Effects of Star-Polymer Confirmations on Polymer Dynamics

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Introduction

Previous work from Starr Lab has shown that variations in star polymer architecture within polymer melts leads to altered dynamics. Specifically, in bulk systems, the glass transition temperature (T_g) of the system has been shown to be dependent on the number of arms (**ƒ**) and number of monomer arm beads (**m**). Additionally, it has been shown that increasing polymer-star interactions (**ε_{ps}**) leads to slower dynamics and higher **T_g**. We believe that one of the factors influencing **T_g** is the degree of interdigitation between the stars and the polymer matrix. We therefore modified the intramolecular star interactions to be purely repulsive to mimic the effect of having the arms spread deeper into the polymer matrix compared to previously studied attractive star systems.

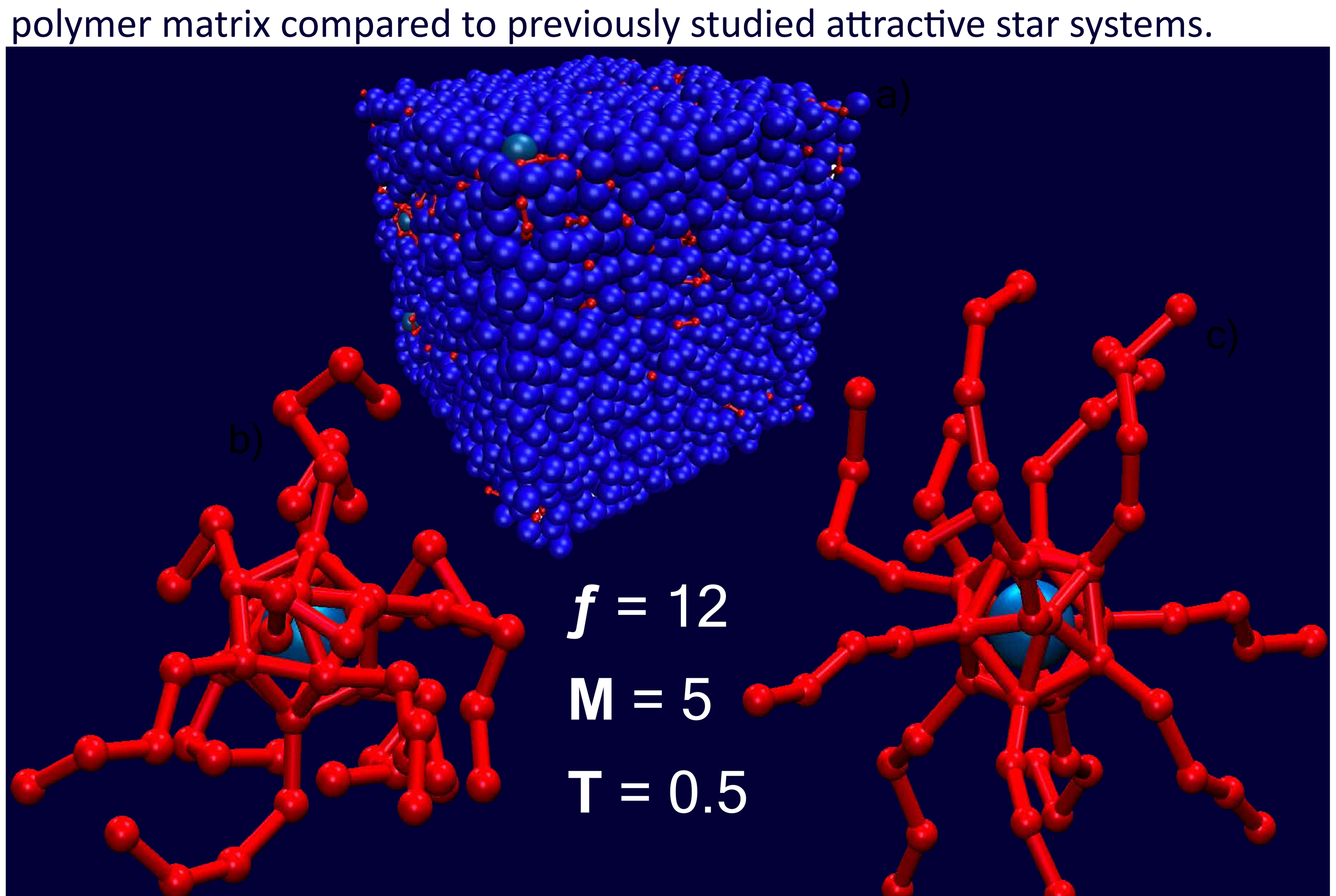


Fig. 1:
a) Polymer matrix (blue) and star polymer additive (red)
b) Confirmation due to attractive interactions
c) Confirmation due to repulsive interactions

