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► **To cite this version:**

Martin Victor V Johansson, Fabrice Testa, Pierre Perrier, Jérôme Vicente, Jean Philippe Bonnet, et al.. Determination of an effective pore dimension for microporous media. *International Journal of Heat and Mass Transfer*, 2019, 142, pp.118412. 10.1016/j.ijheatmasstransfer.2019.07.062 . hal-02196396

**HAL Id: hal-02196396**

**<https://amu.hal.science/hal-02196396v1>**

Submitted on 28 Jul 2019

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# Determination of an effective pore dimension for microporous media

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## Abstract

The transient method of the mass flow rate and permeability measurements through a microporous media, developed previously, is used here to extract different characteristics of the media. By implementing the model of porous media as a bundle of capillaries the effective pore dimension is extracted from the measurements, and its physical interpretation is given. This methodology shows promising results to be used as a non-destructive method of micro-and-nanoporous media analysis. The permeability is also extracted directly from the measurements of the pressure variation in time. By using additional information about the sample porosity, the number of capillaries, the tortuosity and the internal surface of the sample are calculated. The extracted values are very close to that obtained by the mercury porosimetry and by microtomography.

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## 1. Introduction

The determination of characteristics of porous media permeability like the micro and nanoporous membranes or ultra-tight shale-gas reservoirs is still a challenge up to now. The low porous media find a broad application in medicine [1], biotechnology for separation and filtration [2]. The recent development of porous ceramic media with high thermal, chemical and structural stability and the ability to have catalytic properties has opened up new horizons for membranes applications, for example, in high-temperature gas separation and catalytic reactions [3]. Unconventional resources, such as ultra-tight shale-gas reservoirs of very small pores (in nanoscale) play a significant role in securing hydrocarbon energy because of their potential to offset declines in conventional gas production [4]. The morphology of the porous structure dominates the fluid flow through a porous medium. Therefore, it is important to characterize the geometrical properties of a porous medium quantitatively. Different methods exist for the measurements of the average pore size and pore size distribution.

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Preprint submitted to *Elsevier* July 28, 2019

26 The choice of the most appropriate method depends on the application of the  
27 porous solid, its chemical and physical nature and the range of pore size. The  
28 most commonly used methods are [5]: mercury porosimetry, where the pores are  
29 filled with mercury under pressure. This method is suitable for many materials  
30 with pores in the appropriate diameter range from 0.003  $\mu\text{m}$  to 300  $\mu\text{m}$ . From  
31 mesopore to micropore size analysis, BET method [6], can be done by gas ad-  
32 sorption, usually nitrogen, at liquid nitrogen temperature. This method can be  
33 used for pores in the approximate diameter range from 1 nm to 0.1  $\mu\text{m}$ . The pore  
34 size diameter can also be determined via direct observation methods: scanning  
35 electron microscopy (SEM), field-emission scanning electron microscopy (FE-  
36 SEM), environmental scanning electron microscopy (ESEM), and atomic force  
37 microscopy (AFM), [7], [8]. The tomography analysis of a porous structure  
38 can allow the determination of the internal structure of a sample limited by  
39 the characteristics of their spatial resolution [9]. All these methods require ei-  
40 ther preliminary sample preparation or lead to the complete sample destruction,  
41 furthermore, they only use a small part of the sample for analysis.

42 We propose here a simple approach for the non-destructive porous sam-  
43 ple characterization by measuring the pressure variation in the inlet and outlet  
44 tanks (or just the pressure difference between them). The experimental method-  
45 ology, based on the constant volume technique, was initially developed for the  
46 isothermal and non-isothermal measurements of the mass flow rate through the  
47 microchannels [10] and has been recently adapted for the analysis of porous  
48 samples [11]. The gas permeability of the porous sample can be easily obtained  
49 directly from the pressure evolution in time without calculation of the mass flow  
50 rate.

51 The measurements are analyzed by assuming the porous media have similar  
52 behavior as the classical bundle of capillaries model, first suggested by Kozeny  
53 [12] and then extended by Carman [13] to allow for torturous capillaries. In our  
54 analysis we assume that the capillary tubes have the same radius. This allows  
55 us to find an unique parameter (capillary's radius) to characterize the porous  
56 structure. This unique parameter helps also to determine the gas flow regime,  
57 by introducing the Knudsen number as the ratio of the molecular mean free  
58 path and the capillary radius, and then by referring on this Knudsen number  
59 to distinguish the flow regimes. Recently, the models of a bundle of capillary  
60 tubes of variable shape and size cross-section were developed, [14], [15], but all  
61 the models were used either for the liquid or for two phase flows, which physics  
62 is different from the single phase flows.

