Diffusion in Polymers below the Glass Transition Temperature: Comparison of Two Approaches Based on Free Volume Concepts

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Abstract–Theories based on free-volume concepts have been developed to characterize the self and mutual diffusion coefficients of low molecular weight penetrants in rubbery and glassy polymer-solvent systems. These theories are applicable over a wide range of temperatures and concentrations. In this paper, two alternative free-volume based approaches used to evaluate the solvent self-diffusion in glassy polymer-solvent systems are compared in terms of their differences and applicability

Key words: Diffusivity, Self-Diffusion Coefficient, Polymers, Glass Transition, Free-Volume

INTRODUCTION

The diffusion of small molecules in polymers is of considerable practical importance and has been studied extensively. Diffusion theories based on the free-volume concept have been used extensively to correlate and predict solvent self-diffusion in rubbery polymer-solvent systems [Vrentas and Duda, 1977a, b; Zielinski and Duda, 1992; Vrentas and Vrentas, 1994a, 1998]. These methods provide accurate pre- dictions over a wide range of temperatures and concentrations above the glass transition temperature of the pure polymer. As polymer solutions are cooled, the rate of cooling exceeds the rate of relaxation of the polymer sample, and a non-equilibrium state referred to as the glassy state results. This causes extra hole free-volume to be trapped in the polymer. Based on this concept, the free-volume theory has been extended to describe the diffusion of a trace amount of a solvent in a polymer [Vrentas and Duda, 1978; Duda et al., 1994]. The addition of a solvent to a polymer depresses the glass transition temperature of the mixture compared to the glass transition temperature of the pure polymer. The free-volume theory has also been extended to describe self-diffusion below the glass transition temperature of the mixture at finite concentrations of the solvent [Vrentas and Vrentas, 1992, 1994b]. It has been pointed out that some problems exist below the glass transition temperature of the pure polymer in the original extension of the free-volume theory [Vrentas and Vrentas, 1993; Lodge et al., 1990], and methods have been proposed to counter these difficulties [Vrentas and Vrentas, 1994a, b]. In this paper, two free-volume based approaches used to correlate and predict solvent self-diffusion below the glass are compared and their applicability and differences are discussed.

FREE-VOLUME THEORY

According to the free-volume theory, molecular diffusion is

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based on the amount of free space or free-volume between the molecules and was first used to describe the diffusion in liquids [Cohen and Turnbull, 1959]. Cohen and Turnbull envision translational motion in a liquid consisting of spherical molecules to occur when a large enough hole to accommodate that molecule is formed adjacent to the molecule through random thermal fluctuations. According to this point of view, a molecule does not need to attain a specific energy to overcome an activation energy barrier, but can undergo translational motion by simply jumping into a free-volume hole arising from the continuous redistribution of free-volume within the material. By considering the probability of a molecule finding a hole large enough to accommodate it, Cohen and Turnbull developed the following relationship:

$$D_1 = A_O \exp(-\gamma \hat{V}^* / V_f) \tag{1}$$

In this expression, D_1 is the self-diffusion coefficient of the molecule, $\hat{V}^*$ is the minimum volume hole size into which a molecule can jump, and γ is a numerical factor introduced to account for the free-volume being shared by the neighboring molecules. V_f is the average free-volume per spherical molecule in the liquid and A_O is proportionality constant which Cohen and Turnbull consider to be related to the gas kinetic velocities.

The free-volume concepts developed by Cohen and Turnbull to describe the self-diffusion in a liquid have been extended to describe mutual binary diffusion coefficient consisting of a polymeric species and a relatively low molecular weight solvent [Vrentas and Duda, 1977a, b]. For the case of self-diffusion coefficient D_1 of a solvent (component 1) and a polymer (component 2), the free-volume formalism may be written as:

$$D_1 = D_{01} \exp(-E/RT) \exp[-(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)/(\hat{V}_{FH}/\gamma)] \tag{2}$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{K_{11}}{\gamma_1}(K_{21} - T_{g1} + T) + \omega_2 \frac{K_{12}}{\gamma_2}(K_{22} - T_{g2} + T) \tag{3}$$

Here ω_i are the weight fractions of species i, $\hat{V}_i^*$ is the specific hole free-volume required for a diffusional step of component i, and $\hat{V}_{FH}$ is the specific hole free-volume of the system. D_{01}, is

assumed to be a constant pre-exponential factor and is independent of the temperature of the system. The parameter ξ, is the ratio of the molar volume of the jumping unit of the solvent to the molar volume of the jumping unit of the polymer. In this formulation, it is often assumed that for the diffusion of small molecules, it is the complete solvent molecule that is the solvent jumping unit, while the polymer is made up of several small units that jump independently [Vrentas and Duda, 1979]. E, is the energy per mole that a molecule requires to overcome attractive forces which hold it to its neighbors, T is the temperature of the system, and R is the gas constant. Techniques have been developed so that all the parameters, K_{11}/γ_1, K_{12}/γ_2, $K_{21}-T_{g1}$ and $K_{22}-T_{g2}$ can be estimated from properties of the two pure components comprising the mixture [Zielinski and Duda, 1992; Vrentas et al., 1996; Vrentas and Vrentas, 1998]. The free-volume parameters are defined in terms of the thermal expansion coefficients of the two components [Vrentas and Duda, 1977a, b]. This formulation is extremely useful to predict and correlate the self-diffusion coefficient above the glass transition temperature.

