

1 **Impact of surface diffusion on transport through porous materials**

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16 **Abstract.** The peak parking method was applied to evaluate the surface diffusivity D_s of
17 polystyrenes dissolved in a THF/heptane mixture and transported through porous silica
18 materials with various morphologies. With this method, the overall effective diffusivity D is
19 measured experimentally with coarse-grained models like Maxwell equation allowing one to
20 infer the particle diffusivity D_{pz} . Such particle diffusivity has two main contributions: in-pore
21 diffusivity D_p and surface diffusivity D_s . The diffusion within the pores is determined
22 experimentally using either non-adsorbing conditions or calculated from particle porosity,
23 particle tortuosity, and hydrodynamic hindrance. The surface diffusion coefficient D_s is usually
24 determined using models considering parallel diffusion in the pores and at the surface but this
25 assumption is rather crude. In this paper, to address this problem, another approach is proposed
26 using the Brownian motion of molecules in the pore space. These two approaches lead to similar
27 equations relating the effective diffusion coefficient D , the in-pore diffusion D_p and surface
28 diffusion D_s . The surface diffusion is analyzed as a function of the surface affinity of the probes
29 considered here (polystyrenes of different molecular weights/lengths). Such surface affinity
30 depends both on the probe chain length and surface chemistry of the host solid (the latter being
31 characterized here through the silanol surface density). For short chain lengths, a non-
32 monotonic change in the surface diffusion with affinity (i.e. retention factor) is observed in
33 some cases. Yet, generally, as expected, surface diffusion decreases upon increasing the surface
34 affinity. In contrast to short chain lengths, the longest chain lengths are less sensitive to the
35 silanol surface density.

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40 **Keywords:** effective self-diffusion, surface diffusion, peak parking method, porous silica

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1. Introduction

In chromatography, diffusion is generally estimated from the peak broadening which depends on the contribution of several mass transfer processes occurring inside the column [1]. The mass transfer kinetics in the stationary phase have a significant influence on the column efficiency under high flow rates of the mobile phase (with very important implications for many industrial processes such as catalysis and phase separation). The mass transfer kinetics depends mainly on intraparticle diffusion which has two contributions: diffusion in the porous volume and diffusion at the surface of the porous media (D_s). Hydrophilic interaction liquid chromatography (HILIC) [2] and reversed-phased liquid chromatography (RPLC) [3] are the most widely applied retention modes of liquid chromatography. The retention mechanisms at the heart of these techniques have been explained using molecular simulation in both HILIC and RPLC modes [4,5]. While surface diffusion contributes significantly to intraparticle mass transfer in RPLC, it seems negligible in HILIC [4,6,7]. In chromatography, diffusion can be measured using (1) a dynamic method by considering the response to a pulse sollicitation in the framework of the general rate model or (2) a static method through the so-called “stopped flow” or “peak parking” approach. In this context, we note that the peak parking method and pulse method lead to comparable results while being complementary to each other [8]. In general, the peak parking method is preferred for fast particle diffusion as the latter leads to small slopes when plotting the HETP (height equivalent to a theoretical plate) *versus* the mobile phase velocity – the slope being inversely proportional to the particle diffusivity D_{pz} [8].

In 1964, the peak parking method was introduced to determine diffusion coefficient in gas chromatography [9]. Later, this method was applied to liquid chromatography using columns packed with fully porous particles, core-shell particles or monolithic columns [10,11]. In this method, the overall effective diffusivity D – which should be comparable with values obtained using nuclear magnetic resonance experiments because in both experiments gradients of concentration versus time inside the porous medium are analysed– is determined as follows. After very diluted injection in the liquid upstream, the probe molecules are displaced until they reach the middle of the column by using a pump/pressure drop inducing flow. Once the molecules are in the middle of the column, the pump is stopped for a given time during which self-diffusion occurs through the porous medium. The pump is then restarted and the dispersion can be evaluated from the peak spreading increase as compared to the one without parking time. Such self-diffusion has two main contributions: (1) diffusion in the external volume of the

76 spherical particles or in the interskeleton volume for monoliths and (2) diffusion in the porous
77 zones. Desmet *et al.* (2008) showed using theoretical arguments that the residence-time
78 weighted expressions often used in chromatography to determine D are physically inconsistent
79 [12]. Such an important conclusion was also verified experimentally [8,13]. Models such as the
80 effective medium theory (EMT), including the Maxwell model [14], are often used to separate
81 both contributions and to determine the particle diffusion coefficient D_{pz} corresponding to the
82 porous zones. The Maxwell model can also be used to determine the particle tortuosity by
83 means of electrical measurements [15,16]. Higher order models such as Torquato model [17]
84 can also be used but in this model the so-called three-point parameter ζ_2 is unknown. In the
85 present study, the Maxwell model is preferred because it is sufficient to fit correctly the
86 experimental values D_{pz}/D_m where D_m is the bulk self-diffusivity [18]. The particle diffusion
87 coefficient D_{pz} is made up of two contributions: in-pore diffusion D_p and surface diffusion D_s .
88 Our research group has already studied in-pore diffusion of toluene and polystyrenes through
89 bare silica particles and monolithic columns in non-adsorbing conditions [18]. In this previous
90 study, tetrahydrofuran (THF) was used to avoid any adsorption of the solutes on the stationary
91 phase so that no surface diffusion was considered. The in-pore diffusivity was calculated from
92 peak parking experiments by using Maxwell model. Pore diffusion can also be modelled by
93 introducing the friction coefficient as calculated using Renkin equation [19] and the particle
94 tortuosity.