63 The model of a bundle of capillaries with gas flow inside was considerably im-  
64 proved by Klinkenberg [16] taking into account the slip flow regime through the  
65 capillaries. In the present article, from the measured mass flow rate the effective  
66 pore size is estimated by using the fitting procedure via slip flow expression.  
67 The obtained effective pore sizes are then compared to mercury porosimetry  
68 and micro-computed tomography ( $\mu\text{CT}$ ) results. The proposed technique of the  
69 effective pore size measurement can be used as a non-destructive method for  
70 quality verification. Furthermore, this method is independent of the exterior  
71 sample geometry. When the effective pore size is known and by using the infor-

72 mation about porosity the permeability, apparent permeability, and tortuosity  
73 coefficients as well as the surface-to-volume ratio can be easily obtained.

## 74 2. Experimental methodology

75 The experimental methodology, applied in this article, is described in details  
76 in Ref. [11]. We present here only the summary of this technique, essential to  
77 understand the data treatment. From measurements of pressure variation over  
78 time we calculate the important characteristics of porous media such as mass  
79 flow rate and permeability, and then effective pore size dimension.

### 80 2.1. Experimental apparatus

81 The experimental setup is a high vacuum system capable of measuring up to  
82 5 decades of pressure. In the presented experiment the mean pressure is varied  
83 from 75 Pa up to 131 kPa. This large pressure measurement range is achieved by  
84 using three pairings of four Capacitance Diaphragm Manometers (CDM) with  
85 full-scale (CDM<sub>1</sub>-CDM<sub>2</sub>): 133 kPa - 133 kPa, 133 kPa - 13.3 kPa and 13.3 kPa -  
86 1.33 kPa. Four high purity gas bottles with test gases, Helium, Neon, Nitrogen,  
87 Argon (Air Liquide, France) are used. The pumping is performed by a two-  
88 stage Diaphragm Vacuum Pump (DVP) and a Turbomolecular Pump (TMP).  
89 Each side of the porous medium is connected to two reservoirs, of volumes  
90  $V_1$  and  $V_2$ , for the high and low-pressure, respectively. Both tanks volumes,  
91 including the volumes of the valves, connecting tubes and pressure sensors, are  
92 measured accurately, and these volumes are equal to  $V_1 = 255.8 \pm 5.5 \text{ cm}^3$  and  
93  $V_2 = 238.8 \pm 5.1 \text{ cm}^3$ , for the high and low pressure tanks, respectively. The  
94 reservoirs are connected only by a porous sample which is fixed with a vacuum  
95 glue.

96 Two microporous samples, used in the experiments and mentioned in the  
97 following as the first and second discs, have a cylindrical shape (disc) with the  
98 same radius and thickness (in main flow direction) equal to  $4.75 \pm 0.01 \text{ mm}$  and  
99  $L = 2.3 \pm 0.01 \text{ mm}$ , respectively. The characteristics of these microporous discs  
100 are the same as of the ceramic membranes used in micro-to-nano filtration. For  
101 such ceramic microporous media, depending on manufacturer, porosity is in the  
102 range 15% – 30% with pore diameter ranging from 1  $\mu\text{m}$  to 10  $\mu\text{m}$ . The total  
103 volume of each porous disc is  $0.14 \text{ cm}^3$ , so by taking 30% of porosity a gas  
104 volume inside the medium is approximately  $0.042 \text{ cm}^3$ , which is much smaller  
105 than the volume of each tank.

106 The experiments are performed within a narrow temperature range (around  
107 room temperature, 29-31 °C), excluding any heat source in an environment.  
108 The temperature is measured using the thermocouple with the accuracy of 0.6  
109 K.