DIFFUSION BELOW T_g-THE λ APPROACH

As polymer solutions are cooled, the motion of individual polymer chains becomes so constrained that the cooling rate becomes faster than the rate at which the polymer sample can relax. The resulting non-equilibrium condition is referred to as the glassy state. At temperatures above the glass transition temperature, the polymer chains are capable of achieving equilibrium configurations, while they are incapable of attaining equilibrium configurations below the glass transition temperature in conventional time scales [Duda et al., 1994]. Consequently, from the free-volume point of view, extra hole free-volume becomes trapped in the polymer as it is cooled through the glass transition temperature. In addition, although the rate of molecular motion prevents volume relaxation from reaching an equilibrium state in glassy polymers, molecular motion is not eliminated in the glassy state. Using these ideas, the free-volume framework was first extended to predict the self-diffusion coefficient for polymer-solvent systems below the glass transition temperature of both the pure polymer and the mixture [Vrentas and Duda, 1978]. In the limit of trace amount of a solvent diffusing in the polymer, the glass transition temperature of the mixture can be assumed the same as the glass transition temperature of the pure polymer. This idea leads to an extension of the free-volume formulation to describe diffusion of a trace amount of solvent below the glass transition temperature of the pure polymer. In this limit of $\omega_1 \rightarrow 0$ the solvent self-diffusion coefficient D_1 is equal to the mutual binary diffusion coefficient D, and the free-volume formulation for the solvent self-diffusion can be expressed as:

$$D = D_1 = D_{01} \exp\left(\frac{-\gamma \xi \hat{V}_2^*}{\hat{V}_{FH2g}}\right) \quad (4)$$

$$\frac{\hat{V}_{FH2g}}{\gamma} = \frac{K_{12}}{\gamma_2}(K_{22} + \lambda[T - T_{g2}]) \quad (5)$$

Eq. (4) assumes that the activation energy term equals 0. The parameters K_{12} and K_{22} are the same as defined before. The key

parameter in this formulation is λ, which is related to the change in the expansion coefficient of the polymer above the glass transition temperature, α_2, and the expansion coefficient of the glassy polymer, α_{2g} [Vrentas and Duda, 1978].

$$\lambda = 1 - \frac{\hat{V}_2^0(T_{g2})[\alpha_2 - \alpha_{2g}]}{K_{12}} \quad (6)$$

This formulation has been extended to describe diffusion at finite concentrations of solvent and temperatures between the glass transition temperature of the mixture and the glass transition temperature of the pure polymer [Vrentas and Vrentas, 1992]. The polymer is assumed to possess an equilibrium structure between T_{g2}, the glass of the pure polymer and T_{gm}, the glass of the mixture. Under these conditions, the thermal expansion coefficient characterizing the reduction in free-volume with temperature is assumed to be the same as that above the glass transition temperature of the pure polymer. The expression for the free-volume of a polymer-solvent mixture, therefore is the same as that for a rubbery polymer-solvent mixture. However, at finite concentrations of the solvent for temperatures below the glass transition temperature of the mixture the expansion coefficient describing the reduction in polymer free-volume with temperature undergoes a change. Therefore, the free-volume of the polymer decreases at a different rate compared to that above the glass transition temperature of the mixture. It is possible to describe the self-diffusion coefficient if appropriate expressions are available to estimate the free-volume of the glassy polymer-solvent mixture. It must be noted that the free-volume of a glassy polymer-solvent mixture will depend on the sample preparation method, because the properties of a glassy polymer-solvent mixture are history dependent. For a simple sample preparation history, expressions have been derived for the free-volume of a glassy poymer-solvent mixture [Vrentas and Vrentas, 1992].

$$\hat{V}_{FH} = \omega_1 \hat{V}_{FH1} + \omega_2 \hat{V}_{FH2} + \omega_2 \hat{V}_2^0(T_{g2})$$
$$[1 - A\omega_1\alpha_2][T - T_{g2} + A\omega_1][\alpha_{2g} - \alpha_2] \quad (7)$$

$$\hat{V}_{FH1} = K_{11}(K_{21} - T_{g1} + T) \quad (8)$$

$$\hat{V}_{FH2} = K_{12}(K_{22} - T_{g2} + T) \quad (9)$$

In the development of the above equations, a linear approximation has been assumed to describe the concentration dependence of the glass transition temperature of the mixture.

$$T_{gm} = T_{g2} - A\omega_1 \quad (10)$$

A is a factor that is a measure of the depression in glass transition temperature as a function of solvent weight fraction.

