Different Approaches to Understanding the Effect of Additives on Polymer Relaxation

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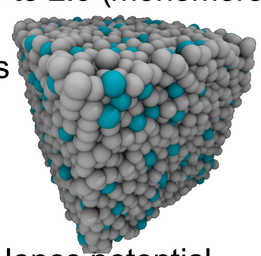
Introduction

When cooling polymers, rather than sharply transitioning from solid to liquid, these materials experience a rapid cooldown called the “glass transition”. In this range of temperatures, monomers (segments of polymer) experience “cooperative relaxation”; that is, they facilitate each other’s movement in the material.

The glass transition is still an ongoing field of study, but by examining different timescales of particle movement, we can build a holistic picture of the phenomenon[1]. Here, we simulate a polymer with small additives and measure the effects of the additives on the glass transition and cooperative relaxation.

Methods

- We use LAMMPS to model the polymer as 6000 spherical monomers.
- We use spherical additives with diameter σ from 0.6 to 2.0 (monomers have σ = 1.0).
- Adjacent monomers are bonded by a harmonic potential, and all non-bonded particles interact through a Lennard-Jones potential.
  - Particle size is the equilibrium distance for particles interacting through the Lennard-Jones potential.
- We examine temperatures from T = 0.45 (close to glass transition) to T = 1.4 (far from glass transition).

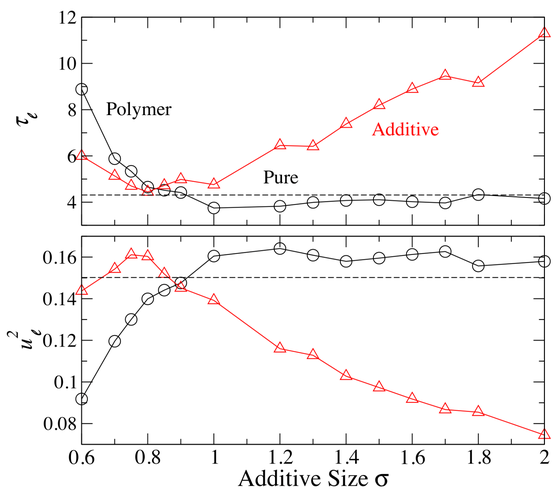


The Localization Model for Relaxation

- We first examine τ and $1/\langle u^2 \rangle$, corresponding to the slowness of dynamics on long and short timescales respectively.
- τ and $1/\langle u^2 \rangle$ can be connected through the Localization Model (LM):

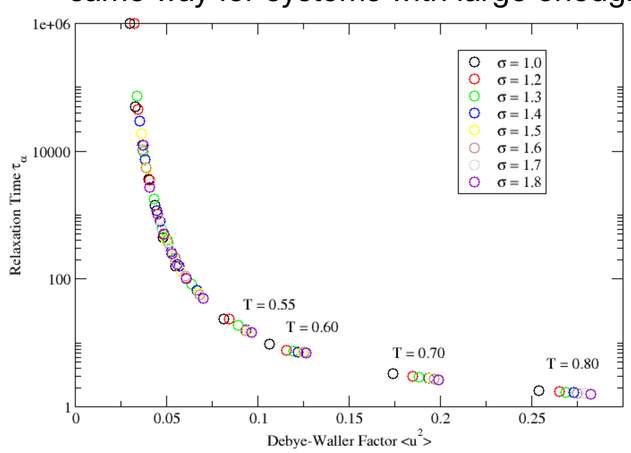
$$\tau = \tau_\ell \, e^{(u_\ell^2/\langle u^2 \rangle)^{3/2}-1}$$

- Each σ has different fit parameters τ_ℓ and u_ℓ^2; the equation describes the relation of τ and $1/\langle u^2 \rangle$ across temperatures.



- LM parameters as a function of additive size σ.
- Polymer data are black circles, additive data are red triangles, and the pure (no additive system) is the dashed lines.

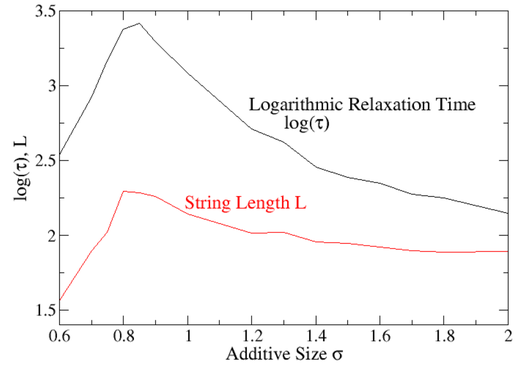
- Notably, both polymer parameters plateau for σ≥1.0 (additives larger than monomers).
  - This means that these two types of relaxation are related in the same way for systems with large enough additives.



- Here we see a different way of looking at the large-particle LM plateau.
- For σ≥1.0, all τ and $\langle u^2 \rangle$ fall on one curve.
- Changing σ is like shifting temperature T.

Strings and Relaxation

- Besides relating τ to $1/\langle u^2 \rangle$ through the LM, we can also relate τ to the “string length” L of the most mobile particles in the system.



This plot illustrates the similar variation with σ of $\log(\tau)$ for the system and string length L.

- “Strings” are formed when particles move together in the same direction.
  - If particle A moves one unit in time t, particle B would move one unit in the same time t, such that particle B ends up where particle A used to be.[2]

Conclusions

- We have shown that τ and $1/\langle u^2 \rangle$ can be related across temperatures for any σ through the LM.
  - And when σ≥1.0, these measures of relaxation are related in the same way for all σ.
- We have also shown that $\log(\tau)$ and string length L have qualitatively similar dependence on σ.
- Overall, since τ, $1/\langle u^2 \rangle$, and L are so connected, it isn’t useful to prioritize one measure as the most fundamental to dynamics.
  - Instead, we must value and further study the connections between these three measures.

1. Pazmiño Betancourt, B. A., Hanakata, P. Z., Starr, F. W., & Douglas, J. F. (2015). Quantitative relations between cooperative motion, emergent elasticity, and free volume in model glass-forming polymer materials. *PNAS* 112(10), 2966–2971.
2. M. Aichele, Y. Gebremichael, F. W. Starr, J. Baschnagel, and S. C. Glotzer (2003). Polymer-specific effects of bulk relaxation and stringlike correlated motion in the dynamics of a supercooled polymer melt. *J. Chem. Phys*. 119, 5290–5304.