95
96 The particle tortuosities obtained by means of the peak parking method are usually comparable
97 to those determined using electrical measurements. The particle tortuosity can also be
98 calculated using the following equation: $\tau_p = 1 - p \ln \varepsilon_{pz}$ in which p is a topological parameter
99 and ε_{pz} the particle porosity. This equation can be established theoretically for freely
100 overlapping spheres (Weissberg equation) [20] and generalized to other systems using p as a
101 free parameter [15,16,21,22, 23,24,25]. The p values obtained by means of the peak parking
102 method are around 1.4 for silica columns. This model, which was recently used by Desmet *et al.*
103 *al.* [26] on reversed C18 columns, led to $p \sim 0.6-0.9$. In the present study, the same columns
104 and solutes are used as in [18] but adsorbing conditions are considered to study the influence
105 of surface diffusion (in practice, a mixture of heptane and THF is used to ensure such adsorbing
106 conditions). The solutes are a series of polystyrenes having different lengths and thus affinities
107 for the surface. The pore diffusion and surface diffusion are often assumed to occur in parallel
108 [1,4,27] but this approximation is rather crude. In the present paper, another model based on

109 intermittence between adsorption steps and self-diffusion relocation of the molecules in the
110 confining pore network [28] is analysed. For such intermittent dynamics, a comparable equation
111 is obtained while adding a constant factor and taking into account detailed balance conditions
112 between proximal fluid in the adsorption layer and distal fluid in the pore network. The model
113 proposed in this paper is applied to the mesoporous zone as well as to the whole column. The
114 peak parking method is used to evaluate experimentally D for polystyrenes of different
115 molecular weights in heptane/THF mixture through porous silica having different
116 morphologies: fully porous and core-shell particles are considered as well as monolithic
117 columns. The Maxwell model is then used to estimate the particle diffusion coefficient D_{pz} .
118 The surface diffusion D_s is also calculated as a function of the retention factor or equilibrium
119 adsorption constant by using either the classical, commonly used equation or the models
120 presented in this paper.

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123 **2. Theory**

124 **2.1. Particle diffusion coefficient**

125 Band broadening in a chromatographic column is mainly due to diffusion inside the particles.
126 In the peak parking method diffusion occurred inside and outside the particles during the
127 parking time leading to band broadening. In the peak parking method, the overall effective
128 diffusion coefficient D is directly obtained from the concentration profile at the end of the
129 column. To calculate the diffusion coefficient D_{pz} inside the particles, effective models are
130 needed. As shown in the literature, the effective medium theory (EMT) can be used to calculate
131 particle diffusion coefficients. Those models describe more accurately the experimental results
132 than the parallel zone or residence time weighted model which is usually used in liquid
133 chromatography. Among EMT models, despite its simplicity, the Maxwell model allows
134 efficient separation of the contributions from the porous and interstitial zones [8].

135

136 2.1.1 Maxwell model for spherical particles

137 *Fully porous particles.* The Maxwell model can be used to relate the effective intraparticle
138 diffusion coefficient D_{pz} to the total diffusion coefficient in the column D or equivalently its
139 value normalized to the bulk self-diffusivity $\gamma = D/D_m$. The Maxwell equation applied to
140 diffusion in a medium with retention writes as [18,26]:

$$\gamma = \frac{D}{D_m} = \frac{1}{\varepsilon(r_m)[1+k']} \frac{1+2\beta[1-\varepsilon_e]}{1-\beta[1-\varepsilon_e]} \quad \text{Eq. (1)}$$

141 where $\varepsilon(r_m)$ is the total porosity accessible to the diffusing molecule of size r_m , ε_e is the
 142 external porosity or the porosity in the macropores, and k' is the retention factor. k' is calculated
 143 from the mean retention time as $k' = (t_R - t_0)/t_0$ where t_R and t_0 are the mean retention times
 144 of the analyte in adsorbing conditions and non-adsorbing conditions, respectively. In practice,
 145 γ is obtained experimentally using the peak parking method as explained in the next section.
 146 The parameter β can be expressed by inverting Eq. (1). Upon introducing $\alpha_{pz} = (1 +$
 147 $2\beta)/(1 - \beta)$, the effective intraparticle diffusion coefficient in adsorbing conditions D_{pz} can
 148 be expressed as:

$$\frac{D_{pz}}{D_m} = \frac{\alpha_{pz}[1-\varepsilon_e]}{\varepsilon(r_m)[1+k']-\varepsilon_e} \quad \text{Eq. (2)}$$

149

150 *Core-shell particles.* In this case, the porosity in the porous zone is calculated as $\varepsilon_{pz} = \varepsilon_p/(1 -$
 151 $\rho^3)$ where ρ is the ratio of the non-porous core radius to the particle radius. To account for the
 152 effect of solid core, it is also important to distinguish between D_{pz} and D_p . While D_p is the
 153 effective particle diffusion, D_{pz} is the effective diffusion in the mesoporous zone (entire particle
 154 in the case of fully porous particles, shell layer in the case of a core-shell particle). For spherical
 155 particles, the relation between the two diffusion coefficients is given by [8]: $D_{pz} =$
 156 $(1 + \rho^3/2)D_p$.

157

158 2.1.2 Maxwell model for monoliths

159 The Maxwell model has also been established for cylinder packings [17]. It is assumed to
 160 provide a reliable representation of the skeleton in monoliths [10]. In this case, Eq. (1) giving
 161 the ratio γ is slightly modified:

$$\gamma = \frac{D}{D_m} = \frac{1}{\varepsilon(r_m)[1+k']} \frac{1+\beta[1-\varepsilon_e]}{1-\beta[1-\varepsilon_e]} \quad \text{Eq. (3)}$$

162 Again, by inverting this last equation, one obtains the following expression for the parameter
 163 β . Like for spherical particles, the intraskeleton effective diffusion coefficient D_{pz} for
 164 monoliths in adsorbing conditions is given by Eq. (3) but with $\alpha_{pz} = (1 + \beta)/(1 - \beta)$.

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167 2.2. Surface diffusion coefficient

168 The intraparticle diffusion coefficient D_{pz} has two contributions: the diffusion in the
 169 mesoporous zone $\gamma_{pz}D_m$ and surface diffusion D_s . In the literature, it is often assumed that the
 170 two phenomena occur in parallel so that the following model is used [26]:

$$\frac{D_{pz}}{D_m} = \frac{\varepsilon_{pz}(r_m)\gamma_{pz} + [1 - \varepsilon_{pz}(r_m)]K_a D_s/D_m}{\varepsilon_{pz}(r_m) + [1 - \varepsilon_{pz}(r_m)]K_a} \quad \text{Eq. (4)}$$

171 where the adsorption equilibrium constant $K_a = k'\varepsilon(r_m)/[1 - \varepsilon(r_m)]$ takes into account the
 172 volumes of the liquid and solid phases. The term γ_{pz} is the ratio between the intraparticle
 173 diffusion coefficient in the porous zone without adsorption and the molecular diffusion
 174 coefficient D_m . The diffusion in the mesoporous zone is hindered by the tortuosity τ_{pz} and the
 175 friction coefficient $k_f(r_m)$ which is due to the collisions between the diffusing molecule and
 176 the pore walls [6]:

$$\varepsilon_{pz}\gamma_{pz} = \varepsilon_{pz}(r_m) \frac{D_{pz}^0}{D_m} = \frac{\varepsilon_{pz}(r_m) k_f(r_m)}{\tau_{pz}(r_m)} \quad \text{Eq. (5)}$$

177 In some literature [e.g. 10] the value of τ_{pz}^2 is used with a factor 2 in the exponent coming
 178 from a difference in the definition of the tortuosity which is then considered as a ratio of length,
 179 whereas in the present paper the definition used is a ratio of lengths to the square.

