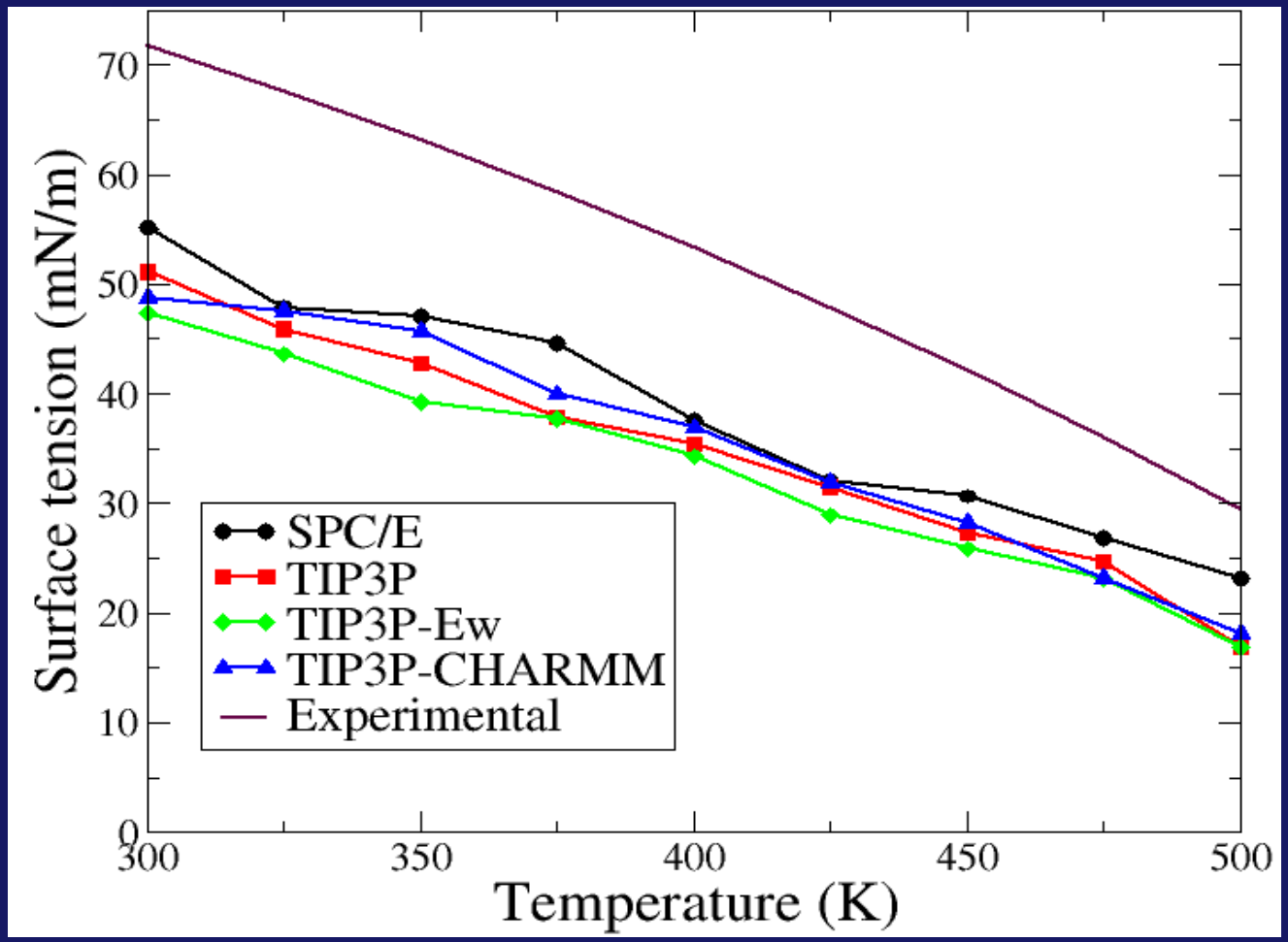
# Surface tension of three-point water models

