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Twinkling Fractal Analysis of Confinement Effects on the Glass Transition of Thin Films RICHARD WOOL, JOSEPH STANZIONE III, Chemical Engineering, Univ Delaware — The Twinkling Fractal Theory (TFT) of the Glass Transition has recently been verified experimentally [J.F. Stanzione, et al., "Observing the twinkling fractal nature of the glass transition", J. Non-Cryst. Solids (2010), doi:10.1016/j.jnoncrysol.2010.06.041] Here we apply the TFT to understand nanoconfinement effects on T_g for amorphous thin films of thickness h with free and adhered surfaces. The TFT states that T_g occurs when the dynamic clusters percolate rigidity at the rate of testing γ. The lifetime τ of these fractal clusters of size R behaves as $\tau \sim R^{\delta}$ exp $\Delta E/kT$, where $\delta = D_f/d_f$ in which D_f is the fractal dimension and $d_f = 4/3$ is the fracton dimension for the vibrational density of states $g(\omega) \sim \omega^{df}$. The activation energy $\Delta E = \beta[T^{*2} - T_g^2]$ in which $\beta \approx 0.3$ cal/mol $^oK^2$ and $T^* \approx 1.2T_g$. In confined spaces, only clusters of size R<h can exist and these have a very fast relaxation time compared to the bulk. Thus, for free surfaces, T_g must be dropped at that test rate to percolate rigidity and we obtain the familiar expression $T_g(h)/T_{g\infty} \approx [1-(B/h)^{\delta}]$ where $\delta \approx 1.8$ when $D_f \approx 2.5$ and B is a known constant. For thin films adhered to solid substrates, T_g increases in accord with the adhesion energyΔA as $\Delta E \rightarrow \Delta E + \Delta A$ and the adhered cluster lifetime increases. As the rate of testing γ increases, the confinement effects diminish as T_g increases in accord with $T_g(\gamma) = T_{go} + (k/2\beta) \ln \gamma/\gamma_o$.

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