DIFFUSION BELOW THE GLASS - THE α APPROACH

One of the problems arising from the λ approach is that the polymer volume in an equilibrium polymer-solvent mixture becomes zero at $T = T_{g2} - K_{22}$. This is a consequence of the assumption that the thermal expansion coefficient of the polymer at temperatures between T_{g2} and T_{gm}, is the same as that above the glass transition temperature of the pure polymer. To counter this

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problem, a second approach has been developed [Vrentas and Vrentas, 1994a, b]. In this approach, three distinct regions are envisaged to exist. Region 1 and region 2 are rubbery polymer-solvent mixtures. Region 1 exists above the glass transition temperature of the pure polymer, while region 2 exists between the glass transition temperature of the pure polymer and the glass of the mixture. Region 3 is a glassy polymer solvent mixture, and exists below T_{gm}, the glass transition temperature of the mixture. For rubbery polymer-solvent systems, expressions for the hole free-volume above and below the glass transition temperature of the pure polymer are given as follows [Vrentas and Vrentas, 1994a]:

$$\frac{\hat{V}_{FH}}{\gamma}=\omega_1\frac{K_{11}}{\gamma_1}(K_{21}-T_{g1}+T)+\omega_2\frac{\hat{V}_{FH2}}{\gamma_2} \quad (11)$$

$$\hat{V}_{FH2}=\hat{V}_2^0(T_{g2})[f_{H2}^G-\int_T^{T_{g2}}(\alpha_2-\alpha_{c2})dT']\ (T<T_{g2}) \quad (12)$$

In these equations T_{gi} is the glass transition temperature of component i, K_{11} and K_{21} are the free-volume parameters of the solvent, γ_i represents the overlap factor for the free-volume of component i and $\hat{V}_{FH2}$ is the specific hole free-volume of the equilibrium liquid polymer at any temperature. $\hat{V}_2^0$ (T_{g2}), is the specific volume of the pure equilibrium liquid polymer at T_{g2}, f_{H2}^G is the fractional hole free-volume of the polymer at its glass transition temperature T_{g2}, α_2 is the thermal expansion coefficient of the equilibrium liquid polymer and α_{c2} is the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial volume of the equilibrium liquid polymer. It is assumed that α_2 is a constant above T_{g2}, but possibly temperature dependent below T_{g2}. It is also assumed that α_{c2} is a constant below T_{g2}, but drops rapidly to zero above T_{g2}, and this drop is idealized as a step change at T_{g2}. The quantities f_{H2}^G, α_{c2}, γ_2 can be computed as follows [Vrentas and Vrentas, 1994a, b]:

$$f_{H2}^G=\alpha_2 K_{22} \quad (13)$$

$$\alpha_{c2}=\frac{\ln\left[\frac{\hat{V}_2^0(T_{g2})(1-f_{H2}^G)}{\hat{V}_2^0(0)}\right]}{T_{g2}} \quad (14)$$

$$\gamma_2=\frac{\hat{V}_2^0(T_{g2})\alpha_2}{K_{12}/\gamma_2} \quad (15)$$

$$\hat{V}_1^*=\hat{V}_1^0(0) \quad (16)$$

$$\hat{V}_2^*=\hat{V}_2^0(0) \quad (17)$$

In these equations, $\hat{V}_i^0(0)$ is the specific volume of component i at 0 K and K_{12} and K_{22} are the free-volume parameters for the polymer. This idea has also been extended for glassy polymer solvent systems, and the specific hole free-volume of the system can be calculated using the expression given below [Vrentas and Vrentas, 1994b]:

$$\frac{\hat{V}_{FH}}{\gamma}=\omega_1\frac{K_{11}}{\gamma_1}(K_{21}-T_{g1}+T)+\omega_2\frac{\hat{V}_{FH2g}}{\gamma_2} \quad (18)$$

In the above expression, $\hat{V}_{FH2g}$ is the specific hole free-volume of the glassy polymer at any temperature below T_{gm}, the glass transition temperature of the mixture. An expression for the

specific hole free-volume of the glassy polymer can be derived by integrating the defining equations for α_{2g}, the thermal expansion coefficient of the glassy polymer and α_{c2g}, the thermal expansion coefficient for the sum of the specific occupied volume and specific interstitial free-volume of the polymer. α_{2g} and α_{c2g} are defined below.