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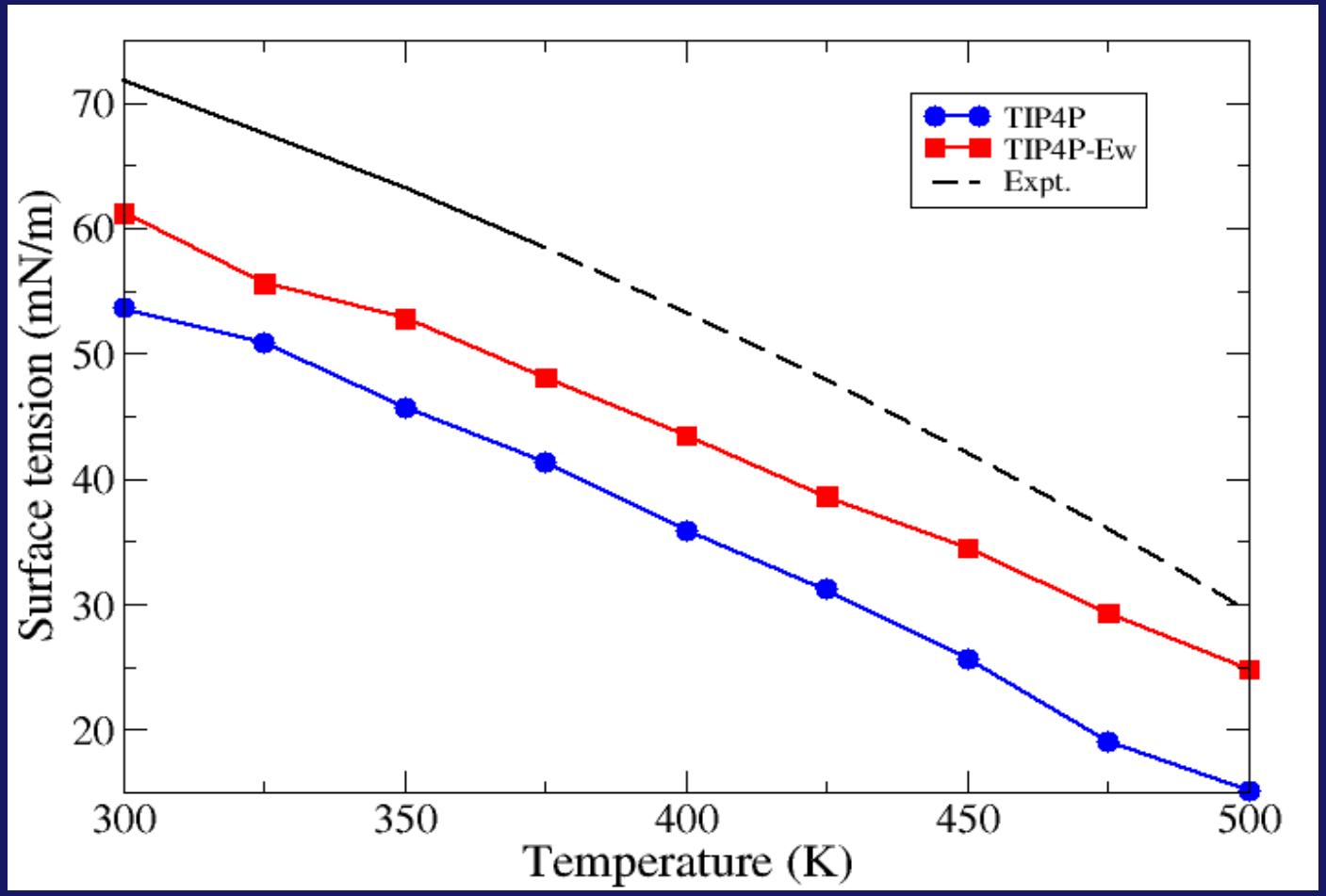
# Surface tension of four-point water models

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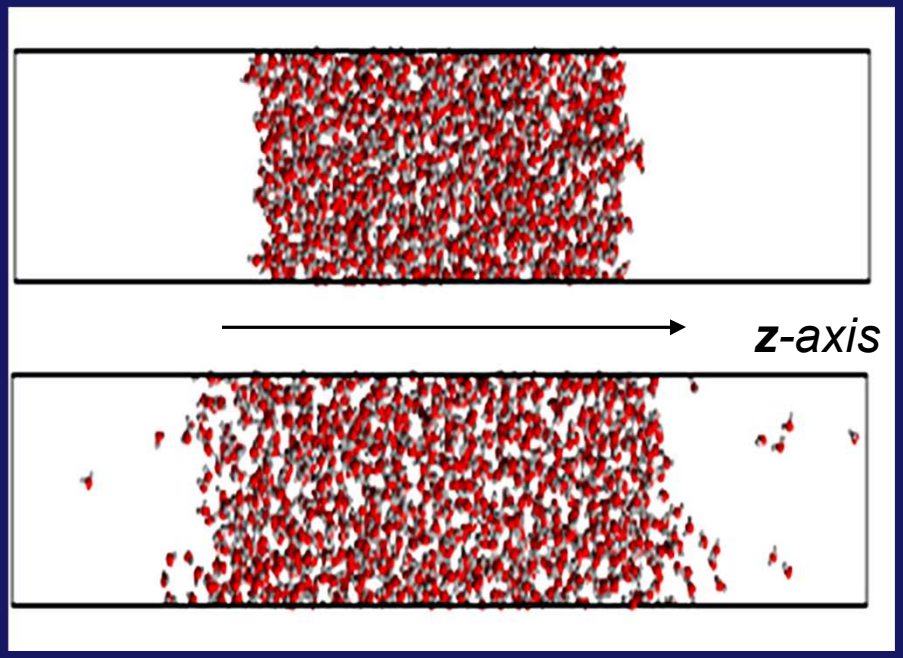
# Capillary wave simulation details