### 110 2.2. Mass flow rate measurements

111 The constant volume technique [17], [18] and the methodology, analogous  
112 to the pulse decay method [19], [11], are implemented here to measure the

113 mass flow rate through samples of a microporous ceramic medium. The applied  
 114 experimental technique allows us to deduce the mass flow rate and also the  
 115 permeability from the pressure variation in time in both tanks. This approach  
 116 needs to have a stable temperature during the measurements, see discussion in  
 117 Ref. [11]. Therefore, if the temperature variations during the experimental time  
 118 are small compared to the pressure variations we can calculate the mass flow  
 119 rate from the pressure variation in each tank as following:

$$\dot{M}_1 = -\frac{dM_1}{dt} = -\frac{V_1}{\mathcal{R}T} \frac{dp_1}{dt}, \quad \dot{M}_2 = \frac{dM_2}{dt} = \frac{V_2}{\mathcal{R}T} \frac{dp_2}{dt}. \quad (1)$$

120 Here  $\dot{M}_i$  and  $p_i$ ,  $i = 1, 2$  are the mass flow rate and pressure in the tank  $i$ ,  
 121 respectively,  $\mathcal{R}$  is the specific gas constant,  $T$  is the gas temperature, the same  
 122 in each tank,  $t$  is the time. Equations (1) are obtained with an assumption that  
 123 the gas follows the ideal gas law. In the present study, the maximal considered  
 124 pressure is slightly above atmospheric pressure (up to 131 kPa); therefore we  
 125 do not consider here the real gas effects. However, the proposed approach can  
 126 be generalized to take into account the real gas effects by using, for example,  
 127 the van der Waals equation instead of the ideal gas law. The estimations of  
 128 the compressibility factor under our experimental conditions are provided in  
 129 [AppendixA](#).

130 The ideal gas law is valid under equilibrium condition; however, the gas  
 131 pressure and gas mass in a tank change in time. Here we assume that we have  
 132 a quasi-steady process, that is, we have a succession of local equilibrium. This  
 133 assumption is true when we have a small unbalancing force which modifies the  
 134 system slower than the system reaches a local equilibrium, see [AppendixB](#) for  
 135 a further discussion.

136 Very often it is convenient to express the mass flow rate in function of the  
 137 pressure difference,  $\Delta p(t) = p_1(t) - p_2(t)$ , between two tanks:

$$\dot{M}(t) = -\frac{V_0}{\mathcal{R}T} \frac{d(\Delta p(t))}{dt}, \quad V_0 = \frac{V_1 V_2}{V_1 + V_2}, \quad (2)$$

138 where  $V_0$  is the effective volume. It is clear that the mass flow rate can be  
 139 calculated using expressions (1) and (2), when the pressure variation in each  
 140 tank or the pressure difference between them in time is known. To measure  
 141 the mass flow rate, first, the initial pressure difference is settled between the  
 142 tanks, then the gas starts to flow from higher to lower pressure tank up to the  
 143 same final pressure  $p_f$  is reached, see Fig. 2 in [11]. During the experiments the  
 144 pressure variations over time in each tank are recorded, then, their difference is  
 145 fitted by using the exponential fitting function [19], [11]:

$$\Delta p(t) = \Delta p_0 \exp(-(t - t_0)/\tau), \quad (3)$$

146 where  $\tau$  is the pressure relaxation time,  $\Delta p_0$  is the initial pressure difference  
 147 between the tanks at time  $t = t_0$ . Similar exponential representations of the  
 148 pressure evolution over time in the first,  $p_1(t)$ , and second,  $p_2(t)$ , tank can be  
 149 also written in a form similar to Eq. (3), see Refs. [19], [11]. The pressure

150 evolution in time in each tank and the pressure difference between two tanks as  
 151 a function of time and their corresponding fitting functions are shown in Fig. 2  
 152 (a) and (b), respectively.

153 By using Eq. (2) for the mass flow rate, the exponential representation of  
 154 the pressure difference in time, Eq. (3), and its analytical derivative, we can  
 155 now express the mass flow rate as

$$\dot{M}(t) = -\frac{V_0}{\mathcal{R}T} \frac{d(\Delta p(t))}{dt} = \frac{V_0}{\mathcal{R}T} \frac{\Delta p_0}{\tau} \exp\left(-\frac{t-t_0}{\tau}\right). \quad (4)$$

156 From Eqs. (1) we can also express the mass flow rate using the analogous  
 157 to Eq. (3) exponential representation of the pressure variation over time in  
 158 each tank, see Refs. [19], [11]. To obtain the mass flow rate from the pressure  
 159 variation measurements, the pressure variation in time,  $\tau$ , is fitted using pressure  
 160 relaxation time as a single fitting parameter, then the mass flow rate can be  
 161 calculated from Eq. (4).

