Supplementary Information for "Activated Penetrant Dynamics in Glass Forming Liquids: Size Effects, Decoupling, Slaving, Collective Elasticity and Correlation with Matrix Compressibility"

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A. Origin of Power Law Behavior in Figure 4

To understand the origin of the power law behavior in Figure 4, we plot in the main frame of Fig. SI1 the integrand of the second term in eqn (14), $q^2 C_{\mathrm{mp}}^2(q) S_{\mathrm{mm}}(q) \Big/ \left[1 + \left(\sigma^2 \tau_{\mathrm{E,p}} / d^2 \tau_{\mathrm{E,m}}\right) n(q) / S_{\mathrm{mm}}(q)\right]$, at a high packing fraction and fixed penetrant size ratio. One sees a nontrivial maximum, which exists (not shown) for all packing fractions and penetrant sizes studied, and which occurs at a nearly *identical* value of wavevector we denote as $q=q^*$. Considering the value of the integrand at the maximum as a metric of the magnitude of the integral in eqn (14), $C_{\mathrm{mp}}^2(q^*)$ and $S_{\mathrm{mm}}(q^*)$ have been calculated. We find $C_{\mathrm{mp}}^2(q^*)$ is essentially constant (not shown), while the pure matrix quantity $S_{\mathrm{mm}}(q^*)$ follows a power law with $g_{\text{mp}}^{\text{contact}}$ as seen in the inset of Fig. SI1. The numerically-deduced apparent power law exponent is 1.42, very close to 4/3, independent of penetrant size. Hence, we can conclude that the origin of the apparent scaling behavior $\tau_{\text{s,p}}/\tau_0 = A\left(g_{\text{mp}}^{\text{contact}}\right)^{7/3}$ is that the short time friction constant is strongly correlated with the matrix cage order parameter , $S_{mm}(q^*)$, and penetrant-matrix collision rate (via $\tau_{\text{E,p}}$), but not with $C_{\text{mp}}(q^*)$.

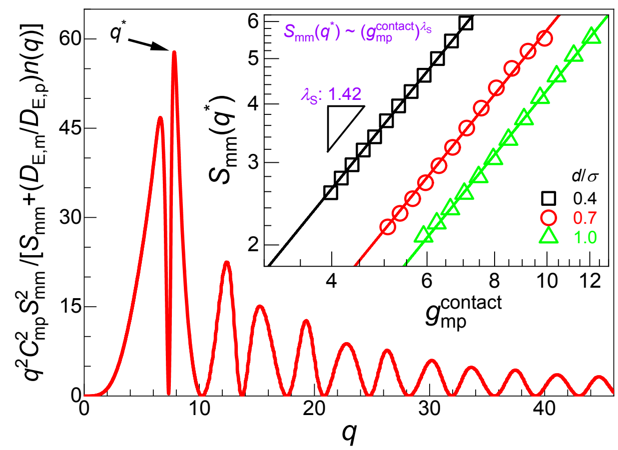

Fig.SI1. The dynamical vertex, defined as $q^2C_{\text{mp}}^2(q)S_{\text{mm}}(q)\Big/\left[1+\left(\sigma^2\tau_{\text{E,p}}\big/d^2\tau_{\text{E,m}}\right)n(q)\big/S_{\text{mm}}(q)\right]$ in eqn (14), is plotted as a function of $q\sigma$ for a representative example at $\phi = 0.61$ and $d = 0.7\sigma$. The inset plots the value of $S_{\text{mm}}(q^*)$ as a function of the cross contact value where the vertex maximum wavevector (peak q^*) is slightly lower than the location (q_{max}) of the first maximum of $S_{\text{mm}}(q)$[1].

