

**SI Appendix: Why We Need to Look Beyond the Glass
Transition Temperature to Characterize the Dynamics of Thin
Supported Polymer Films**

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I. DETAILS ON MOLECULAR MODELING AND SIMULATIONS

Polymers are modeled as unentangled chains of 10 beads linked by harmonic springs. We use the harmonic spring potential

$$U_{\text{bond}} = \frac{k_{\text{chain}}}{2}(r - r_0)^2$$

to connect nearest-neighbor monomers within a polymer chain. The equilibrium bond length is $r_0 = 0.9$ and the spring constant is $k_{\text{chain}} = 1111$ [1]. To inhibit crystallization of the film, we choose r_0 smaller than that chosen in Ref. 2. We use the same substrate model as that in Ref. 3 for all the films studied. The substrate consists of 528 particles arranged in a triangular lattice (the (111) face of an FCC lattice). We tether substrate particles via a harmonic potential

$$V_{\text{sub}}(r) = (k/2)(r - r_0)^2,$$

where r_0 is the ideal lattice position and $k = 50$ is the spring constant [4, 5]. We use Lennard-Jones (LJ) interactions between non-bonded monomers and substrate particles. The interactions are truncated at pair separations $2.5\sigma_{ij}$, where σ is equivalent to the particle diameter in the LJ potential, and the subscript ij indicates the possible combinations of interactions (ss substrate-substrate, ps polymer-substrate, pp polymer-polymer). The LJ parameters are $\sigma_{pp} = 1.0$, $\varepsilon \equiv \varepsilon_{pp} = 1.0$, $\sigma \equiv \sigma_{ps} = 1.0$, $\sigma_{ss} = 0.8$, $\varepsilon_{ss} = 1.0$, and we use interaction strengths between monomers and substrate particles $\varepsilon_{ps} = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5$, and 3.0 . Since we only vary ε_{ps} , we simply refer to this quantity as ε .

Periodic boundary conditions are used in the directions parallel to the substrate with a box length 19.76σ (determined by the lattice spacing of the triangular lattice substrate). We conducted all simulations using the LAMMPS [6] simulation package with a time step $dt = 0.002$. For cooling and heating simulations of the bulk polymers, we use an NPT ensemble at $P = 0$. We performed at least 3 independent heating and cooling runs for both the pure polymer and polymer films at the same rate 10^{-5} . To generate trajectories from which we study the dynamics at fixed T , we carry out NPT simulations starting from configurations taken from the heating runs at $T > T_g$ with pressure $P = 0$. For the supported polymer films, we use an NVT ensemble where the box dimension in the z -direction is large compared to the film thickness. The temperatures are varied from 0.45 to 0.65, above (the heating rate dependent) $T_g(h = 15) \approx 0.40$ of the thickest polymer film. We equilibrate

each trajectory for at least 100 times the overall polymer relaxation time τ_{overall} .

