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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 solicitation 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  $\zeta_2$  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  $\varepsilon_{pz}$  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.

121

122

## 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  $r_m$ ,  $\varepsilon_e$  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  $\gamma$  is obtained experimentally using the peak parking method as explained in the next section.  
 146 The parameter  $\beta$  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  $\rho$  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  $\gamma$  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  $\beta$ . 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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 166

## 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  $\gamma_{pz}$  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  $\tau_{pz}$  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  $\tau_{pz}^2$  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  $\varepsilon_{pz}^0$  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  $\tau_{pz}$  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  $\tau_r$  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.  $\varepsilon$  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  $\varepsilon_{pz}$ . 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[C<sub>6</sub>H<sub>5</sub>]-CH<sub>2</sub>-)<sub>n</sub> 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.

278

279

#### 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 $\mu$ L loop, an autosampler and a thermoregulated column compartment. The  
284 injection volume was set at 1  $\mu$ 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 nm<sup>2</sup>) 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  $\sigma_R^2$  are the mean retention time and variance of  
306 the peak with the stainless-steel tube, and  $t_i$  and  $\sigma_i^2$  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<sup>-1</sup>. 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  $\sigma_t^2$  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  $\varepsilon_e$  and  $\varepsilon$  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  $\text{H}^+$  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  $r_m$ ,  $\varepsilon_e$  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  $\varepsilon$ ,  $D_m$ ,  $\frac{D^0}{D_m}$ ,  $\frac{D_{pz}^0}{D_m}$ . 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 ml.min<sup>-1</sup> 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<sup>2</sup> determined by TGA for the three columns are given in  
405 Table I. The number of OH per nm<sup>2</sup> 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<sup>2</sup> 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  $\text{nm}^2$ . 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 nm<sup>2</sup>. For larger molecules (e.g. P02,  $P = 6$ ), the effect of the number of OH groups per nm<sup>2</sup>  
 492 is less pronounced; this indicates that the surface diffusion mechanisms depend strongly on the  
 493 number of OH groups per nm<sup>2</sup> 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  $\alpha$  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  $\alpha$  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]).  $\alpha$  is given in Table 3 for the different models and columns used. For the  
 517 Lichrospher column,  $\alpha$  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,  $\alpha$  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,  $\alpha$  is around 0.5 and 0.7 according to the  
 522 model used ( $P = 1-10$ ). Such  $\alpha$ -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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574

575

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## Glossary

$D$	Overall effective Diffusion coefficient (adsorbing conditions)	$\text{m}^2.\text{s}^{-1}$
$D^\circ$	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	$\text{mol}^{-1}$
$N$	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 <sup>-1</sup>
$\alpha_{pz}$	Parameter in the Maxwell equation	
$\beta$	Parameter in the Maxwell equation	
$\varepsilon$	Total porosity	
$\varepsilon_e$	external porosity or porosity in the macropores	
$\varepsilon_{pz}^0$	Total particle porosity in the mesoporous zone	
$\varepsilon_{pz}(r_m)$	Particle porosity in the mesoporous zone accessible to a molecule of size $r_m$	
$\gamma$	Ratio between D and $D_m$	
$\lambda$	Ratio of molecule to pore radius	
$\rho$	Ratio of the non porous core radius and the particle radius	
$\sigma_r^2$	Peak variance of the solute in time units	s <sup>2</sup>
$\tau_p$	Particle tortuosity	
$\tau_r$	Pore network tortuosity	
$\tau_{pz}$	Tortuosity in the mesoporous zone	