Methods & Refrences

Simulation Protocols

- **Reduced units** - easily mapable to real units
- **Periodic boundary conditions** - uniform distribution of the polymers

Interactions

- **Bonded Polymers** - harmonic spring potential
- **All other interactions** - Lenard-Jones potential

Star Polymers

- ƒ arms
- **m** beads per arm
- One central core

Polymer Matrix

- 6000 monomer beads
- 600 chains

Parameters Studied

- **ε_{ps}** = 1.0, 1.2, 1.5, 1.7
- **ƒ** = 2, 3, 6, 12, 16
- **m** = 5, 10
- **T** = 0.425, 0.45, 0.475, 0.5, 0.525, 0.55, 0.6, 0.7, 0.8, 0.9, 1.0
- 330+ simulations

Program (s)

- Large Atomic/Molecular Massively parralel Simulator

Procedure

Simulation

- Equillibrate Systems
- Production Runs
- Sanity Check

Extracting Relaxation Time (τ)

- Calculate the incoherent part of the intermediate scattering function $F_{self}(q, t)$
- τ defined when $F_{self}(q,t) = 0.2$

$$F_{self}(q,t) = \frac{1}{N}\sum_{j=1}^{N}\langle e^{-i\mathbf{q}(\mathbf{r}_j(t)-\mathbf{r}_j(0))}\rangle$$

Extracting Glass Transition Temperature (T_g)

- Fit τ to the Vogel-Fulcher-Tammann (VFT) equation
- T_g defined to be the point where τ(t) = 10^4

$$\tau = \tau_0 e^{(DT_0/T-T_0)}$$

Data Analysis

- Sanity Check
- Discussions
- Litterature Comparison

Refrences

1) Fan, J., Emamy, H., Chremos, A., Douglas, J. F., & Starr, F. W. (2020). Dynamic heterogeneity and collective motion in star polymer melts. The Journal of Chemical Physics, 152(5), 054904. doi:10.1063/1.5135731
2) Hatanaka, T., Saito, T., Fukushima, T., Todo, H., Sugibayashi, K., Umehara, S., . . . Okamura, Y. (2019). Potential of biocompatible polymeric ultra-thin films, nanosheets, as topical and transdermal drug delivery devices. International Journal of Pharmaceutics, 565, 41-49. doi:10.1016/j.ijpharm.2019.04.059

Conclusions & Results

Star polymers in "fluffly" confirmations tend to significantly alter dynamics by increasing relaxation times and glass transition temperatures of the systems

