The University of Akron
College of Polymer Science and Polymer Engineering

# Surface and Interfacial Tension of Graft Polymer Melts

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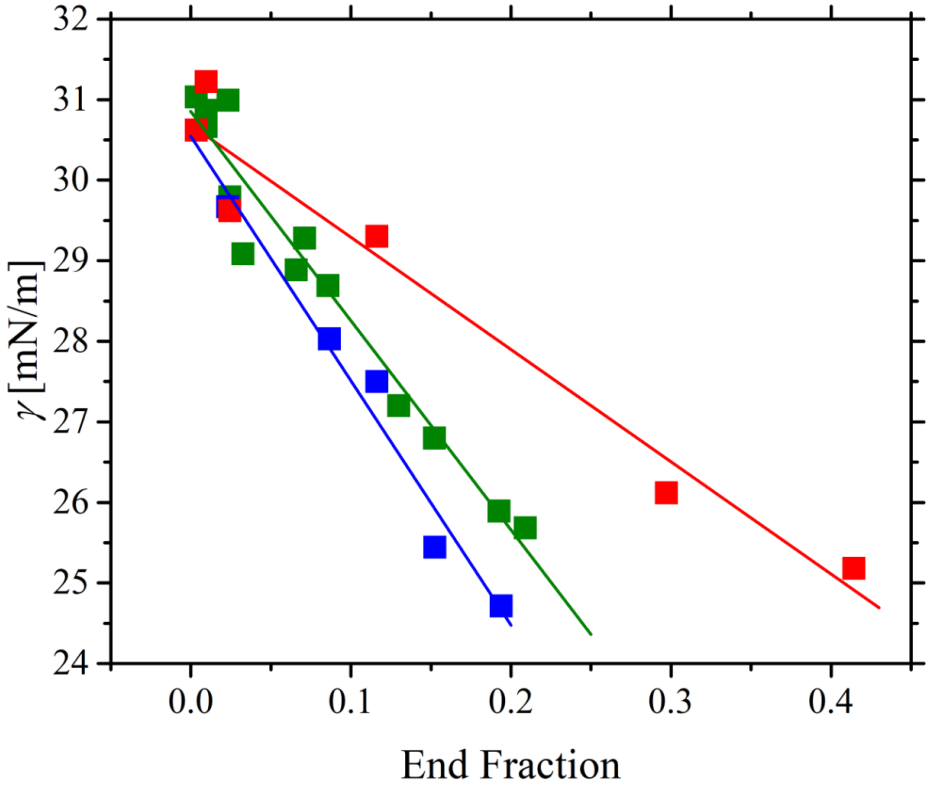
# Surface Tension of Polymer Melts

Dependence of surface properties on physical chain architecture

## Motivation

- Coatings and Adhesives
  - $W = \gamma_{LV}(1 + \cos\theta)$
- Miscibility of blends




Dee, G.T. and B.B. Sauer. Journal of colloid and interface science, *1992.* ***152(1).***
Fleischer, C.A., et al. Macromolecules, *1993.* ***26(16).***
Sauer, B.B. and G.T. Dee. Macromolecules, *1991.* ***24(8).***