180 The particle porosity $\varepsilon_{pz}(r_m)$ accessible to a molecule of a given size r_m can be estimated in
 181 non-adsorbing conditions with the same molecule or can be directly calculated with the
 182 following equation (which considers a spherical molecule in a cylindrical pore): $\varepsilon_{pz}(r_m) =$
 183 $\varepsilon_{pz}^0(1 - \lambda)^2$ where ε_{pz}^0 is the total particle porosity calculated from the porous volume obtained
 184 by classical characterization methods (e.g. nitrogen adsorption or inverse size exclusion
 185 chromatography with an analyte molecule very small compared to the pore size). In this
 186 equation, $\lambda = r_m/r_p$ is the ratio between the molecule radius r_m and the pore radius r_p . The
 187 friction coefficient is usually calculated using Renkin equation [19]: $k_f(r_m) = 1 - 2.10\lambda +$
 188 $2.09\lambda^3 - 0.95\lambda^5$.

189
 190 While the particle tortuosity τ_{pz} may be taken as a constant which usually lies between 1.4 and
 191 2, it can also be considered as dependent on the particle porosity accessible to a molecule of a
 192 given size r_m . In previous publications [8,18], it was shown that the Weissberg equation could
 193 be used to calculate the particle tortuosity. The Weissberg equation writes $\tau_{pz}(r_m) = 1 -$
 194 $p \ln \varepsilon_{pz}(r_m)$ where p is a topological factor that depends on the morphology of the solid. The
 195 tortuosity of the silica used here has been measured previously by electrical measurements and

196 the details are given in [18]. D_{pz}/D_m was calculated from the overall effective diffusion
 197 coefficient and the Maxwell model introduced above. By using Eq. (4), the surface diffusion
 198 coefficient D_s can be calculated in a second step.

199

200 Because the assumption of parallel in-pore diffusion and surface diffusion is rather crude,
 201 another approach is proposed here. We consider the molecular trajectory as an intermittent
 202 dynamic made of a succession of adsorption steps and relocation steps in the pore network
 203 between two adsorption events. Some statistical properties of this rich dynamics type were
 204 already analyzed [28,29]. Various statistics can be chosen to describe elementary molecular
 205 displacement inside the pore, such as overdamped Langevin dynamics, Pearson statistics [28]
 206 or Brownian motions based on Gaussian probability. In any case, the trajectory of a molecule
 207 can be decomposed in N steps involving successive displacements inside the pores, \vec{r}_i , and
 208 displacements at the surface, \vec{e}_i , (with i varying between 1 and N). For a sufficiently long path
 209 (N very large), the mean square displacement can be written as (e.g. [30]):

$$210 \quad \langle \vec{r}^2 \rangle = \langle [\sum_{i=1}^N \vec{r}_i]^2 \rangle + \langle [\sum_{j=1}^N \vec{e}_j]^2 \rangle \quad \text{Eq. (6)}$$

211 where complete decorrelation between adsorption and bulk self-diffusion segments is assumed.
 212 At long time (large N), the mean square displacement associated to molecular self-diffusion can
 213 be written as $\langle \vec{r}^2 \rangle = 6D_{app}N[t_a + t_r]$ where D_{app} is the apparent self-diffusion coefficient in
 214 the considered porous system and t_a (resp. t_r) is the mean residence time on the surface (resp.
 215 mean duration of a path inside the pore between two contacts with the surface). For non-
 216 adsorbing conditions, *i.e.* $t_a = 0$, we get

$$217 \quad \langle [\sum_{i=1}^N \vec{r}_i]^2 \rangle = 6D_{app}^0 N t_r = \frac{6D_{m,p} N t_r}{\tau_r} \quad \text{Eq. (7)}$$

218 where D_{app}^0 is the self-diffusion coefficient in the porous network without adsorption and τ_r the
 219 associated pore network tortuosity. $D_{m,p}$ is the local self-diffusion coefficient inside a pore; it
 220 is here considered as different from the bulk diffusion coefficient D_m as local confinement
 221 effects might lead to non-negligible departure between these two values. The second right hand
 222 side of Eq. (6) reads $\langle [\sum_{j=1}^N \vec{e}_j]^2 \rangle = 4D_s N t_a$ where the surface self-diffusion D_s is considered
 223 bidimensional and independent of pore curvature, which means that the lengths covered by
 224 adsorbed molecules on the surface are lower than pore size. This leads to the following
 225 equation:

$$226 \quad D_{app} = \frac{t_r}{t_r + t_a} \times \frac{D_{m,p}}{\tau_r} + \frac{t_a}{t_r + t_a} \times \frac{4}{6} \times D_s \quad \text{Eq. (8)}$$

227 At this point, it is needed to take into account detailed balance conditions which allow imposing
 228 thermodynamic equilibrium between the adsorbed layer and the molecular population in the
 229 pore network. This condition reads $t_a/[t_a + t_r] = f_{ads}$, where f_{ads} is the average molar fraction
 230 of molecules that are adsorbed at equilibrium (in this equation, we use assume ergodicity which
 231 imposes that the fraction of time spent by a molecule in one of the phases is proportional to its
 232 molar fraction in this phase). Using the later condition into Eq. (8), we get $D_{app} = (1 -$
 233 $f_{ads})D_{app}^0 + \frac{4}{6}f_{ads} D_S$. This equation was proposed to analyse gas diffusion inside porous
 234 media [31].