162 The classical uncertainty calculation technique is used to estimate the mea-  
 163 surement uncertainty of the mass flow rate, which for our experimental condi-  
 164 tions lies in the range 3.6 – 5.1%, see Ref. [11] for more details.

### 165 2.3. Gas permeability measurements

166 The Darcy law [20] allows us to relate the instantaneous discharge (or vol-  
 167 umetric) flow rate through a porous medium,  $Q$ , to the pressure drop over a  
 168 given distance  $L$ , which is the thickness of a porous sample (disc):

$$Q = \frac{KS}{\mu} \frac{\Delta p}{L}, \quad (5)$$

169 where  $K$  is the permeability,  $S$  is the cross-section of the porous sample,  $\mu$  is  
 170 the viscosity, which is calculated as [21]:

$$\mu = \mu_{\text{ref}} \left(\frac{T}{T_{\text{ref}}}\right)^{\omega}, \quad (6)$$

171 where  $\omega$  is the gas viscosity index,  $\mu_{\text{ref}}$  is the gas viscosity at temperature  
 $T_{\text{ref}} = 273.15$  K [21], see also Table 1.

Gas	$\mu_{\text{ref}} \times 10^{-5}$ [Pa · s]	$\omega$	$\mathcal{R}$ [J · kg <sup>-1</sup> · K <sup>-1</sup> ]	Molar mass $\mathcal{M}$ [g · mol <sup>-1</sup> ]
He	1.865	0.66	2077.1	4.003
Ne	2.976	0.66	412.02	20.18
N <sub>2</sub>	1.656	0.74	296.80	28.00
Ar	2.117	0.81	208.13	39.95

Table 1: Useful characteristics of the gases [21] used in present experiments

172 The volumetric flow rate, used in Eq. (5), is related to the mass flow rate  
 173 and the gas density  $\rho$  as:  
 174

$$Q = \frac{\dot{M}}{\rho} = \dot{M} \frac{\mathcal{R}T}{p}, \quad (7)$$

175 then by integrating along the porous sample and by using the mass conservation  
 176 property, we obtain the expression, analogous to Eq. (5), which relates the mass  
 177 flow rate, instead of volumetric flow rate, to the permeability

$$\dot{M} = \frac{KS}{\mu} \frac{\Delta p}{L} \frac{p_m}{RT}. \quad (8)$$

178 Here  $p_m$  is the mean pressure between two tanks,  $p_m = 0.5(p_1 + p_2)$ . Then, using  
 179 the expression of the mass flow rate via the pressure variation in tanks, Eq. (2),  
 180 and following the technique developed in Ref. [11] we can relate permeability  
 181 to the pressure difference variations between the tanks and finally obtain the  
 182 expression of the gas permeability through the fitting parameter,  $\tau$ , pressure  
 183 relaxation time, see Ref. [11] for more details:

$$K = \frac{\mu}{\tau p_m} \frac{LV_0}{S}. \quad (9)$$

184 It is worth to note that the previous expression is obtained under the condition  
 185 of the mean pressure constancy during an experimental run. This condition is  
 186 satisfied, when the tanks volumes are equal,  $V_1 = V_2$ . For the case of different  
 187 tanks volumes  $V_1 \neq V_2$ , the analytical expression was derived in [11]. This ex-  
 188 pression relates the variation of the mean pressure during the experimental time  
 189 to the tanks volumes ratio,  $V_1/V_2$ , and the initial pressure ratio,  $p_1(t_0)/p_2(t_0)$ ,  
 190 between the tanks.

191 The uncertainty of the permeability measurements, when using Eq. (9), is  
 192 calculated by the classical way, similar to the calculation of the uncertainty  
 193 on the mass flow rate. Under our experimental conditions the measurement  
 194 uncertainty on the permeability lies in the range 5.0 – 6.4%.