II. DETAILS ON THERMODYNAMIC DEFINITIONS OF T_g

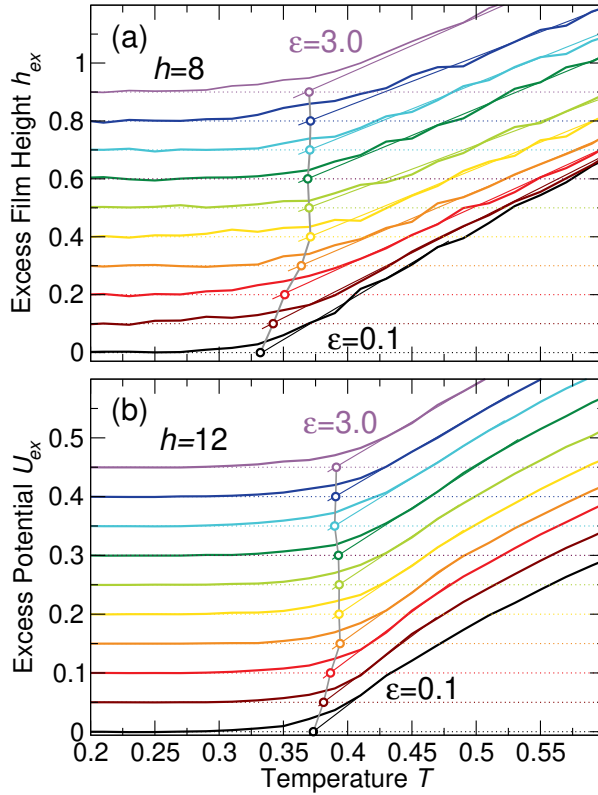


FIG. S1: The excess film height $h_{\text{ex}}(T)$ (a) and excess potential energy $U_{\text{ex}}(T)$ (b) of thin polymer films for all polymer-substrate interaction strengths $\epsilon = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, 3.0$ (from bottom to top). For each ϵ , the film height is averaged over at least 3 independent runs. The circles are the resulting T_g for each ϵ . Each curve (except for $\epsilon = 0.1$) is shifted vertically for clarity in the figure.

We first explain how we obtain thermodynamic estimates of T_g from film thickness or potential energy. To estimate T_g by a method comparable to ellipsometry measurements, we evaluate the temperature dependence of film thickness $h(T)$ on heating. To determine results comparable to DSC measurements, we evaluate the T -dependence of potential energy $U(T)$ during heating. We collect both $U(T)$ and $h(t)$ from heating supported polymer films at a fixed rate of 10^{-5} for all ϵ and h studied starting from $T = 0.01$. Note that this rate is substantially faster than rates used experimentally, and our T_g estimate is thus significantly

higher than would be reported experimentally. However, it is expected that T_g changes will be comparable in both simulation and experiment. In the glass regime below $T \lesssim 0.25$, $U(T)$ is well described by a quadratic function, and $h(T)$ is well described by a linear function. The quadratic behavior of U_{glass} corresponds to the commonly observed linear temperature dependence of specific heat in the glass state; the linear behavior of film height in the glass regime is also commonly observed in experiments. To eliminate this trivial dependence of potential energy and thickness on the temperature in the glass, we focus on the T -dependence of excess film height relative to the glass,

$$h_{\text{ex}}(T) = h(T) - h_{\text{glass}}(T), \quad (1)$$

shown in Fig. S1 (a), and excess potential energy relative to the glass,

$$U_{\text{ex}}(T) = U(T) - U_{\text{glass}}(T), \quad (2)$$

shown in Fig. S1 (b). We define T_g as the vanishing temperature $h_{\text{ex}}(T_g) \rightarrow 0$ or $U_{\text{ex}}(T_g) \rightarrow 0$ from a linear extrapolation of the T dependence of $h_{\text{ex}}(T)$ and $U_{\text{ex}}(T)$ in the fluid state, as indicated by the fits in the Fig. S1. Notably, T_g for all films is reduced compared to that of the bulk polymer. It is also noteworthy that the breadth of the glass transition region grows with increasing substrate interaction strength, an effect that is also observed experimentally [7, 8].

A. Local Thermodynamic T_g

As a complement to the dynamical estimates of T_g in the different regions (free interface T_g^{int} , middle layer T_g^{mid} , and substrate layer T_g^{sub}) of the film discussed in the main text, we have also evaluated the thermodynamically defined T_g in the corresponding regions. The specific definitions of these regions are given in the main paper. We use the same methods to define T_g as described in the text above, except that we only examine the potential energy of that specific layer (free interface, middle layer, and substrate layer), defined by the pair potential energy within the region. The resulting T_g estimates from the potential energy are shown in Fig. S2. The local thermodynamic estimates of T_g in the substrate and middle layer decrease with decreasing film thickness and T_g of the free interface (T_g^{int}) remains nearly a constant with film thickness, consistent with the findings in Ref. [9]. As a result,

