

Correlation Between Fractional Free Volume and Diffusivity of Gas Molecules in Glassy Polymers

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ABSTRACT: Despite its oversimplifications, the free-volume approach has proven to provide very useful correlative and even semipredictive capabilities. This article is concerned with the correlation between the diffusivity, D , of gas molecules in glassy polymers and the fractional free volume, FFV, determined by the Bondi method. The diffusivities were taken from a database, generated by the authors in connection with work on the new Landolt Börnstein series "Diffusion in Non-Metallic Solids", which encompasses a very large variety of glassy polymers. For a given diffusant $\log D$ is a linear function of $1/\text{FFV}$ as predicted by the free volume theory. However, the deviations from this relationship are significant and strongly correlated between O_2 , N_2 , CO_2 , and CH_4 . The systematic deviations are opposite to the predicted effect of the polymer jumping unit size in the free-volume concept of Vrentas and Duda and are interpreted in terms of an increase in the activation energy with increasing chain stiffness. Correlation analysis further suggests that the diffusion mechanisms of H_2 and particularly of He differ markedly from that of larger gas molecules. Furthermore the influence of the cohesive energy and the glass-transition temperature of the polymers is investigated. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 3344–3358, 1999

Keywords: gas diffusion; glassy polymers; free volume; cohesive energy; chain stiffness

INTRODUCTION

Diffusion of gas molecules through polymeric materials has been studied extensively during the last decades and is of considerable practical concern,^{1–5} for example, for permselective membranes for gas separation, food packing, and protective coatings. From the various factors controlling the diffusion behavior of small weakly interacting molecules free volume appears to be the most important one and lends itself to correlative and, to some extent, even predictive purposes.^{4–9}

In the free volume approach, originally developed by Cohen and Turnbull¹⁰ for diffusion in simple liquids, it is assumed that a certain part of the free volume, often termed "hole free volume", can be redistributed without a significant energy change. Then a molecule can migrate if a void of a critical size v^* , large enough for the molecule to jump into, is formed by random volume fluctuations. The probability for such a process is given by $\exp(-\gamma v^*/v_f)$, where v_f is the mean hole free volume per molecule and γ is an overlap factor, typically between 0.5 and 1, which considers that the same free volume is available to more than one molecule.

Several adaptations of the original Cohen and Turnbull model to diffusion of penetrants in polymers above the glass-transition temperature have been reported [see, e.g., (3, 11–14) for reviews].

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The most elaborate one, which was also applied to glassy polymers,¹⁵ was developed by Vrentas and Duda.¹⁶ Taking into account the critical energy, E^* , a penetrant molecule must obtain to overcome the attractive forces holding it to its neighbors, Vrentas and Duda derived the following expression for the diffusivity in the limit of zero penetrant concentration:

$$D(0) = \tilde{D}_0 \exp\left(-\frac{E^*}{RT}\right) \exp\left(-\frac{\gamma \xi \hat{v}^*}{\hat{v}_f}\right). \quad (1)$$

Here \hat{v}^* and \hat{v}_f are the critical local hole free volumes required for the displacement of a polymer jumping unit per gram of polymer and the average hole free volume per gram of polymer, respectively. Diffusion of solute molecules is described in terms of its coupling to polymer self-diffusion. The coupling parameter $\xi = v_s^*/v^*$ is the ratio of the critical volume of the penetrant to the critical volume of the polymer jumping unit.

A number of different schemes, resulting in different values, are available for estimating \hat{v}_f .^{11,17,18} \hat{v}_f can be defined as $\hat{v}_f = \hat{v} - \hat{v}_0$, where \hat{v} is the reciprocal of the density, and \hat{v}_0 is the specific volume occupied by the polymer molecules themselves. Bondi¹⁷ showed that for complex organic molecules the occupied volume can be well approximated by $1.3 \cdot \hat{v}_W$. The van der Waals volume, \hat{v}_W , can be reliably estimated from group contributions, which have been compiled for most commonly encountered organic groups in ref. 8. The factor 1.3 was estimated from the packing density of molecular crystals at 0 K and accounts for the fact that the zero point volume is greater than the molecular volume. The specific free volume is then given by $\hat{v}_f = \hat{v} - 1.3\hat{v}_W$, where \hat{v}_W is the specific van der Waals volume.

This method has most frequently been used to correlate diffusion data mainly in glassy polymers.⁵⁻⁷ A fairly good linear correlation was generally found between $\log D$ and $1/\hat{v}_f$ for penetrants like gas molecules exhibiting a weak interaction with polymers. In many cases, a better correlation was obtained for the fractional free volume $\text{FFV} = \hat{v}_f/\hat{v}$, according to

$$D = A \cdot \exp(-B/\text{FFV}). \quad (2)$$

So far all these correlations are based on rather limited data sets, and the scatter is considerable. Recently, Park and Paul¹⁹ have introduced an empirical free-volume-based group contribution

method, which involves a penetrant-specific fractional free volume. The method was applied to permeability data for gas molecules in a large number of glassy polymers with rigid backbones. It was demonstrated that the scatter in correlations analogous to eq 2 can be reduced significantly if the penetrant-specific fractional free volume, which is evaluated from permeation data, is used instead of FFV values from the Bondi method.