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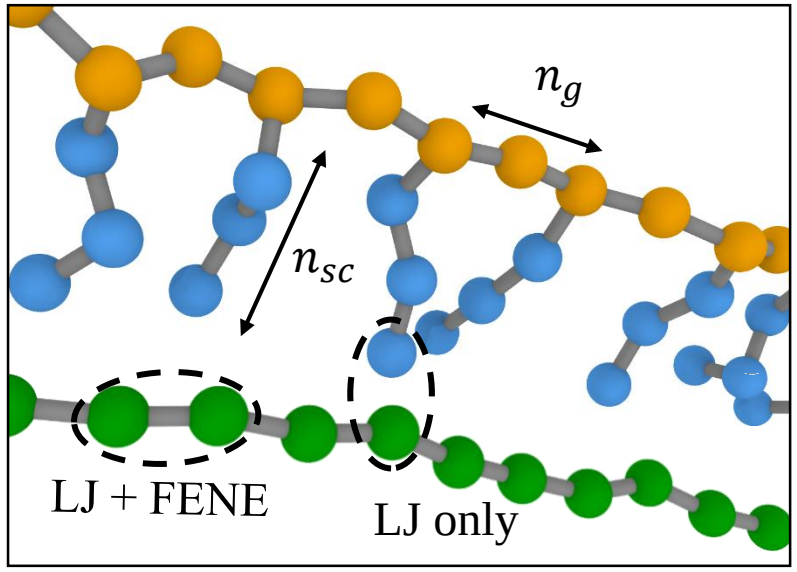
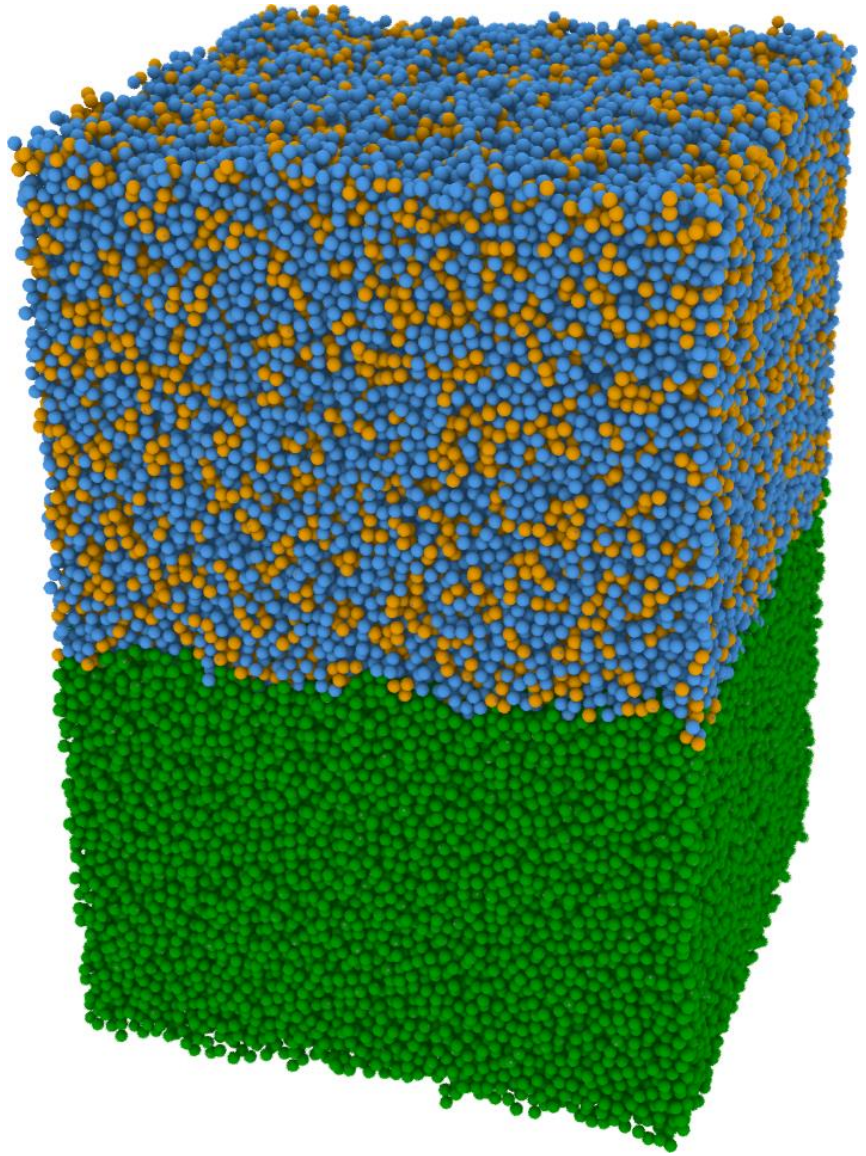
# Molecular Dynamics Simulations



**LJ Interaction Potential**

$$U_{LJ} = \begin{cases} 4\,\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_{cut}}\right)^{12} + \left(\frac{\sigma}{r_{cut}}\right)^{6}\right], & r \le r_{cut} \\ 0, & r > r_{cut} \end{cases}$$

**FENE Bond Potential**

$$U_{FENE} = -\frac{1}{2} k_{spring} R_{max}^2 \ln\left(1 - \frac{r^2}{R_{max}^2}\right)$$

| | |
|---|---|
| $\varepsilon_{LL}$ | 1.5 $k_B T$ |
| $\varepsilon_{GG}$ | 1.0 $k_B T$ |
| $\varepsilon_{GL}$ | $\sqrt{\varepsilon_{LL}\varepsilon_{GG}}$ |