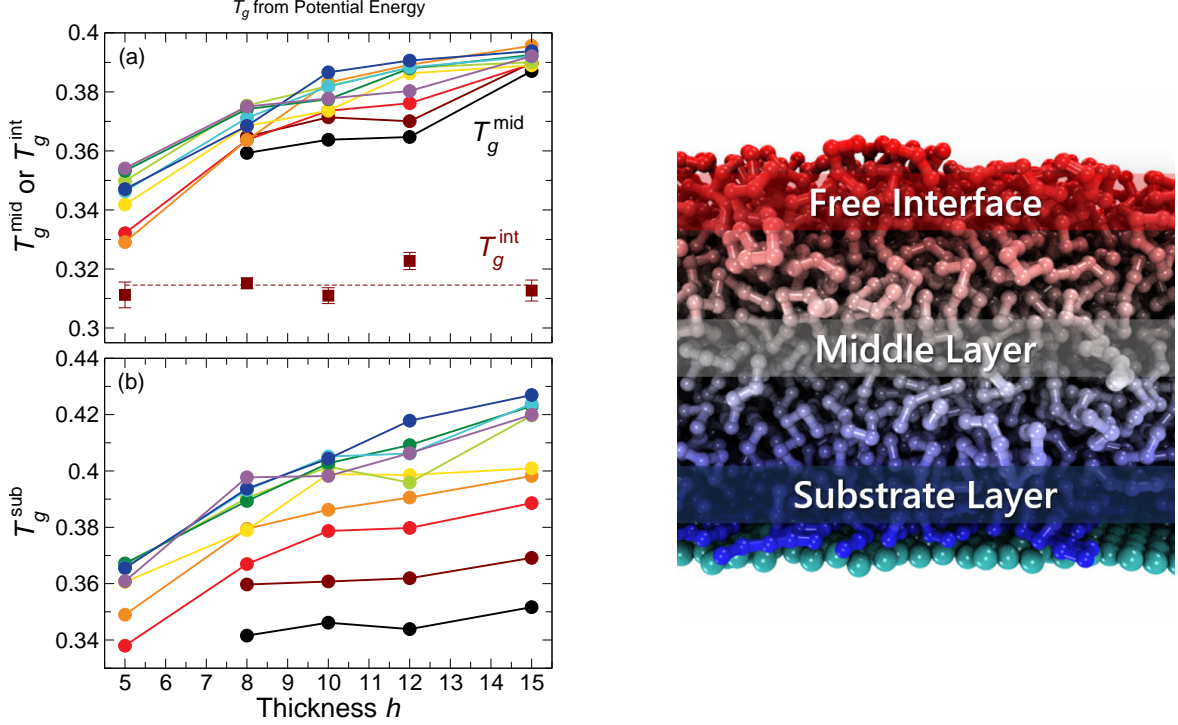


FIG. S2: The thermodynamic glass transition temperatures T_g from (a) middle film and free surface layers, and (b) substrate layer of the film, defined by excess potential energy, as a function of film thickness h for all ϵ studied. T_g from U_{sub} decreases with decreasing film thickness. Similarly, T_g from U_{mid} decreases with decreasing film thickness for all ϵ . T_g from U_{int} is nearly identical for all thicknesses and ϵ . Therefore, we average T_g^{int} over all ϵ for each film thickness and the error bars indicate the standard error of T_g^{int} . The picture illustrates the free interface, middle, and substrate layer of thin polymer film with a strongly interacting substrate; colors indicate the logarithmic scaled relaxation time from red (most mobile) to blue (least mobile).

the overall thermodynamic T_g estimates decrease as the films become thinner. We have also determined the thermodynamic T_g in the different regions of the film based on the density of these regions, leading to the same trends that we have found for the potential energy. This data is inherently noisier than the potential energy data, so we only show position dependent thermodynamic estimates of T_g here based on potential energy.

Most notably, T_g of the substrate layer (T_g^{sub}) obtained from potential energy does not increase with decreasing film thickness, whereas the dynamically defined substrate T_g increases with decreasing film thickness (Fig. 5(b) in the paper). Thus, the data suggest that the ther-

modynamic measure of T_g decreases for thinner films, both for the film as a whole, as well as locally. A similar issue has been examined in Ref. [3]; the bound layer near the substrate acts as a compatible interface to the film interior and this bound layer effectively cloaks the film upper layer (everything except the substrate layer) from the substrate interaction. On heating, the upper layer exhibits glass transition before the bound substrate layer turns into fluid-like state. Since the thickness of the bound layer are only a few nanometers (see inset of Fig. 3 and Ref. [10]), the upper layer of the film dominates the overall thermodynamically defined T_g .