235
 236 t_a and t_r can be related directly to the experimental retention times with adsorption t_R and
 237 without adsorption t_0 . Indeed, the latter can be decomposed into contributions from inside t_0^{pz}
 238 and outside t_0^{ext} the mesoporous zone:

$$239 \quad t_R = t_0^{ext} + t_0^{pz} + t_{ads} = t_0^{ext} + N(t_r + t_a) \quad \text{Eq. (9)}$$

$$240 \quad t_0 = t_0^{ext} + t_0^{pz} = t_0^{ext} + Nt_r$$

241 where $t_0^{pz} = Nt_r$ is the porous zone retention time without adsorption, $t_{ads} = Nt_a$ is the time
 242 spent in the adsorption phase, while the external retention time t_0^{ext} can be determined in non-
 243 adsorbing conditions of excluded molecules. While N is generally unknown, the effective
 244 diffusivity formula for D_{app} allows using experimental data for f_{ads} (see in line equation
 245 above). In more detail, the equilibrium adsorption constant K_a can be calculated from
 246 chromatographic experiments as $K_a = C_a/C_s = \varepsilon k'/(1 - \varepsilon)$ where C_a is the concentration of
 247 adsorbed molecules expressed as moles per volume of solid phase and C_s the bulk solution
 248 concentration. ε is the porosity of the considered porous medium and k' the corresponding
 249 retention factor. By imposing the mass balance condition, it is easy to verify that: $f_{ads} =$
 250 $(1 - \varepsilon)K_a/[\varepsilon + (1 - \varepsilon)K_a]$.

251
 252 Coming back to chromatography experiments, one can now consider two cases.

253 **(1) The considered porous medium is the mesoporous zone.** In that case $D_{app} = D_{pz}$
 254 (adsorbing conditions) and $D_{app}^0 = D_{pz}^0$ (non-adsorbing conditions) are those of the
 255 mesoporous zone whose porosity is ε_{pz} . Using the mass balance condition, the equation for
 256 D_{app} given above becomes:

$$257 \quad D_{app} = D_{pz} = \frac{\varepsilon_{pz}(r_m)}{\varepsilon_{pz}(r_m) + [1 - \varepsilon_{pz}(r_m)] K_a} D_{pz}^0 + \frac{4}{6} \times \frac{[1 - \varepsilon_{pz}(r_m)] K_a}{\varepsilon_{pz}(r_m) + [1 - \varepsilon_{pz}(r_m)] K_a} D_S \quad \text{Eq. (10)}$$

258 **(2) The considered porous medium is the column itself.** In that case, $D_{app} = D$ and $D_{app}^0 =$
259 D^0 are those of the whole column and correspond to the total diffusion coefficients with and
260 without adsorption, respectively:

$$261 \quad D = \frac{\varepsilon(r_m)}{\varepsilon(r_m) + [1 - \varepsilon(r_m)] K_a} D^0 + \frac{4}{6} \times \frac{[1 - \varepsilon(r_m)] K_a}{\varepsilon(r_m) + [1 - \varepsilon(r_m)] K_a} D_S \quad \text{Eq. (11)}$$

262 Interestingly, starting from a microscopic description based on serial molecular transport, a
263 macroscopic parallel description of the diffusion coefficient is obtained where the surface
264 diffusion is simply multiplied by a factor 4/6 (which is the ratio between surface/bulk
265 dimensions).

266

267

268 **3. Material and methods**

269 3.1 Chemicals

270 The organic solvents used are tetrahydrofuran (THF) purchased from Carlo Erba Reagents
271 (SDS) and n-heptane. Toluene (T) was purchased from Aldrich. A series of twelve polystyrenes
272 (-CH[C₆H₅]-CH₂-)_n with various molecular weights and molecular sizes was provided from
273 Polymer Standards Service (Mainz, Germany). They are named from P01 for the monomer to
274 P12 for the biggest polymer. THF was used for non-adsorbing conditions while a heptane:THF
275 mixture (97:3) was used for adsorbing conditions. Toluene and polystyrenes were dissolved in
276 the mobile phase at a concentration of 1 g/L. Detection of the polymers was done using UV-
277 VIS spectroscopy at a wavelength of 262 nm.

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280 3.2. HPLC system

281 The experiments were done using the 1200 HPLC system (Agilent Technologies) including a
282 quaternary gradient pump with a multi-diode array UV-VIS detector, an automatic sample
283 injector with a 100 μ L loop, an autosampler and a thermoregulated column compartment. The
284 injection volume was set at 1 μ L and all experiments were conducted at 298 K. The system was
285 controlled using the Chemstation software. The columns used in this study were composed of
286 porous silica with various morphologies: fully porous silica particles (Lichrospher Si100,
287 Merck), core-shell silica particles (Poroshell 120, Agilent) and monolithic silica (Chromolith,
288 Merck). The main characteristics of the columns and their characterization made by means of
289 mercury porosimetry, nitrogen adsorption and ISEC can be found in Ref. [18]. The tortuosities
290 determined by electrical measurements are also given in Ref. [18]. The main characteristics are

291 summarized in Table I. The silicas were characterized by thermogravimetry (TGA) using the
292 TA Instruments TGA Q500. Around 10 mg of sample are placed in a platinum crucible and
293 lowered into a temperature-controlled oven. The evolution of the sample mass was followed
294 under argon atmosphere as a function of temperature from 25 to 850 °C with a heating rate of
295 5°C/min. The number of silanol groups (number of OH per nm²) was determined from the
296 weight loss between 175 and 800°C. All results are given in Table I.

297

298 3.3. Molecular diffusion coefficients

299 The molecular diffusion coefficients of toluene and of the smallest polymers (P01-P03) in the
300 mixture heptane:THF 97:3 were determined by Taylor Dispersion Analysis (TDA). Such TDA
301 experiments were done three times with a stainless-steel tube (0.876 mm internal diameter,
302 length 1.20 m) at three different flow rates. The molecular diffusion coefficient D_m was
303 calculated using the following equation:

$$304 D_m = R_C^2(t_R - t_i)/24(\sigma_R^2 - \sigma_i^2) \quad \text{Eq. (12)}$$

305 where R_C is the capillary internal radius, t_R and σ_R^2 are the mean retention time and variance of
306 the peak with the stainless-steel tube, and t_i and σ_i^2 correspond to the retention time and the
307 variance obtained without the stainless-steel tube. Eq. (12) is valid as long as the two following
308 conditions are fulfilled: (1) The dimensionless residence time $t' = D_m t_R R_C^2$ should be $t' > 1.4$
309 and (2) and the Peclet number should be $Pe > 70$. Those conditions are verified here. The
310 hydrodynamic radius of the polymers r_m in the mixture is then calculated by using Stokes-
311 Einstein equation. D_m and r_m for T, P01, P02 and P03 in the mixture 97:3 (heptane:THF) at
312 298 K are given in Table II. The molecular diffusion coefficients and size of polystyrenes in
313 non-adsorbing conditions, i.e. using pure THF as solvent, can be found in Ref. [18].

