

Supporting Information: Local dynamics and failure of inhomogeneous polymer networks

Ziyu Ye,[†] Han Zhang,[‡] and Robert A. Riggleman^{*,‡}

[†]*Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA*

[‡]*Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA*

E-mail: rriggle@seas.upenn.edu

Calculation of the Stress

To calculate the stress in our simulations, we employ the virial expression for stress tensor where the α, β components of the stress tensor are given by $\tau_{\alpha,\beta} = \frac{1}{V} \sum_i r_{i,\alpha} f_{i,\beta}$, where $r_{i,\alpha}$ and $f_{i,\alpha}$ are the $\alpha \in \{x, y, z\}$ components of the position and force of particle i , respectively. For the total stress, the sum is taken over all particles, while when we break it into the rubbery and glassy components, the sum is restricted to the monomers of the rubbery and glassy components. To account for the differences in volume occupied by the rubbery and glassy domains, the volume prefactor is scaled by f_g and $(1 - f_g)$, respectively.

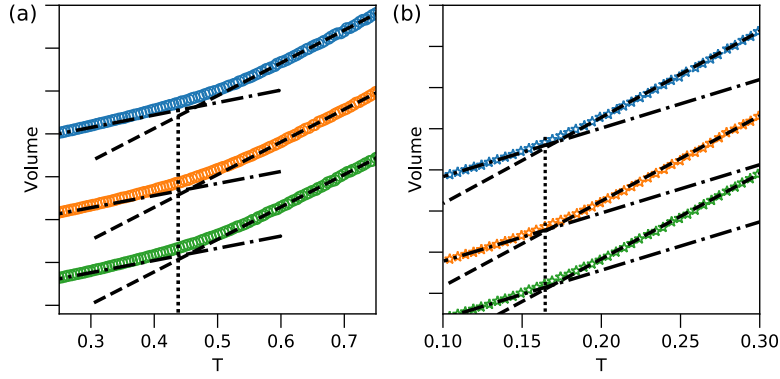


Figure S1: Data used to determine T_g for pure networks of $N = 5, 10,$ and 20 for the high T_g (left) and low T_g (right) networks.

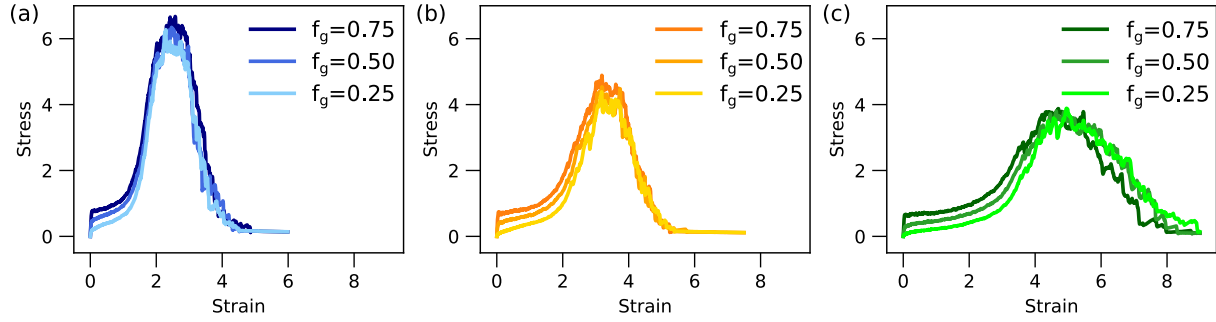


Figure S2: Data from Figure 7a replotted to show the slight shift in the onset of strain hardening. From left to right, we have $N = 5, 10,$ and 20 .

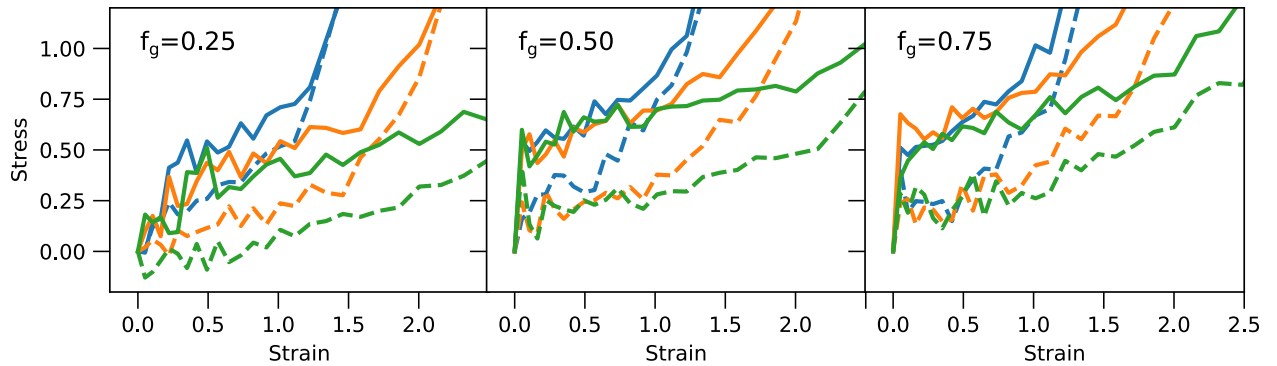


Figure S3: Same as Figure 8 main text, but zoomed into the low stress region to more clearly view the small-strain response of the rubbery and glassy domains.