Water slab at 300 K




Water slab at 500 K

- SPC/E water
- 16,000 to 400,000 molecules
- Surface area between 84.6 $nm^2$ and 2116 $nm^2$
- 10 Å cutoff for LJ
- PPPM for Ewald summation
- NVT MD simulations:
  - 300 K, 400 K, and 500 K
  - 1-2.75 ns (timesteps of 1 fs), 250 ps-2 ns equilibration
  - Densities every 5 ps

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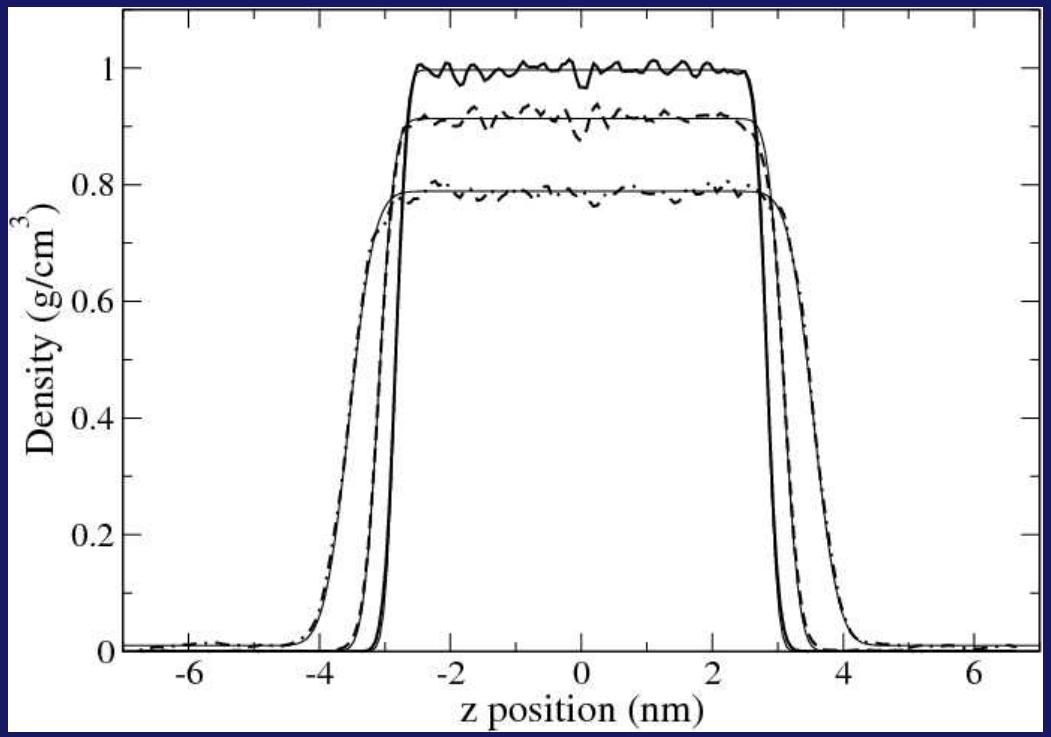
# Determining the surface tension

Fit density profile to functional form:

$$\Psi_t(z) = \tanh\left(\frac{2z}{w_t}\right)$$

$$\Psi_e(z) = \mathrm{erf}\left(\frac{\sqrt{\pi}z}{w_e}\right)$$

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# Determining the surface tension

Capillary-wave calculation of $\gamma$:

Intrinsic interfacial width

$$\Delta^2 = \Delta_0^2 + \frac{k_B T}{2\pi\gamma} \ln \frac{L}{B_0}$$

Total observed interfacial width

Length of interfacial surface

$$\Delta^2 = \begin{cases} \pi^2 w_t^{\,2}/48, & \tanh \\ w_e^2/2\pi, & \text{erf} \end{cases}$$

