



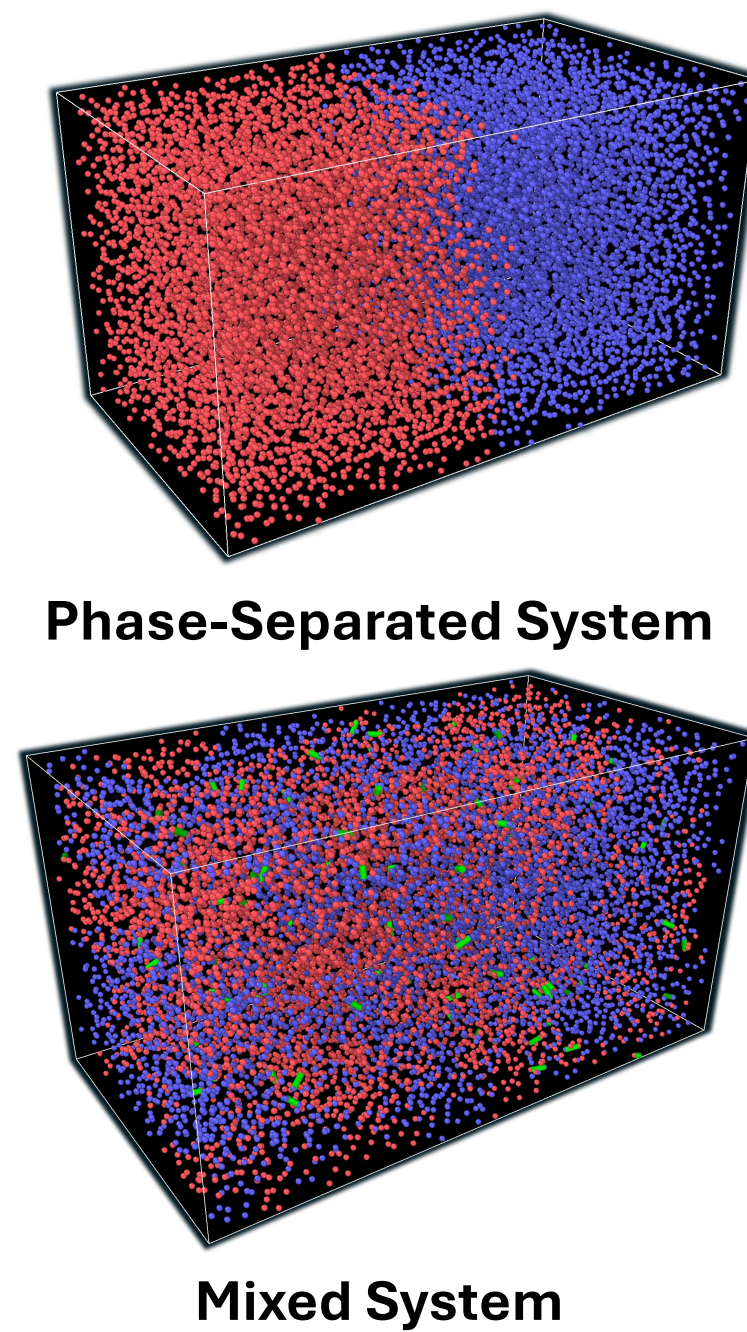
# Dynamic Crosslinks as a Method to Improve Polymer Compatibilization in Mixed-Plastics Recycling



Evelyn Grandfield, Max Hanrahan, Francis Starr  
Wesleyan University Physics Department

## Polymer Phase Behavior in Recycled Materials

Poor miscibility in polymer blends is a major obstacle for the recycling of mixed-waste plastics. The recycling process requires intensive plastic-waste sorting because phase separation in inhomogeneous polymer blends weakens the tensile strength of recycled materials.<sup>1</sup> Adding crosslinks is one path toward compatibilization. As opposed to the static crosslinks often suggested in literature, dynamic crosslinks are advantageous because they can break and reform over time, which facilitates large-scale rearrangement in the material.<sup>2</sup> This project conducts molecular simulations to study the effect of dynamic crosslinks on polymer miscibility. Our goal is to use dynamic crosslinks to reduce the surface tension between the interface of the two polymers. The resulting material will be the most robust over multiple recycling processes if polymers can repeatedly mix and demix. Therefore, it is desirable to increase physical miscibility without significantly reducing the temperature of phase separation.

