

# On Free Volume of Polymers Above the Glass Transition

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## Synopsis

The magnitude of the activation energy for diffusion,  $E_D$ , is shown to be inversely dependent on the fractional free volume of the polymer above  $T_g$ . From the proportionality of  $E_D$  above and below  $T_g$ , the magnitude of  $E_D$  below  $T_g$  is also inversely dependent on the free volume in that temperature range. While this correlation holds very well for our determinations of fractional free volume above  $T_g$ , it does not correlate with the Simha-Boyer fractional free volume below  $T_g$ , contrary to expectations.

## INTRODUCTION

A characteristic temperature of polymer,  $T_R$ , was recently described<sup>1,2</sup> as the temperature at which the number of nonbonded nearest neighbors of each segment is one less than at the glass transition temperature  $T_g$ . The  $T_R$  is also defined as the temperature at which the extrapolated strength of a polymer reaches zero and becomes independent of the loading rate.<sup>3</sup> The value of  $T_R$  is determined by the combined effect of two variables: the amount of free volume present in the polymer at  $T_g$  and the rate of expansion above  $T_g$ . Numerically,  $T_R$  is calculated<sup>2,4</sup> from  $T_g$  and  $\Delta\alpha$ , the difference between the coefficients of expansion above and below  $T_g$ . It has recently been shown<sup>5</sup> that there exists an indirect dependence of  $T_R$  on  $\sigma$ , the characteristic ratio which reflects the restrictions on torsional rotation and overall chain flexibility.

From packing density considerations it was demonstrated<sup>1,2</sup> that  $(FFV)_{T_R} = 0.113 \pm 0.002$  above and beyond  $(FFV)_{T_g}$  with FFV standing for the fractional free volume at the subscripted temperature. Assuming that a polymer chain is simulable by a string of hard spheres and that it is in a state of equilibrium,  $T_R$  is determinable through the equation

$$T_R = T_g + T_g^{-1/2}(0.113/\Delta\alpha)^{3/2} \quad (1)$$

deriving from the critical exponent equation

$$0.113 = (T_R - T_g) \frac{(\alpha_L - \alpha_G)}{(T_R/T_g - 1)^{1/3}} \quad (2)$$

where

$$\alpha_L - \alpha_G = \Delta\alpha$$

Taking into consideration the fact that at  $T_g$  the polymers are usually not in a state of equilibrium, the fractional free volume at  $T_R$  is defined by

$$(FFV)_{T_R} = (\alpha_L - \alpha_G)(T_R - T_g) = \Delta\alpha \Delta T \quad (3)$$

It should be noted here that the Simha-Boyer<sup>6</sup> (SB) equation for fractional free

volume at  $T_g$ ,  $SB(FV)_{T_g}$ , is a very special case of eqs. (2) and (3), in which  $T_R = 2T_g$  exactly and where  $SB(FV)_{T_g} \cong 0.113 \cong (FFV)_{T_R}$ .

## DISCUSSION

It has been noted by several workers<sup>7-13</sup> that for a given amorphous, or for the amorphous part of a semicrystalline polymer, the activation energy for diffusion,  $E_D$ , is an increasing function of the penetrant's molecular size but is nearly independent of the structure of the diffusant molecule. This is especially true for inorganic diffusants that have poorer affinity toward the polymer than organic penetrants. It was also found that, especially for inorganic diffusants, the molecular cross section  $d^2$  ( $d$  is the molecular diameter) is directly correlated with  $E_D$  so that  $E_D/d^2$  is close to constancy for each polymer.<sup>14</sup> The use of this ratio, then, eliminates the effects of the penetrant's molecular size and can be used as a probe to investigate material parameters such as  $FFV$ . In the glassy region, below  $T_g$ , the activation energy for diffusion is lower, by a more or less constant ratio<sup>13,14</sup> than in the rubbery region above  $T_g$ , for many gaseous diffusants.<sup>13,15,16</sup> Sufficiently small diffusants, such as  $H_2$  or  $He$ , often give the same  $E_D$  above and below  $T_g$ .