### 195 3. Modeling of the porous structure

196 Different type of modeling can be used to characterize the flow through  
 197 microporous media. One of the simplest and, in the same time, efficient models  
 198 of a microporous medium is its representation as a bundle of several numbers  
 199 of capillaries with the circular cross-section of the same or different diameters  
 200 [12], [20]. All the capillaries (pores) can be parallel and have a length  $L_c$  equal  
 201 to the length  $L$  (thickness) of the porous medium, see Fig. 1 (left). However,  
 202 in the real samples, this capillary length can be different from the length of  
 203 the porous medium because of the random orientation of the capillaries. As a  
 204 result, the capillary length is generally longer than the medium thickness, see  
 205 Fig. 1 (right). To account for this fact a tortuosity  $l_\tau$  [22] is introduced as

$$l_\tau = \frac{L_c}{L}. \quad (10)$$

206 The sample porosity  $\varepsilon$  is defined as

$$\varepsilon = \frac{V_c}{V}, \quad (11)$$

207 where  $V_c$  is the volume of void-space (such as fluids) and  $V$  is the total or bulk  
 208 volume of a solid material.

209 If the porous medium is represented as a bundle of  $N$  capillaries of the same  
 210 radius  $a$  and of the length  $L_c$ , different from the membrane thickness  $L$ , Eq.  
 211 (10), the porosity is calculated as:

$$\varepsilon = \frac{N\pi a^2 L_c}{SL} = \frac{N\pi a^2 l_\tau}{S}. \quad (12)$$

212 With the same set of parameters a very useful characteristic of porous medium  
 213 can be calculated, the Specific Surface Area (SSA) defined as the the ratio of  
 214 the internal surface to the sample volume

$$\mathcal{S}_A = \frac{2\pi a L_c N}{SL} = \frac{2\pi a N l_\tau}{S} \left[ \frac{\text{m}^2}{\text{m}^3} \right]. \quad (13)$$

215 Finally the used here model of the porous medium has 4 unknown parameters.  
 216 Three among them, the parameters  $a$ ,  $N$  and  $l_\tau$  (or  $\varepsilon$ ) are defined above. The  
 217 fourth parameter, the velocity slip coefficient,  $\sigma_p$ , (or the accommodation coef-  
 218 ficient,  $\alpha$ ), are presented in Section 4.2, where their physical meaning and the  
 219 typical values are given. In the following, we will show how these characteristics  
 220 of a porous medium can be extracted when using the presented above model of  
 221 a bundle of capillaries.

## 222 4. Expressions of the mass flow rate through a single capillary

### 223 4.1. Flow regimes

224 The microporous medium is modeled here as a bundle of capillaries, so it is  
 225 worth to define first different possible flow regimes in a capillary and to present  
 226 then the expressions of the mass flow rate through a capillary for these flow  
 227 regimes. Usually the flow regimes could be identified through the Knudsen  
 228 number, which is calculated as the ratio between the equivalent molecular mean  
 229 free path  $\ell$  and the characteristic dimension  $a$  of the capillary (its radius):

$$Kn = \frac{\ell}{a}. \quad (14)$$

230 The equivalent molecular mean free path  $\ell$  is defined as

$$\ell = \frac{\mu v_0}{p_m}, \quad (15)$$

231 where  $v_0$  is the most probable molecular speed

$$v_0 = \sqrt{2\mathcal{R}T}. \quad (16)$$

232 It is convenient to introduce also the rarefaction parameter  $\delta$  which is directly  
 233 proportional to the pressure and related to the Knudsen number as

$$\delta = \frac{a}{\ell} = \frac{1}{Kn}. \quad (17)$$



234 We adopt here the classical definition of gas flow regimes in terms of the Knudsen  
 235 number or rarefaction parameter [23]: continuum flow regime ( $Kn < 0.01$  or  
 236  $\delta > 100$ ); slip flow regime ( $0.01 < Kn < 0.1$  or  $10 < \delta < 100$ ); transitional flow  
 237 regime ( $0.1 < Kn < 10$  or  $0.1 < \delta < 10$ ); free molecular flow regime ( $Kn > 10$   
 238 or  $\delta < 0.1$ ).