III. DYNAMICAL DEFINITION OF T_g

Following Refs. 3, 11, we first define the overall relaxation time τ_{overall} and the center of mass relaxation time τ_{cm} of the polymer film by the time at which $F_s(q_0, \tau)$ has decayed by a factor $1/e$ relative to its plateau value A ; the plateau value $A \approx 0.75$ is nearly constant for all films and temperatures studied, and so we can define $F_s(q_0, \tau) = A/e \approx 0.28$. To mimic the experimental criterion of a fixed relaxation time at T_g , we choose $\tau(T_g) = 10^3$ (in LJ units), the same definition as in Refs. 3, 11; note that due to inherent differences in accessible time scales between simulation and experiment, this time scale is substantially smaller than that chosen experimentally, so that T_g from the simulation is substantially higher than would be obtained from standard experimental criteria. Despite the difference in the absolute time scale used, it is expected trend in the changes in T_g due to changing film thickness or interfacial interaction strength will be similar between simulation and experiment. The resulting T_g estimates for the film as a whole and for all film thicknesses h and polymer-substrate interaction strengths are shown in Fig. 1 (c) in the main text. A similar plot for T_g from the chain dynamics is shown in Fig. S3.

IV. THE THICKNESS DEPENDENCE OF T_g

We use a Gibbs-Thomson inspired model [1] to fit the thickness dependent of $T_g(h)$,

$$\frac{T_g(h)}{T_g(h \rightarrow \infty)} = 1 - \frac{l_p a}{h}, \quad (3)$$

where $l_p \approx 1$ is the persistence length for spring-bead polymer model, and a is the fitting parameter. Note that the Keddie *et al.* [12] have proposed an empirical function for the T_g

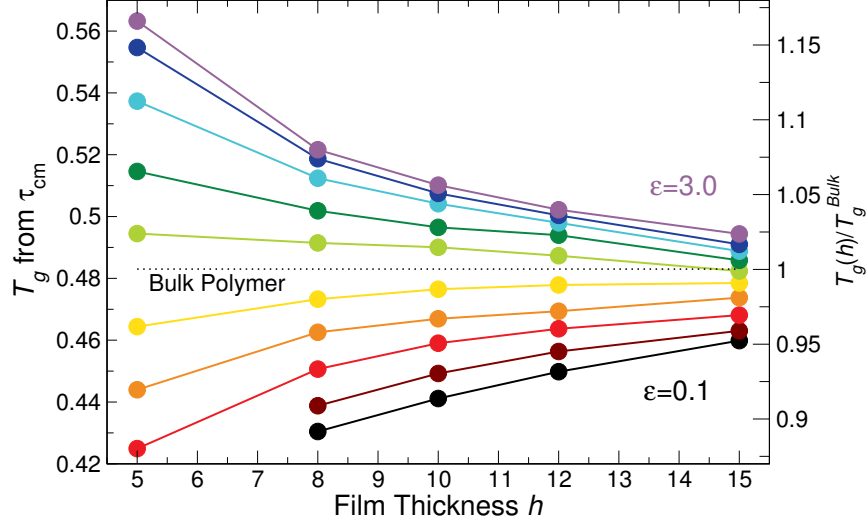


FIG. S3: Dynamic glass transition temperature T_g estimates of thin polymer films, defined from the relaxation time of the center of mass of polymers [$\tau_{\text{cm}}(T_g) = 10^3$] plotted as a function of film thickness h for polymer-substrate interaction strengths $\varepsilon = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5$ and 3.0 . On the right side of the vertical axis, we normalize T_g by the corresponding glass transition temperature of the bulk polymer T_g^{Bulk} .

shifts of thin polymer films,

$$T_g(h) = T_g^\infty \left[1 - \left(\frac{a}{h} \right)^\delta \right], \quad (4)$$

where δ is the fitting exponent. Equation 3 is appropriate for the description of a second order phase transition, while Eq. 3 is motivated by a change in the cohesive energy of the film due to confinement 1, an argument for both the shift of the melting temperature and the glass transition temperature.

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