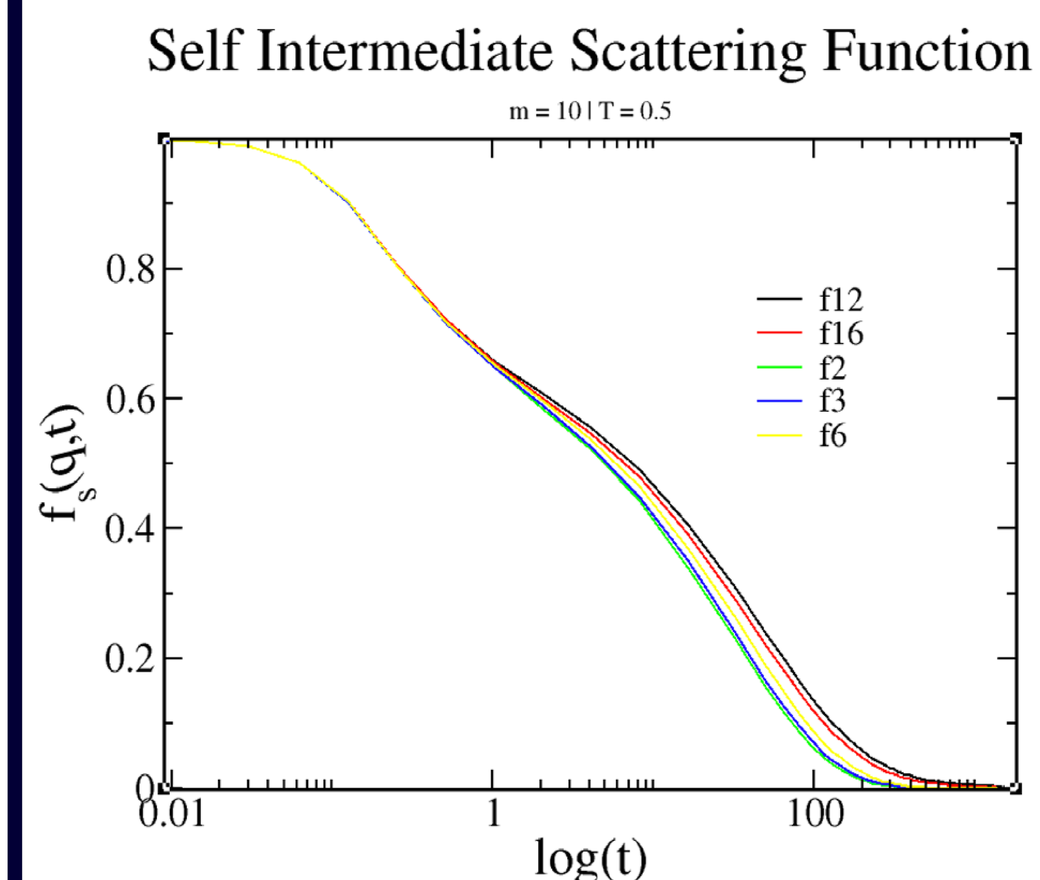


Fig. 3: The self part of the intermediate scattering function displaying a range of ƒ for m = 10 and T = 0.5 at ε_{ps} = 1.0. We observe a non linear trend in dynamics for different functionalities. Specifically, we observe the fastest dynamics for linear like star polymers (ƒ = 2) and slowest for ƒ = 12 as shown in