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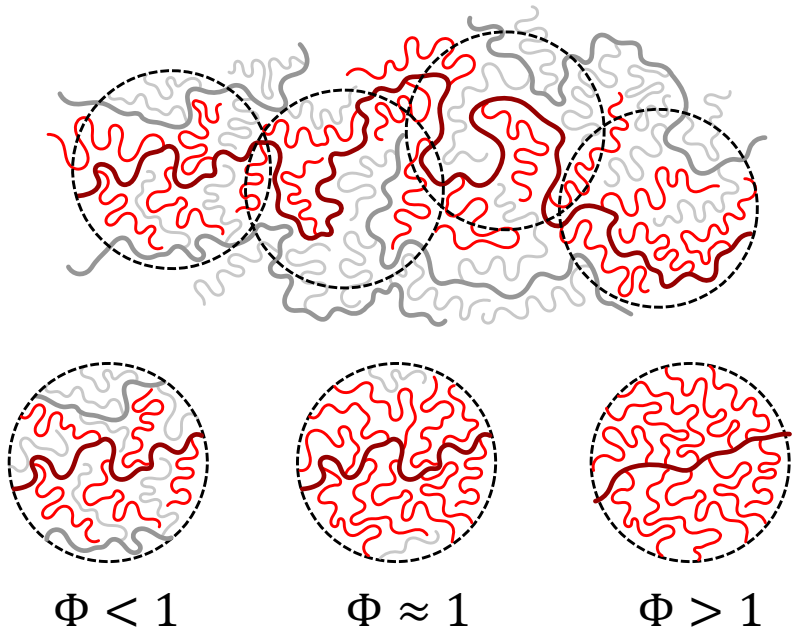
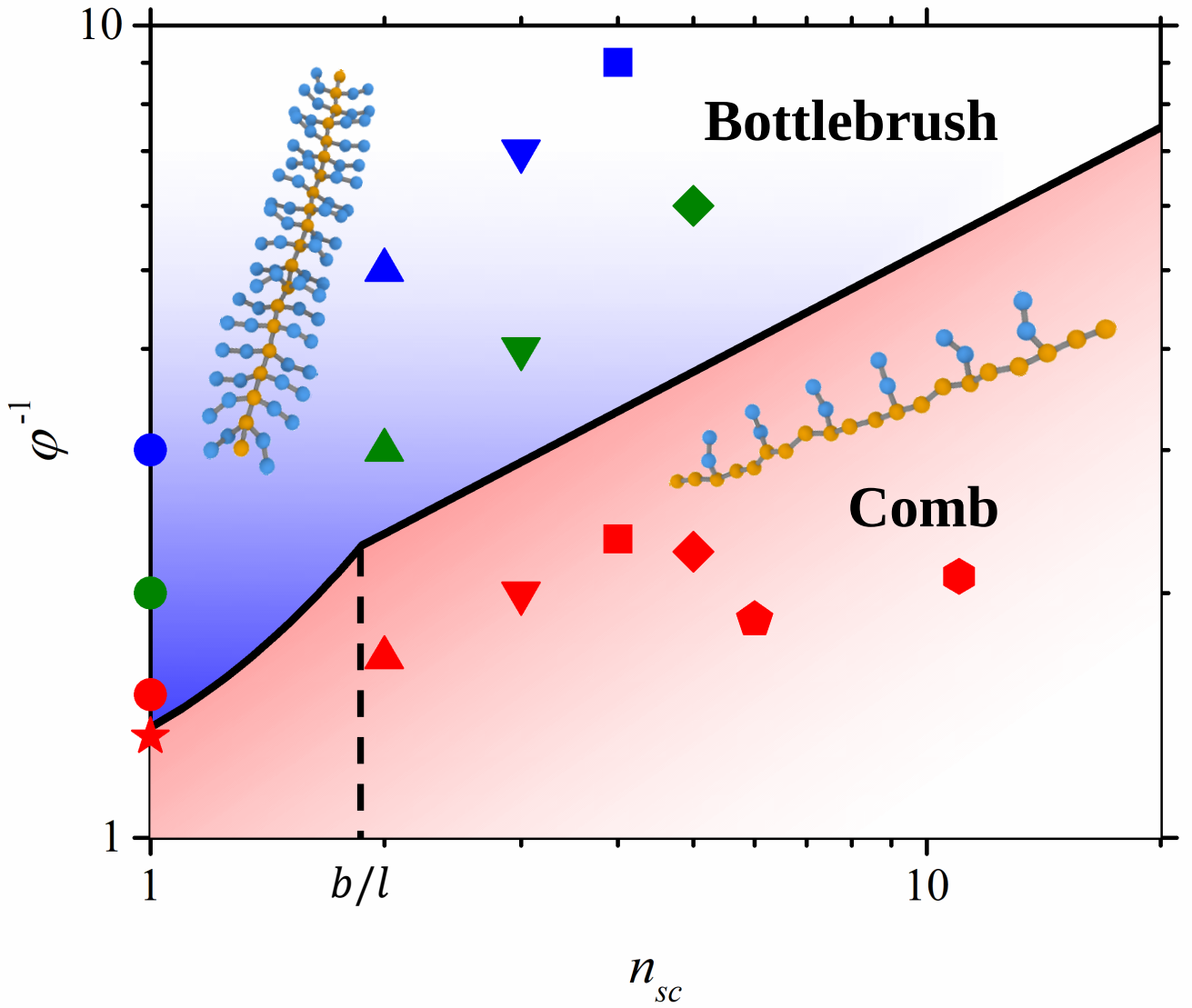
# Diagram of States

$$\Phi \equiv \frac{\text{Volume of side chain monomers}}{\text{Pervaded volume of side chains}}$$