#### 239 4.2. Mass flow rate expressions for a single capillary

240 In the case of the slip flow regime ( $10 \leq \delta \leq 100$ ) the mass flow rate through  
 241 a tube (capillary) of a radius  $a$  can be obtained from the Stokes equation

$$\frac{\mu}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) \right) = \frac{dp}{dz} \quad (18)$$

242 subjected to the velocity slip boundary condition at the solid surface

$$u = \sigma_p \ell \left. \frac{\partial u}{\partial r} \right|_{r=a}. \quad (19)$$

243 In the previous relations  $u$  is the longitudinal flow velocity,  $z$  is the longitudinal  
 244 flow direction,  $p$  is the local gas pressure,  $\sigma_p$  is the velocity slip coefficient, which  
 245 depends on the type of the gas-surface interaction. Using the kinetic theory  
 246 the velocity slip coefficient was calculated in Ref. [23] to be equal to 1.018  
 247 in the case of diffuse gas-surface interaction. The accommodation coefficient,  
 248  $\alpha$ , characterizes also the gas-surface interaction: it is equal to 1 for the case  
 249 of diffuse interaction (complete accommodation) in the frame of Maxwellian  
 250 scattering kernel [24]. Both coefficients are related between them: the authors  
 251 of Refs. [25], [26] suggested to use the following relation:

$$\sigma_p(\alpha) = \frac{2 - \alpha}{\alpha} (\sigma_p(\alpha = 1) - 0.1211(1 - \alpha)). \quad (20)$$

252 By integrating Eq. (18) with the boundary condition (19) and the symmetry  
 253 condition on the tube axis we obtain the velocity profile over the capillary cross-  
 254 section. Next, by integrating this velocity profile and then, by integrating along  
 255 the tube (according to  $z$  variable) from 0 to the capillary length  $L_c$  and using  
 256 the mass conservation property we obtain finally the mass flow rate through a  
 257 single tube (capillary) for the slip flow regime:

$$\dot{M} = \dot{M}_P \left( \frac{1}{4} + \frac{\sigma_p}{\delta} \right), \quad (21)$$

258 where  $\dot{M}_P$  is the classical Poiseuille mass flow rate through a capillary of a  
 259 radius  $a$  and the length  $L_c$  in the hydrodynamic flow regime ( $\delta \geq 100$ ):

$$\dot{M}_P = \frac{\pi a^4}{L_c} \frac{\Delta p p_m}{\mu v_0^2} = \frac{\pi a^4}{L_c} M_{S0}, \quad (22)$$

260 where

$$M_{S0} = \frac{\Delta p p_m}{\mu v_0^2} \left[ \frac{\text{kg}}{\text{s}} \text{m}^{-3} \right]. \quad (23)$$

261 In the hydrodynamic flow regime the molecule-molecule collisions dominate  
 262 the molecule-surface collisions. Contrarily, in the free molecular flow regime  
 263 ( $\delta \leq 0.1$ , Knudsen diffusion regime) the molecule-molecule collisions can be  
 264 practically neglected and the molecule-surface collisions guide the flow. In this  
 265 regime the mass flow rate is calculated from following expression [27]:

$$\dot{M}_{\text{FM}} = \frac{2 - \alpha}{\alpha} \frac{8}{3\sqrt{\pi}} \dot{M}_{\text{G}}, \quad (24)$$

266 with

$$\dot{M}_{\text{G}} = \frac{\pi a^3 \Delta p}{L_c v_0} = \frac{\pi a^3}{L_c} M_{\text{G}0}, \quad (25)$$

267 where

$$M_{\text{G}0} = \frac{\Delta p}{v_0} \left[ \frac{\text{kg}}{\text{s}} \text{m}^{-2} \right]. \quad (26)$$

268 In the case of the transitional flow regime ( $0.1 \leq \delta \leq 10$ ) the mass flow rate can  
 269 be found only numerically by the solution of the linearized Boltzmann equation  
 270 (or of others model kinetic equations [28], [29]). In this flow regime the number  
 271 of molecule-surface collisions is comparable to the number of intermolecular  
 272 collisions.