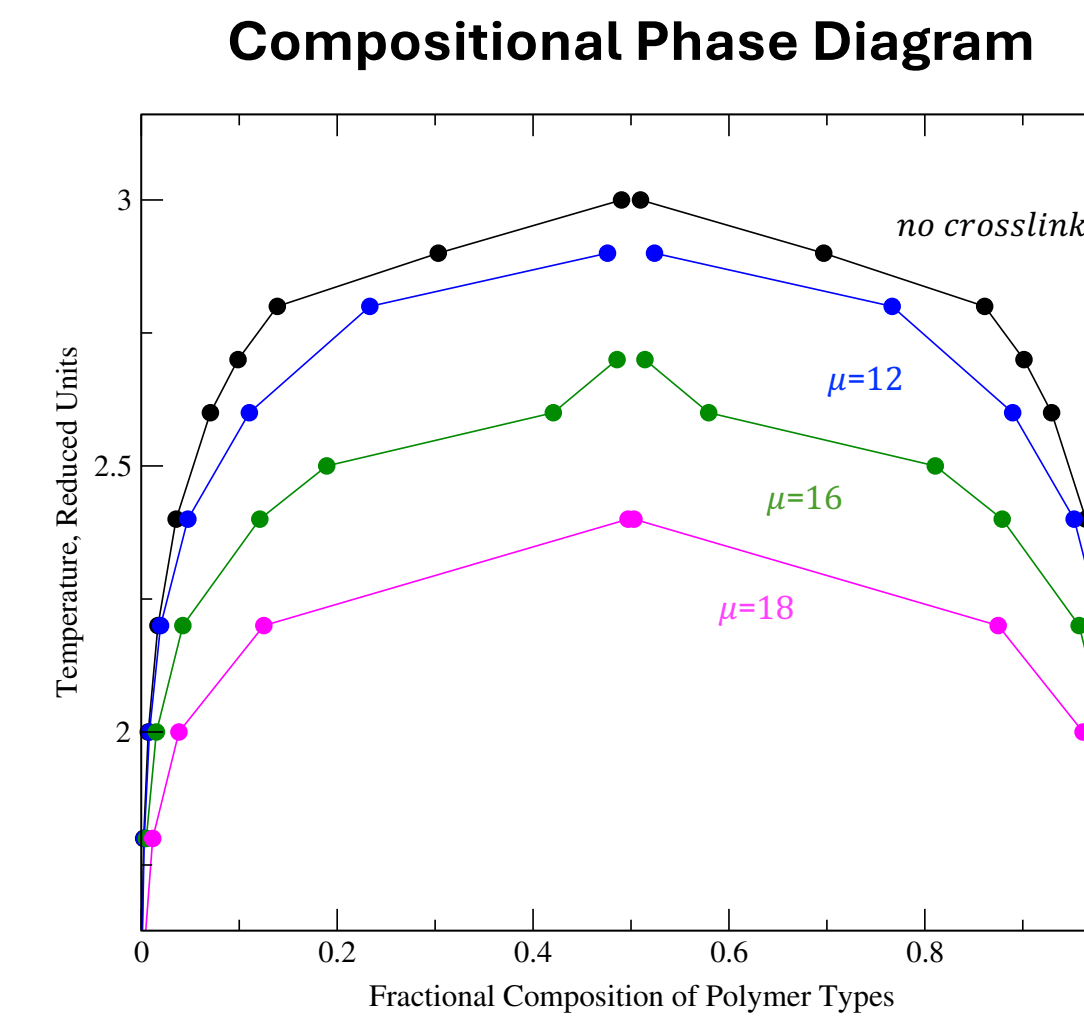


Phase-Separated System

Mixed System

## Critical Temperature for Phase Separation

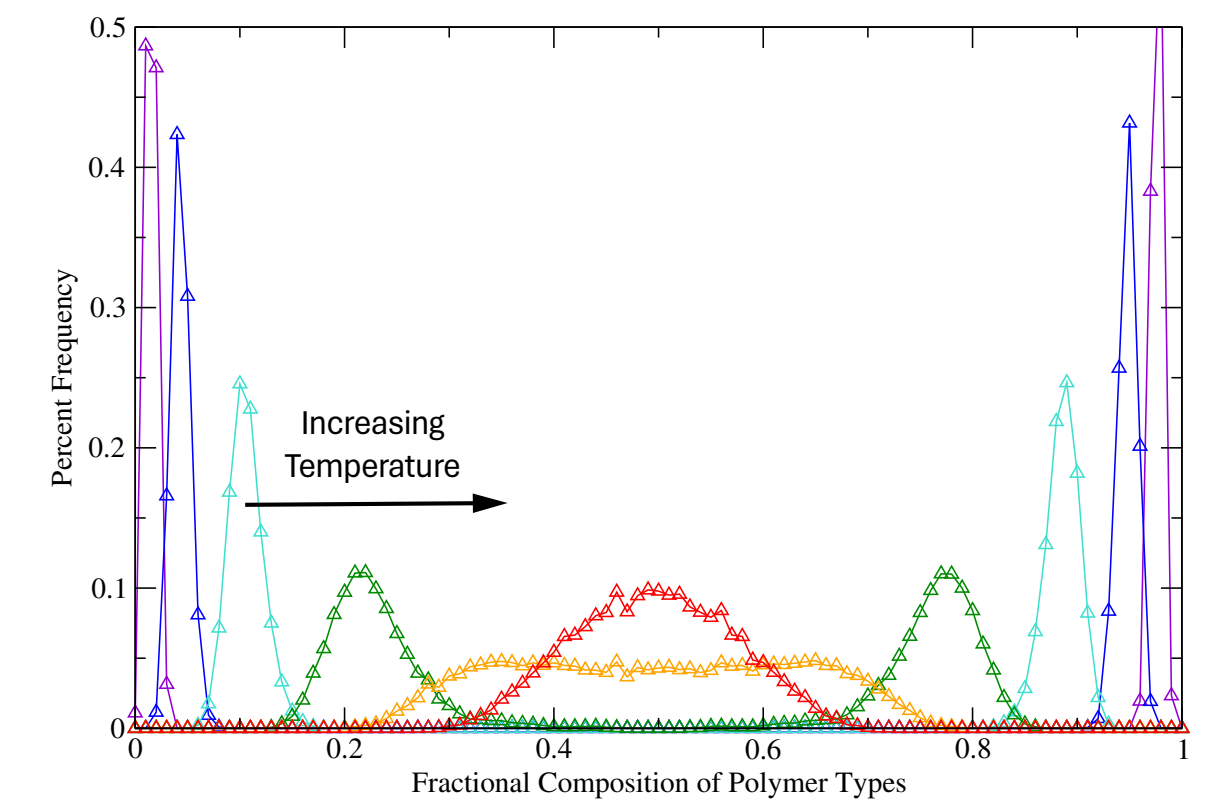
Polymer blends will be mixed above a critical temperature,  $T_C$ . To determine the compositional phase diagram, we conduct simulations using the semi-grand ensemble, where polymers probabilistically swap types based on energy differences. At the critical temperature, the composition of polymer types will fluctuate around 50/50. We find that dynamic bonds reduce the critical temperature, and the magnitude of this effect depends on the chemical potential,  $\mu$ .



