

From the schematic given by Figure 6, it is clear that the fictive temperature is between the temperature, T , and the glass transition temperature, T_g . A quantitative relationship for fictive temperature may be developed using the expression for the difference in configurational entropy between the real glass and the equilibrium glass, as given by

$$S_c(T) - S_c^e(T) = \int_T^{T_g} \frac{\Delta C_p^{l,g}}{T} dT, \Delta C_p^{l,g} = C_p^l - C_p^g \quad (9)$$

where C_p^l is the heat capacity of the liquid or "equilibrium glass," and C_p^g is the heat capacity of the "real" glass. Performing the integration in equation (9), assuming the quantity $T\Delta C_p^{l,g}$ is independent of temperature, and combination with the integrated forms of equation (7) then leads to the desired expression for fictive temperature

$$\frac{1}{T_f} = \frac{(1 - \gamma_c)}{T} + \frac{\gamma_c}{T_g}; \quad T \leq T_g \quad (10)$$

$$\gamma_c \equiv \frac{\Delta C_p^{l,g}}{\Delta C_p} = \frac{C_p^l - C_p^g}{C_p^l - C_p^{x\text{stal}}}$$

where $C_p^{x\text{stal}}$ is the heat capacity of the crystalline phase. All heat capacities are evaluated at the glass transition temperature. The combination of equations (8) and (10) constitutes a generalization of the Adam-Gibbs theory for the temperature dependence of the structural relaxation time. Above the glass transition temperature, fictive temperature and temperature are identical, and the expression for relaxation time given by equation (8) reduces to the usual expression (i.e., equation 5). Below T_g , equation (10) is used to evaluate the fictive temperature, and the expression for relaxation time differs from the usual expression, the magnitude of the change depending on the value of γ_c . Note that if the configurational heat capacity of the real glass is zero (i.e., the heat capacities of the real glass and the crystal are identical), $\gamma_c = 1$, and the fictive temperature is equal to the glass transition temperature at all temperatures below T_g . In this case, the relaxation time shows Arrhenius temperature dependence below T_g . At the other extreme, if the configurational heat capacities of the real glass and the liquid differ only slightly, $\gamma_c \approx 0$, $T_f \approx T$, and the relaxation time expression is the same both below and above T_g . We note that since enthalpy relaxation is nonexponential, a real glass consists of a number of substates, each having a different configurational entropy and a different fictive temperature. Thus, the results given in equations (8) to (10) refer to an average of substates for temperatures below T_g .

While most treatments of this subject assume that the heat capacities of the crystalline and glassy phases are essentially the same, and therefore Arrhenius temperature dependence is predicted below T_g , experimental heat capacity data for sucrose (47,48,50) indicate that the heat capacity of glassy sucrose is significantly higher than the heat capacity of crystalline sucrose, and $\gamma_c \approx 0.8$. Figure 7 shows calculated relaxation times for two hypothetical amorphous materials with $T_g = 70^\circ\text{C}$, but with different fragilities (i.e., $D = 7$ and $\gamma_c = 0.8$ for a fragile glass like sucrose and $D = 23$ and $\gamma_c = 0.94$ for a representative strong