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Dynamic Cluster Size Effects on the Glass Transition of Thin Films RICHARD WOOL, University of Delaware — During cooling from the melt of amorphous materials, it has been shown experimentally that dynamic rigid clusters form in equilibrium with the liquid and their relaxation behavior determines the kinetic nature of T_g [Stanzione et al, J. Non Cryst Solids 357(2): 311-319 2011]. The fractal clusters of size R ~ 5-60 nm (polystyrene) have relaxation times $\tau \sim R^{1.8}$ (solid-to-liquid). They are analogous to sub critical size embryos during crystallization as the amorphous material tries to crystallize due to the strong intermolecular forces at $T < T_m$; they are not related to density fluctuations or surface capillary waves. In free-standing thin films of thickness h, several important events occur: (a) The large clusters with R > h are excluded and the thin films have an average faster relaxation time compared to the bulk; consequently T_g decreases as h decreases. (b) The segmental dynamics at the 1 nm scale are largely not affected by nanoconfinement since T_g is determined only by the cluster dynamics with $R \gg 1$ nm. (c) The mobile layer on the surface of free standing films is due to the presence of smaller clusters on the surface which will disappear with increasing rate of testing. (d) With adhesion to a solid substrate, the surface mobile layer disappears as the surface clusters size grow and the change in T_g is suppressed. (e) Physical aging is controlled by the relaxation of the rigid fractal clusters and in thin films, physical aging will occur more rapidly compared to the bulk. (f) The large effect of molecular weight M on T_g appears to be related to the effect on the cluster size distribution giving smaller clusters and faster relation times with increasing M. These results are in accord with the Twinkling Fractal theory of the glass transition.

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