314

315 3.4. Peak parking experiments

316 The peak parking method was used to measure the apparent effective diffusion coefficient of
317 molecules through the different porous media under study. In these experiments, 1 µL of a
318 dilute sample solution was injected at a rate of 0.5 mL min⁻¹. The columns were eluted during
319 the time needed for the liquid sample to arrive about half length of the column. Then, the flow
320 was stopped and the molecules left to diffuse freely during a given time called the parking time
321 t_p . The flow was then started again to the same flow rate and the peak variance of the solute
322 band σ_t^2 was measured. In more detail, the peak variance is measured by fitting the
323 chromatograms with a Gauss function. To correct for other band broadening effects (injector,

324 connecting tubing), the peak variances obtained without parking were subtracted from the peak
 325 variance values obtained with parking. The variance in time unit was then plotted versus the
 326 parking time to infer from the slope the effective diffusion in the column:

$$327 \quad D = \frac{1}{2} \frac{\Delta\sigma_t^2}{t_p} \left(\frac{\varepsilon_e}{\varepsilon(r_m)[1+k']} \right)^2 u^2 \quad \text{Eq. (13)}$$

328 where the porosities ε_e and ε are obtained by ISEC, u is the interstitial linear velocity and k' is
 329 the retention factor. k' is given by $k' = [t_R - t_0]/t_0$ where t_R and t_0 are the mean retention
 330 times of the analyte in adsorbing and non-adsorbing conditions, respectively.

331

332

333 4. Results and discussion

334 4.1. Peak identification and polydispersity index

335 The analyte molecules used in this study are toluene and a set of polystyrenes having different
 336 sizes. While P01 is the monomer used for the polystyrene synthesis, the polystyrenes ranging
 337 from P02 to P12 are polydisperse with a polydispersity index $\text{PDI} > 1.0$. In practice, this means
 338 that each polystyrene is a mixture of polymers having a different number of units. In adsorbing
 339 conditions, toluene and P01 have only one peak but for the other polystyrenes many peaks are
 340 observed in the chromatograms. The heptane/THF mixture (97/3) was chosen to ensure a good
 341 separation of the fractions contained in each polystyrene. It was shown that adsorption increases
 342 usually with the molecular weight of the polymer, therefore leading to a significant polymer
 343 separation according to their affinity for the silica surface [32]. For the polymerisation of
 344 polystyrene, n-butyllithium ($\text{C}_4\text{H}_9\text{Li}$) is added to styrene monomer to react with another styrene
 345 radical in the next step and so on. At the end of this stage, the terminating agent proton H^+ is
 346 added to remove lithium at a given time. At end, the molecular weight of the polystyrenes is
 347 given by $M_w = 104P + 58$ where P is the number of units.

348

349 The PDIs given by the supplier are 1.09 and 1.05 for P02 and P03, respectively. Such PDI,
 350 which corresponds to the width of the molecular weight distribution, is defined as the ratio of
 351 the average molecular weight M_w to the number average molecular weight M_n , i.e. $\text{PDI} = M_w/M_n$.
 352 M_w is calculated from the weight fraction distribution of molecules of different size, $M_w =$
 353 $\sum_{i=1}^n M_i w_i$ where n is the degree of polymerization while w_i and M_i are the mass fraction and
 354 molecular weight of each fraction. M_n is the total weight of all polymer molecules in the sample
 355 divided by the total number of polymer molecules: $M_n = \sum_{i=1}^n N_i M_i / \sum_{i=1}^n N_i$ where N_i is the
 356 number of molecules of size i : $N_i = N_A m_i / M_i$ (in this equation, m_i is the total mass for each

357 fraction while N_A is Avogadro's number). From the chromatograms shown in figure 1 for the
358 column filled with fully porous silica particles, one can obtain the mass fraction of each peak.
359 When doing so, the number of units for each peak must be assumed. For the polymer P02, the
360 first peak has been assumed to correspond to 3 units, 4 units for the second peak, and so on.
361 Then, the highest peaks for P02 and P03 are assumed to correspond to 6 and 13 units,
362 respectively. By using the equations above, the PDI for P02 and P03 are found to be 1.07 and
363 1.08, respectively. These values are close to those provided by the supplier. Similar
364 chromatograms were obtained with Poroshell and Chromolith columns.

365

366 4.2. Porosities and diffusivities in non-adsorbing conditions

367 To calculate the surface diffusion coefficients, it is necessary to estimate or measure
368 experimentally a number of parameters such as the mean retention time t_0 , the porosities ($\varepsilon(r_m)$
369 the total porosity of the column accessible to a probe of size r_m , ε_e the external porosity) the
370 molecular diffusion coefficients D_m , the total diffusion coefficient in the column D^0 and the
371 effective diffusion in the mesoporous zone D_{pz}^0 in non-adsorbing conditions for each polymer
372 length. Those parameters have been published previously in non-adsorbing conditions for the
373 three columns and polystyrenes under study (by using THF instead of the mixture heptane/THF
374 as solvent [18]). The parameters were estimated by taking the mean values of the molecular
375 weights for the polystyrenes. In adsorbing conditions, each polystyrene is divided in fractions
376 having different unit numbers and thus different molecular weights. To calculate each fraction
377 contribution, it is necessary to rely on a simple mathematical equation. In practice, a second
378 order equation can be used for the retention time and porosity ($y = a + bM_w + cM_w^2$) while a
379 power law can be used for the diffusion coefficients ($y = aM_w^b$). These equations were used
380 to calculate the following parameters for each fraction in non-adsorbing conditions (THF): t_0 ,
381 ε , D_m , $\frac{D^0}{D_m}$, $\frac{D_{pz}^0}{D_m}$. Typical illustrative fits are provided in figure 2 for the retention time t_0 in non-
382 adsorbing conditions for the three columns (the regression coefficient R is such that $R^2 > 0.95$
383 for all parameters and columns under study).