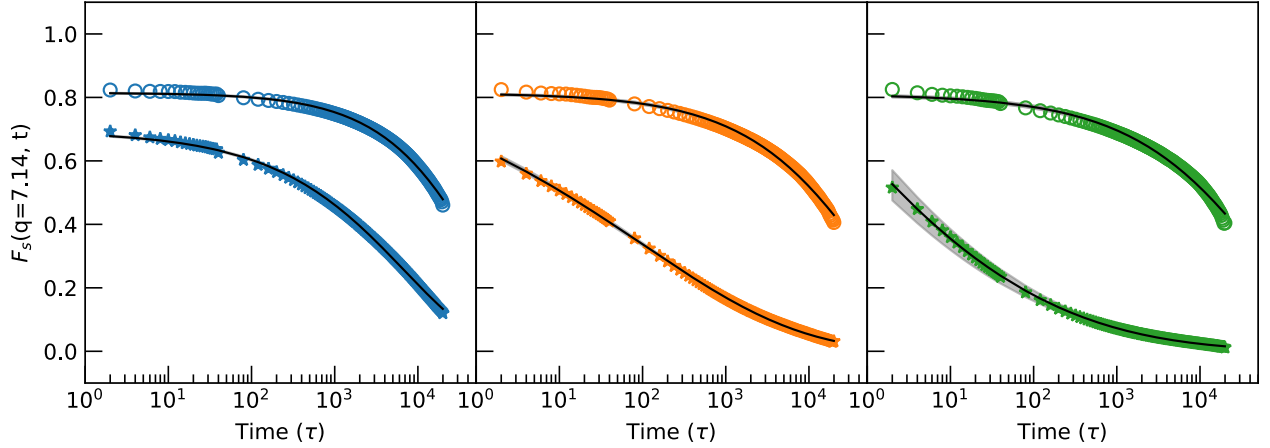


Figure S4: Relaxation of the intermediate scattering function for the $N = 5, 10$ and 20 systems (left to right) in the glassy (open circles) and rubbery (stars) domains. Solid black lines are fits to the KWW fitting function, and the shaded grey domains represent the 95% confidence interval on the fitting function.

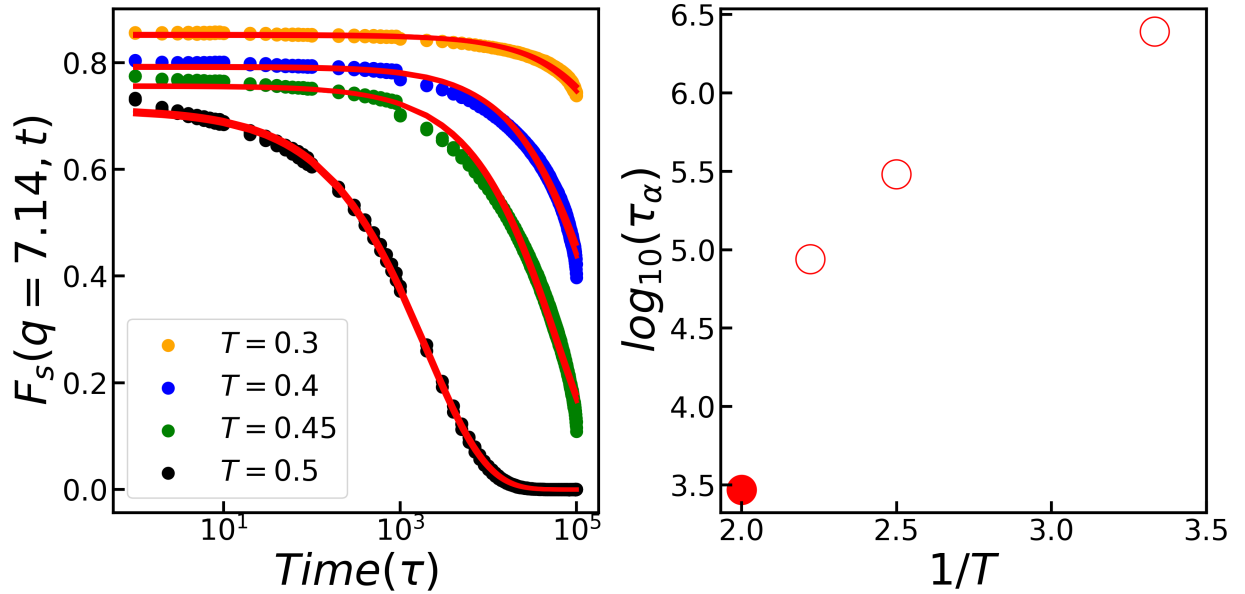


Figure S5: Left plot: Self-part of the intermediate scattering function ($F_s(q = 7.14, t)$) for the pure high- T_g (glassy) $N = 10$ network at various temperatures, with red curves representing KWW function fittings. Three individual configurations are generated at each temperature. Right plot: Extracted τ_α values as a function of $1/T$, averaged over three configurations. The same approach to extract τ_α is used as described in the main text. For the highest temperature ($T = 0.5$) systems, the $F_s(q = 7.14, t)$ curves fully decay. While for the rest systems, the $F_s(q = 7.14, t)$ curves do not fully decay. Open circles are used to represent $\tau_\alpha(T)$ values extrapolated from the KWW fittings.