273 The approximate expression of the dimensionless mass flow rate  $G$  ( $G =$   
 274  $\dot{M}/\dot{M}_{\text{G}}$ ) through a capillary of the radius  $a$  and the length  $L_c$ , which covers all  
 275 flow regimes, was proposed in [30] for the diffuse scattering,  $\alpha = 1$ :

$$G(\delta) = \dot{M}/\dot{M}_{\text{G}} = \frac{8}{3\sqrt{\pi}} \frac{1 + 0.04 \delta^{0.7} \ln \delta}{1 + 0.78 \delta^{0.8}} + \left( \frac{\delta}{4} + \sigma_p \right) \frac{\delta}{1 + \delta}. \quad (27)$$

276 The typical shape of the normalized mass flow rate,  $G$  function, Eq. (27), for  
 277 a capillary is shown on Fig. 3. The function  $G$  has the finite limit in the free  
 278 molecular regime, *i.e.* when  $\delta \rightarrow 0$ . In the case of diffuse scattering of the  
 279 molecules from the surface,  $\alpha = 1$ ,  $\lim_{\delta \rightarrow 0} G(\delta) = 8/(3\sqrt{\pi})$ , see Eqs. (24) and  
 280 (27). In the opposite limit case,  $\delta \rightarrow \infty$ , the hydrodynamic flow regime, the  
 281 normalized mass flow rate,  $G$  function, Eq. (27), tends to infinity. Therefore, in  
 282 the following to have a finite value of the mass flow rate in the hydrodynamic  
 283 flow regime, we will use the representation of the mass flow rate in form (21),  
 284 which limit case for  $\delta \rightarrow \infty$  gives very known Poiseuille flow rate, Eq. (22).

## 285 5. Determination of porous medium characteristics from pressure 286 measurements

287 In the previous Section, we introduced the complete description of the flow  
 288 through a single capillary. In this Section, the model of the porous media as  
 289 a bundle of capillaries is presented, and its parameters as the capillary radius,  
 290 capillary number, tortuosity, and specific surface area are extracted from the  
 291 measurements. The proposed geometrical model corresponds to a homogeneous  
 292 porous medium with a signature of a single pore size.

293 *5.1. Fitting range*

294 The analytical expressions for the mass flow rate through a single capillary,  
 295 provided in the previous Section, could be used to calculate the mass flow rate  
 296 through a microporous sample by representing it as a bundle of capillaries. To  
 297 choose the analytical expression for the mass flow rate the flow regime in a  
 298 capillary must be known. However, the flow regimes depend on the rarefaction  
 299 parameter (Knudsen number), which includes the characteristic dimension of a  
 300 flow (capillary radius), which is *a priori* unknown.

301 To have an idea about the flow regime it is useful to note that the mass flow  
 302 rate through a capillary in free molecular regime is proportional to  $\Delta p/v_0$ , this  
 303 motivates our definition of the dimensionless quantity  $G_0$  as

$$G_0 = \dot{M}/(\Delta p/v_0) = \dot{M}/M_{G0} \quad [\text{m}^2]. \quad (28)$$

304 By defining the dimensionless quantity  $G_0$  in this way, we eliminate its depen-  
 305 dence from the geometrical parameters,  $a$ , and  $L_c$ , which are unknown *a priori*  
 306 in this model. By analogy, in the hydrodynamic flow regime, the mass flow rate  
 307 is proportional to  $\Delta p p_m/(\mu v_0^2)$ , so we define dimensionless quantity  $S_0$  as

$$S_0 = \dot{M}/\left(\frac{\Delta p p_m}{\mu v_0^2}\right) = \dot{M}/M_{S0} \quad [\text{m}^3]. \quad (29)$$

308 When we plot these normalized quantities,  $G_0$  and  $S_0$ , as a function of inverse  
 309 molecular mean free path  $\ell^{-1}$  and molecular mean free path  $\ell$ , respectively, we  
 310 find similar behavior as for the mass flow rate through a tube. That is, with  
 311 these normalizations we find a constant value in the respective regime and we  
 312 can make the first identification of two known limits, the free molecular and  
 313 hydrodynamic regimes.

314 However, it is more complicated to identify the slip flow regime. The  $G_0$   
 315 curve for the first disc is presented in Fig. 4. It is clear that the analytical curve  
 316 of dimensionless mass flow rate  $G$  through a single capillary, Fig. 3, has a very  
 317 similar shape to the experimental curve of the normalized quantity  $G_0$  through  
 318 the microporous medium, see Fig. 4. Therefore, by analogy, we can identify  
 319 the slip flow regimes visually in terms of inverse molecular mean free path. In  
 320 Table 2 different flow regimes are represented by different molecular mean free  
 321 path ranges.