384

385 4.3. Retention factor k'_i as a function of number of polysterene unit

386 Each chromatogram peak corresponding to a given fraction i was fitted with a Gauss function
387 to determine the peak width and mean retention time $t_{R,i}$. Finally, the retention factor for each
388 fraction in the n -heptane/THF mixture can be calculated by applying for each fraction i the
389 following equation: $k'_i = [t_{R,i} - t_{0,i}]/t_{0,i}$. The mean retention time $t_{0,i}$ is obtained from the

390 equations given in Section 4.2. The evolution of retention factor of the different fractions for
391 P01, P02 and P03 through the Lichrospher Si 100, Poroshell and Chromolith columns at a flow
392 rate of $0.5 \text{ ml}\cdot\text{min}^{-1}$ is shown in figure 3. As expected, the retention factor increases with
393 increasing the number of units. Such behaviour has also been observed in high-performance
394 liquid chromatography of polystyrene oligomer on the bare silica column in the THF/*n*-hexane
395 mixture. Mass spectrometry was further used to recognize the degree of polymerization for the
396 oligomer peaks in this case [33]. For the three columns, the retention times for the P02 fractions
397 agree with that of the P03 fractions with the same numbers of units. This indicates that the P02
398 and P03 fraction affinity for the silica surface in the column with the same numbers of units is
399 comparable: there is apparently no competition between these fractions of a given polymer
400 sample. Moreover, this result confirms that our peak assignment to a given polymer chain length
401 is correct. Figure 3 also shows that the retention factors for P02 and P03 in the Si 100 column
402 are larger than for the other columns. This suggests that the surface chemistry in these two
403 materials differ: for silica-based materials, it is often related to the surface density of silanol
404 groups. The number of OH per nm^2 determined by TGA for the three columns are given in
405 Table I. The number of OH per nm^2 is 3.1 for Lichrospher Si100, 2.4 for Poroshell and 1.1 for
406 the Chromolith columns. The retention factor k' increases with the number of OH per nm^2 as
407 seen in figure 3; the largest and smallest k' are obtained for Lichrospher Si100 and
408 Chromolith columns, respectively.

409

410 4.5. Effective diffusion coefficient by peak parking method

411 Typical chromatograms are given in figure 4 for the monomer P01 and the polystyrene P02
412 with the column Lichrospher Si100. The peaks are symmetrical and broaden with increasing
413 parking time due to diffusion. For P02 and P03, each polymer fraction was fitted with a
414 Gaussian function. The variance of each peak was evaluated for each parking time to determine
415 the effective diffusion coefficient from the Gauss fit. The peak variance is plotted as a function
416 of the parking time in figure 5 for P01 and some fractions of P02 for the Lichrospher column.
417 Similar results were obtained for the two other columns (they are not shown here for the sake
418 of brevity). It should be noticed that all the curves are straight lines. The slope decreases as the
419 molecular size increases due to the expected decrease in effective diffusion. By applying Eq.
420 (13), the effective diffusion coefficient D for each probe can be determined. The total accessible
421 porosity $\varepsilon(r_m)$, retention factor k' and molecular diffusivity D_m were estimated for each
422 fraction using fits against a second order or power law equation as explained in Section 4.2.
423 The ratios D/D_m as a function of the adsorption equilibrium constant K_a is shown in figure 6.

424 The relative error in the determination of D/D_m is $\pm 10\%$ ($\pm 5\%$ error for the determination of
425 D_m by TDA measurements and $\pm 5\%$ for the determination of the slope of the peak variance
426 *versus* peak parking time). As expected, for all columns, D/D_m decreases significantly upon
427 increasing the adsorption constant K_a . The effective diffusion D is larger in the monolithic
428 column compared to fully porous and core-shell particle columns. This result may be explained
429 by the fact that the monolithic column possesses a much more open structure than packed
430 columns [34]. In fact, the external porosity of the monolithic column is around 70% against
431 40% for packed columns while the total porosity is around 90% for monolithic columns against
432 80 % for fully porous particles and 70% for core-shell particles columns. The values for $K_a =$
433 0 were published previously [18] and were obtained with P01 and P02 in non-adsorbing
434 conditions with the same columns in pure THF. For small K_a , a maximum is observed for the
435 Lichrospher Si100 and Poroshell columns, which could be explained by diffusion in the
436 mesoporous zone and at the surface of the solid as discussed in the next part.

437

438 4.4. Diffusion in the mesoporous zone and surface diffusion

439 Experimentally, D_{pz}/D_m was derived from the experimental values D/D_m using the Maxwell
440 model as explained in Section 2.1. D_{pz}/D_m is plotted in figure 7 as a function of the adsorption
441 equilibrium constant K_a for the three columns (the relative error over D_{pz}/D_m is about $\pm 10\%$).
442 D_{pz}/D_m values for the fully porous and core-shell particle columns go through a maximum for
443 low K_a values and then continuously decrease. A different behaviour is observed for the
444 monolithic column where D_{pz}/D_m decreases monotonously with K_a . The occurrence of this
445 maximum which indicates that diffusion may be higher in the presence of adsorption than in its
446 absence is of course interpreted by the contribution of surface diffusion which is now calculated.