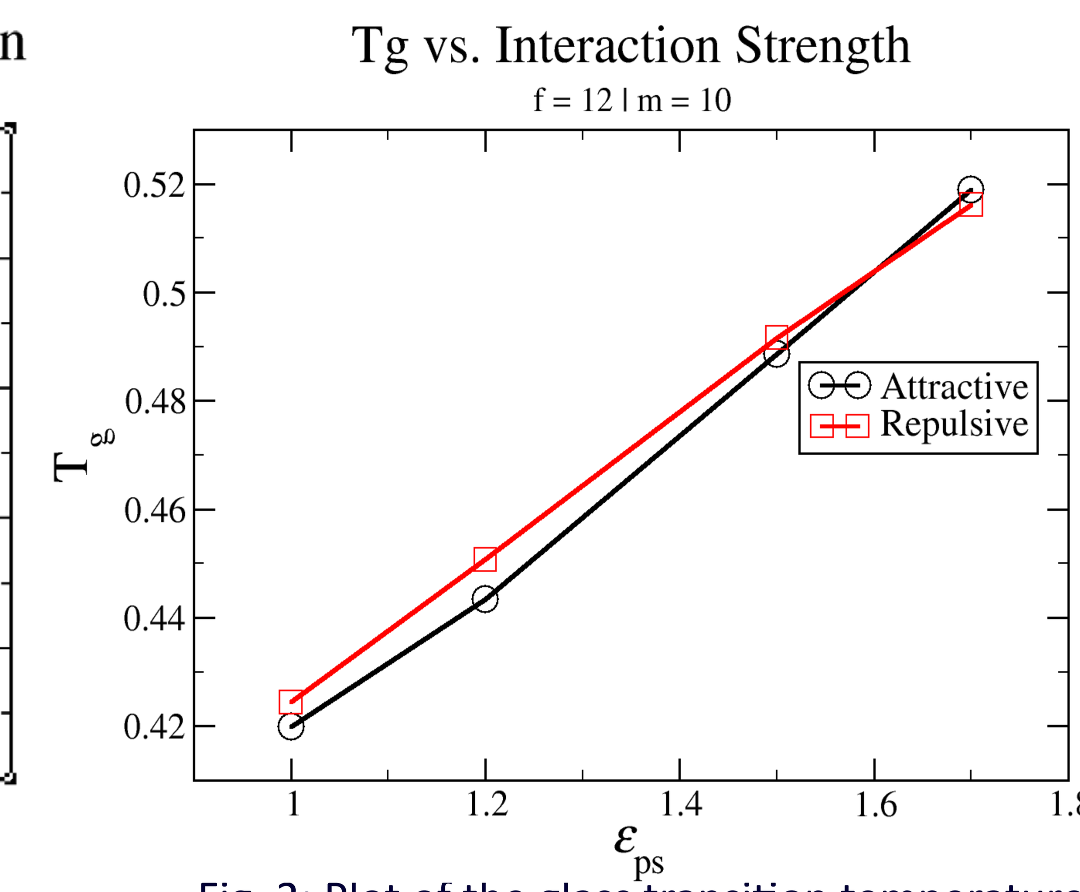


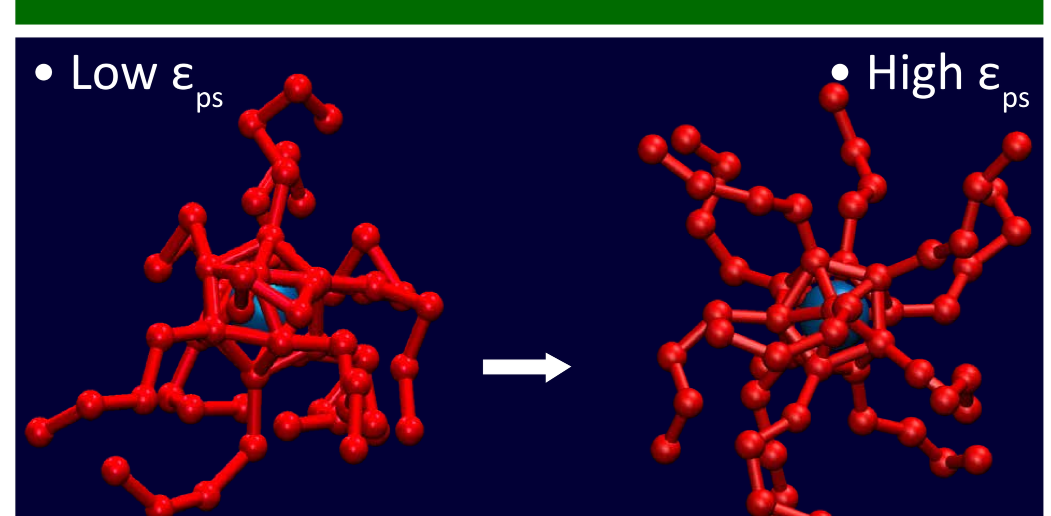
Fig. 2: Plot of the glass transition temperature T_g as defined in the methods section versus polymer-star interaction strength ε_{ps}. For low ε_{ps} we observe a significant difference in T_g between attractive and repulsive stars. Likewise, for large ε_{ps} we observe a significant convergence of T_g.

Previous Work Summarized

- Glass transition temperatures follow non-linear trends with functionality
- Moderate functionalities (**ƒ ≈ 12**) have the largest effect on T_g
- Believed to be caused by "maximizing surface area" available to polymers
- Increasing ε_{ps} leads to fluffier stars

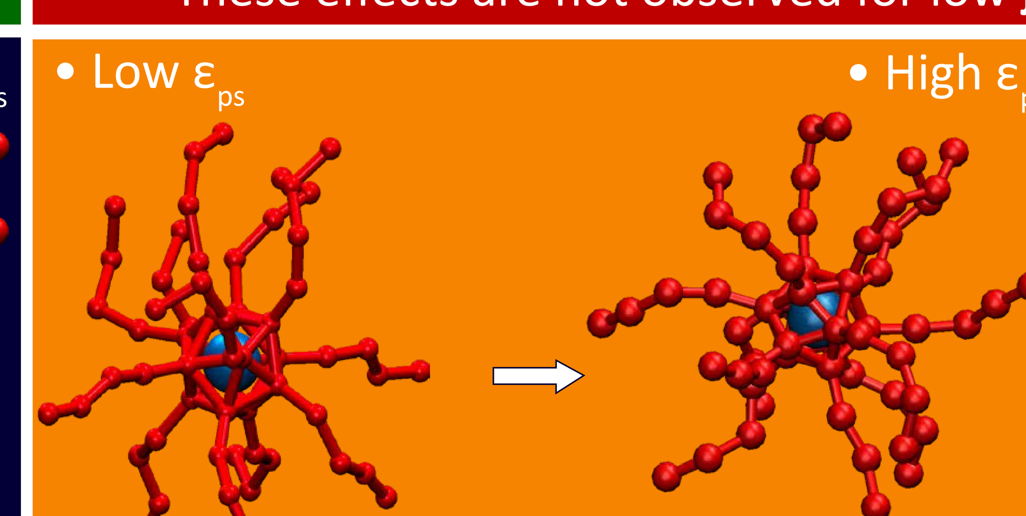
New Findings

- Stars assuming fluffy confirmation states have larger T_g
- Difference in T_g diminishes as ε_{ps} increases
- At large ε_{ps} fluffiness is fully saturated
- Star confirmation is responsible for this difference in T_g
- These effects are not observed for low **ƒ**



Repulsive Star

- Initially we observe a condenced confirmation, but as ε_{ps} increases, it assumes a fluffy confirmation



Attractive Star

- We observe a fluffy confirmation in both cases even as ε_{ps} increases indicating a saturated system

Future Work & Acknowledgments

Transitioning to the thin-film systems

- **Bulk data -** Reference point
- Addition of a fixed substrate
- Film dynamics are more complex

Analysis

- **g(r)-** develop working radial distribution density profiles for film systems
- **Radius of gyration -** Quantify Fluffiness

Acknowledgments

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Bulk System
Red = Polymer Melt

Film System
Green = Substrate | Blue = Star Arms
Yellow = Star Core | Red = Polymer M.