Fractal Analysis and Synergetics of Catalysis in Nanosystems

G. V. Kozlov

G. E. Zaikov

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G.V. KOZLOV AND G.E. ZAIKOV

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Preface

By Sergeev's definition [1], nanochemistry is a field of science connected with obtaining and studying physical-chemical properties of particles measurable on a nanometer scale. According to this definition, polymer synthesis is automatically a nanochemistry by virtue of Melikhov's classification [2]: polymeric macromolecules (more precisely macromolecular coils) are nanoparticles, and polymeric sols and gels are classified among nanosystems. Catalysis of nanoparticles is one of the most important sections of nanochemistry [1-4].

The majority of catalytic systems are nanosystems [3]. At heterogeneous catalysis the active substance attempts to deposit on a carrier in nanoparticle form in order to increase its specific surface. At homogeneous catalysis active substance molecules have often in themselves had nanometer sizes. The most favourable conditions for homogeneous catalysis are created when reagent molecules are adsorbed rapidly by nanoparticles and are desorbed slowly but have high surface mobility and, consequently, high reaction rate on the surface, from the reaction, molecules of such structures are formed in which desorption rate is increased sharply. If these conditions are realized in nanosystem with larger probability than in macrosystem, then nanocatalyst has the raising activity that was observed for many systems. In this connection, such questions arise as adsoption and desorption rate, surface mobility of molecules and characteristics. Frequency of reagent interaction acts depends on the size, molecular relief and composition of nanoparticles and the carrier [2].

Quite a large number of examples are cited of practical application of nanoparticles as catalysts in chapter 8 [8]. However, to keep up the tradition in catalytic effects analysis, the main attention is paid to the chemical aspects of the problem.

The new direction in polymers synthesis is the reaction performance in inorganic compounds which on the one hand perform the function of reaction catalyst and on the other hand function as nanofiller of the forming nanocomposite [5]. In these reactions, the main property of nanosystems puts into effect – the large area of contact surface of catalyst – a reactionary medium because of the small size of solid-phase catalyst particles [6]. In this case the interaction catalyst – reaction product by virtue of the cited above classification should be considered as two fractals interaction, as it is well known that both particulates surface with sizes of nanometer interval [7] and macromolecular coil [8] are fractal objects. The indicated circumstance makes structural study of catalysis inevitable within the framework of the fractal analysis. This aspect was studied in Meakin, 1986 [9] for the first time.

The solution of the actual problem of nanomeasured particles and nanomaterials on their base requires an interdisciplinary approach to the study of self-governed synthesis of

nanoparticles. This follows from Shevchenko-Kadomtsev quantum-mechanical approach [10, 11] to nanoworld structure on the base of synergetics principles. Ivanova [12] confirmed this property on the basis of self-governed synthesis analysis of stable structures of periodic system atoms and nanoparticles with the sizes smaller than 100 nm. Therefore, just one more method of catalysis study on nanoparticles is the use of synergetics principles. In this book, the application of fractal analysis and synergetics methods was considered on the example of both model reaction of transesterification in nanoparticles presence and for the case of a number of widely used in practice polymerization reactions.

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Contents

Chapter 1

The Fractal Models of Gas Transport Processes for Polymeric Materials

It is obvious that for chemical reaction realization in solutions or melts, the necessary condition is the contact of reagent-diffusible molecules. This makes processes of reagent diffusion in reactionary medium important and often the key moment of polymerization reactions. Specific features of such diffusive processes will be studied in the subsequent chapters. In the present chapter we consider the main rules of gas transport fractal models for polymeric materials as a general case and also some practical applications of these conceptions.

