Twinkling Fractal Theory of the Glass Transition.\textsuperscript{1} RICHARD WOOL, Department of Chemical Engineering, University of Delaware — A new approach to the glass transition temperature $T_g$ considers the interaction of particles with an anharmonic potential $U(x)$, and Boltzmann population $\phi(x) \sim \exp -U(x)/kT$. As $T_g$ is approached from above, solid clusters of atoms form and percolate at $T_g$. However, the solid percolation cluster is in dynamic equilibrium with its surrounding liquid and “twinkles” as solid and liquid atoms interchange. The twinkling frequency $F(\omega)$ is related to the vibrational density of states $G(\omega) \sim \omega^{d_f}$ and the energy difference $\Delta U \sim (T^2 - T_g^2)$ via $F(\omega) \sim G(\omega) \exp -\Delta U/kT$, where $d_f = 4/3$ is the fracton dimension. $F(\omega)$ controls the rate dependence of $T_g$, physical aging, yield stress, heat capacity $C_p$, $T_g$ of thin films, etc. When $T < T_g$, the non-equilibrium volume development $\Delta V$, is determined by the fractal structure at $T_g$. The thermal expansion coefficients in the liquid and glass are related via $\alpha_g = p_c \alpha_L$. For a Morse potential $U(x) = D_o[1-\exp ax]^2$, we predict that $T_g = 2D_o/9k$, and $\alpha_L = 3k/[4D_o a R_o]$. For atoms with $R_o \approx 3 \text{ Å}$, bond energy $D_o \approx 2-10$ kcal/mol and anharmonicity factor $a \approx 2/\text{Å}$, we obtain $\alpha_L \approx 0.03$, and modulus $E \sim 1/\alpha_L$, which were found for a broad range of polymers. The yield stress $\sigma_y$ is determined by the onset of the twinkling fractal state as $\sigma_y = \{0.16 E [p_c-p_s] D_o/V_m\}^{1/2}$ where $V_m$ is the molar volume.

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