

# Supplementary Information

---

## Simulation methodology

We perform classical molecular dynamics simulations of freestanding polymer films comprised of unentangled 20-bead chains. Nonbonded beads interact via a 12-6 Lennard Jones potential,  $E_{LJ} = 4\epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right]$  where  $\epsilon$  and  $\sigma$  are characteristic energy and lengthscale parameters, respectively, and where interactions are truncated and shifted to zero at a distance of  $2.5\sigma$ . Both  $\epsilon$  and  $\sigma$  are set to unity for all simulations performed here. Bonded beads interact *via* the Finitely Extensible Nonlinear Elastic (FENE) potential,  $E_{FENE} = -0.5KR_0^2 \ln \left[ 1 - (r/R_0)^2 \right] + E_{LJ} + \epsilon$ , where  $K = 30$  is an inelastic spring constant and  $R_0 = 1.5$  is a maximum bond length. This model, modified from the earlier work of Kremer and Grest, has previously been employed to study polymer glass formation, both in the bulk and under confinement.

Simulations of the 1h thickness film and interface-free system are taken from a previously published study<sup>1</sup>. For other systems, four independent trials are performed. Initial random configurations are produced with the polymer chains in a freestanding film morphology generated by PACKMOL<sup>2</sup>. The freestanding film morphology is maintained by employing periodic boundary conditions in all directions and performing simulations in the NVT ensemble. The systems are initially equilibrated at a temperature of  $T = 1.5$  for a time of  $10,000\tau$ . The systems are then quenched from  $1.5T$  to  $0.3T$  at a rate of  $10^{-6}T/\tau$ . Configurations saved regularly during the quench are then subject to an additional equilibration of at least  $100\tau_\alpha$ , where  $\tau_\alpha$  is the structural relaxation time as determined from the self-part of the intermediate scattering function. Data collection runs are then performed from these resulting configurations.

Simulations are performed in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package<sup>3</sup>. Simulations employ a RESPA time stepping scheme, with a nonbonded timestep of  $0.01\tau$  and a bonded timestep of  $0.0025\tau$ . Temperature is controlled via the Nose-Hoover thermostat, as implemented in LAMMPS, with a damping parameter of  $2\tau$ . The net linear momentum is set to zero every  $1\tau$  to prevent any possible buildup of momentum.

We quantify relaxation dynamics via the self-part of the intermediate scattering function,

$$F_s(\mathbf{k}, t) = \frac{1}{N} \sum_j^N \left\langle \exp \left[ -i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \right] \right\rangle \quad \backslash * \text{MERGEFORMAT (1)}$$

where  $\mathbf{k}$  is the wavevector,  $N$  is the number of particles, and  $\mathbf{r}_j(t)$  is the position of particle  $j$  at time  $t$ . We employ a wavenumber  $k = 7.07$ , comparable to the first peak in the structure factor data, with data averaged over multiple randomly chosen wavevectors  $\mathbf{k}$  corresponding to this wavenumber. The structural relaxation time  $\tau_\alpha$  is defined as the time at which  $F_s(k, t)$  decays by 80%, with a stretched exponential fit to the data employed for interpolation and data smoothing.

In order to quantify dynamics locally within the film, we sort particles into spatial bins of thickness  $0.875\sigma$  as a function of distance from the interface, with the interface defined as the point at which the density is equal to half that in the film center. For the purpose of determining interfacial position, the density is calculated for bins with thickness of less than  $0.16\sigma$ . We first identify the film center by identifying the point halfway between the two positions at which the density is equal to 0.5; the central film density is then determined based upon the average over a region at least  $1\sigma$  thick centered on this point. A precise position for the interface is determined by performing a linear interpolation using the two consecutive bins with values on either side of half of the central density. We denote the position of the interface as  $z = 0$  and average all  $z$ -dependent data over the two interfaces.

## References

1. R. J. Lang and D. S. Simmons, *Macromolecules*, 2013.
2. L. Martinez, R. Andrade, E. G. Birgin, and J. M. Martinez, *Journal of Computational Chemistry*, 2009, **30**, 2157–2164.
3. S. J. Plimpton, *J. Comp. Phys.*, 1995, **117**, 1–19.