For this article, we have analyzed diffusion data for six gases and 71 polymers from a new database generated in connection with work on the new Landolt Börnstein series "Diffusion in Semiconductors and Non-Metallic Solids".²⁰ The database encompasses a large variety of glassy polymers, which makes it a powerful basis for investigating correlations between diffusion coefficients and polymer properties like chain stiffness, cohesive energy, and glass-transition temperature and to check general trends reported in the literature.

EXPERIMENTAL

Data Analysis

All diffusivities used for the present analysis were taken from the above-mentioned Landolt Börnstein volume. It is a compilation of data from critically examined original papers, the references of which are given there.²⁰ For the present investigations only the diffusivities in fully amorphous glassy polymers at the lowest concentrations were taken into account, although the diffusivity of gas molecules depends only slightly on concentration.^{13,14,20} In those cases where more than one diffusivity was available for a given polymer/gas system, we used an average value. The fractional free volume, calculated by the Bondi method, was taken from the original papers. In a few cases the FFV values originate from other sources if no values were found in the original papers. Since the fractional free volume depends on temperature it is important to use the FFV value at the temperature of the diffusion experiment. Therefore, both diffusion and free volume data were taken from a narrow temperature range of $25 \pm 15^\circ\text{C}$, which comprises most of the reported results, anyhow.

The gas molecules chosen for the analysis are O_2 , N_2 , CO_2 , CH_4 , as well as He and H_2 because for these molecules, diffusion measurements have

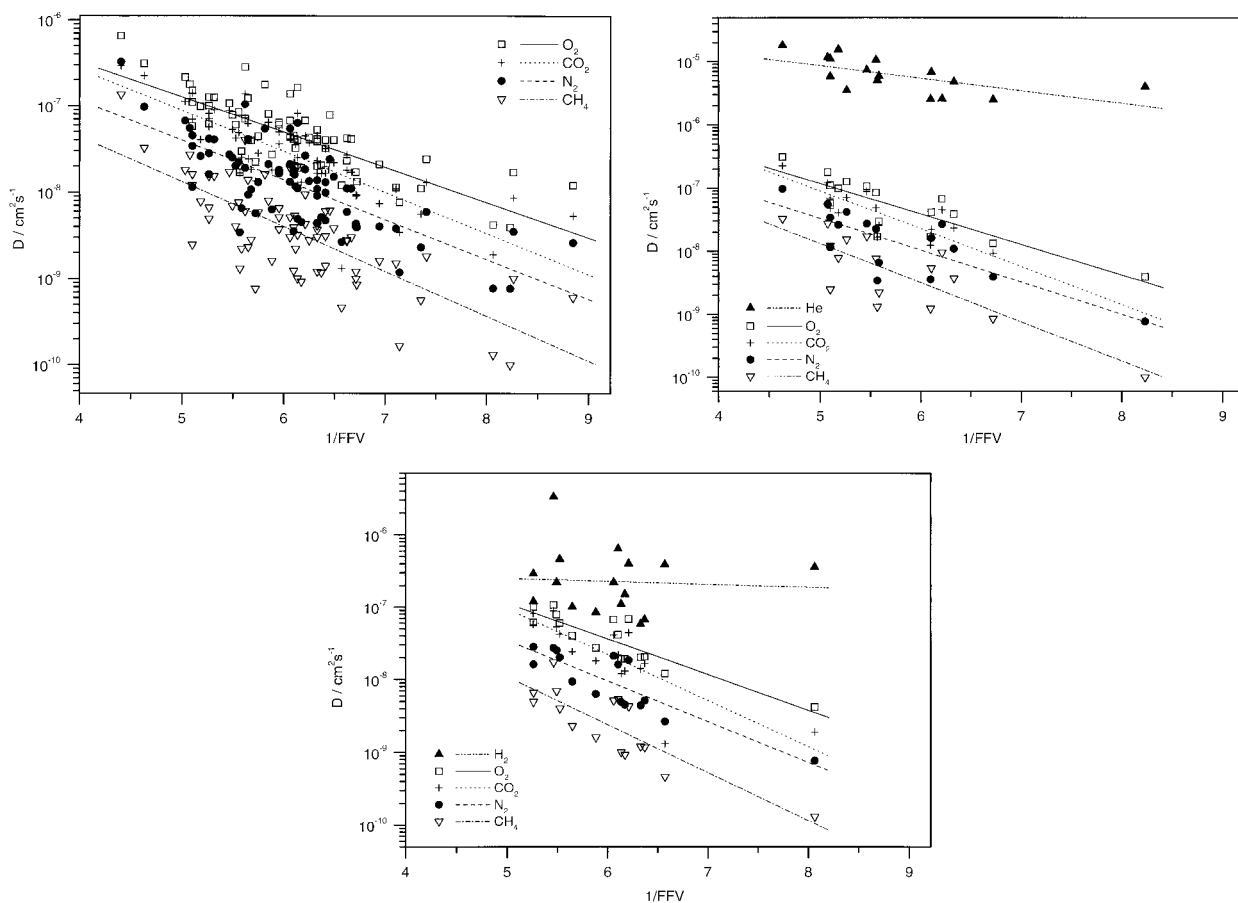


Figure 1. Plot of $\log D$ versus $1/\text{FFV}$ for diffusion of He, H_2 , O_2 , N_2 , CO_2 , and CH_4 , in various polymers. In the different plots, only those polymers are chosen for which data are available for all gas molecules indicated in the plot.

been performed in many different polymers. Figure 1(a) shows a plot of $\log D$ versus $1/\text{FFV}$ for O_2 , N_2 , CO_2 , and CH_4 . To achieve good comparability between results for different gases only those polymers are selected for which diffusivities of all gas molecules are available. Corresponding plots, which include He and H_2 are depicted in Figures 1(b) and 1(c), respectively. The slopes of straight lines fitted to the data according to eq 2 are plotted in Figure 2 against the van der Waals volumes²¹ of the gas molecules.