To identify the critical temperature more precisely, we examine the probability distribution of polymer-type composition. Our system is part of the Ising universality class, wherein it is established that the probability distribution at the critical temperature will be bimodal with a ratio  $X \sim 2.54$  between local maxima and minima.<sup>4</sup> At each chemical potential,  $T_C$  must exist in the temperature range where  $X$  crosses the threshold value.

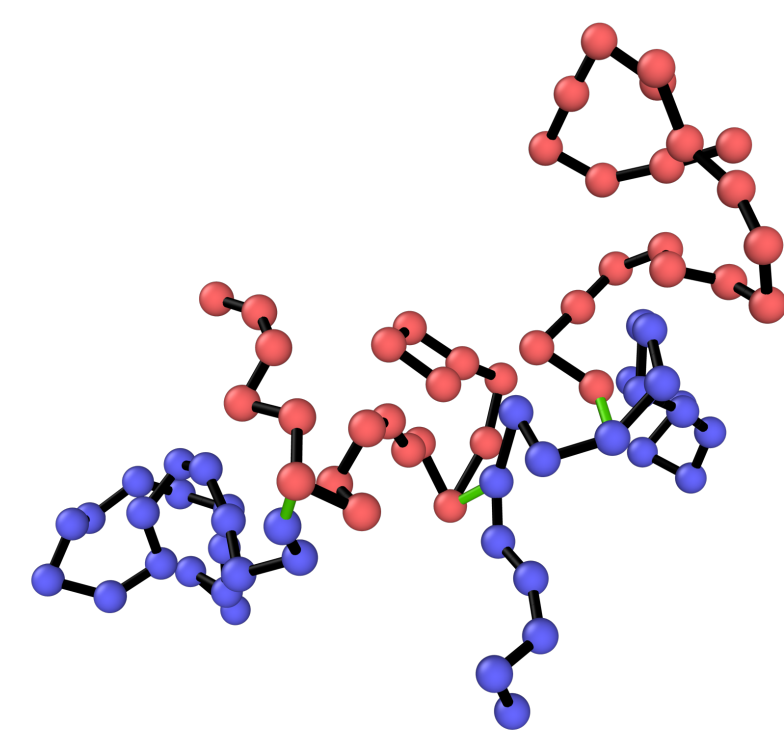
System	$T_C$ Range	Average Dynamic Bonds in $T_C$ Range
no bonds	2.9< $T$ <3.0	0
$\mu=12$	2.8< $T$ <2.9	88.98
$\mu=16$	2.6< $T$ <2.7	335.06
$\mu=18$	2.2< $T$ <2.3	545.66

Probability Distribution for  $\mu = 16$



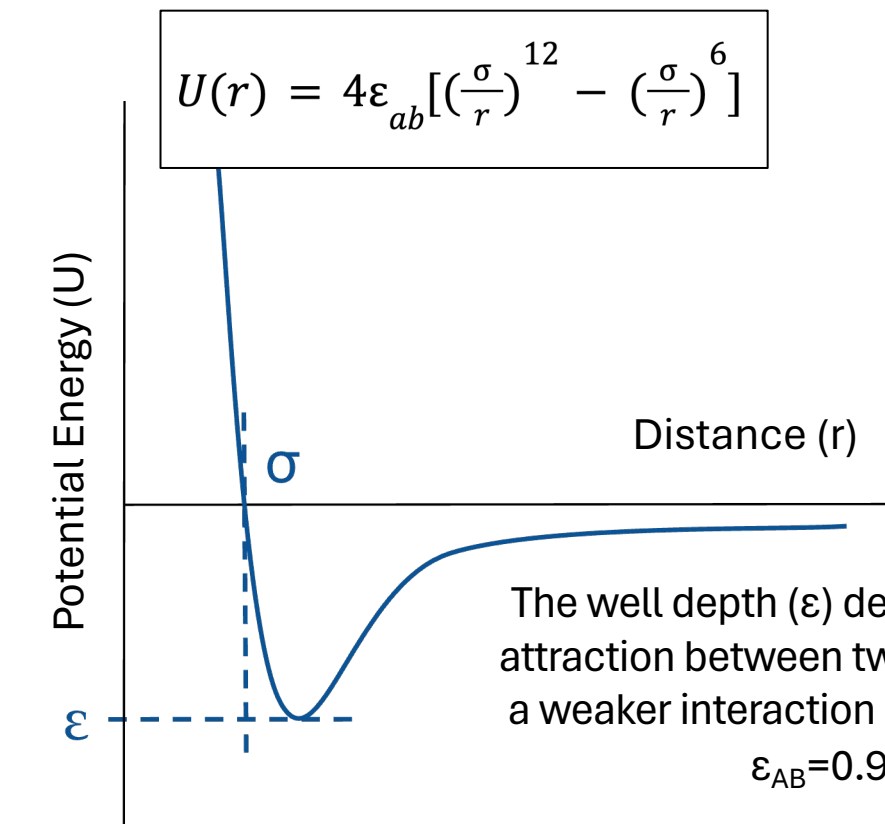
## Mathematical and Computational Methods

This project uses the molecular dynamics software package LAMMPS to simulate a blend of 800 polymers with two types, A and B. Each polymer is represented as a coarse-grained chain, 19 monomers in length. The Lennard Jones (LJ) potential determines the interaction energy between non-bonded monomer pairs at a distance  $r$ . Bonded monomer pairs interact via the finitely extensible, non-linear elastic (FENE) potential.