$$\frac{\partial \ln(\hat{V}_{2g}^0)}{\partial T}=\alpha_{2g} \quad (19)$$

$$\frac{\partial \ln(\hat{V}_{FI2g}+\hat{V}_{2g0})}{\partial T}=\alpha_{c2g} \quad (20)$$

$$\hat{V}_{FH2g}=\hat{V}_{2g}-[\hat{V}_{FI2g}+\hat{V}_{2g0}] \quad (21)$$

In the above equations, $\hat{V}_{2g}^0$ is the specific volume of the glassy polymer, $\hat{V}_{FI2g}$ is the specific interstitial volume of the glassy polymer, and $\hat{V}_{2g0}$ is the specific occupied volume of the glassy polymer. It is assumed that an expression of the form $\exp(\alpha T)=(1+\alpha T)$ is an accurate representation in the temperature range of interest. Using the above definitions and assumptions, the expression for the free-volume of the polymer below the glass transition temperature of the mixture is written as,

$$\hat{V}_{FH2g}=\hat{V}_2^0(T_{g2})[f_{H2}^G-\int_{T_{gm}}^{T_{g2}}(\alpha_2-\alpha_{c2})dT'-\int_T^{T_{gm}}(\alpha_{2g}-\alpha_{c2g})dT']\ T<T_{gm} \quad (22)$$

To estimate α_{c2g}, the assumption that $(\alpha_{c2g}/\alpha_{c2})=(\alpha_{2g}/\alpha_2)_{T=T_{g2}}$ is invoked.

This equation reduces to a simple form if it is assumed that a trace amount of solvent does not alter the glass transition temperature of the mixture significantly when compared to the glass transition temperature of the pure polymer.

$$\hat{V}_{FH2g}=\hat{V}_2^0(T_{g2})[f_{H2}^G-(\alpha_{2g}-\alpha_{c2g})(T_{g2}-T)] \quad (23)$$

RESULTS AND DISCUSSION

Using the equations given in the preceding sections, the differences between the λ approach and the α approach are compared using the Polystyrene-toluene system as an example. The values of the parameters used in generating this figure are shown in Table 1. Fig. 1 shows that the free-volume of the pure polymer at various temperatures above and below the glass transition temperature of the pure polymer. Above the glass transition temperature, identical values of free-volume are obtained using both approaches. A break is observed at the glass transition temperature because of a change in the expansion coefficient at this point. It is observed that the free-volume calculated using the α approach is greater than that calculated using the α approach below the glass transition temperature. This is a consequence of the assumption that a change in the expansion coefficient for the sum of the occupied and interstitial free-volume occurs at the glass transition temperature. This change is idealized as a step change at the glass transition temperature.

Figs. 2 and 3 compare the free-volume of a PS-Toluene mixture as an example, at different weight fractions of the solvent, 5 and 15 wt% respectively. The values of the parameters used in the above mentioned figures are listed in Table 1. Since the addition of a solvent to a polymer depresses the glass transition
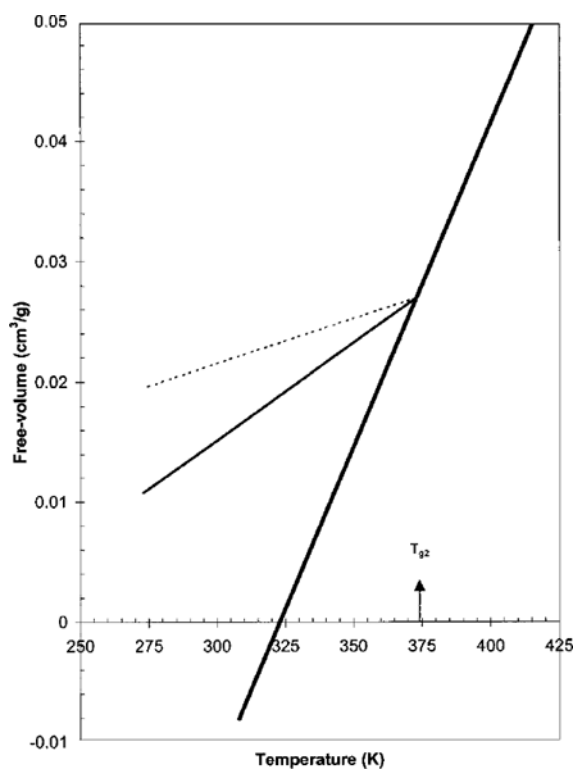
Fig. 1. Free-volume of the pure polymer above and below T_{g2}. Bold solid line represents free-volume in an equilibrium structure. Thin solid line shows free-volume using λ approach and the dotted line shows free-volume using the α approach.
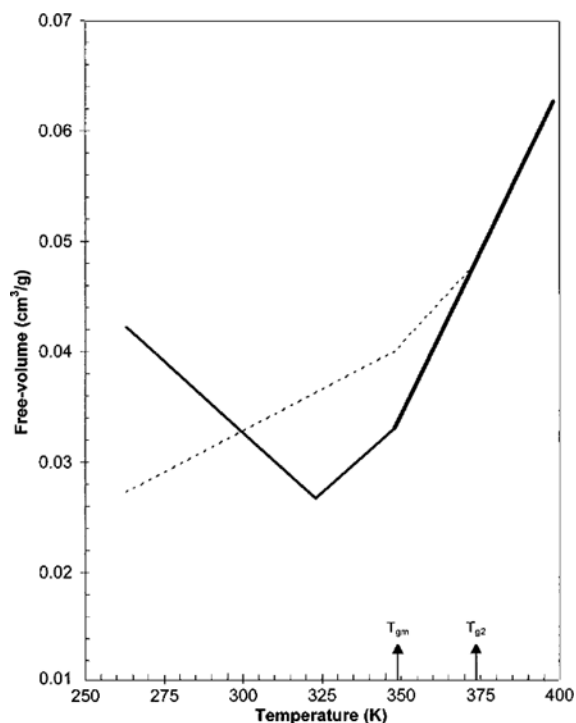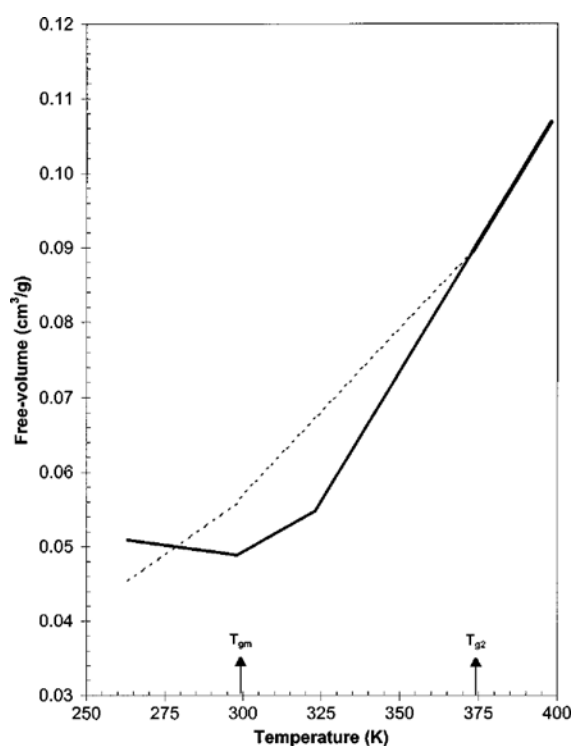