One notes a considerable scatter of the data in Figure 1 around the fits according to the free volume theory:

$$\log_{10}[D(\text{FFV})] = A' - B'/\text{FFV} \quad (3)$$

which are linear regressions, when $\log D$ is plotted versus $1/\text{FFV}$ ($A' = \log_{10} A$, $B' = B/\ln 10$; A , B from eq 2). In order to check whether the scat-

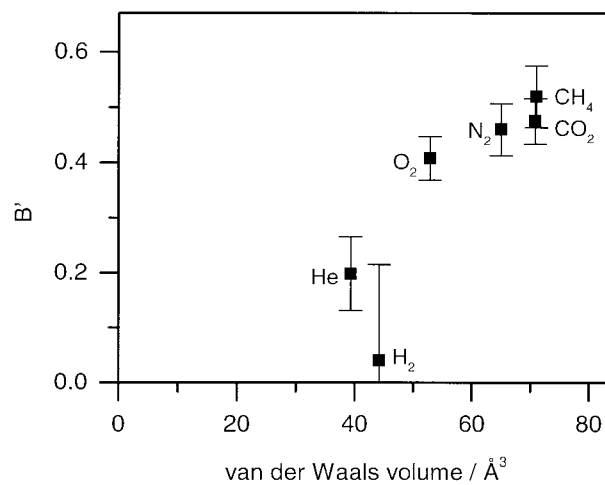


Figure 2. Plot of the B parameter defined in eq 2 against the van der Waals volume of the gas molecules. B was determined from linear fits to the data in Figure 1.

Table I. Correlation Factors $\rho(i, j)$, Defined in Eq 5, Calculated from the Data in Figure 1

	He	H ₂	O ₂	N ₂	CO ₂	CH ₄
He	1	—	0.32	0.24	-0.01	0.15
H ₂	—	1	0.57	0.56	0.23	0.66
O ₂	0.32	0.57	1	0.98	0.82	0.93
N ₂	0.24	0.56	0.98	1	0.81	0.95
CO ₂	-0.01	0.23	0.82	0.81	1	0.85
CH ₄	0.15	0.66	0.93	0.95	0.85	1

ter is purely statistical or whether the deviations from the linear regressions correlate for different gases, we performed a correlation analysis, that is, we looked for correlations between the logarithmic deviations from the regression lines defined as

$$\delta(p, g) = \log D(p, g) - \log[A(g)\exp(-B(g)/FFV(p))] \quad (4)$$

for a given gas g and polymer p . In this case the correlation coefficient $\rho(g_1, g_2)$ is given by 22

$$\rho(g_1, g_2) = \frac{(\sum_p \delta(p, g_1))(\sum_p \delta(p, g_2))}{(\sum_p \delta(p, g_1)^2)^{1/2}(\sum_p \delta(p, g_2)^2)^{1/2}} \quad (5)$$

$\rho = 1$ corresponds to perfect correlation, that is, $\delta(p, g_1)$, when plotted versus $\delta(p, g_2)$, yields a straight line for all polymers p , while $\rho = 0$ indicates the lack of any correlation, that is, random scattering. The resulting ρ values are displayed in Table I.

One notes that the ρ values for O₂, N₂, CO₂, and CH₄ are close to unity, reflecting strong correlation. This clearly shows that the deviations δ from the linear fits in Figure 1 strongly depend on the type of polymer. Therefore, in order to learn more about the influence of the polymer properties the different polymers are sorted in Table II according to the mean logarithmic deviations

$$\langle \delta \rangle(p) = [\delta(p, O_2) + \delta(p, N_2) + \delta(p, CO_2) + \delta(p, CH_4)]/4. \quad (6)$$

In order to find out which polymer properties are responsible for the scattering of the data in Figure 1(a), the connection of the diffusivities with two other available parameters of the polymers—the cohesive energy and the glass-transition temperature—was investigated. Since the cohesive

energy is a macroscopic measure of the internal energy resulting from the interaction of adjacent polymer chains, it may also be correlated to the energy necessary for the opening of a diffusion channel. The glass-transition temperature is correlated to the chain flexibility⁹ and therefore may have an influence on the diffusivity of gases. Two approaches in the literature are revised in the next section. The cohesive energy of polymers was, if possible, evaluated following ref. 24, the glass-transition temperature values are given in ref. 20.