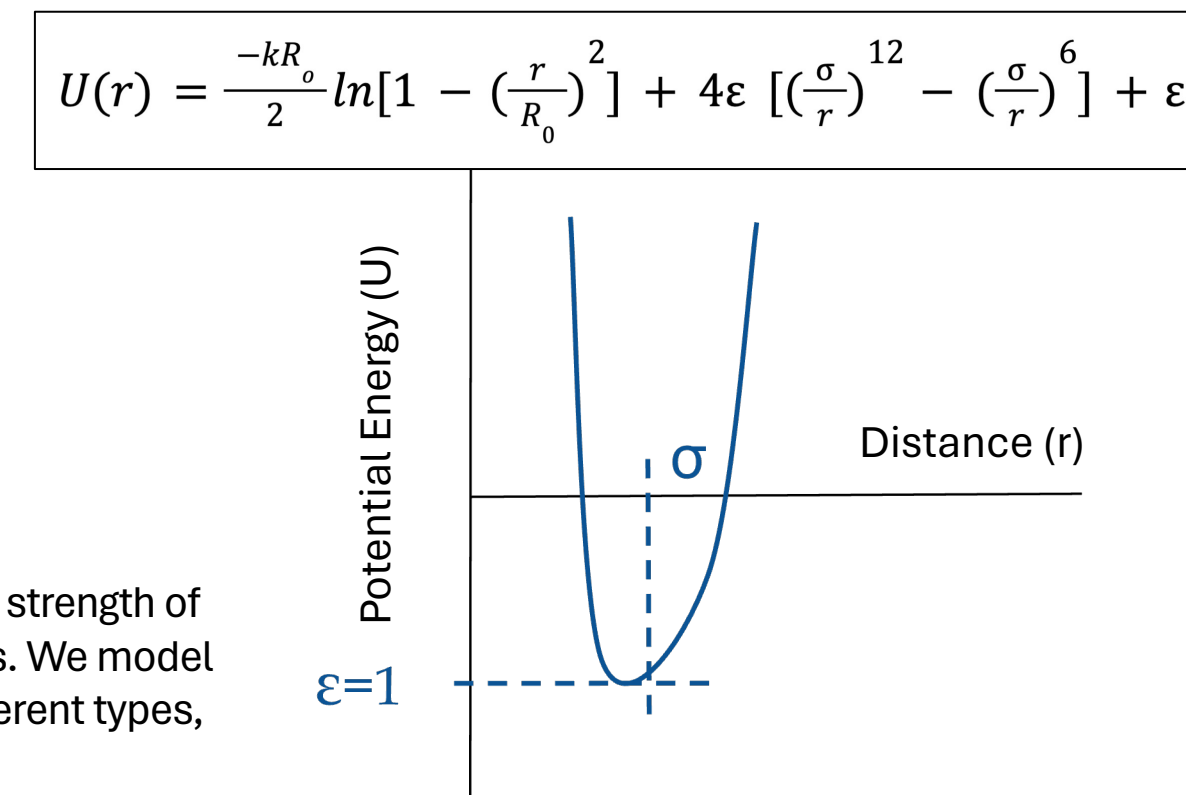
Dynamically Bonded Copolymer

LJ Potential



The well depth ( $\epsilon$ ) determines the strength of attraction between two monomers. We model a weaker interaction between different types,  $\epsilon_{AB}=0.9\epsilon_{AA}=0.9\epsilon_{BB}$

FENE Potential



Dynamic bonds form and break stochastically using an algorithm that satisfies detailed balance, a necessary condition for thermodynamic equilibrium. Detailed balance requires that the probability to be in each thermodynamic state stands in equal ratio to the probabilities to transition between states. Mathematically,  $\frac{P(s_{bond})}{P(s_{open})} = \frac{P(s_{open} \rightarrow s_{bond})}{P(s_{bond} \rightarrow s_{open})} = e^{(\mu - \Delta U)/kT}$ , where  $\Delta U$  is the energy difference between bonded and non-bonded states.<sup>3</sup> Increasing chemical potential  $\mu$  increases the propensity to form bonds. This project simulates exclusively inter-type crosslinks between A and B polymers. The unit system is reduced such that temperature is measured relative to interaction strength,  $T = \frac{\epsilon_{AA}}{k}$ , and can be scaled for any polymer system.

## Quantifying Miscibility with Surface Tension

The surface tension,  $\gamma$ , quantifies how much force is needed to distort the interface between two polymer types. Systems can spontaneously mix when  $\gamma = 0$ . Our goal is to find the combination of parameters that reduces the surface tension in systems cooler than the critical temperature. We evaluate the surface tension of the mixture using two methods developed by Irving-Kirkwood (1949) and Gloor (2005)<sup>5</sup> and find close agreement.