Fig. 3. Free-volume of a 15 wt% Polystyrene-toluene mixture. Bold solid line represents free-volume in an equilibrium structure. Thin solid line shows free-volume using λ approach and the dotted line shows free-volume using the α approach.

temperature of the mixture, the three regions discussed in the preceding section are observed on the graph for the calculated free volume using the α approach. Region 1 as stated before lies above the glass transition temperature of the pure polymer. Region 2 exists between the glass transition temperature of the pure polymer and the glass transition temperature of the mixture while region 3 is located below the glass transition temperature of the mixture. In this example, the depression in the glass transition temperature is accounted for using the approximate linear relationship given in Eq. (10) with A=500. This value results from plotting the approximate theory of Chow in the concentration range of 0-16 wt% solvent [Chow, 1980]. A break in the

Table 1. Free-volume parameters used to generate Figs. 1-3

K_{11}/γ_1 (cm^3/g K)	0.00157
K_{12}/γ_2 (cm^3/g K)	0.000539
$K_{21}-T_{g1}$ (K)	−90.5
K_{22} (K)	50
f_{H2}^G	0.0265
$\hat{V}_2^0(T_{g2})$ (cm^3/g)	0.972
α_2 (K^{-1})	0.00053
α_{c2} (K^{-1})	0.000288
α_{2g} (K^{-1})	0.00016
α_{c2g} (K^{-1})	0.000087
A (K)	500
λ	0.3
T_{g2} (K)	373

Fig. 2. Free-volume of a 5 wt% Polystyrene-toluene mixture. Bold solid line represents free-volume in an equilibrium structure. Thin solid line shows free-volume using λ approach and the dotted line shows free-volume using the α approach.

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free-volume is observed at the glass transition temperature of the mixture. This occurs because there is a change in the thermal expansion coefficient of the equilibrium liquid polymer and the sum of the occupied and interstitial free-volumes at this point. The break in free-volume becomes more difficult to detect at high solvent concentrations, since the contribution of the polymer free-volume is small compared to the solvent. At $T=T_{g2}-K_{22}$, using the λ approach, the free-volume of the polymer becomes zero and at temperatures below this value assumes negative values, as demonstrated by the thick solid line in Fig. 1. Since negative values of free-volumes are not consistent with the free-volume theory, the free-volume is set to zero. This leads to an artificial break in the graph of free volume as a function of temperature using the λ approach. It is also observed that the free-volume calculated using the λ approach increases after the free-volume of the polymer is set to zero. This is an artificial effect and caution must be exercised when utilizing this expression. It must be noted that in this illustrative case, constant values of α_2 and α_{2g} are used. However, if the thermal expansion coefficients are available as a function of temperature, they must be used since this could lead to a significantly higher free-volumes being calculated at low temperatures [Vrentas and Vrentas, 1994a]. If data are available describing depression in the glass transition temperature with addition of solvent, they must be used. In the absence of any data, an approximate theory developed by Chow may be used [Chow, 1980].