RESULTS AND DISCUSSION

The strong correlation between the deviations of the diffusivities of O₂, N₂, CO₂, and CH₄ from the linear regressions in Figure 1 allows experimental errors in the diffusion coefficients to be ruled out as the main cause of the scattering in Figure 1(a) because these would lead to statistical scattering with $\delta = 0$. Therefore, large experimental errors in the determination of the FFV or shortcomings of the FFV in describing the transport properties of a polymer have to be considered. Since large experimental errors in FFV are not expected,⁸ we conclude that the FFV is not the optimum polymer property to forecast diffusion coefficients in polymers. This holds also for the specific free volume originally suggested by Lee and for the FFV, when 0 K volumes are evaluated after Sugden.²⁵ Apparently, the deviations are mainly a polymer property. A closer examination of the molecular structures of the polymers in Table II suggests that the chain stiffness plays a crucial role. Large positive $\langle \delta \rangle$ values are mostly found for polymers with a highly flexible backbone, whereas polymers with a high chain stiffness tend to have large negative $\langle \delta \rangle$ values. But there are some exceptions showing that chain

Table II. Polymers Listed in Order of Increasing Mean Logarithmic Deviations, $\langle \delta \rangle$ Defined in Eq 4^a

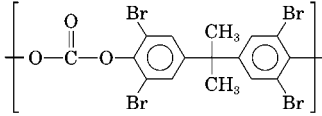
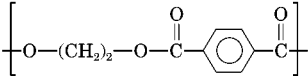
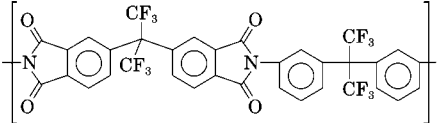
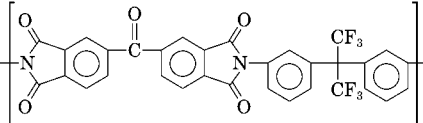
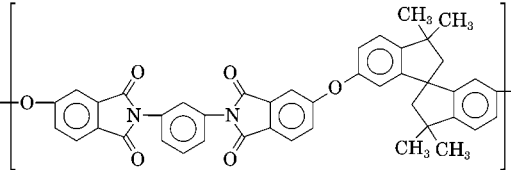
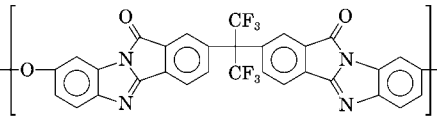
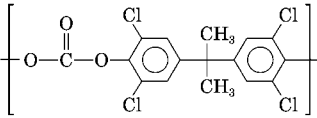
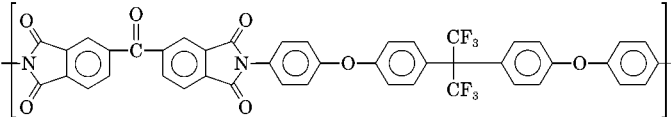
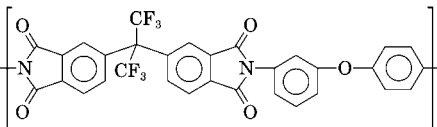
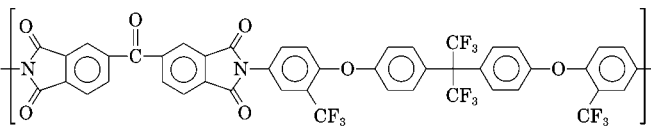
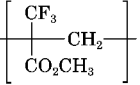
Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$							$\langle \delta \rangle$
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄	FFV ⁻¹	
TBPC		499	—	1.69	0.34	1.66	0.13	5.57	-0.655
PET		—	39	1.2	0.265	0.131	0.046	6.57	-0.641
6FDA-6FmDA		—	—	2.23	0.569	1.34	0.076	5.72	-0.58
BTDA-6FmDA		—	—	0.764	0.118	0.343	0.017	7.14	-0.519
SBI-PEI		253	—	1.68	0.353	1.22	0.123	6.1	-0.445
6FDA-TADPO		578	—	5.77	1.14	4.76	0.245	5.1	-0.424
TCPC		583	—	2.95	0.65	2.53	0.22	5.58	-0.414
BTDA-BAPHF		—	11	1.9	0.49	1.2	0.1	6.13	-0.403
6FDA-mp'ODA		—	15	1.9	0.45	1.3	0.092	6.17	-0.395
BTDA-BATPHF		—	8.4	2.7	0.63	1.8	0.16	5.88	-0.36
PMMA		400	—	0.39	0.077	0.079	0.01	8.23	-0.347

Table II. Continued

Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$							
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄	FFV ⁻¹	$\langle \delta \rangle$
BPDA-BATPHF		—	10	4	0.93	2.4	0.23	5.65	-0.312
FBPC		—	—	3.93	1.07	1.82	0.28	5.68	-0.294
BTDA-pp'ODA		—	36	0.42	0.077	0.19	0.013	8.06	-0.291
BPDA-BAPHF		—	5.8	2	0.44	1.4	0.12	6.33	-0.282
PCZ		—	—	1.8	0.47	0.97	0.14	6.41	-0.272
6FDA-TADPOAA		248	—	1.32	0.39	0.92	0.085	6.72	-0.241
BTDA-BAHF		—	6.7	2.04	0.51	1.64	0.117	6.37	-0.231
6FDA-BATPHF		—	12	6.1	1.6	5.7	0.49	5.26	-0.212
DMPSF		—	—	1.7	0.4	0.94	0.1	6.71	-0.195
3,4'-PSF		—	—	1.7	0.43	0.9	0.12	6.71	-0.172

