Supporting Information

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SI Text

Variation of the Vogel–Fulcher–Tammann Prefactor. The widely used empirical Vogel–Fulcher–Tammann (VFT) relation

$$\tau = \tau_0 \exp[DT_0/(T - T_0)], \quad \textbf{[S1]}$$

has three adjustable parameters. Whereas many works discuss the meaning and variation of D (inversely proportional to fragility) and T_0 (proportional to T_g), considerably less attention is given to the prefactor τ_0. We find that τ_0 can vary substantially in thin-film systems and nanocomposite materials, and this variation has been important in assessing the predictive nature of our model of relaxation, and in physically understanding the dynamic properties of polymer films and nanocomposites.

Fig. S1 shows that τ_0 can vary by many orders of magnitude in thin polymer film simulations, a point which gave us great concern when we first analyzed the data, because the values of τ_0 seem unphysically small. We have since come to appreciate the physical explanation for this variation, which is discussed at length in ref. 1. In short, in the context of the string model extension of the AG formulation, this prefactor is not a "free parameter" but rather is completely determined by the activation parameters of classical transition state theory. The confinement of the film has a significant effect on the entropy of activation ΔS, which is absorbed into the definition of τ_0 in the VFT formulation. The resulting exponential dependence of τ_0 on ΔS means that changes of ΔS give rise to changes in τ_0 by orders of magnitude.

Bässler Relation. One alternate to the empirical VFT relation is the Bässler equation,

$$\tau = \tau_0 \exp\left[(T/T_0)^2\right], \quad \textbf{[S2]}$$

derived in the context of the dynamics of spin models (2). Fig. S2 shows the best fit of our data to this relation. It is apparent that the quality of the data collapse is inferior to the VFT representation (Fig. 1 of main text) for the wide range of fragility covered by our simulation data.

Isotropic Free Volume Limit of the Localization Model. As discussed in the main text, the localization model of ref. 3 proposes that

$$\tau(\langle u^2\rangle) = \tau_u \exp\left[\left(u_A^2/\langle u^2\rangle\right)^{\alpha/2}\right], \quad \textbf{[S3]}$$

where α is a measure of free-volume anisotropy. One would expect $\alpha = 3$ for roughly spherical volumes on dimensional grounds. The main text shows that $\alpha > 3$ generally offers the best fit. However, it is still instructive to consider the case $\alpha = 3$, because, in this case, there are no free parameters (as τ_A and u_A^2 are obtained directly from the simulation data). Fig. S3 shows that the quality of the collapse is inferior to the case when α is allowed to vary, but already provides a surprisingly good reduction of the data.

1. Hanakata PZ, Pazmiño Betancourt BA, Douglas JF, Starr FW (2014) A unifying framework to quantify the effects of boundary stiffness, polymer-substrate interactions and substrate roughness on the dynamics of thin supported polymer films. arXiv: 1502.02626.
2. Bässler H (1987) Viscous flow in supercooled liquids analyzed in terms of transport theory for random media with energetic disorder. *Phys Rev Lett* 58(8):767–770.
3. Simmons DS, Cicerone MT, Zhong Q, Tyagi M, Douglas JF (2012) Generalized localization model of relaxation in glass-forming liquids. *Soft Matter* 8(45):11455–11461.

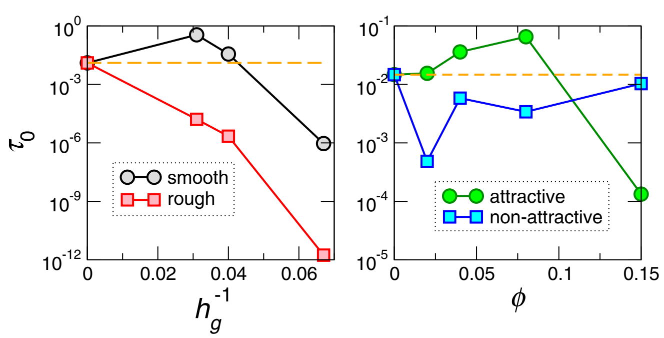

Fig. S1. Variation of the prefactor τ_0 of the VFT relation for thin films (as a function of inverse thickness h_g^{-1}) and for composites (as a function of nanoparticle concentration ϕ).

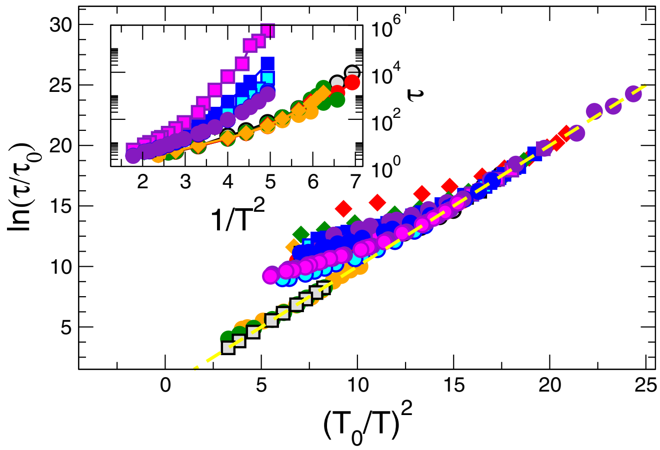

Fig. S2. Relaxation time data fit to the Bässler equation.

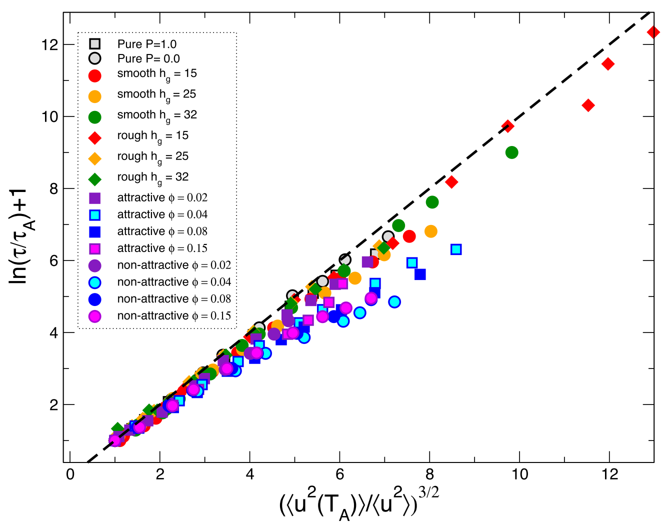

Fig. S3. Fit to the localization model, constraining $\alpha = 3$, so that the model has no free parameters.