As noted by Meares,<sup>17</sup> " $E_D$  is certainly far larger than would be needed to make a hole of volume just sufficient for the diffusate to jump into," and "it may be concluded that the activation energy is required to open up a passage through which the particle can travel." The work required to open up a passage of a unit length is greater below  $T_g$  than above, since the surrounding chains in the glassy state are far less mobile below  $T_g$ .<sup>17</sup> The lower  $E_D$  below  $T_g$  is explained by Meares as resulting from the mean jump length of the diffusant molecules being very much smaller below  $T_g$  than above it.<sup>17</sup>  $E_D$  is hence dependent on two variables: the volume affected by each jump of the diffusant molecule and the amount of work which is invested in pushing aside the segments in the polymeric matrix. From this, one may hypothesize that when a polymer is very dense with practically no free volume, a very large amount of work, per unit distance, must be invested in order to open a passage for a diffusing molecule, resulting in a very high  $E_D$ . On the other extreme, when a polymer has a very high amount of free volume, its chains are easily shoved aside, leading to a low  $E_D$ . In other words,  $E_D$  for a flexible-chain polymer above  $T_g$  is directly proportional to the amount of free volume existing in the system. From the proportionality of  $E_D$  above and below  $T_g$ , the same argument should hold below  $T_g$ . The statement above is in agreement with the fluctuation theory,<sup>18,19</sup> which states that a lower  $E_D$  indicates a smaller excess volume fluctuation.

Now,  $(FFV)_{T_R}$  reflects the amount of free volume formed in the polymer in the  $\Delta T$  temperature interval: the larger  $(FFV)_{T_R}$ , the larger is the free volume at  $T_R$ . When normalized with respect to temperature, under the assumption of uniform expansion in the  $\Delta T$  interval ( $\alpha_L = \text{constant}$ ), a larger  $(FFV)_{T_R}$  reflects a larger free volume at any reduced temperature in the  $T_R - T_g$  range. A large  $(FFV)_{T_R}$  should hence lead to a small  $E_D$  over the whole  $\Delta T$  interval, and a small  $(FFV)_{T_R}$  should lead to a large  $E_D$  value. For a given diffusant molecule with a cross-sectional area of  $d^2$ , the ratios of  $E_D/d^2$  should follow the same relationship as above. From the proportionality of  $E_D$  above and below  $T_g$ , the above  $FFV - E_D$  relationship should hold also below  $T_g$  but with different numerical values.

The relationship between  $E_D/d^2$  above  $T_g$  and  $(FFV)_{T_R}$  is shown in Figure 1. It is obvious that  $E_D/d^2$  decreases as  $\Delta\alpha \Delta T$  increases, in accord with our expectations. Bearing in mind the difficulties in accurately determining the diffusion and the expansivity parameters, and the fact that they were obtained on different samples in different laboratories, the fit is remarkably good. All but one of the thermal data appear in references 1 and 5. For fluorinated ethylene-propylene (FEP)<sup>20</sup>  $T_g = 343^\circ\text{K}$  and  $\Delta\alpha = 2.83 \times 10^{-4}$ , leading to  $T_R = 774^\circ\text{K}$  and  $\Delta\alpha \Delta T = 0.1220$ . The diffusion data, mostly from the range of  $T_g + 40^\circ\text{C}$  to  $T_g + 100^\circ\text{C}$ , were obtained from references 9, 10, 13, 14, 15 and 21–37, with the data for PTFE and PC being extrapolated from the glassy to  $T_g + 40^\circ\text{C}$ . Because the  $E_D/d^2$  data per each polymer for several diffusants such as  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  were rather close together, an average value was used in the plot in Figure 1. The line was visually fitted to the data points and is described by

$$(E_D/d^2) \times 10^3 = 3.34 - 20.5(\Delta\alpha \Delta T) \quad (4)$$

The equation indicates that, on the average, when a polymer has an  $(FFV)_{T_R}$  of about 0.16, the transport of gas molecules through it becomes practically effortless. Since  $FFV$ 's reflect significantly larger total free volumes at  $T > T_g$ ,<sup>2</sup>