Table II. Continued

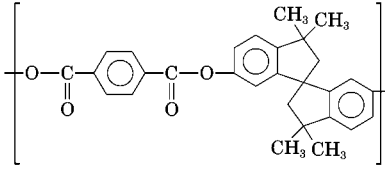
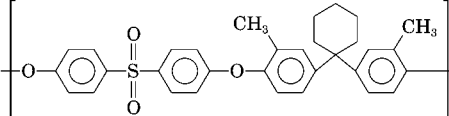
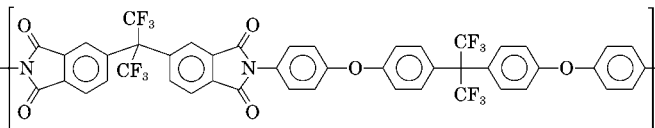
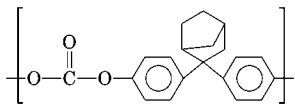
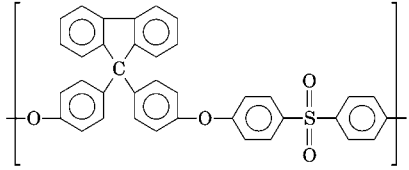
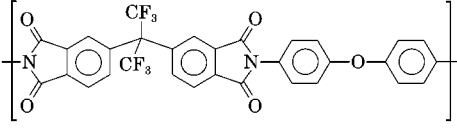
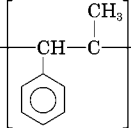
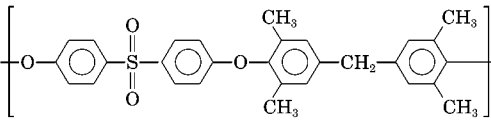
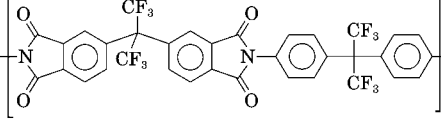
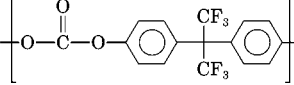
Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$							$\langle \delta \rangle$
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄	FFV ⁻¹	
SBI/iso		1550	—	9.83	2.59	4.04	0.775	5.18	-0.133
DMPSF-Z		—	—	1.1	0.23	0.56	0.056	7.35	-0.123
6FDA-BAPHF		—	46	6	2	4.2	0.4	5.52	-0.123
NBPC		—	—	4.4	1.3	2.8	0.58	5.75	-0.103
FBPSF		—	—	4.34	1.31	2.01	0.3	6.06	-0.066
6FDA-ODA		—	—	3.2	1.16	3.58	0.22	6.12	-0.057
PaMS		—	—	2.1	0.4	0.74	0.16	6.94	-0.039
TMPSF-F		—	—	4	1.1	2.5	0.32	6.13	-0.028
6FDA-BAHF		—	29	10	2.8	8.1	0.66	5.26	-0.027
HFPC		1100	—	11	3.4	6.95	1.2	5.1	-0.022

Table II. Continued

Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$						FFV ⁻¹	⟨δ⟩
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄		
PPS		—	—	1.13	0.38	1.09	0.15	7.11	-0.001
PMDA-BATPHF		—	22	7.8	2.5	5.3	0.69	5.49	0
TMPC		1050	—	8.42	2.22	4.86	0.757	5.56	0.025
PC-AP		—	—	4.48	1.78	2.18	0.39	6.1	0.026
HMBIPSF		—	—	7	1.9	7.2	0.6	5.62	0.034
PSF		—	—	4	0.986	1.66	0.309	6.41	0.04
PC		673	64	4.11	1.59	2.19	0.533	6.11	0.042
BPA/iso		477	—	3.83	1.08	2.29	0.367	6.33	0.061
PSF-AP		—	—	5.25	1.37	1.65	0.3	6.33	0.064
PSF-M		—	—	2.3	0.59	2.7	0.28	6.62	0.065
6FDA-IPDA		—	—	6.36	1.64	4.93	0.371	5.95	0.07

Table II. Continued

Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$						FFV ⁻¹	$\langle \delta \rangle$
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄		
6FDA-MDA		—	—	4.26	1.34	3.7	0.276	6.25	0.08
TMPSF-P		—	—	6	1.7	5	0.51	5.95	0.104
HFPSF		—	—	6.3	1.8	3.6	0.65	5.95	0.106
BPI-PC		349	—	12.6	4.14	7.04	1.52	5.26	0.116
TMPSF-M		—	—	4.1	0.91	4.5	0.41	6.33	0.135
TMHFPSF		—	—	15	4.5	14	1.6	5.1	0.149
PSF-F		—	—	4.2	1.1	1.8	0.27	6.62	0.15
PDPP0		—	—	12.5	4.05	8.9	1.53	5.31	0.163
PMDA-BAPHF		—	22	6.7	2.1	4.1	0.51	6.06	0.168
PSF-O		—	—	4.1	1.1	1.7	0.3	6.67	0.173