1.1. Structural Model of Strange (Anomalous) Diffusion in Polymers

As it was known [1-3], the diffusivity value D for the same polymer can vary as the function of gas-diffusant molecule sizes and testing temperature and for different polymers – as function of glass transition (melting) temperature. This variation can make up several orders of magnitude. Therefore for diffusive processes, descriptions often use power functions [4-7]. Such strong D variation assumes diffusion processes division on slow and rapid ones [8]. In the base of this division is placed the dependence of gas molecule displacement S on time t [9]:

$$S \sim t^{\beta}, \tag{1.1}$$

where for a classical case $\beta=1/2$, for slow diffusion $\beta<1/2$ and for a rapid one $\beta>1/2$.

Within the framework of fractional differentiation theory, it was shown that its main parameter – fractional exponent α is connected with both β and structure characteristic – fractal (Hausdorff) dimension d_f by different functional forms is dependent on diffusion type. In other words, structures with the same d_f can have very different diffusivities D. Therefore the authors [10] studied the possibility and conditions of realization of the indicated diffusion

types in polymers and offereda structural model explaining a change in diffusion type. It was made using the example of methane (CH_4) diffusion in 11 polymers [2, 11-13].

In paper [1] the following dependence D on molecular weight M of gas-diffusant was used:

$$D = KM^{-b_M}, \tag{1.2}$$

where K and b_M are constants.

The authors [4] offered a systematic increase of exponent b_M with the growth of glass transition temperature T_g of polymers and explained the observed law by the chain kinetic rigidity increase with T_g rising. However, as constants K and b_M are empirical, this makes it difficult to predict D value with the aid of the equation (1.2).

The diffusivity D value within the fractal model of gas transport processes can be defined according to the equation [14-16]:

$$D = D_0^{'} f_g \left(d_h / d_m\right)^{2(D_t - d_s)/d_s}, \tag{1.3}$$

where $D_0^{'}$ is a universal constant, equal to 3.8×10^{-7} cm^2/s, f_g is relative free volume, d_h is this volume microvoid diameter, d_m is a diameter of gas-diffusant molecule, D_t is the dimension controlling gas transport processes, d_s is the spectral dimension of the structure accepted for use in paper [10] 11 polymers equal to 1.0 [17].

As the dimension D_t dependent on the ratio (d_h/d_m) value is accepted either fractal (Hausdorff) dimension of structure d_f (at $(d_h/d_m)>1.70$) or the dimension of localization regions of excessed energy D_f^e (at $(d_h/d_m)<1.70$) [18, 19]. The values d_f and D_f^e are connected by the relationship [20]:

$$D_f^e = 1 + \frac{1}{3 - d_f}. \tag{1.4}$$

It is not difficult to see, that the equations (1.2) and (1.3) give the same functional form of D dependence on gas-diffusant molecule sizes: D value decreases rapidly in virtue of power dependence at M or d_M rise. However, the equation (1.3) does not contain empirical (fitting) parameters that allow its use for D prediction. The exponent $2(D_t-d_s)/d_s$ value in the equation (1.3) can be determined by the slope of linear plots $D(1/d_m)$ in double logarithmic coordinates. In Fig. 1.1 the dependence, determined by such method, of dimension D_t on the difference of glass transition temperatures T_g (or melting temperatures T_m for semicrystalline polymers) and testing temperature T for 11 polymers is shown. As one can see, up to $[T_g(T_m)-T]< 120$ K D_t weak growth is observed and above the indicated temperature difference, the D_t value increases considerably more rapidly. From the equation (1.3) it follows, that the dimension D_t makes the main contribution in polymers diffusivity change at d_m=const in virtue of the power character of this equation and as changes of fluctuational free volume characteristics f_g and d_h are small and antibate [21]. Therefore the dimension D_t can be accepted as some main general characteristic of diffusion in polymers [10].