$\Phi < 1$ $\Phi \approx 1$ $\Phi > 1$

$$\Phi = \begin{cases} \dfrac{v\left(n_{sc}/n_g + 1\right)}{(lb)^{3/2} n_{sc}^{1/2}}, & n_{sc} \geq b/l \\ \dfrac{v\left(n_{sc}/n_g + 1\right)}{l^3 n_{sc}^2}, & n_{sc} < b/l \end{cases}$$



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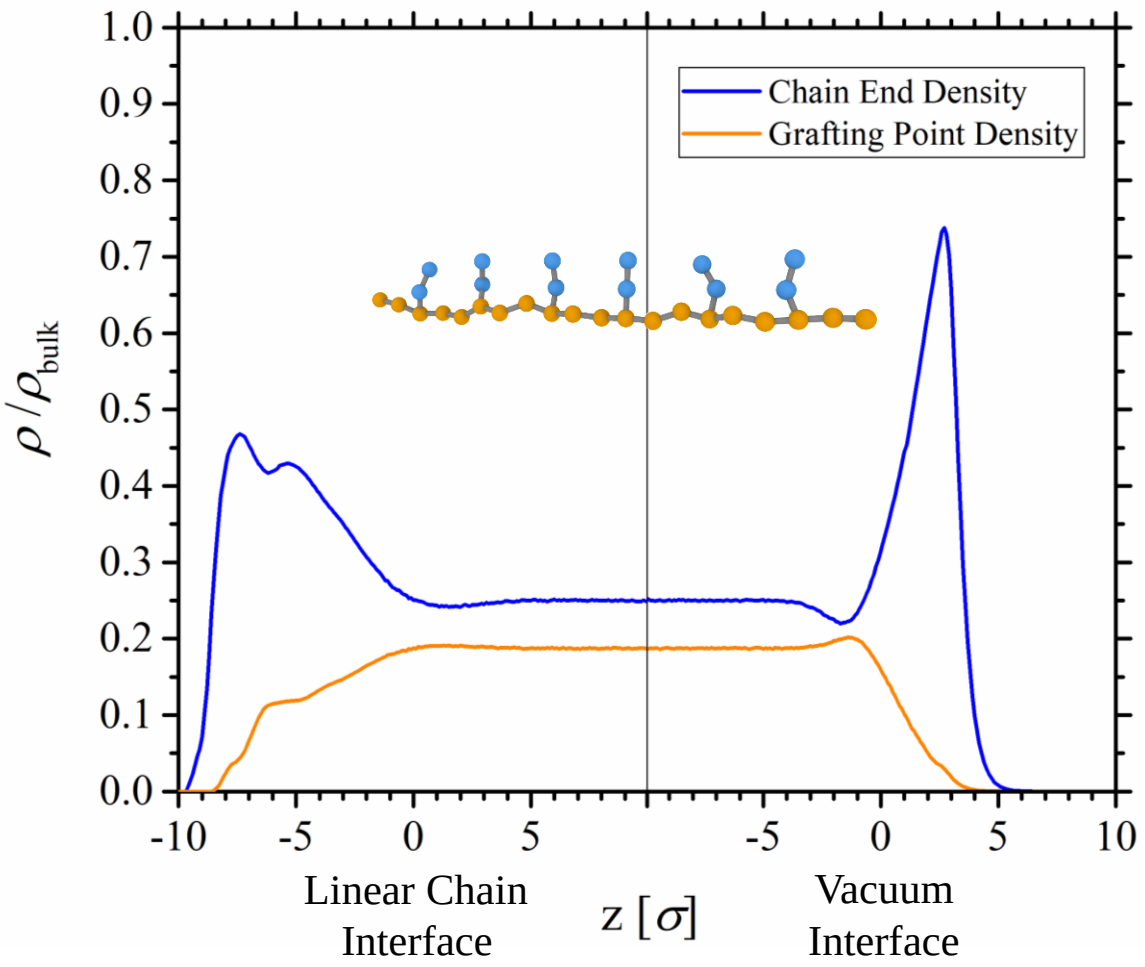
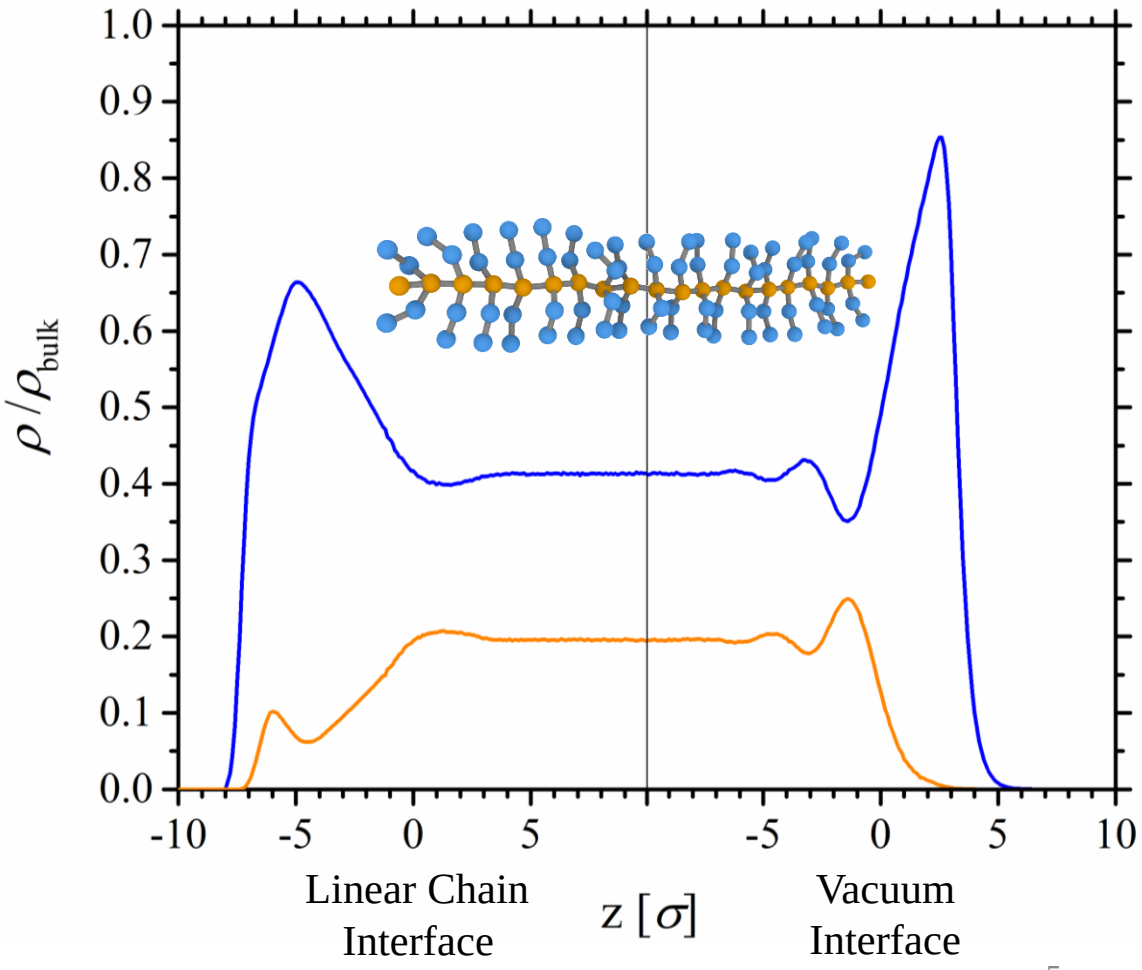
# Density of Chain Ends and Grafting Points