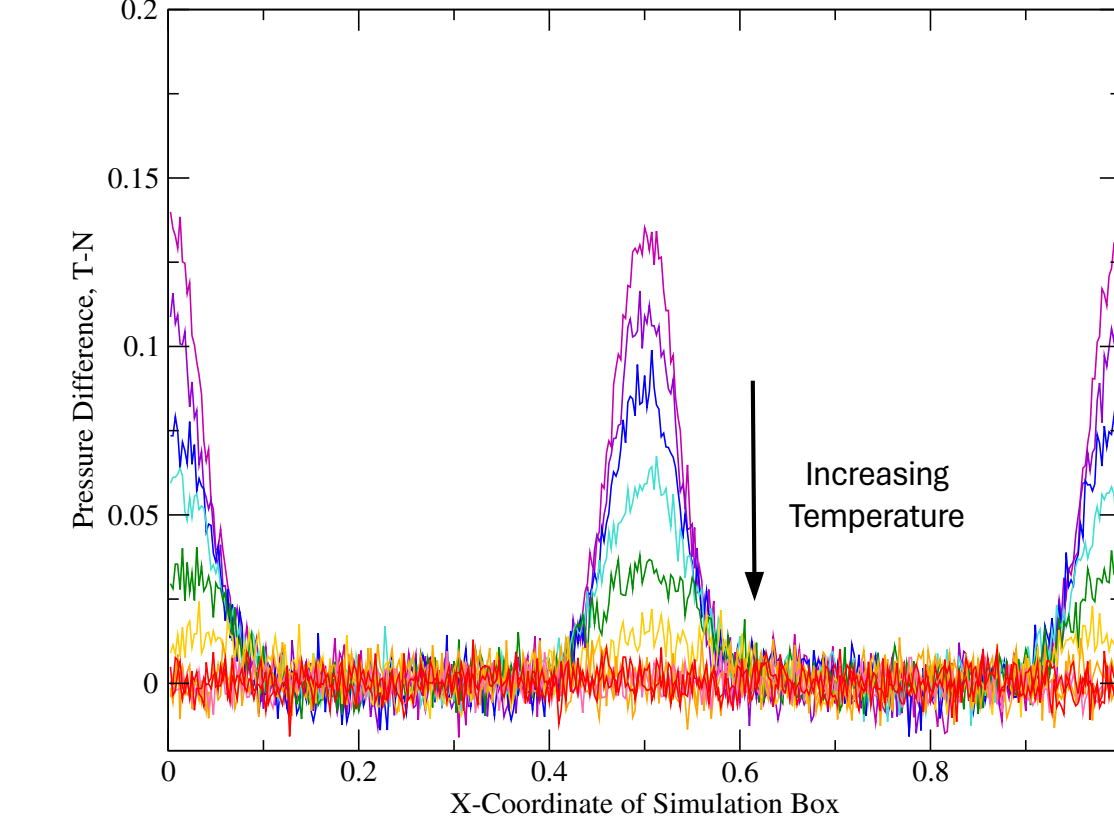
Method 1:  $\gamma_{IK} = \int (P_T - P_N) dx$

The Irving-Kirkwood surface tension is defined as the integral of the difference between normal and tangential components of the pressure tensor over the tangential direction of the simulation box. The interface is in the y-z plane, so x tangential. Energy differences cause atoms near the interface to experience larger tangential pressure, which increases the surface tension. The cumulative integral creates a surface tension profile across the simulation box, which is flat at  $\gamma = 0$  in mixed systems.

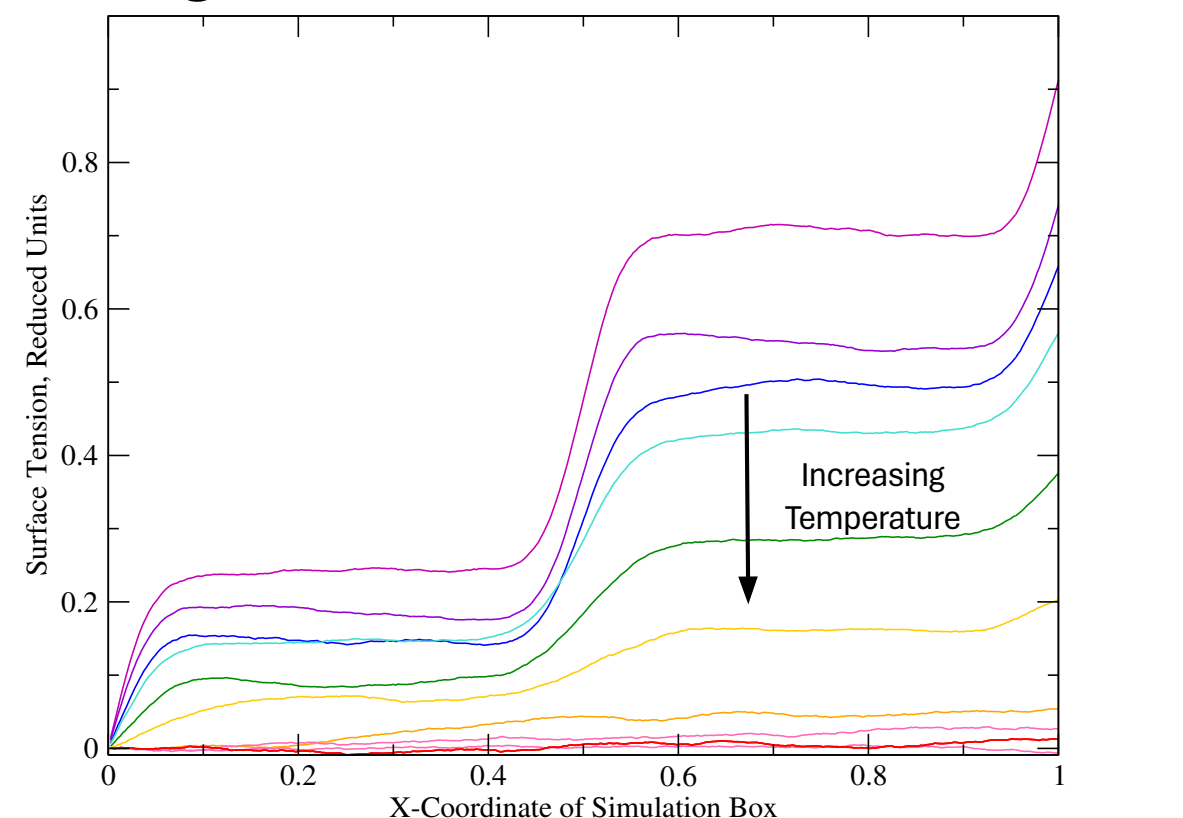
Method 2:  $\gamma_G = -\frac{kT}{\Delta A} \ln \langle e^{-\frac{\Delta E}{kT}} \rangle$

The method of Gloor perturbs the area of the simulation box,  $A$ , and measures the resulting change in energy,  $\Delta E$ . Phase-separated systems will be more resistant to stretching, which corresponds to a larger change in free energy and a larger surface tension.