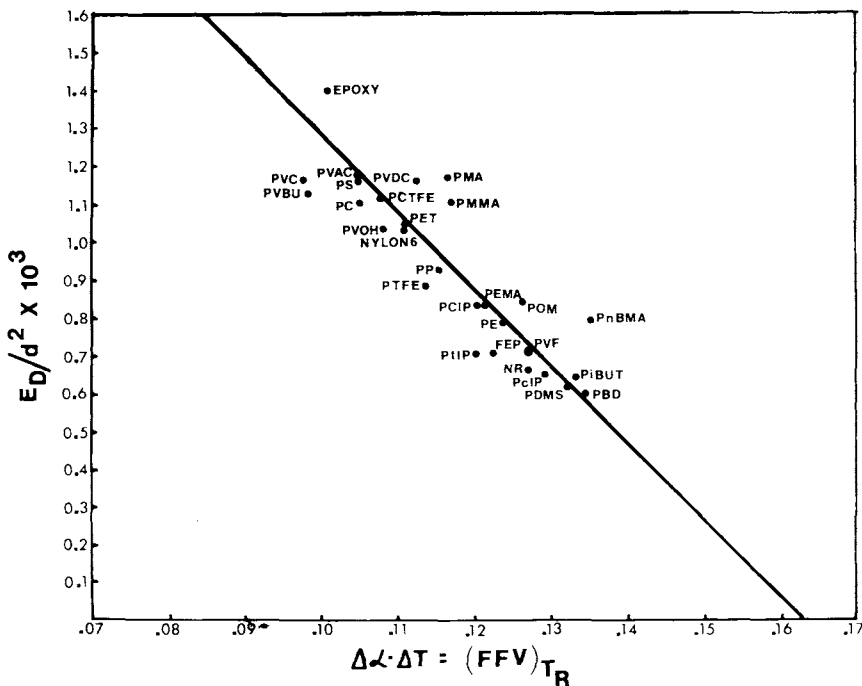


Fig. 1. Plot of  $E_D/d^2$  vs.  $(FFV)_{T_R}$ . Abbreviations: poly(vinyl acetate) (PVAC), poly(vinyl chloride) (PVC), poly(vinylbutyral) (PVBU), polystyrene (PS), poly(vinylidene chloride) (PVDC), poly(methyl acrylate) (PMA), poly(chlorotrifluoroethylene) (PCTFE), polycarbonate of bisphenol A (PC), poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), poly(vinyl alcohol) (PVOH), polypropylene (PP), poly(tetrafluoroethylene) (PTFE), poly(ethyl methacrylate) (PEMA), polychloroprene (PCIP), poly(oxymethylene) (POM), poly(*n*-butyl methacrylate) (PnBMA), polyethylene (PE), poly(vinyl fluoride) (PVF), fluorinated ethylene propylene (FEP), poly-*trans*-isoprene (PtIP), natural rubber (NR), poly-*cis*-isoprene (PciIP), polyisobutylene (PiBUT), poly(dimethylsiloxane) (PDMS), polybutadiene (PBD).