Diffusion of a tracer, TTI (tetra-hydrothiophene indigo) has been studied in PS (polystyrene) [Ehlich and Silescu, 1990]. Table 2 lists the values of the parameters used in this correlation. Fig. 4 compares the diffusion coefficient of this tracer, TTI in PS calculated using the α approach and the λ approach. From this figure, we observe that the diffusion coefficient calculated using the two approaches is the same above the glass transition temperature of pure polystyrene. This is consistent with the results of Fig. 1, where no difference in the free-volume above the glass transition temperature of the pure polymer is observed. However, a difference is observed in the estimated diffusion coefficient be-
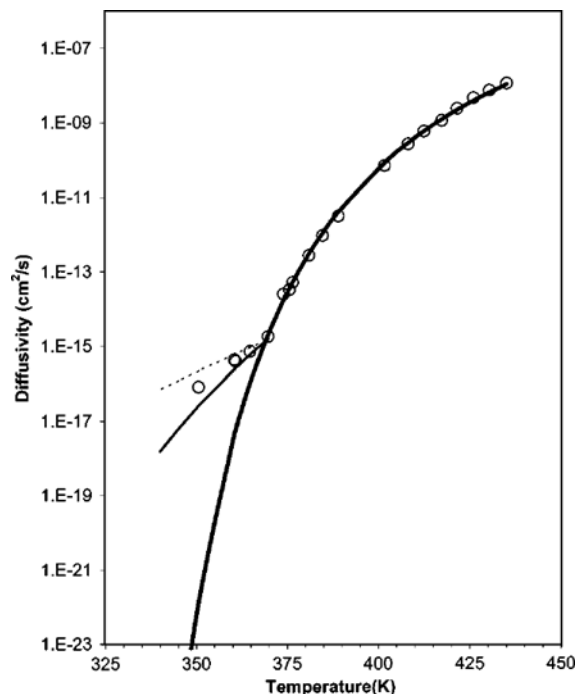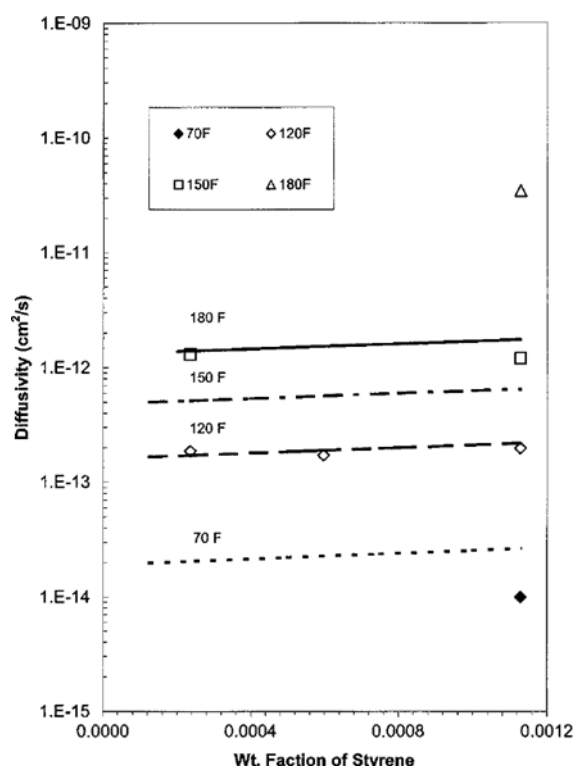

Fig. 4. Comparison of correlation for TTI (tetra hydrothiophene indigo) in polystyrene using the α and λ approaches. Bold solid line represents free-volume in an equilibrium structure. Thin solid line shows free-volume using λ approach and the dotted line shows free-volume using the α approach. Data from Ehlich and Sillescu [Ehlich and Sillescu, 1990].

