

# Supplementary Information for Surface and Bulk Relaxation of Vapour-Deposited Polystyrene Glasses

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From Fig. 8 in the main manuscript, it is observed that the temperature dependence of the experimentally defined surface relaxation time  $\tau$  appears to be different than that of the surface mobility obtained from the best fits to the numerical solutions of the GTFEN model. From high temperatures to above  $1/T \sim 3.25 \times 10^{-3} \text{ K}^{-1}$ , the relaxation time  $\tau$  transforms from an Arrhenius behaviour to an athermal one, while the same saturation is absent in the surface mobility  $M$ . Similarly Fig. 8(a) in the main manuscript shows no differences between surface relaxation times of as-deposited and rejuvenated films whereas the mobility shows a small but clear difference.

These differences appear to be due to the choice of the physical quantity used in characterizing the surface relaxation time. While the doubling time of a specific  $d^*$  is a very convenient way to quantify the time scale of the surface relaxation, the choice of  $d^*$  itself can lead to quantitatively and sometimes even qualitatively different results. For example, both Fig. S1(a) and Fig. S1(b) show the doubling time of some width  $d^*$  defined from the surface profile. In Fig. S1(a) the definition of  $d^*$  is exactly the same as presented in Fig. 8(a) in the main manuscript, which is the minimal value of the radial coordinate  $r$  at which the height crosses 0 nm, while in Fig. S1(b)  $d^*$  is chosen as the minimal value of the radial coordinate  $r$  at which the height crosses 2 nm (such as that used in ref [1]). It is readily seen that a shift of 2 nm in the observed location changes the temperature dependence of  $\tau$  significantly. While a  $d^*$  at 0 nm leads to an order of magnitude of change in  $\tau$  within the temperature range investigated, a  $d^*$  at 2 nm gives almost two orders of magnitude of

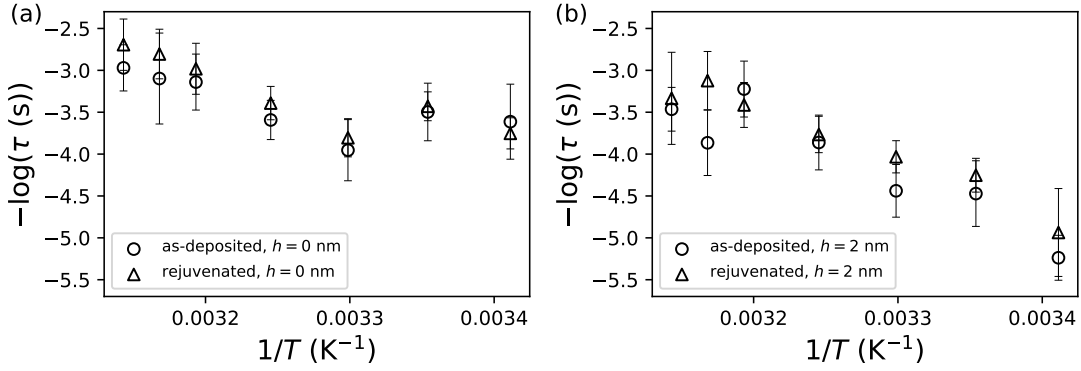


Figure S1: The doubling time of a peak width  $d^*$  defined in two different ways. In panel (a)  $d^*$  is defined as the minimal value of the radial coordinate  $r$  at which the height crosses 0 nm, while in panel (b) it is defined as the minimal value of the radial coordinate  $r$  at which the height crosses 2 nm.

change in  $\tau$ . The transition from an Arrhenius to an athermal behaviour is also only present in one case and not the other. Similarly, while still within quoted uncertainties the as-deposited and rejuvenated samples appear to be less similar when a  $d^*$  of 2 nm is chosen.

In obtaining the surface mobility  $M$ , the experimental surface profiles, from  $r = 0$  to very far from the nanoparticle, are fit to the numerical solutions of the GTFEN model. Unlike the surface mobility  $M$  which is a global characteristic of the surface flow, the peak width  $d^*$  is a single point, and not every point is equally sensitive to changes in the mobility. For example, in ref [2], it is clear that not every point could be used to determine mobility, and the midpoint of the step in that case is in fact a fixed point and completely insensitive to changes in mobility. In general, the globally determined  $M$  value is a more reliable and sensitive way to characterize the surface property, while the report from any locally defined doubling time is less sensitive to changes in mobility and also appear to depend strongly on the geometry and the choice of  $d^*$ . As a test of this idea we used the profiles generated from the GTFEN model to generate a  $d^*$  as a function of time and plotted that doubling time as a function of  $M$ . This exercise, the results of which are displayed in Fig. S2 revealed that as mobility changes by two orders of magnitude, the times derived from  $d^*$  values determined from numerically generated profiles did not similarly change. This demonstrates conclusively that local measurements can result in loss of sensitivity to changes in mobility.

This discrepancy is also reflected in the literature investigating surface properties of glassy films using different methods. In the study of the relaxation of nanoholes on PS thin films [3], the depth of holes are measured and a relaxation time  $\tau$  is extracted from their time evolution. A levelling-off in the temperature dependence of  $\tau$  at low temperatures is observed, similar to that of  $\tau$  in the current study, and even their transition temperatures are strikingly similar. In contrast, in the

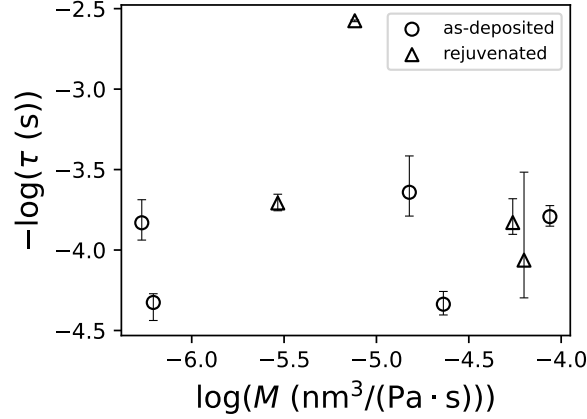


Figure S2: The doubling time of a peak width  $d^*$  determined from numerically generated profiles for different values of the mobility  $M$

stepped PS films study by Chai *et al* [2] and in the study of surface evolution of PS films upon annealing by Yang *et al* [4], an Arrhenius behaviour in the surface mobility is observed in both studies, similar to that of  $M$  in the current study. It is worth noting that in all of the latter three studies, a mathematical model is built, starting from the Stokes equation, to extract the mobility from experimental surface profiles which cover a wide range of the surface. This apparent disagreement between  $\tau$  and  $M$  can be easily understood with the argument above. When the surface property is described by the time dependence of the profile at a local point, it is influenced by the choice of the point and may not be a good representation of the global relaxation.

## References

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