447

448 Surface diffusivity D_s was determined from (i) the equations proposed in this paper by
449 considering the mesoporous zone [Eq. (10)] or the whole column [Eq. (11)] and (ii) the equation
450 which is usually employed when considering parallel diffusion [Eq. (4)]. Figure 8 shows
451 D_s/D_m as a function of the adsorption constant K_a for the three columns. These data show that
452 D_s/D_m obtained by considering the mesoporous zone or the whole column are similar except
453 for the monolithic column for which D_s/D_m are slightly higher when considering the whole
454 column. The Maxwell model is used for the determination of D_{pz} and D_{pz}^0 in eq. 10, but for eq.
455 11 no model is necessary for the determination of the total diffusion coefficient, all the
456 parameters being determined experimentally. These results indicate that the Maxwell model

457 provides a good estimate of the porous zone diffusion coefficient. Higher order models like the
458 Torquato model could also be used but the Maxwell model despite its simplicity gives a good
459 estimation of surface diffusion as also concluded in [10]. D_s/D_m obtained by considering the
460 classical parallel diffusion model are slightly lower than the values obtained by using Eqs. (10)
461 or (11) because of the factor 4/6. Eq. (11) is simpler to use because D_s is directly determined
462 from D_0/D_m and D/D_m obtained by the peak parking method in non-adsorbing and adsorbing
463 conditions, respectively. Regardless of the model used, D_s significantly decreases upon
464 increasing adsorption strength. For $K_a > 3$, D_s/D_m are around 0.1-0.3 for the Lichrospher and
465 Poroshell columns and around 0.3-0.6 for the monolithic column. Upon increasing K_a , surface
466 diffusion is faster in the monolithic column compared to the Lichrospher and Poroshell columns,
467 therefore indicating that the interactions of molecules with surface are probably different. For
468 low $K_a < 2$, D_s/D_m reaches values larger than 1 whatever the model in the case of packed
469 columns. $D_s/D_m > 1$ indicated that surface diffusion of the solutes is faster than bulk diffusion
470 in the mobile phase. In other words, for such D_s/D_m , the solutes are more mobile near the
471 surface which lowers their mass transport resistance. Fast surface diffusion was also observed
472 in reversed-phase liquid chromatography [4]. For the monolithic column, even at low K_a ,
473 $D_s/D_m < 1$ regardless of the model used. The three columns are made of pure silica with
474 surface silanol groups which have a polar character due to the polarity of the covalent bond
475 between hydrogen and oxygen atoms. In this study, a heptane/THF mixture is used; those
476 solvents can interact with the silanol surface groups due to non-specific interactions (van der
477 Waals forces). In particular, THF may exhibit polar interactions with silanol groups. A part of
478 the silanol groups is probably covered with THF molecules. In pure THF, the polystyrene
479 molecules are not adsorbed on the silica surface so that polystyrene is not able to displace the
480 THF molecule from the silica surface. The adsorption of polystyrene molecules on silica, which
481 can be due to the interaction of benzene ring with silanols, is enhanced in the presence of
482 heptane which contributes to the displacement of THF. At low K_a , the surface diffusion D_s is
483 close or even larger than D_m for Lichrospher and Poroshell columns. A different behavior is
484 observed for the monolithic column where $D_s/D_m < 1$ even at low K_a (regardless of the model
485 used). These results indicate that, at low K_a , the behaviour with the three silica columns is
486 different; this could be explained by the silanol surface density which differs between these
487 three columns (see Table I). D_s/D_m as obtained from the three proposed equations are plotted
488 in figure 9 as a function of the number of OH groups per nm^2 . These data are shown for the
489 three silica columns upon transport of the monomer P01 and the fraction of P02 having 6 units.

490 For a small molecule such as P01, D_s/D_m increases with increasing the number of OH groups
 491 per nm². For larger molecules (e.g. P02, $P = 6$), the effect of the number of OH groups per nm²
 492 is less pronounced; this indicates that the surface diffusion mechanisms depend strongly on the
 493 number of OH groups per nm² but also on the size of the molecule. Zhang et al. [35] studied by
 494 means of simulation the diffusion of polystyrene on silica surfaces grafted with different
 495 densities of hydroxyl groups. These authors showed that, at low or full grafting, diffusion is
 496 facilitated compared to moderate grafting density because the activation energy required to
 497 induce diffusion is smaller and polystyrene chain prefer a shrinking configuration leading to
 498 faster diffusion. For the three columns, $\frac{D_s}{D_m}$ decreases strongly upon increasing K_a and/or the
 499 polymer length. Our results are compared hereafter with theory and simulation of polymer
 500 surface diffusion previously published by assuming a two-dimensional model for displacement.
 501 Such modeling predicts that surface diffusion should scale as $D_s \sim P^{-\alpha}$ with α ranging between
 502 0.75 and 1.5 (we recall that P is the number of units of monomer) [36]. While $\alpha = 1$ for the
 503 Rouse model (free lateral motion of the polymer chain) [37], $\alpha = 1.5$ for a reptation-type model
 504 (hindered lateral motion of the polymer chain) [38, 39]. The difference between these two
 505 mechanisms generally depends on surface roughness at the nanoscale. Generally, the Rouse
 506 model is verified on smooth surfaces while α becomes larger than 1 on rougher surfaces [38,
 507 39]. Skaug et al. [36], who found $\alpha \sim 0.6 \pm 0.2$, proposed an intermittent-hopping mechanism
 508 dominated by a desorption-mediated mechanism; in this model, polymers desorb from the
 509 interface, diffuse in the bulk liquid, and adsorb again on another surface site. The log of the
 510 surface diffusion coefficient obtained with Eq. (13) is plotted as a function of $\log P$ in figure 10
 511 for the three columns. These data are shown for P ranging between 1 and 10 corresponding to
 512 the monomer ($P = 1$) and the different fractions of the polymer P02 ($P = 3-10$). Similar plots
 513 were obtained for the two other models used to infer D_s . As expected by the models proposed
 514 in the literature, a linear relation is obtained between $\log D_s$ and $\log P$ (which is, in particular,
 515 consistent with the fact that D_s was found to scale as $1/n$ where n is the hydrocarbon chain
 516 length in [40]). α is given in Table 3 for the different models and columns used. For the
 517 Lichrospher column, α is close to unity (0.9-1.1 depending on the model used) for the smallest
 518 polymers ($P = 1-5$). For the poroshell column, α is around 0.9 for P ranging between 1 and 10.
 519 For the Lichrospher column, the results for $P = 5-10$ are not shown because D_s/D_m is very close
 520 to zero and the error bar becomes very large. Surface diffusion for those columns seems to
 521 follow the Rouse model. For the Chromolith column, α is around 0.5 and 0.7 according to the
 522 model used ($P = 1-10$). Such α -values are close to that obtained by Skaug et al. [36] who

523 proposed an intermittent hopping mechanism. It is finally logical that the transition from a
524 mechanism to the other depends on silanol surface density. For example, the Rouse mechanism
525 can be associated with high silanol density whereas hopping mechanism are observed when
526 distance between sites is large, *i.e.* low silanol density. It means that the activation energy to
527 jump between two adjacent sites increases when distance increases. All in all, these data show
528 that the surface diffusion mechanisms differ between the three columns.