Table II. Continued

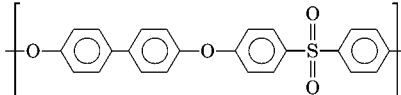
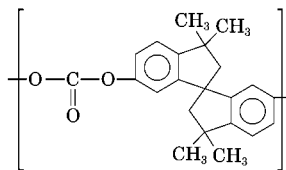
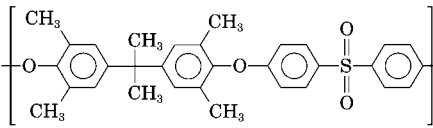
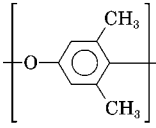
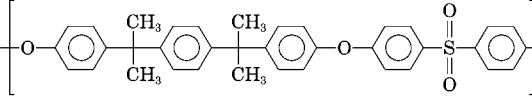
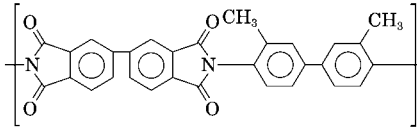
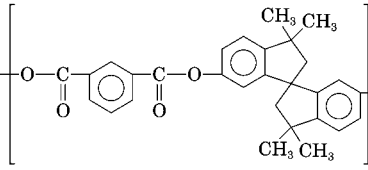
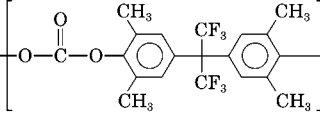
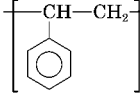
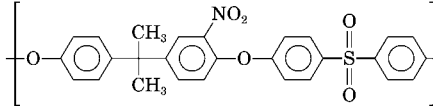
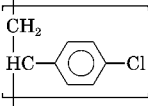
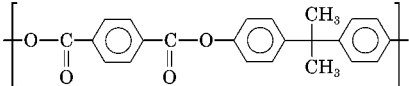
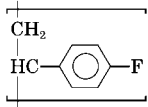
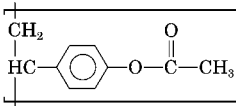
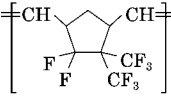
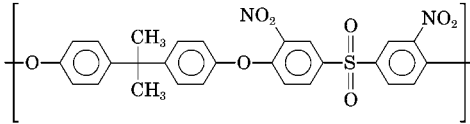
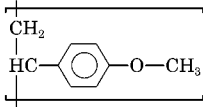
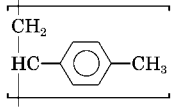
Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$						FFV ⁻¹	$\langle \delta \rangle$
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄		
BIPSF		—	—	4	1.5	2.2	0.38	6.49	0.177
SBIPC		730	330	10.6	2.7	8.8	1.7	5.46	0.181
TMPSF		—	—	8	2.1	6.4	0.79	5.85	0.184
PDMPO		—	—	21.5	6.68	11.2	1.79	5.03	0.186
PSF-P		—	—	3.2	1.3	3.2	0.6	6.41	0.189
BPDA-BAHF		—	40	6.79	1.83	4.42	0.6	6.21	0.213
SBI/tere		1170	—	17.7	5.5	12	2.7	5.08	0.217
TMHFPC		1800	—	31	9.7	22.4	3.24	4.63	0.219
PS		—	—	12.2	4.1	6.185	1.38	5.65	0.265
PSF-NO ₂ (50%)		—	—	2.4	0.59	1.3	0.18	7.41	0.308

Table II. Continued

Name	Monomerstructure	Diffusion Coefficients/ $10^{-8} \text{ cm}^2 \text{ s}^{-1}$							$\langle \delta \rangle$
		He	H ₂	O ₂	N ₂	CO ₂	CH ₄	FFV ⁻¹	
PCS		—	—	7.8	2.4	2.2	0.61	6.45	0.333
BPA/tere		258	—	6.66	2.64	4.47	0.935	6.21	0.337
PFS		—	—	17.6	5.4	5.8	1.6	5.81	0.422
PAS		—	—	13.7	5.4	4.6	1.9	6.06	0.503
PSF-NO ₂ (98%)		—	—	1.7	0.35	0.86	0.1	8.26	0.504
DFHFPNB		—	—	65	32.5	29	13.5	4.41	0.51
PSF-NO ₂ (192%)		—	—	1.2	0.26	0.53	0.06	8.85	0.598
PMxS		—	—	16.3	6.3	8.1	2	6.13	0.641
PMS		—	—	28.1	10.4	13.7	4	5.62	0.646

^a The values of the fractional free volumes and gas diffusivities used in the present study are given, too. T_g and E_{coh} of the polymers will be listed in ref. 23.

stiffness is not the only important quantity. It would be interesting to verify the influence of the chain stiffness by comparing the δ values with quantitative parameters of the chain flexibility like the persistence length,²⁶ but this quantity has been measured for only a few polymers in Figure 1.

Because chain stiffness appears to be one crucial polymer property that gives rise to the sys-

tematic deviations from eq 2, we now discuss the effect of the polymer chain stiffness on the parameters A and B . The effect on the B parameter is implied by the free-volume model of Vrentas and Duda and has been noted before.¹³ Comparison of eqs 1 and 2 yields

$$A = \tilde{D}_0 \exp\left(-\frac{E^*}{RT}\right), \text{ and} \quad (7)$$

$$B = \frac{\gamma \xi \hat{v}^* \text{FFV}}{\hat{v}_f} = \frac{\gamma v_s^* \hat{v}^* \text{FFV}}{v^* \hat{v}_f} \approx \gamma \frac{v_s^*}{v^*}, \quad (8)$$

since $\text{FFV} = (V - V_0)/V \approx \hat{v}_f/\hat{v} \approx \hat{v}_f/\hat{v}^*$.

The overlap factor γ should not vary much from polymer to polymer. Although v^* cannot be determined directly, it was shown to increase with chain stiffness.⁹ This means that polymers with a stiff backbone have a large jumping unit, whereas flexible chains have a small one. This is also immediately plausible from a simple geometrical picture. Consequently, the B parameter is predicted to decrease with increasing chain stiffness, that is, gas molecules should diffuse faster in stiffer polymers than in more flexible ones with the same fractional free volume. Since the $\langle \delta \rangle$ values in Table II decrease with increasing chain stiffness, that is, the experimental observations are opposite to the predicted influence of the polymer jumping unit on the B parameter, the free-volume term with the B parameter cannot explain the observed polymer dependence.