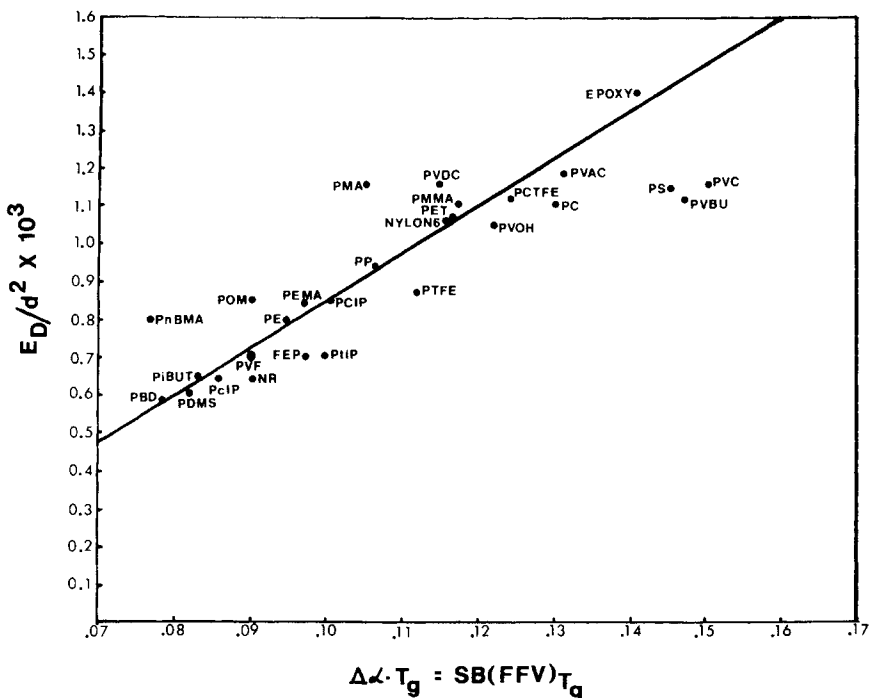


Fig. 2. Plot of  $E_D/d^2$  vs.  $SB(FFV)_{T_g}$ . Same abbreviations as in Fig. 1.

one deals here with volume increases of the order of 0.25 above the total free volume at  $T_g$ . On the other hand, when  $(FFV)_{T_g} = 0$ , the value of  $E_D/d^2$  is enormous, indicating that molecular rupture and material destruction will occur before transport will take place.

When experiments were performed over a wide temperature interval above  $T_g$ , it became obvious that a gradual decrease in  $E_D$  takes place with the increase in temperature. This was observed for such diverse systems as natural rubber,<sup>8,38</sup> poly(vinyl acetate),<sup>39</sup> poly-*cis*-isoprene,<sup>40,41</sup> polyethylene,<sup>42</sup> poly(methyl acrylate),<sup>43</sup> chloroprene,<sup>41</sup> possibly polystyrene,<sup>44</sup> and a host of other rubbery substances.<sup>7,8,40,42</sup> These relationships are all in agreement with our conclusion that an increase in  $FFV$  above  $T_g$  is associated with a corresponding decrease in  $E_D d^2$ . From the proportionality of  $E_D$  above and below  $T_g$ , this conclusion carries over to temperatures below  $T_g$ , too. From his experimental data, van Amerongen concluded<sup>8</sup> that it appears that the experimental points for a given gas fall along curves of the shape

$$E_D = a - b(T + T_g) \quad (5)$$

This equation bears a remarkable similarity in form and content to our eq. (4). Due to the scarcity of data, it is impossible yet to determine whether these two equations are in essence one and the same. Nevertheless, the expectations from our model are in perfect agreement with van Amerongen's conclusion.

To be physically meaningful, the Simha-Boyer fractional free volume at  $T_g$  should show an inverse dependence on the magnitude of  $E_D/d^2$  both above and below  $T_g$ . That is, the larger  $SB(FFV)_{T_g}$ , the smaller is  $E_D/d^2$ . The similarity in the dependence of  $SB(FFV)_{T_g}$  above and below  $T_g$  should arise from the constant proportionality between  $E_D/d^2$  above and below  $T_g$ . The experimental

observations, however, contrast the expected  $SB(FFV)_{T_g}-E_D/d^2$  relationship. This relationship is plotted in Figure 2. Here,  $E_D/d^2$  increases with the increase in  $SB(FFV)_{T_g}$ , and the visually fitted line is described by the equation

$$(E_D/d^2) \times 10^3 = -0.35 + 12.3(\Delta\alpha T_g) \quad (6)$$

According to this equation, the larger the free volume, the higher is the activation energy for diffusion through the polymer. Since this contradicts experimental results, cohesive energy considerations, and diffusion theory, the physical meaning of  $SB(FFV)_{T_g}$  should be reexamined.

Finally, the correlation between  $E_D/d^2$  and  $(FFV)_{T_R}$  is useful in estimating unknown parameters such as  $\Delta\alpha$  or  $E_D$  above  $T_g$ . This is demonstrated in this work by the case of poly(vinyl fluoride) (PVF) for which  $E_D$  but not  $\Delta\alpha$  was known. By placing the PVF point on the line in Figure 1 at a point corresponding to  $E_D/d^2$ , and from the knowledge of  $T_g$  and  $T_R$ ,  $\Delta\alpha$  was calculated.  $E_D$  can be estimated in a similar fashion.

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