Slope of semi-log plot inversely proportional to $\gamma$

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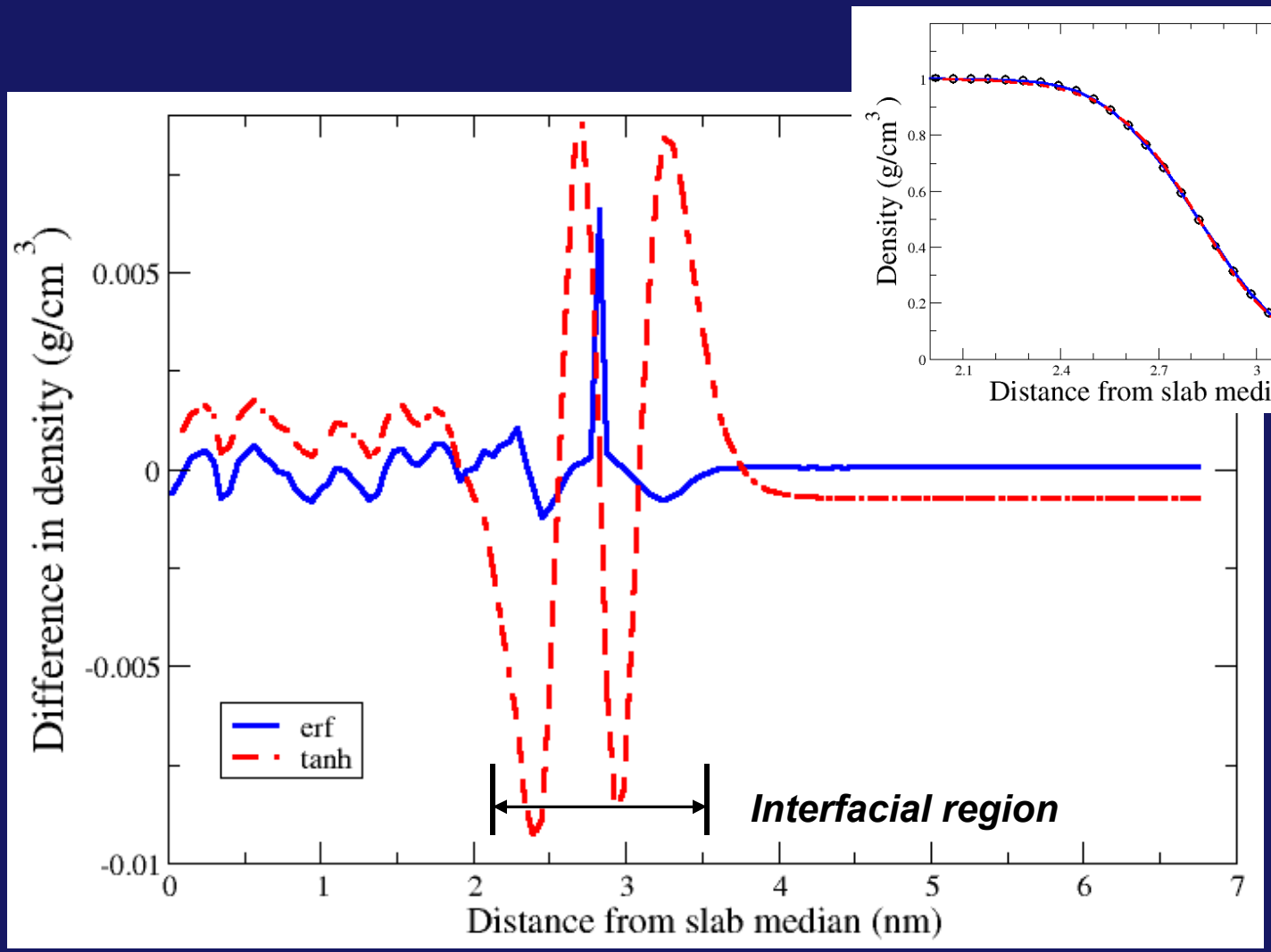
# Comparison of erf and tanh profiles