Therefore, in glassy polymers, the polymer dependence of $\langle \delta \rangle$ values in Table II originates essentially from the A factor in eq 7. If one assumes that the pre-exponential factor D_0 does not vary much between different polymers, the experimental data in Table II imply an increase in the activation energy E^* with increasing chain stiffness. Then in glassy polymers there would not only be an activation barrier for overcoming the attractive forces holding a diffusant to the neighboring polymer chains—this energy should be very small for the weakly interacting gas molecules, anyhow—but also to surmount potential barriers resulting from attractive forces between the polymer segments. In these terms the decrease of $\langle \delta \rangle$ with increasing chain stiffness (cf. Table II) appears to reflect the expected increase in the activation energy for stiffer polymers.^{14,27,28}

While the present study demonstrates the importance of the activation energy term in glassy polymers, it is generally assumed that diffusion is free-volume dominated for diffusion of weakly interacting molecules, and hence the E^* term can be absorbed into the pre-exponential factor \tilde{D}_0 .¹⁶

So far we have only used Table I to discuss the mean of the δ values for O_2 , N_2 , CO_2 , and CH_4 because of the large correlations. A closer look at Table I reveals that the correlation coefficients of CO_2 with N_2 , O_2 , and CH_4 are somewhat smaller than the correlation coefficients between the latter gases. This may result from the fact that the

CO_2 molecule is less spherical and more polar than the other three gases. Both properties can result in a slightly different diffusion mechanism. Another explanation is a greater experimental scatter in the CO_2 diffusion coefficients because of the greater tendency to plasticization¹⁴ of the polymers. In contrast to the larger gas molecules N_2 , O_2 , CO_2 , and CH_4 , the correlation factors between diffusion of H_2 and these molecules are distinctly smaller than among these molecules, but still indicate some correlation (cf. Table II). The correlation factors between He and the other molecules are very low. These results suggest that the diffusion behavior of O_2 , N_2 , CO_2 , and CH_4 is very similar, whereas the smaller molecules H_2 and He diffuse via different mechanisms.

The influence of the diffusant shape is also reflected in the plot of the B parameter against the van der Waals volume of the diffusant (Fig. 2). Within the free-volume concept B should be proportional to the critical free volume, v_s^* , of the diffusant (cf. eq 1), which should be approximately equal to the diffusant volume.¹⁶ In accord with this expectation one notes the tendency of an increase in B with increasing van der Waals volume. However, H_2 and He behave again quite differently. The B value of H_2 is much smaller than that for He. The differences in the B values of CH_4 and CO_2 are not as pronounced but also seem to reflect the influence of the shape of the diffusant, since CH_4 is an almost spherical molecule, whereas CO_2 has an elongated shape. This shape effect is not accounted for in present free-volume theories.

The different diffusion behavior of O_2 , N_2 , CO_2 , and CH_4 on the one hand and of the much smaller molecules H_2 and He on the other, as well as the differences between the latter molecules, lends support to the notion of a diffusant-dependent free volume. In particular, the very small B value of H_2 suggests that molecules that are very small at least in one direction are able to diffuse within the nonfluctuating interstitial free volume without much assistance of free-volume fluctuations. This also explains why diffusion of such molecules is almost completely decoupled from the glass transition, where the hole free volume increases strongly.²⁹

Besides the free volume, the cohesive energy E_{coh} of the polymers has an effect on the diffusion coefficient. Meares³⁰ related the activation energy of diffusion to the cohesive energy density by calculating the energy E_h required to open a cylindrical cavity before a diffusion jump takes place:

Table III. Regression Parameters Found for Four Gases in the Linear Regression of Eqs 3 and 10 to the Diffusion Coefficients^a

	Linear Regression of Eq 3			Multiple Regression of Eq 10			
	B'	A'	$ R $	B	C_0	C_1 (cm ³ /J)	R
O ₂	0.408	-4.86	0.782	0.385	-3.77	0.00264	0.869
N ₂	0.460	-5.10	0.761	0.421	-3.87	0.00316	0.842
CO ₂	0.475	-4.68	0.812	0.54	-3.78	0.0012	0.86
CH ₄	0.519	-5.28	0.743	0.474	-3.71	0.004	0.853

^a Note that both regressions are not based on the same set of diffusion coefficients, because E_{coh} in eq 10 was not available for all polymers.

$$E_d = E_h = 0.25\pi d_A^2 \lambda E_{coh}. \quad (9)$$

Here d_A is the diameter of the gas molecule and λ the length of a diffusion jump. According to this rather crude estimation a linear relationship between $\log D$ and E_{coh} is to be expected. Indeed a correlation coefficient of $R = 0.4$ for both variables, determined for 49 polymers, is found. Additional information on the influence of the cohesive energy is obtained from the multiple linear regression of a linear function of both the inverse fractional free volume and the cohesive energy to the logarithms of the diffusion coefficients.

$$\log_{10} D = C_0 - B/\text{FFV} - C_1 E_{coh}. \quad (10)$$

The regression coefficients for four gases are listed in Table III together with the regression parameters of the linear regressions in Figure 1(a) according to eq 3.