B. Penetrant and Matrix Particle Jump Distances

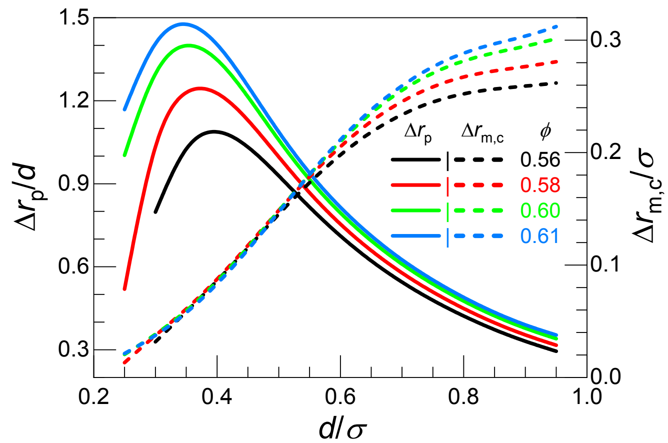

Fig. SI2 Penetrant jump distance (solid curves, normalized by the penetrant diameter) and corresponding matrix displacement (dash curves, normalized by the matrix particle diameter) as a function of size ratio for various packing fractions. The key information in this plot is discussed in the main text.

C. Size Ratio Dependence of Penetrant Relaxation Time Based on PY Structural Input

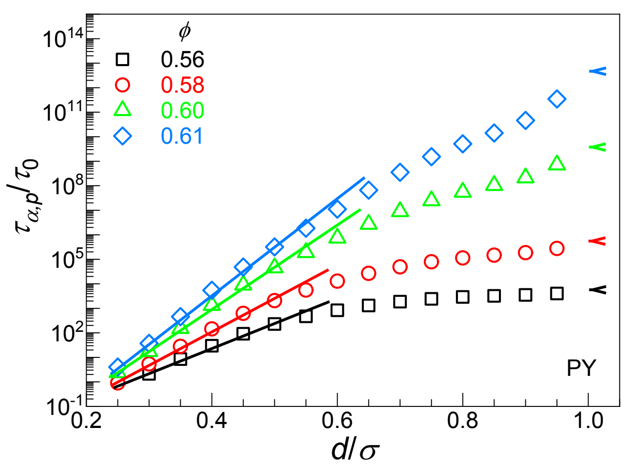

Fig. SI3 Penetrant mean alpha relaxation time (in units of τ_0) as a function of size ratio for various matrix packing fractions. This is the same as in Fig. 7 in the main text but based on using the PY closure to calculate the required structural input to the dynamical theory. The significant quantitative differences between the dynamical theory predictions based on the MV and PY structural inputs are discussed in the main text.

D. Contributions to the Collective Elastic Barrier for Penetrant Hopping

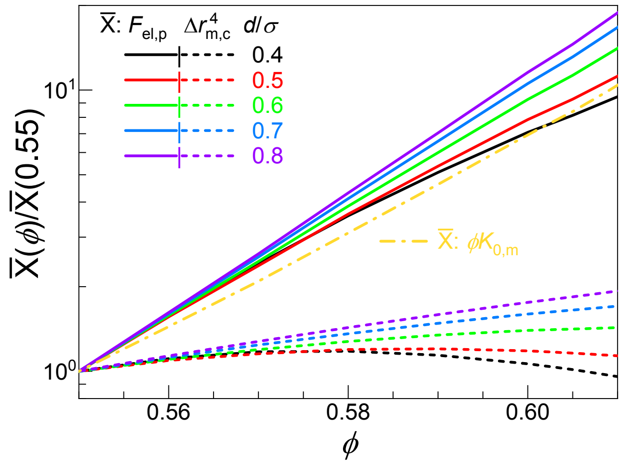

Fig. SI4 Relative importance of the key factors $\Delta r^4_{m,c}$ and $\phi K_{0,m}$ that enter the penetrant elastic barrier in eqn (17), reduced by their corresponding values at ϕ=0.55, plotted versus matrix packing fraction for various size ratios. The key conclusion from this plot is discussed in the main text.

References

1 We note that if q^* is defined as the q value corresponding to the first maximum of the vertex in Fig. SI1, then q^* is much lower than the q_{max} of $S_{mm}(q)$ (particularly at lower packing fraction, e.g., $q^* < q_{max}/2$ at $\phi = 0.55$), and $S_{mm}(q^*)$ can be very small and does not grow as a power law of the cross contact value.