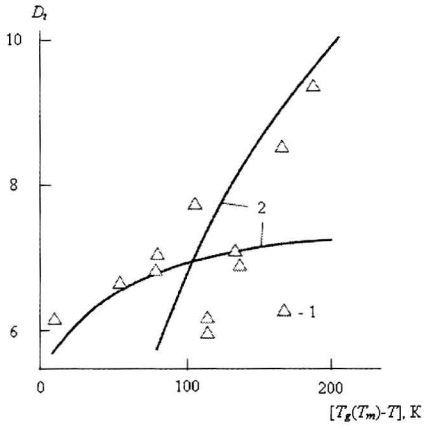

Figure 1.1. The dependence of dimension D_t controlling gas transport processes on difference of glass transition T_g (melting T_m) temperature and testing temperature T. 1 – experimental data; 2 – calculation according to the equation (1.8) [10].

The sharp change of the D_t dependence on $[T_g(T_m)-T]$ at the last parameter value ~ 120K assumes that this reduced temperature is the boundary between slow and rapid diffusion. The interrelation d_f and α for three-dimensional Euclidean space can be obtained by analogy with paper [9] as follows. Let's assume, that Hurst exponent H is connected with d_f according to the equation [10]:

$$d_f = 3 - H. \tag{1.5}$$

The authors [9] showed that in the equation (1.1) the exponent β is equal to $(1-\alpha)/2$ for slow diffusion and $1/(1+\alpha)$ – for a rapid one. Equaling H to the mentioned expressions for α according to the technique [9], let's obtain the interrelation between α and d_f:

$$\alpha = \frac{3 - d_f}{2} \tag{1.6}$$

for slow diffusion and

$$\alpha = \frac{1}{d_f - 1} \tag{1.7}$$

for rapid one.

It was not difficult to see, that allowing for polymers structure in three-dimensional space variation $2 \le d_f < 3$ value α changes in the interval 0-0.5 for slow diffusion and 0.5-1.0 – for a rapid one.

Accounting for D_t increase at the difference of temperature $[T_g(T_m)-T]$ growth (Figure 1.1), the authors [22] obtained the interrelation between these parameters in the following general form:

$$D_t = c\left[T_g(T_m) - T\right]^{\alpha}, \tag{1.8}$$

where c is constant.

As follows from Figure 1.1 data, at the assumed transition from slow diffusion to a rapid one, D_t value ≈6.5 or, according to the equation (1.4), d_f≈2.81. The exponent α in the equation (1.8) is equal to 0.095 for slow diffusion and 0.55 – for a rapid one. The values c for these cases were accepted as equal to 4.45 and 0.52, accordingly. In Figure 1.1 the dependences of D_t on $[T_g(T_m)\text{-}T]$ calculated according to the equation (1.8) at indicated α and c values are shown. As one can see, they describe experimentally obtained D_t variation well. This means that at $[T_g(T_m)\text{-}T]$<120 K slow diffusion is observed and above this temperatures difference – rapid one [10].

In Fig. 1.2 the dependence of methane diffusivity D_{CH_4} on glass transition T_g (melting T_m) temperature for 11 polymers is shown. This dependence reveals an interesting feature: up to $T_g(T_m)$≈450 K small values D_{CH_4} are observed and at $T_g(T_m)$>450 K begins the rapid growth of diffusivity. Let's note, that $T_g(T_m)$ ≈450 K corresponds to the value $[T_g(T_m)\text{-}T]$≈157 K, i.e. the plots of Figures. 1.1 and 1.2 are approximately in conformity. The similar picture of dependence of diffusivity by CO_2 in case the of polyethylene D_{CO_2} as a function of testing temperature T was observed in papers [23, 24], where rapid growth of D_{CO_2} at T>263 was connected with fractal properties of fluctuational-free volume. As was shown in the papers [24, 25], representation of fluctuational-free volume microvoid as a three-dimensional sphere is too simplified and it is more precise to consider this microvoid as D_f^e-dimensional sphere. In this treatment microvoid volume v_h^{fr} is given by the following equation [20]:

$$v_h^{fr} = \frac{\pi^{D_f^e/2} r_h^{D_f^e}}{\left(D_f^e/2\right)!}, \tag{1.9}$$

where r_h is a radius of free volume microvoid.