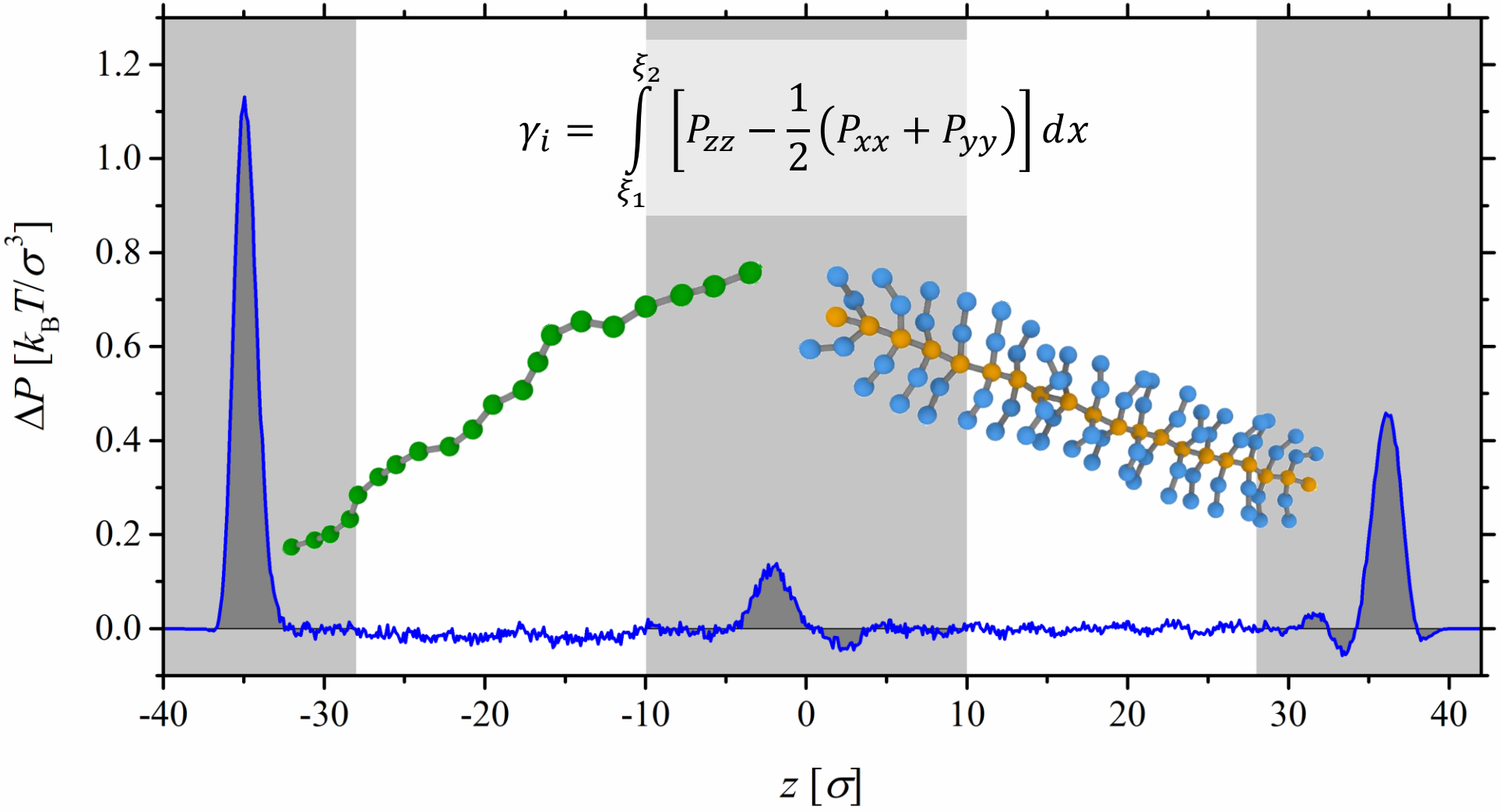
## Comb




## Bottlebrush

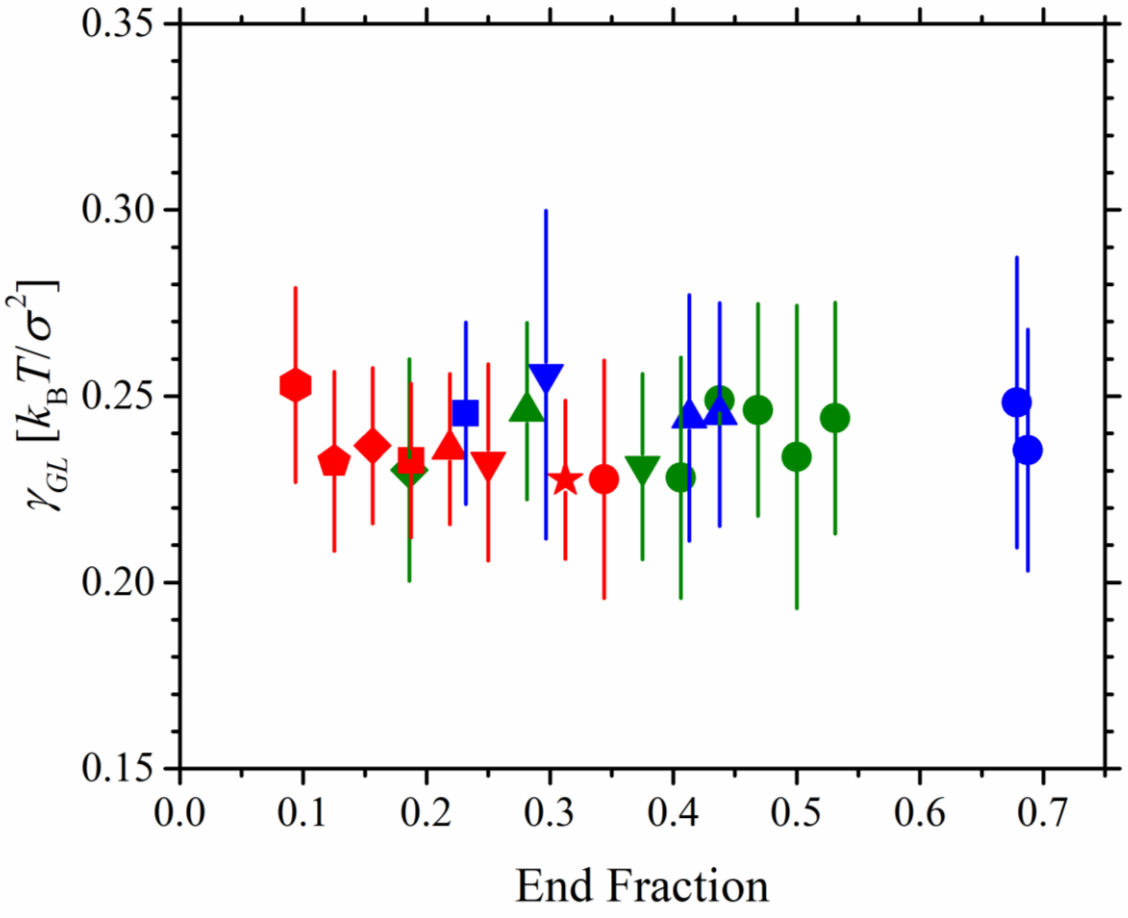


# Surface Tension

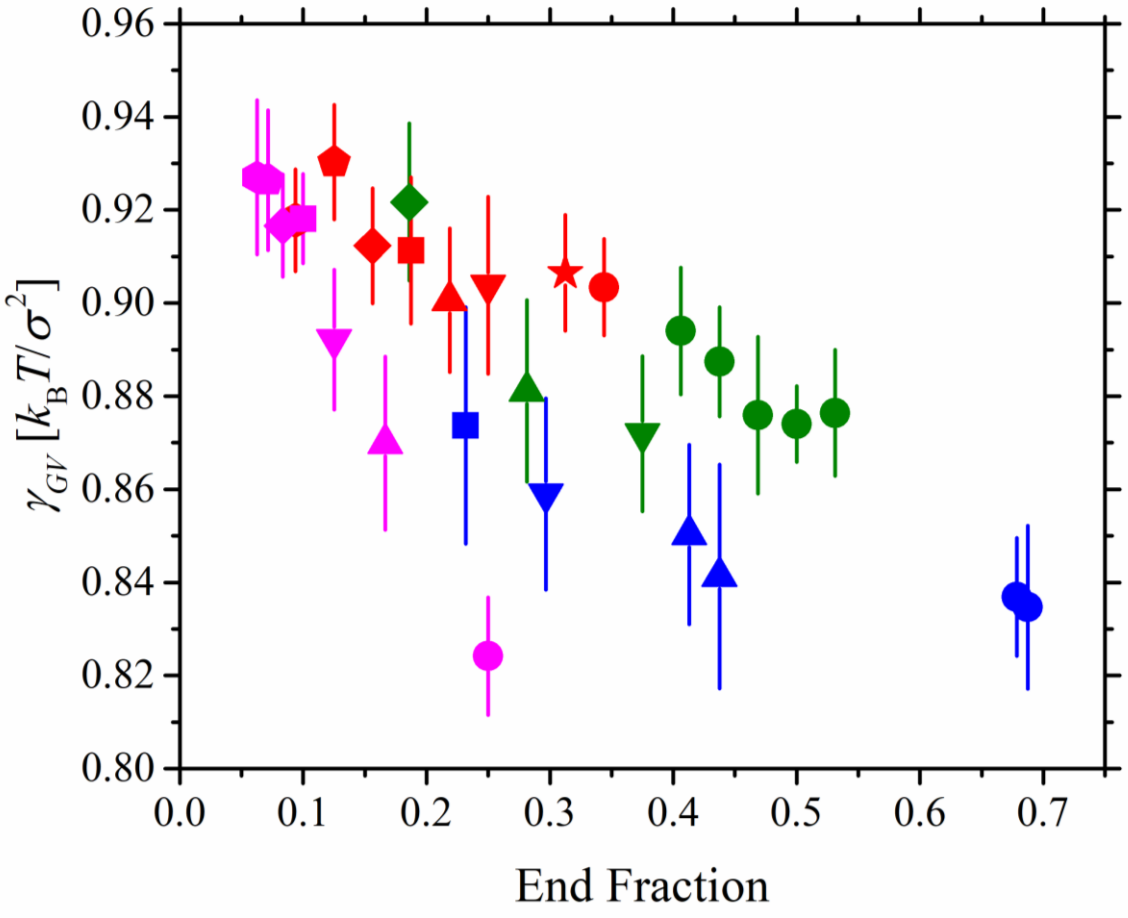


# Surface Tension

## Linear Chain Interface




## Vacuum Interface



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# Surface Tension

$$f_{be} = 2/N$$

$$f_{se} = \begin{cases} f_{gr} = \frac{n_{gr}}{N}, & n_g \geq 1 \\ 2f_{gr} = \frac{n_{gr}}{N}, & n_g = 0.5 \end{cases}$$

$$\gamma_{GV} = \gamma_\infty - \gamma_{be} f_{be} - \gamma_{se} f_{se} + \gamma_g f_{gr}$$

$$\boxed{\gamma_{GV} = \gamma_\infty - \gamma_{be} f_{be} - \Delta\gamma f_{se}}$$