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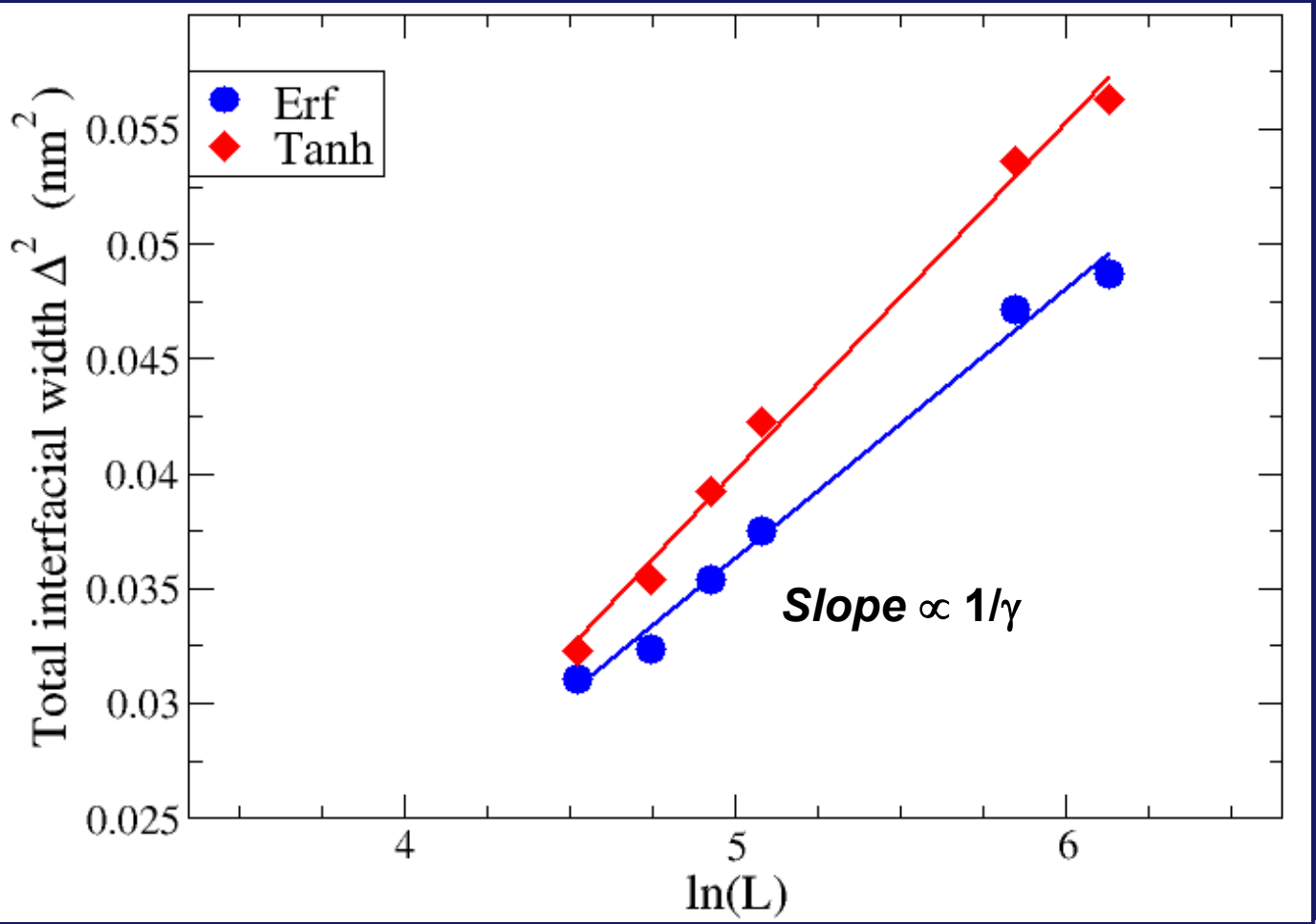
# Comparison of erf and tanh profiles

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# Comparison of calculated surface tensions

| | Surface tension $\gamma$ (mN/m) | | |
|---|---|---|---|
| Temperature | Erf | Tanh | Pressure-integration |
| 300 K | 55.5 | 42.6 | 50.2 |
| 400 K | 32.0 | 27.8 | 33.3 |
| 500 K | 24.3 | 20.9 | 20.5 |
| S.D. | ±3.0 | ±1.9 | ±3.0 |

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# Conclusions

- Existing three-point models do not agree with experimental data, although temperature dependence is in good agreement
- TIP4P agrees with experiment at high temperatures, but not low temperatures
- Studying capillary wave behavior offers alternate route to computing surface tension
- Agreement with pressure-integration approach is better for erf than tanh profiles

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# Acknowledgments


- Steve Plimpton
- Paul Crozier
- Amalie Frischknecht
- Scott Sides


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