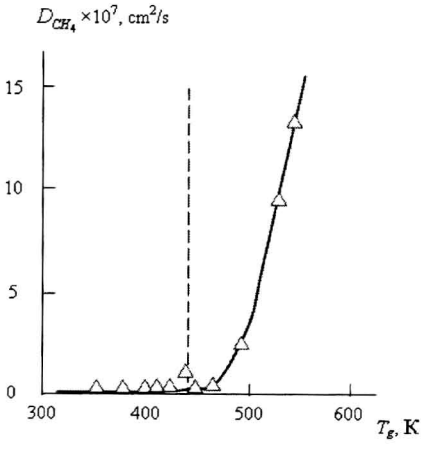

Figure 1.2. The dependence of methane diffusivity D_{CH_4} on glass transition T_g (melting T_m) temperature for 11 polymers. The vertical shaded line indicates the T_g value at which percolation of f_g^{fr} occurs [10].

If one designates microvoid volume in three-dimensional representation as ν_h then relative fractal free volume f_g^{fr} can be calculated as follows [10]:

$$f_g^{fr} = f_g \frac{\nu_h^{fr}}{\nu_h}, \tag{1.10}$$

where relative fraction of fluctuational free volume f_g can be accepted equal to 0.060 for solid-phase polymers [21].

For the estimation of the value ν_h there exists a number of methods and in paper [10] the following one was used. The experimental magnitude ν_h was calculated according to the formula [26]:

$$\tau_3 = 7.8\nu_h - 1.29, \tag{1.11}$$

where τ_3 is a life time of orthopositronium in experiments on positrons annihilation. The values τ_3 were accepted for the studied polymers according to the data of papers [13, 27-29]. In the equation (1.11) τ_3 is given in ns, ν_h – in nm^3.

The dependence of the value calculated by such method f_g^{fr} at the condition $D_f^e = D_t$ on $T_g(T_m)$ is shown in Figure 1.3. As it was expected f_g^{fr} increase is observed at $T_g(T_m)$ growth and at $T_g(T_m) \approx 440$ K, that corresponds to $[T_g(T_m)\text{-}T] \approx 147$ K (compare it with Figure 1.1), value f_g^{fr} reaches percolation threshold in assumption of the scheme of overlapping spheres (microvoids), which is equal to 0.34±0.01 [30]. In other words, according to the percolation theory at $[T_g(T_m)\text{-}T] \approx 147$ K or $T_g(T_m) \approx 440$ K in polymeric membrane a network of connected free volume microvoids is formed that facilitates diffusion conditions of gas-diffusant and sharply raises diffusivity [10].

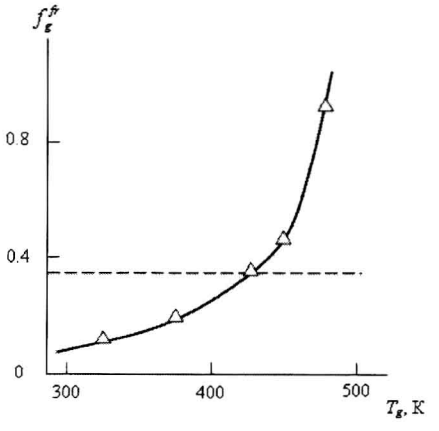

Figure 1.3. The dependence of relative fractal free volume f_g^{fr} calculated according to the equation (1.10) on glass transition T_g (melting T_m) temperature. Horizontal shaded line indicates percolation threshold f_g^{fr}, which is equal to 0.34±0.01 [10].

It is necessary to give explanations concerning absolute values f_g^{fr} which, calculated according to the equation (1.10), can exceed 1.0 which at first seems to be physical nonsense. As a matter of fact, this means local "splash" of value f_g^{fr} within the limits of fluctuation of average value f_g when $\nu_h^{fr} > 16.7\nu_h$. In accordance with a large general quantity of microvoids (~ 10^{28} m^{-3}) such "splash" for their limited number leaves value f_g practically invariable but can be effected on local properties of polymers on the molecular level.