529

530 Recently Bousige et al. [41] proposed a novel strategy by mapping molecular dynamics
531 simulations onto intermittent Brownian motion to describe fluid diffusion in disordered
532 nanoporous media. These authors showed that surface diffusion decreases linearly $E/k_B T$
533 where E is the adsorption energy of an adsorbed molecule (see Supplementary Fig. S7 in Ref.
534 [41]). In this study, the adsorption constant K_A is such that it can be written as $\ln K_A = E/k_B T$.
535 D_s is plotted as a function of $\ln K_A$ in figure 11; a linear relation is obtained for the three
536 columns as expected from the multiscale approach proposed in [41]. The slope is different from
537 a sample to another as this reflects an expected impact of the surface chemistry at play. The
538 largest slope is obtained for Si100, which clearly shows a higher affinity for the molecules
539 studied here (as already shown in figure 3). The behaviours observed in figure 8 and figure 11
540 are intriguing; at low affinity, the surface diffusion is higher on Si100 whereas it is lower than
541 for the other samples at high affinity. This apparent behaviour is somewhat qualitatively
542 comparable to the simulation data obtained in Ref. [41]; surface affinity is increased by
543 increasing the polymer chain length in the present work while the adsorption energy is directly
544 increased in the simulation part at constant molecule size. This expected behaviour is confirmed,
545 for example, by calorimetry experiments which indicate that, at low equilibrium concentration,
546 molecules are adsorbed in a rather flat conformation (making the adsorption energy
547 proportional to the chain length) [32]. When the solid is varied, the affinity changes despite an
548 overall identical chemical nature. As already discussed, the difference may arise from the
549 density of silanol groups on the surface. Moreover, the activation energy for a molecule to jump
550 between adjacent surface groups may depend both on the surface group distance and molecule
551 size. As shown above, figure 9 shows that surface diffusion is less affected by OH density when
552 molecules are larger.

553

554 **5. Conclusion**

555 In this paper, an approach based on the intermittent dynamics of molecules in pore space is
556 proposed. It appears that this approach leads to a simple equation that relates the apparent

557 diffusion coefficient, the pore diffusivity and surface diffusivity like in similar, classical
558 approximations based on parallel transport between pore fluid and surface fluid. The evolution
559 of surface diffusion is analyzed in the present work as a function of the affinity of the probe for
560 the surface. This affinity is found to depend both on the probe chain length and surface
561 chemistry – the latter being characterized here by the OH silanol density at the silica surface.
562 For short chain lengths, a non-monotonic evolution of the surface diffusion with affinity (or
563 retention factor) may be observed in some cases. However, generally, the surface diffusion
564 decreases upon increasing the surface affinity. Interestingly, the longest chain lengths are less
565 sensitive to the OH silanol surface density. Further investigation including calorimetric studies
566 is needed to evaluate polymer/surface interactions; this would help understand the mechanisms
567 of surface diffusion by looking for complementary correlations between these parameters and
568 the measured surface diffusion coefficients.

569

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571
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576 **References**

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Glossary

D	Overall effective Diffusion coefficient (adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
D°	Overall effective Diffusion coefficient (non-adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
D_{app}	Apparent self-diffusion coefficient in the porous network under adsorbing conditions	$\text{m}^2.\text{s}^{-1}$
D_{app}^0	self-diffusion coefficient in the porous network (non-adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
D_m	Bulk self diffusivity	$\text{m}^2.\text{s}^{-1}$
$D_{m,p}$	local self-diffusion coefficient inside a pore	$\text{m}^2.\text{s}^{-1}$
D_p	In-pore diffusion coefficient	$\text{m}^2.\text{s}^{-1}$
D_{part}	Effective particle diffusion coefficient	$\text{m}^2.\text{s}^{-1}$
D_{pz}^0	Particle diffusion coefficient in the mesoporous zone (non-adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
D_{pz}	Particle diffusion coefficient in the mesoporous zone (adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
D_s	Surface diffusion coefficient	$\text{m}^2.\text{s}^{-1}$
\vec{e}_i	Displacement at the surface	m
f_{ads}	Average molar fraction of molecules adsorbed at equilibrium	
k'	Retention factor	
Ka	Constant of adsorption	
k_B	Boltzmann Constant	$\text{m}^2.\text{kg}.\text{s}^{-2}.\text{K}^{-1}$
k_f	Friction factor	
Mn	Number average molecular weight of the sample	$\text{g}.\text{mol}^{-1}$
Mw	Molecular weight of the sample	$\text{g}.\text{mol}^{-1}$
N_a	Avogadro's number	mol^{-1}
N	Number of steps in Brownian motion	
P	Number of units in the polystyrene molecule	
p	Topological factor	
Rc	Capillary internal radius (TDA)	m
\vec{r}_i	Displacement inside the pores	m
r_m	Molecule hydrodynamic radius	m
r_p	Pore radius	m
t_a	Mean residence time on the surface	s
t_{ads}	time spent in the adsorption phase	s
t_0	Experimental mean retention time (non-adsorbing conditions)	s
t_0^{ext}	Time spent outside the mesoporous zone (external porosity) (non-adsorbing conditions)	s
t_{oint}	Internal retention time without adsorption	s
t_0^{pz}	Time spent inside the mesoporous zone (non-adsorbing conditions)	s
t_p	Parking time	s

t_r	Mean duration of a path inside the pore between two contacts with the surface	s
t_R	Experimental mean retention time (adsorbing conditions)	s
u	Interstitial linear velocity	m.s ⁻¹
α_{pz}	Parameter in the Maxwell equation	
β	Parameter in the Maxwell equation	
ε	Total porosity	
ε_e	external porosity or porosity in the macropores	
ε_{pz}^0	Total particle porosity in the mesoporous zone	
$\varepsilon_{pz}(r_m)$	Particle porosity in the mesoporous zone accessible to a molecule of size r_m	
γ	Ratio between D and D_m	
λ	Ratio of molecule to pore radius	
ρ	Ratio of the non porous core radius and the particle radius	
σ_r^2	Peak variance of the solute in time units	s ²
τ_p	Particle tortuosity	
τ_r	Pore network tortuosity	
τ_{pz}	Tortuosity in the mesoporous zone	