low the glass transition temperature. The predicted value of diffusivity using the λ approach is smaller than that using the α approach, especially at low temperatures. This is a consequence of the higher free-volume predicted by the α approach when compared to the λ approach. For diffusion of TTI in PS, the λ approach does a better job of correlating the data of Ehlich and Sillescu. However, at the lowest temperature, deviations are seen between the correlation and the datum point for both approaches. It must be noted that the values of α_2, α_{2g} and T_{g2} were used from the data provided by Ehlich and Sillescu, while the values of D_0 and ξ were regressed from the data above the glass transition temperature of the pure polymer. In the analysis, the glass transition temperature was taken as 369 K, the temperature on the D vs. T curve where a break in diffusivity is observed. The two parameters D_0 and ξ were correlated independently for the two approaches, however, their values were identical.
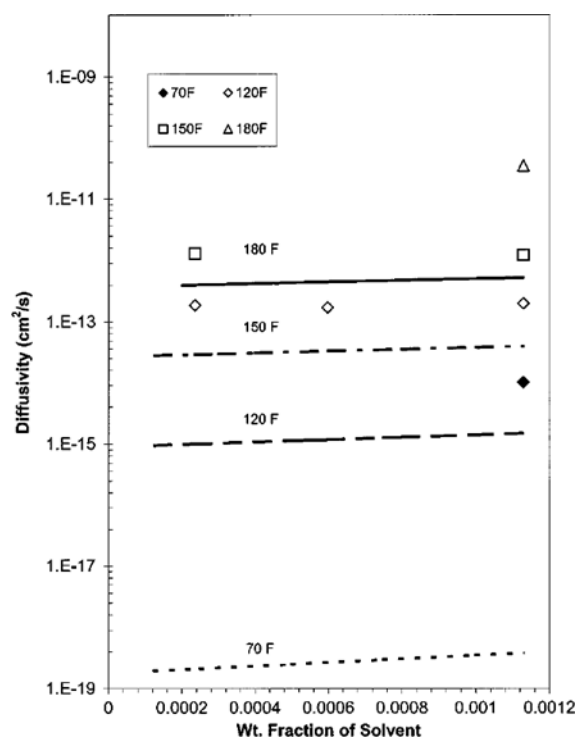
The diffusion of styrene diffusing in polystyrene has been measured by Murphy and co-workers at different residual levels of styrene and at different temperatures below the glass transition temperature [Murphy et al., 1992]. These experimental results have been compared with the predictions of the two approaches of the free-volume theory. These data were obtained over a small range of concentrations and a relatively large range of temperatures. In this analysis, the thermodynamic term relating the change in activity with change in solvent concentration has been neglected, since in the limit of pure polymer, the thermodynamic term approaches 1. Hence, the predicted values of the self-dif-

Table 2. Free-volume parameters used in the correlation presented in Fig. 4

D_{01} (cm^2/s)	0.0017 (α), 0.00156 (λ)*
$\hat{V}_2^0(T_{g2})$ (cm^3/g)	0.972
f_{H2}^G	0.028
α_2 (K^{-1})	0.00056
α_{2g} (K^{-1})	0.00019
α_{c2g} (K^{-1})	0.000097
K_{22} (K)	50
A (K)	500
λ	0.34
T_{g2} (K)	369
γ_2	1.0
ξ	0.9
K_{12}/γ_2 (cm^3/g K)	0.000544
E (kcal/mole)	0

*The α and λ approaches result in different values for D_{01}.

Table 3. Free-volume parameters used in the prediction for the Styrene-Polystyrene system, Figs. 5 and 6

D_{01} (cm²/s)	0.000461
$\hat{V}_2^0(T_{g2})$ (cm³/g)	0.972
f_{H2}^G	0.0265
α_2 (K⁻¹)	0.00053
α_{2g} (K⁻¹)	0.00016
α_{c2g} (K⁻¹)	0.000087
K_{22} (K)	50
λ	0.30
T_{g2} (K)	373
γ_2	0.956
ξ	0.9
K_{12}/γ_2 (cm³/g K)	0.000539
E (kcal/mole)	0

Fig. 5. Prediction of Styrene diffusion in Polystyrene-α approach. Data from Murphy and co-workers [Murphy et al., 1992].

fusion coefficient are equivalent to the mutual binary diffusion coefficient. Since free-volume parameters were not available for Styrene, free-volume parameters for ethylbenzene, a molecule of similar size and structure were used instead. It must be noted that as a first approximation the activation energy for diffusion as defined in Eq. (2) was assumed to be zero. The parameters used to predict the self diffusion-coefficient of styrene in polystyrene were obtained from several sources [Zielinski and Duda, 1992; Vrentas and Vrentas, 1994a, b; Vrentas et al., 1996], and are listed in Table 3. The free-volume predictions for the diffusion of styrene in polystyrene using the α approach and λ the approach are shown in Fig. 5 and Fig. 6 respectively. It is clear

Fig. 6. Prediction of Styrene diffusion in Polystyrene-λ approach. Data from Murphy and co-workers [Murphy et al., 1992].

that the self-diffusion coefficient of styrene is a weak function of the concentration of styrene in the concentration range studied by Muphy and co-workers.

At low concentration levels, the agreement between predicted values using the α approach and experimentally measured values are good at all temperatures except 180 °F. At low temperatures the difference between the predicted value of diffusivity using the two approaches becomes clearly evident, and values predicted using the λ approach are smaller than the experimentally measured values at all temperatures. This clearly illustrates the effect of the smaller free-volume predicted by the λ approach.

The diffusion coefficient of a small molecule at high polymer concentrations is controlled by the hole free-volume of the system. An increase in temperature as well as an increase in the concentration of the low molecular weight penetrant can cause an increase in the free-volume of the system and hence an increase in the diffusion coefficient.