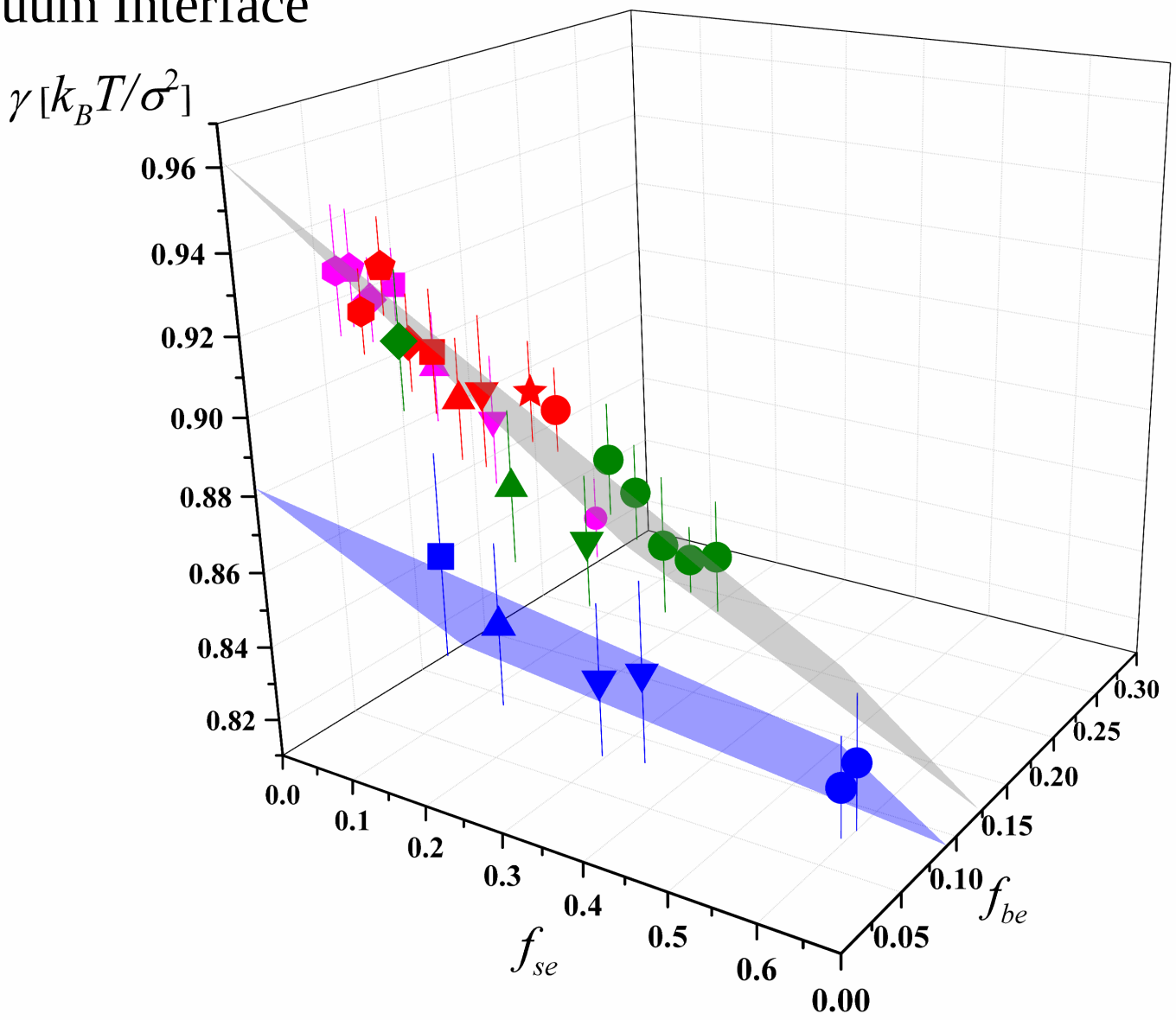
Fitting:

$\gamma_\infty = 0.96 k_B T/\sigma^2$
$\gamma_{be} = 0.55 k_B T/\sigma^2$
$\Delta\gamma = 0.12 k_B T/\sigma^2$

Fitting with $n_g = 0.5$,
fixing $\gamma_{be} = 0.55 k_B T/\sigma^2$:

$\gamma_\infty = 0.88 k_B T/\sigma^2$
$\Delta\gamma = 0.032 k_B T/\sigma^2$

Vacuum Interface



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## Collaborators

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