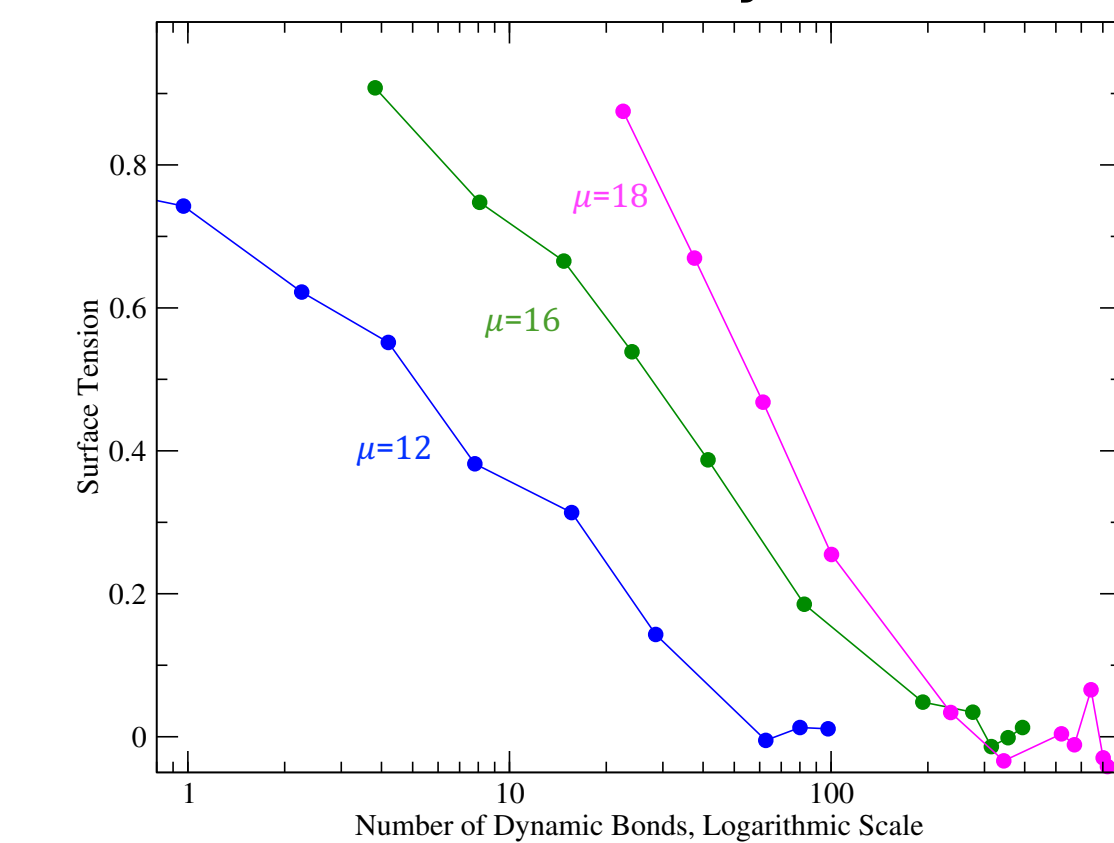
Irving-Kirkwood Pressure Profiles



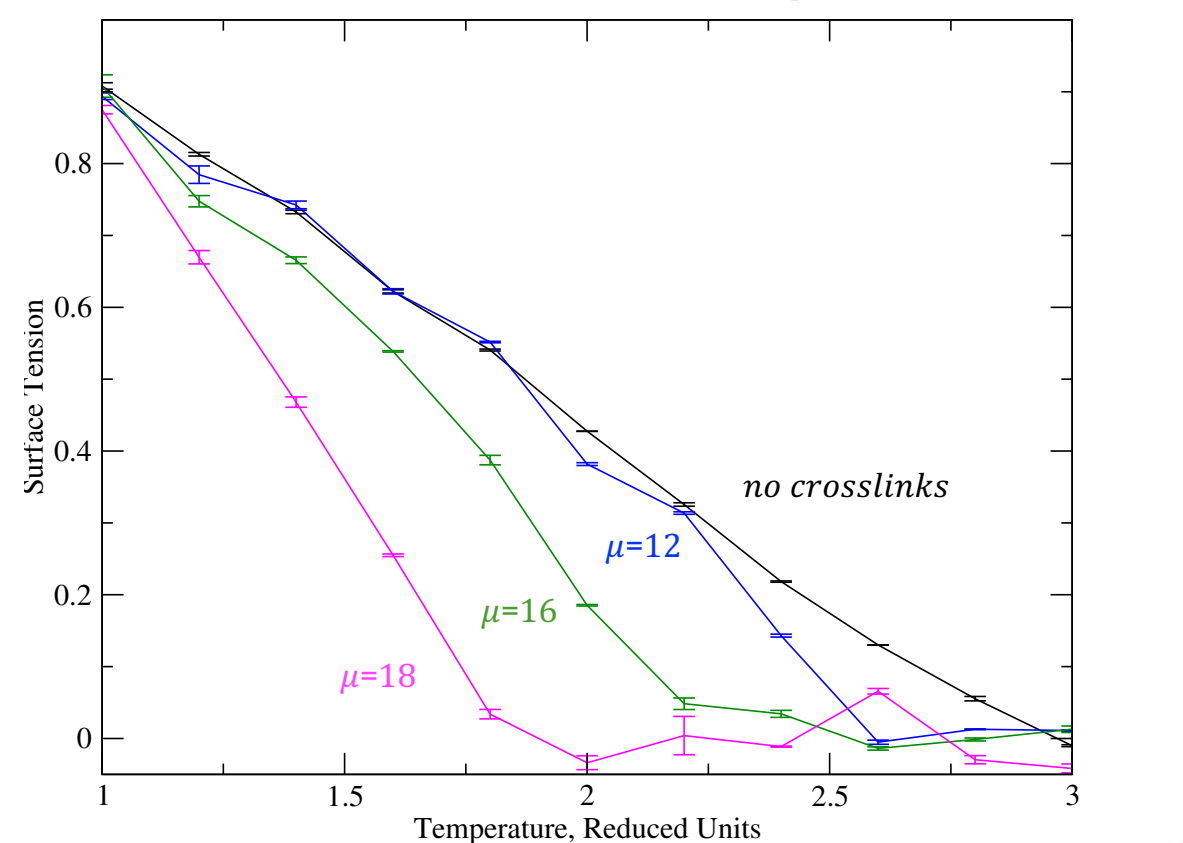
Irving-Kirkwood Surface Tension Profile



Surface Tension vs. Dynamic Bonds



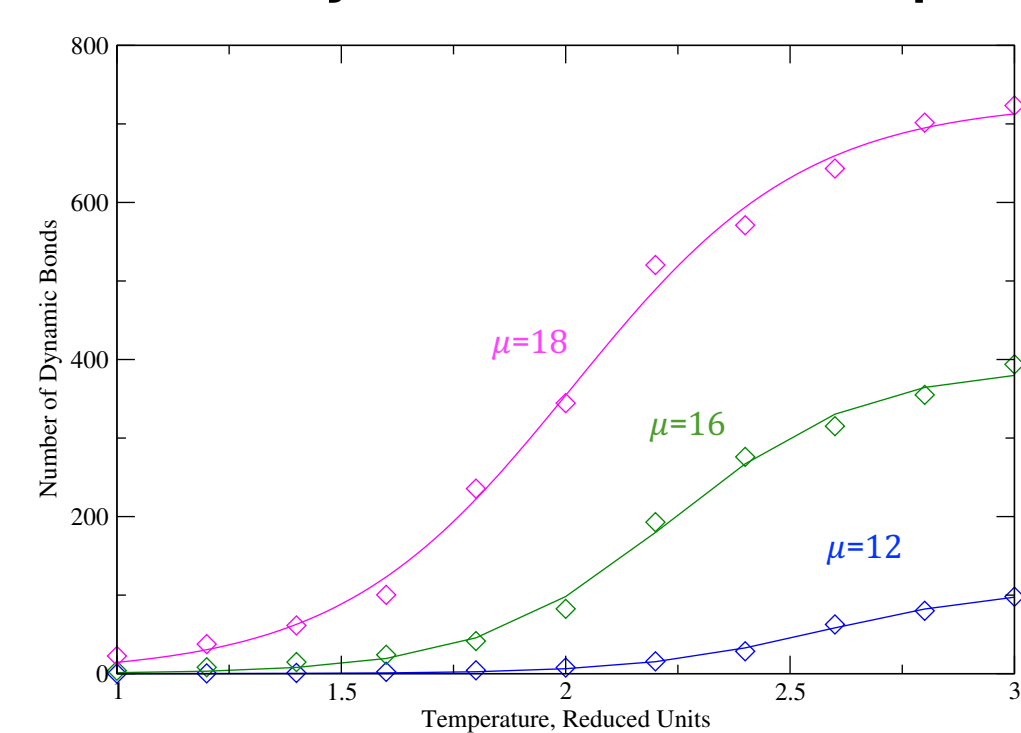
Surface Tension vs. Temperature