Hence, the results cited above showed that in polymers both slow and rapid diffusion processes can be realized. The transition from the first type of diffusion to the second one is defined by glass transition (melting) temperature of polymers, i.e. by their chains' degree of flexibility and results in a sharp increase of diffusivity at the same fractal dimension of polymer structure. The application of percolation theory and fractal analysis allows one to give structural treatment of this change – the transition from slow diffusion to rapid one is due to formation through percolation network of overlapping microvoids of fluctuational free volume [10].

The authors [31] studied oxygen diffusion in nonbornens series with different T_g and obtained them from solutions by two methods – with rapid (method 1) and slow (method 2) solvent evaporation. It was found that the diffusivity growth with T_g for the films obtained by method 1 is much stronger than in method 2 (Figure 1.4).

Therefore it was assumed that in films with more equilibrium structure (method 2) slow diffusion is realized and in nonequilibrium films (method 2) a rapid one. To check this assumption, the authors [31] made at first the calculation of α according to the cited above technique [10], then D_f according to the equation (1.8) at the cited above coefficient c values and at last D_{O_2} values according to the equation (1.3). At D calculation the ratio (d_h/d_m)=const=1.15 for slow diffusion and (d_h/d_m)=1.06-1.31 for a rapid one in virtue of ν_h^{fr} change (ν_h=const). In Figure 1.4 the comparison of theory and experiment is shown from which follows their good correspondence. Hence, the transition to more equilibrium structure of polymers changes the mechanism of gas diffusion in polymers from rapid to slow. Properties of fractal free volume in connection with gas transport processes will be considered in the following section in detail.

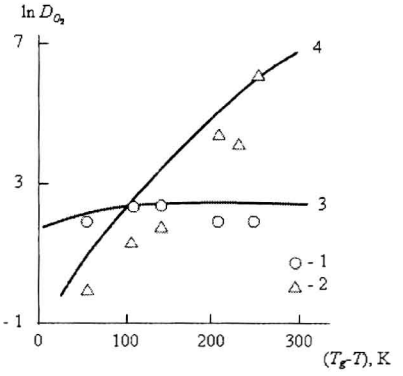

Figure 1.4. The dependences of diffusivity D_{O_2} by oxygen on differences in glass transition temperatures and testing temperatures (T_g-T) in logarithmic coordinates for nonbornenes. Experimental (1, 2) and calculated according to the equation (1.3) (3, 4) data for slow (1, 3) and rapid (2, 4) diffusion [31].

1.2. Fractal Free Volume and Gas Diffusion in Polymers

At present it is assumed [1, 2], that gas diffusion in polymers is realized by gas molecules passing through free volume microvoids, which in the present case is an analog of porosity in crystalline solids. However, for gas-diffusant molecules passing through a polymeric membrane it is necessary to form through channels or, in other words, a percolation network of microvoids. Besides, in the case of an overlapping spheres scheme the percolation threshold is equal to 0.34±0.01 [30], that is much larger than maximal possible value of relative free volume f_g, which is equal to 0.159 for polymers [32]. This apparent discrepancy has two alternative explanations. In classical models, the diffusion process is considered as sequence of jumps by gas-diffusant molecules from one free volume microvoid to another, which are formed and annihilated as a result of thermal fluctuations. Also, the mentioned microvoids are simulated by a three-dimensional sphere that exludes reaching by f_g value the percolation threshold [33]. However, simulation of a microvoid as a three-dimensional sphere with smooth walls is far from reality [34]. Microvoid walls represent the surface of macromolecules segment oscillating about their equilibrium states [35]. Therefore the authors [24, 25] offered to simulate the indicated microvoid by D_f^e - dimensional sphere this is the main postulate of the free volume fractal conception. As shown above, in this treatment f_g^{fr} value can reach percolation threshold and this condition is the boundary for realization of rapid and slow diffusion processes in polymers [10]. The authors [36, 37] demonstrated reality of fractal free volume in polymers using general models of fractal structures dynamics [38] and experimental data on the dependence of diffusivity on temperature [39], which were obtained for the diffusion of carbon dioxide in high density polyethylene (HDPE) according to the equation of Arrenius type [39]:

$$D_{CO_2} = D_0 \exp\left(-\frac{E_a}{RT}\right), \tag{1.12}$$

where D_{CO_2} is diffusivity for carbon dioxide, D_0 is the constant, E_a is the diffusion activation energy, R is universal gas constant, T is testing temperature.

