Supplementary Information (SI) for Soft Matter.

Supporting Information: Generalized Entropy Theory Investigation of the Relatively High Segmental Fragility of Many Glass-Forming Polymers

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S1 Segmental Fragility and Extent of Cooperative Motion for Polymer Melts Having Variable Cohesive Interaction Strength and Applied Pressure

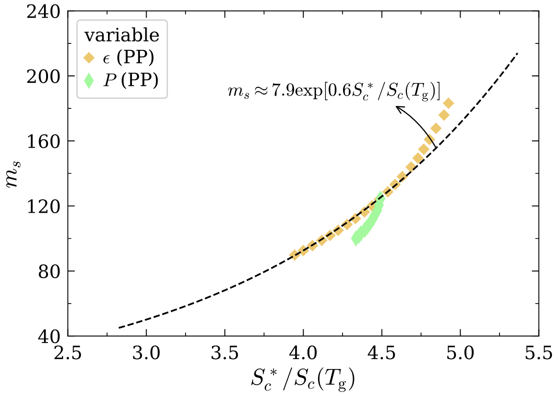

Figure S1: Variation of the segmental fragility m_s as a function of $S_c^*/S_c(T_\mathrm{g})$ calculated from the GET for the PP structure having variable ϵ and P.

In Section 3.1 of the main text, we have shown that the near universal relation between m_s and $S_c^*/S_c(T_\mathrm{g})$ applies to a broad range of polymer models when the cohesive interaction strength ϵ and applied pressure P are fixed. However, this relation does not hold anymore when either ϵ or P is varied. For reference, we show the corresponding result in Figure S1. In particular, we see that the data deviate progressively from the universal curve with decreasing ϵ or increasing P. We discuss this "anomalous" behavior in Section 3.3 in connection with understanding the inverted trend between m_s and T_g caused by a significant change of the cohesive interaction strength in the GET, a correlation pattern that is observed in certain types of polymer materials,[1–9] as discussed in the main text.

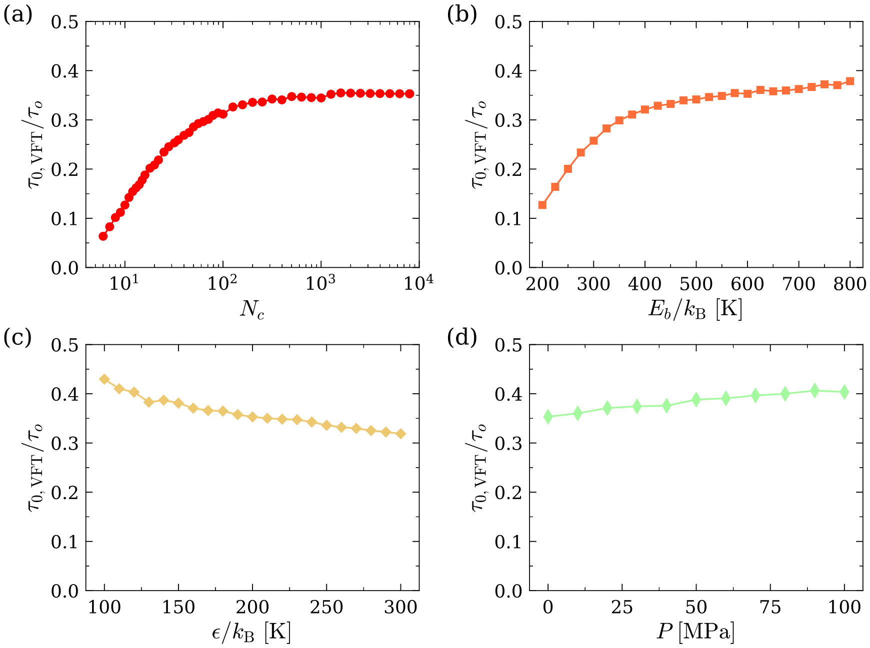

Figure S2: Variation of $\tau_{0,\mathrm{VFT}}$ with molecular and thermodynamic parameters for the PP model. Panels (a–d) show $\tau_{0,\mathrm{VFT}}/\tau_o$ as a function of N_c, E_b, ϵ, and P, respectively.

S2 High Temperature Vibrational Prefactor as a Function of Molecular and Thermodynamic Parameters

Figures S2 and S3 summarize $\tau_{0,\mathrm{VFT}}/\tau_o$ as a function of molecular and thermodynamic parameters predicted from the GET. While $\tau_{0,\mathrm{VFT}}$ is found to generally vary with molecular parameters, this time scale has roughly the same order of magnitude as τ_o. In the present

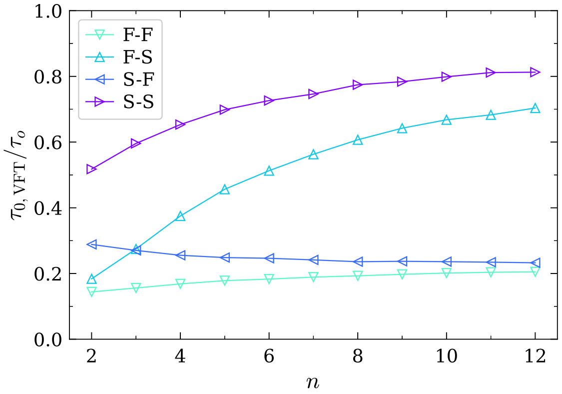

Figure S3: $\tau_{0,\mathrm{VFT}}/\tau_o$ as a function of n for different classes of polymers.

work, we assume τ_o to equal 10^{-13} s so that $\tau_{0,\mathrm{VFT}}$ is predicted by the GET to be somewhat smaller in magnitude.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data used to generate the figures in this manuscript are available at Open Science Framework at https://osf.io/fzheg/.

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