The higher correlation coefficients show, that eq 10 represents the data substantially better than the linear regression with $1/\text{FFV}$ as the only independent variable. According to eq 9 the constant C_1 increases with increasing kinetic diameters of the gas molecules. The values of $C_1 \approx 0.003 \text{ (J/cm}^3\text{)}^{-1}$ corresponds to a Boltzmann factor $\exp(-E_h/kT)$ with $E_h = 2.3 \cdot 10^{-23} \text{ cm}^3 \cdot E_{coh}$. The volume of 0.023 nm^3 found here yields λ in the range $0.13\text{--}0.33 \text{ nm}$ using eq 9 and kinetic diameters reported in ref. 13. Despite the crude approximations, these values are very close to an expected jump length of several Å.

Some related approaches can be found in the literature, where connections between diffusivity data and other properties of the polymers are investigated. For example, Jia et al.³¹ found the

permeability in more than 60 polymers to be best described by the formula

$$\log P = a_1 + b_1 v_f / E_{coh} \quad (11)$$

where a_1 and b_1 are constants dependent on the gas and v_f the molar free volume. This result cannot be reproduced here for diffusion coefficients, the correlation found between $\log D$ and v_f/E_{coh} is lower than the one in Figure 1(a). There may be several causes why eq 11 is not as successful in describing the diffusion data underlying this article.

1. The data bases encompass different classes of polymers, because Jia et al. allowed for rubbery and partially crystalline polymers, whereas in our study only fully amorphous glassy polymers are included. Because crystallites in the polymers lower the mean diffusion coefficient considerably, in the study of Jia et al. physical effects are concerned, which cannot play a role in our analysis.
2. Even if Jia et al. would have concentrated on data based only on amorphous glassy polymers, different results may occur because of the scattering. Statistics cannot be applied here strictly, because a set of polymers is never known to be representative for all polymers. That is why estimations of error bars would not make sense here and a comparison of the different analyses would be difficult.
3. In eq 11 Jia worked with permeability coefficients P , whereas we consider diffusion coefficients D . However, this difference

should not lead to largely different results, because $P = D \cdot S$ and the absorption coefficient S does not differ much from polymer to polymer compared to D values.

4. Experimental errors in the diffusion data and different tables for evaluation of polymer properties are, of course, sources for different results. But as for the last point, these differences should not lead to qualitatively different results.

Recently Tokarskie et al.³² analyzed structure–property relationships with the help of a generic function approximation, which searches for the best combination of parameters to describe a given property, here the diffusion coefficient. They analyzed diffusion coefficients of O₂, N₂ and CO₂ measured for 16 polymers together with nine physicochemical properties. They found strong correlations ($R \approx 0.82$) between the bulk moduli of the polymers and the logarithms of the diffusion coefficients, but also between the cohesive energy and log D values ($R \approx 0.63$), corresponding to our findings.

The glass-transition temperature of a polymer is an important property, easy to measure and available in the literature for most polymers. A direct correlation between T_g and diffusion coefficients is not found in our database. In contrast to this Plate et al.³³ compiled diffusivities of H₂, He, N₂, CH₄ and lower hydrocarbons measured in more than 40 polymers and found that the diffusion coefficients at room temperature (RT) increase with increasing $|T_g - RT|$, that is, for rubbery polymers diffusion coefficients increase the more T_g is below room temperature and—in contrast to our results—for glassy polymers diffusion coefficients increase with increasing T_g . The points 1, 2, and 4 in the above list of causes for differences in the results can be applied here analogically. Additionally, the number of diffusion coefficients in glassy polymers in the study of Plate et al. was probably too low for significant conclusions.

A more indirect relationship between diffusion coefficients and T_g has been noticed by Haraya et al.³⁴: In a plot of O₂ diffusion coefficients versus the inverse specific free volume $SFV = \hat{v} - \hat{v}_0$ polymers with a high glass-transition temperature lie on a line called “HTG line” by the authors, whereas diffusion coefficients of polymers with low T_g were found on an “LTG line” more declining than the HTG line and intersecting it near the middle of the 13 data points. If this observation

was universally valid, the diffusivity of gases in glassy polymers could be well described by the function

$$\log D = C_0 - B/SFV + C_2 T_g (1/SFV - C_3) \quad (12)$$

with additional free parameters C_2 and C_3 . Indeed the 3rd term in eq 12 leads to a small decrease in the sum of squares, but the effect is not very prominent and does not seem to be worth an ample discussion here.

CONCLUSION

The fractional free volume strongly determines the diffusivity of small weakly interacting molecules in glassy polymers. There is, however, a considerable scattering. This polymer dependence appears to originate mainly from the chain stiffness and the cohesive energy and is opposite to the effect implied by the free-volume fluctuation term in eq 1. The polymer dependence can well be explained by means of the activation energy term. This reveals that there is an activation barrier in addition to the barrier for overcoming the attractive forces between diffusant and polymer and that the activation energy term cannot be neglected, that is, absorbed into the pre-exponential factor, even for essentially noninteracting molecules. He and particularly H₂ seem to diffuse mainly via the nonfluctuating interstitial free volume. Equation 10, involving the cohesive energy in addition to the fractional free volume, is proposed for correlative and semipredictive purposes instead of eq 3. It is based on physical grounds, and both the cohesive energy and the fractional free volume are accessible via group contribution methods. Certainly, improved theories with real predictive capabilities would be very desirable but are not available at present. Much additional insight into the mechanisms of diffusion of small molecules in polymers is expected from molecular dynamics simulations in the near future.

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