Stanley [38] considered fundamental laws of diffusion and transport for the mediums representing a random mixture of components **A** and **B** in which there are sections conducting both well and badly. It was obvious that the concretization of this general model for gas diffusion in polymers looks like this: polymer is considered as random mixture of free volume **A** (conductor) and actual polymeric material (macromolecules, occupied volume) **B** (insulator) having zero diffusivity. This is the so-called random network of resistors (RNR) or limit of "ant" [38]. In the RNR limit, the larger conductivity is assumed equal to unit and the smaller one is equal to zero. At the approach of component **A** concentration, i.e. f_g^{fr}, to the percolation threshold p_c from above (p_c=0.34±0.01 [34]) the macroscopic conductivity Σ is rushing to zero and its behaviour is described by critical exponent μ [38]:

$$\Sigma \sim \left(f_g^{fr} - p_c\right)^{\mu}. \tag{1.13}$$

For the case $f_g^{fr} < p_c$ the limit of random superconducting network (RSN) is used, where the smaller conductivity is equal to unity and the larger conductivity is infinite. At the approach to p_c from below the conductivity rushes to infinity according to the law [38]:

$$\Sigma \sim \left(p_c - f_g^{fr}\right)^{-s}. \tag{1.14}$$

The macroscopic conductivity value is connected with diffusivity D according to the relationship of Nernst-Einstein:

$$\Sigma \sim nD, \tag{1.15}$$

where n is density of charge carriers.

Let's consider a concrete form of the relationship between Σ and D. Diffusive form J represents substance quantity Q (analog of n) passing through the surface element A during time unit t [33]:

$$J = \frac{Q}{At}. \tag{1.16}$$

In stationary regime of diffusion J value can be defined as follows [33]:

$$J = \frac{D\left(c_1 - c_2\right)}{l}, \tag{1.17}$$

where c_1 and c_2 are diffusant concentrations on both external and internal surfaces of the polymeric membrane, l is thickness of this membrane.

In a stationary diffusion regime c_1=const, c_2=const, l=const, A=const and for t=const according to the equations (1.16) and (1.17) let's obtain [36]:

$$D \sim Q, \tag{1.18}$$

or

$$D \sim n. \tag{1.19}$$

Further according to the relationships (1.15) and (1.19) follows:

$$\Sigma \sim D^2. \tag{1.20}$$

The exponents μ and s in the relationships (1.13) and (1.14), respectively, are defined as follows. The value μ is given like this [38]:

$$\frac{\mu}{\nu_p} = (d-2) + (d_w - d_f), \tag{1.21}$$

where ν_p is percolation critical index, which is equal to 0.80-0.88 [30, 40, 41], d is dimension of Euclidean space, in which fractal is considered (it is obvious, in our case d=3), d_w is dimension of trajectory of random walk on fractal, d_f is fractal dimension of structure.

The value d_f can be calculated according to the equation [42]:

$$d_f = 3 - 6\left(\frac{\varphi_{cl}}{SC_\infty}\right)^{1/2}, \tag{1.22}$$

where φ_{cl} is a relative fraction of local order regions (clusters), S is a macromolecule cross-section area (for HDPE S=18.7 Å^2 [43]), C_∞ is characteristic ratio which is an indicator of polymer chain statistical flexibility [44] and is equal 5.8 to for HDPE [45].