## Thermodynamic Properties of Dynamically Crosslinked Systems

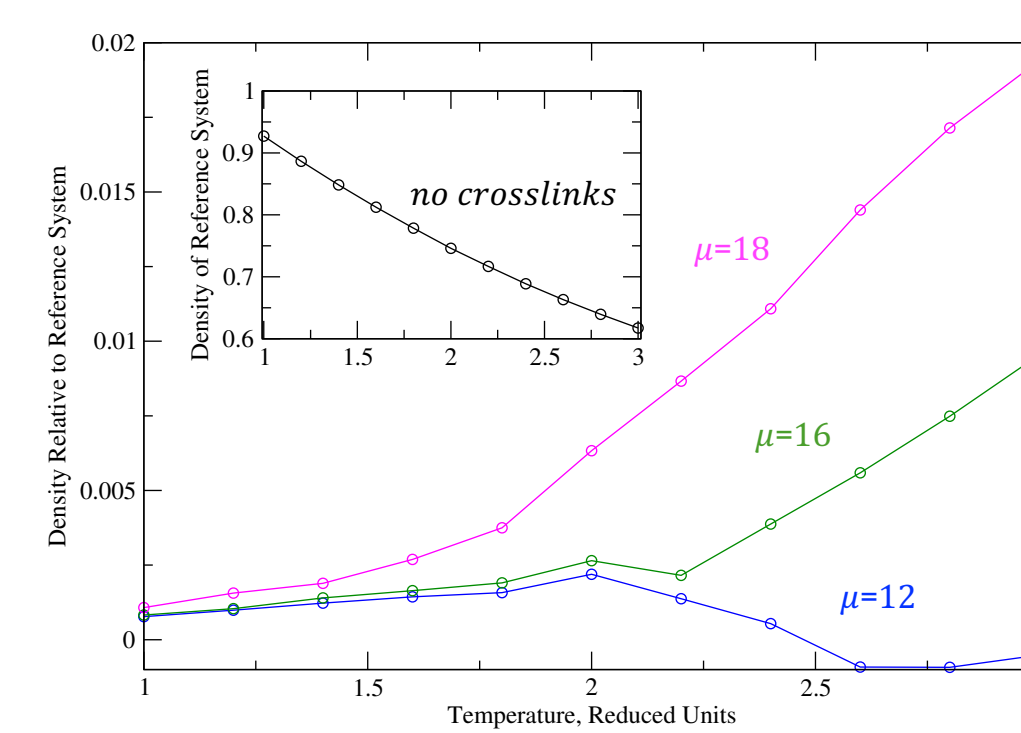
We simulated polymer blends at fixed pressure over a range of chemical potentials and temperatures. At equilibrium, all relevant properties fluctuate around stable averages.