CONCLUSIONS

Two approaches to correlate and predict self-diffusion coefficients below the glass transition temperature of the pure polymer and mixture are the α approach and the λ approach. These approaches have been compared in terms of the values that they yield for free-volume of the polymer, and free-volume of the mixture. It has been pointed out that the free-volume calculated using the λ approach decreases quickly, and this leads to the non-physical result of a zero or even negative free-volume of the polymer in equilibrium mixtures. The α approach however, obviates this difficulty to some extent. It must however, be noted that

both these approaches provide approximations to the actual behavior and the λ approach is applicable for diffusion of trace amounts of a penetrant, in the vicinity of T_{g2}. If methods become available to accurately determine the occupied and interstitial volume at all temperatures, and especially at temperatures below the glass transition temperature, the basic equations given in the preceding sections can be used to obtain more precise predictions.

Diffusion of the tracer, TTI in PS has been used to illustrate the differences in results that can be obtained using the two approaches. A higher diffusion coefficient has been predicted below the glass transition temperature using the α approach, while a smaller value was predicted using the λ approach at the lowest temperature. This result is consistent with the free-volume behavior calculated using the two approaches. This result also indicates that the actual behavior of free-volume may be something between the values predicted by the two approaches.

The predictions have been compared to the experimental results of Murphy and co-workers and the results indicate that the predictions are consistent with experimental results. These data clearly elucidate the differences in the predictions between the two approaches, which become apparent at low temperatures.

The α approach has been used successfully to predict the diffusion coefficient of styrene in general purpose polystyrene at low concentrations of styrene and temperatures below the glass transition temperature of the pure polymer. However, one of the practical problems with the α approach is that all the parameters are usually not available to effectively utilize this approach. Much of the data available below the glass is at an infinite dilution of the penetrant. Therefore, in many cases, the λ approach is used to correlate diffusion coefficients with λ as an adjustable parameter. Since the glassy state is a non-equilibrium state, the thermal expansion coefficients of the polymer are history dependent and are likely be different for the same polymer depending on the history of the sample. At high solvent concentrations and low temperatures, diffusion is typically coupled with relaxation. Analysis of data obtained under these conditions is not trivial and this is one of the reasons that the preponderance of data available is at infinite dilution.

NOMENCLATURE

A_0	: pre-exponential factor in Eq. (1)
A	: constant characterizing the depression in T_g [K]
D	: mutual binary diffusion coefficient [cm^2/s]
D_1	: self-diffusion coefficient [cm^2/s]
D_{01}	: constant pre-exponential factor [cm^2/s]
E	: energy/mole required to over-come attractive forces of neighboring molecules
f_{H2}^G	: fraction free-volume of the polymer at the glass
K_{11}/γ_1	: free-volume parameter of component 1 [cm^3/g K]
K_{12}/γ_2	: free-volume parameter of component 2 [cm^3/g K]
K_{21}	: free-volume parameter of component 1 [K]
K_{22}	: free-volume parameter of component 2 [K]
R	: gas constant
T	: temperature [K]
T_{g1}	: glass transition temperature of component 1 [K]
T_{g2}	: glass transition temperature of component 2 [K]

T_{gm}	: glass transition temperature of the mixture [K]
$\hat{V}_{FH}/\gamma$	: hole free-volume of the system [cm^3/g]
$\hat{V}_2^0(T_{g2})$	: specific volume of the polymer at T_{g2} [cm^3/g]
$\hat{V}_1^*$	: specific hole free-volume for component 1 to jump ($= \hat{V}_1^0(0)$) [cm^3/g]
$\hat{V}_2^*$	: specific hole free-volume for component 2 to jump ($= \hat{V}_2^0(0)$) [cm^3/g]
$\hat{V}_{FH2g}$	: free-volume of a glassy polymer [cm^3/g]
$\overline{V}^*$	: minimum size of hole required for molecular jump
V_f	: average free-volume per molecule
$\hat{V}_{FH1}$	: specific hole free-volume of component 1
$\hat{V}_{FH2}$	: specific hole free-volume of component 2
$\hat{V}_{FH2g}$	: specific hole free-volume of glassy polymer
$\hat{V}_{2g}^0$	: specific volume of glassy polymer
$\hat{V}_{FI2g}$	: specific interstitial volume of glassy polymer
$\hat{V}_{2g0}$	: specific occupied volume of glassy polymer
α_2	: thermal expansion coefficient of the polymer above T_g [K^{-1}]
α_{2g}	: thermal expansion coefficient of the polymer below T_g [K^{-1}]
α_{c2}	: thermal expansion coefficient of the occupied and interstitial free-volume below T_{g2} [K^{-1}]
α_{c2g}	: thermal expansion coefficient of the occupied and interstitial free-volume below T_{gm} [K^{-1}]
γ	: parameter describing sharing of free-volume
λ	: parameter describing relaxation above and below T_g
ω_1	: weight fraction of component 1
ω_2	: weight fraction of component 2
ξ	: ratio of molar volume of jumping unit of the solvent to that of the polymer

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