In its turn, φ_{cl} value as T function can be calculated as follows [46]:

$$\varphi_{cl} = 0.03(1-K)(T_m - T)^{0.55}, \tag{1.23}$$

where K is crystallinity degree, T_m is melting temperature.

According to the Aharony-Stauffer rule dimension d_w is defined as follows [38]:

$$d_w = d_f + 1. \tag{1.24}$$

The exponent s can be calculated according to the equation [38]:

$$\frac{s}{\nu_p} = d_u - (d-2), \tag{1.25}$$

where d_u is dimension of nonscreening perimeter of fractal object which is equal to [47]:

$$d_u = (d_f - 1) + \frac{d - d_f}{d_w}. \tag{1.26}$$

In Figure 1.5 the dependence of relative fractal free volume f_g^{fr} on testing temperature T for HDPE is shown, calculated according to the equations (1.9) and (1.10).

As one can see, f_g^{fr} value can be essentially higher than the limiting value f_g in classical treatment (0.159 [32]) and at T≈270 K reaches percolation threshold (compare with Figure 1.3 data). Further according to the relationships (1.13) and (1.14) one can determine value Σ above and lower percolation threshold, i.e. above and lower T=270 K, and then to calculate according to the relationship (1.20) diffusivity D^T in relative units. In Fig. 1.6 the comparison of temperature dependences D^T, calculated according to the equation (1.12), are shown. As

one can see, the full similarity of the dependences $D^T(T)$ and $D_{CO_2}(T)$ is observed, that indicates the reality of fractal free volume for polymers. Besides, in Figure 1.6 the dependence $D^T(T)$ (the curve 3) is shown calculated according to the relationship (1.14) in assumption, that f_g value changes in limits 0.060-0.110, i.e. as classical theories of free volume [1, 2] assume. As one can see, in this case D^T increase in interval T=173-293 K is ~ 10 %, that obviously does not correspond to the experimental data [37].

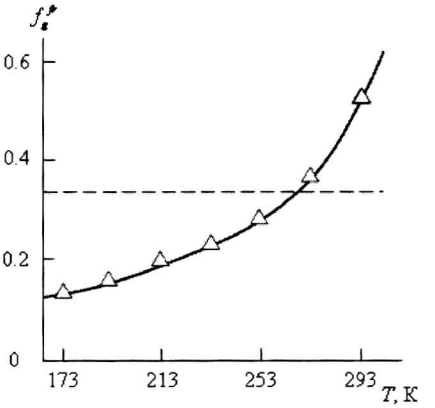

Figure 1.5. The dependence of fractal fluctuational free volume f_g^{fr} on testing temperature T for HDPE. The shaded horizontal line indicates the percolation threshold value pc [25].

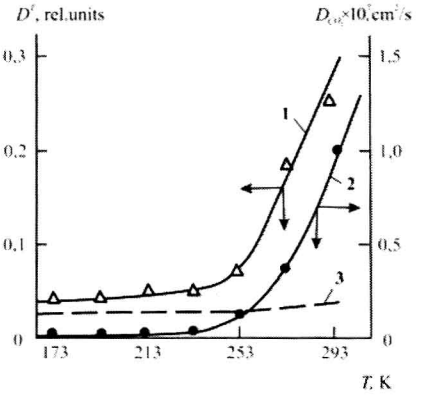

Figure 1.6. The dependences of diffusivities D^T and D_{CO_2} calculated according to the relationships (1.13) and (1.14) (1) and (1.12), respectively, on testing temperature T for HDPE. The curve 3 shows the dependence $D^T(T)$ calculated according to the relationship (1.14) with f_g use [36].

Adduced in Figure 1.5 f_g^{fr} values reach ~ 0.55 and in principle can be larger than 1.0 (see Figure 1.3), that at first sight seems to be physical nonsense. However, if we consider the formula (1.10) for f_g^{fr} estimation then it is obvious, as it was noted above, that it is a matter of local increase of microvoid volume in comparison with the assumed one of free volume by