Number of Dynamic Bonds vs. Temperature



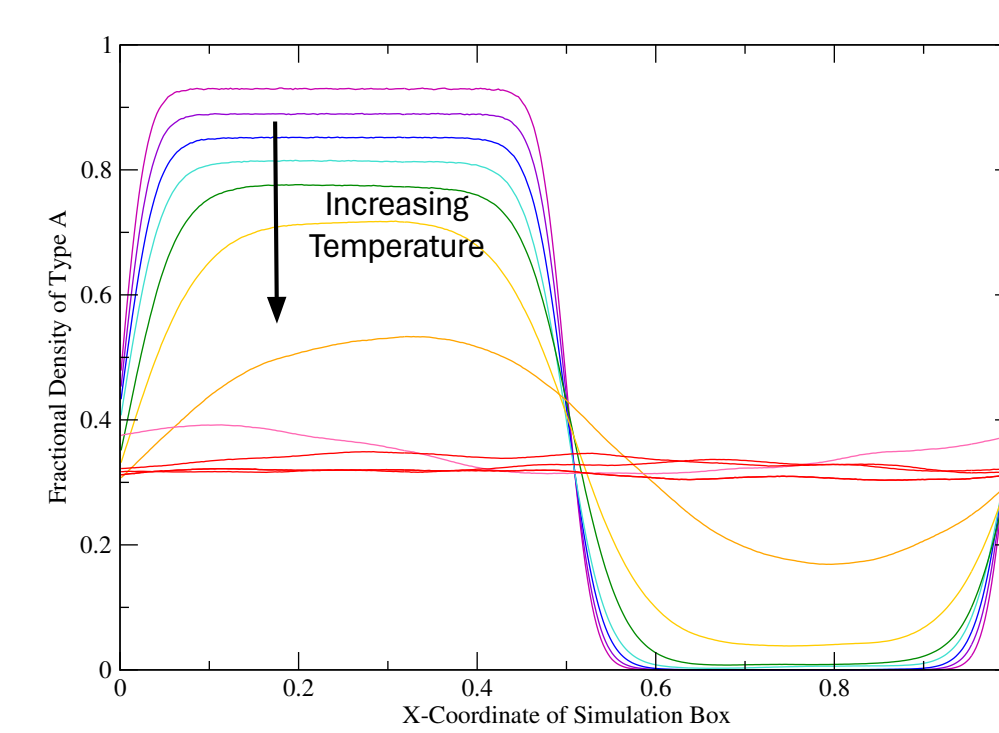
The number of dynamic bonds increases with chemical potential and temperature. The increase is steepest close to the critical temperature.

Density vs. Temperature



Equilibrium density decreases with temperature. Systems with dynamic bonds deviate from the reference system at higher temperatures and chemical potentials because bonds decrease the equilibrium distance between atoms.

Density Profile of Type A, for  $\mu = 16$



At low temperatures, type A polymers will exist at high density on one side of the simulation box and low density on the other. As temperature increases, A-type polymers become evenly distributed and have flat density profiles.

## Conclusion

This project confirms that the presence of dynamic bonds enhances compatibilization in polymer blends. Miscibility, as measured by surface tension, varies differentially with temperature at various chemical potentials. The current analysis is limited to dynamic bonds that form exclusively between A and B polymer types. In the future, we expect that dynamic bonds between polymers of the same type will reduce surface tension without a significant decrease in critical temperature from the reference system. This project produces a guideline for a range in which compatibilization is possible in a system with chain length 19 and interaction strength  $\epsilon_{AB}=0.9\epsilon_{AA}$ . We also hope to expand this analysis to determine a wider range of parameters for compatibilization.

## References

- Goring, P. & Priestly, R. (2023). "Polymer Recycling and Upcycling: Recent Developments toward a Circular Economy." *Journal of the American Chemical Society*, 3(10). doi:10.1021/jacsau.3c00544
  - Clarke, R. et al (2022). "Dynamic Crosslinking Compatibilizes Immiscible Mixed Plastics." *Nature* 616. doi:10.1038/s41586-023-05858-3
  - Allen & Tildesley (2017). "Computer Simulation of Liquids," *Oxford Press*.
  - Tsypin, M. & Blöte, H. (2000). "Probability distribution of the order parameter for the three-dimensional Ising-model universality class." *Physical Review*, 62(1). doi:10.1103/PhysRevE.62.73
  - Gloor, J. (2005). "Test-area simulation method for the direct determination of the interfacial tension of systems with continuous or discontinuous potentials." *J. Chem Phys*, 123(13). doi:10.1063/1.2038827
- And a huge thank you for the help of our collaborators Sanat Kumar and Rahul Karmakar.