322 When the flow regime is determined the corresponding analytical mass flow  
 323 rate expression can be chosen and then the measured mass flow rate can be fitted  
 324 to determine the characteristic flow dimension, pore radius, and the number of  
 325 capillaries in the representation of the porous medium as a bundle of capillaries.  
 326 Once the flow dimension has been extracted, it is useful to calculate the Knud-  
 327 sen number and the rarefaction parameter and compare how close the chosen  
 328 Knudsen number (rarefaction parameter) range is to the classical definition of  
 329 the slip regime range for a capillary. For the slip flow regime, we should find the  
 330 Knudsen number  $Kn \approx 0.1$  and the rarefaction parameter  $\delta \approx 10$ . We can use  
 331 this point as a guideline to further refine our definition of the regimes. This is

332 done by reiterating the process of fitting and extracting the equivalent flow di-  
 333 mension and again calculating the Knudsen number and rarefaction parameter  
 334 until become close to the theoretical values of a tube.

335 Once the definition of the slip flow regime has been done in a suitable way,  
 336 we have to find three properties which present the additional argumentation  
 337 that we have defined our regime correctly. First, the Knudsen number and  
 338 rarefaction parameter are close to the theoretical values for a tube. Second, the  
 339 relative difference of our linear fit in the slip flow regime and the measured values  
 340 do not have a trend but is rather scattered around a constant value. Third, the  
 341 intrinsic permeability is gas independent within experimental uncertainty.

### 342 5.2. Effective pore size

343 Let us use the analytical expression for the mass flow rate through one tube,  
 344 Eqs. (21) and (22), and write it for a bundle of  $N$  capillaries, where the capillary  
 345 length  $L_c$  can be different from the thickness  $L$  of the porous sample (disc). In  
 346 this case the mass flow rate through a bundle of  $N$  capillaries reads:

$$\dot{M} = \frac{N\pi a^4}{L_c} \frac{\Delta p p_m}{\mu v_0^2} \left( \frac{1}{4} + \frac{\sigma_p}{\delta} \right). \quad (30)$$

347 In the previous expression four parameters are unknown:  $N$ ,  $a$ ,  $L_c$  and  $\sigma_p$ . To  
 348 determine them from experimental data we can write the previous expression  
 349 in the following form

$$S_0 = \dot{M}/M_{S0} = \frac{N\pi a^4}{L_c} \left( \frac{1}{4} + \frac{\sigma_p}{\delta} \right), \quad (31)$$

350 where  $M_{S0}$  is defined in (23). Then we fit previous expression according to the  
 351 linear regression:

$$\mathcal{F}_S = \mathcal{A}_S X + \mathcal{B}_S, \quad (32)$$

352 where

$$\mathcal{A}_S = \sigma_p \frac{\pi a^3 N}{L_c}, \quad \mathcal{B}_S = \frac{\pi a^4 N}{4L_c}, \quad X = \ell, \quad (33)$$

353  $\mathcal{A}_S$  and  $\mathcal{B}_S$  are the fitting coefficients of the S-fit. The mass flow rate is fitted via  
 354 the molecular mean free path,  $X = \ell$ , Eq. (15). From the previous expressions,  
 355 it is clear that the slope of the fitting curve,  $\mathcal{A}_S$  coefficient, depends on the gas  
 356 nature only via the slip coefficient  $\sigma_p$ .

357 As it was mentioned previously, initially the characteristic dimension  $a$  of the  
 358 flow are not known, and we can refer to different flow regimes only by using the  
 359 molecular mean free path. The intervals associated with different flow regimes  
 360 and expressed in term of the molecular mean free path are presented in Table 2.  
 361 The S-type fit, Eq. (32), is realized in the hydrodynamic and slip flow regimes,  
 362 so for  $\ell > 0.19 \mu\text{m}$  for the first disc.

363 The fitting coefficients,  $\mathcal{A}_S$  and  $\mathcal{B}_S$ , for the first disc and various gases are  
 364 shown in Table 3. It is worth to note that even if the measurements for four  
 365 gases are carried out for the first disc only for two gases, Nitrogen and Argon,

366 the number of the experimental points in slip regime is large enough to obtain  
 367 the good fitting curves. The measured mass flow rate normalized using Eq. (31),  
 368 and the fitting curve, according to Eq. (32), are shown in Fig. 5 for Argon. The  
 369 quality of the fit is also tested by plotting the relative deviation between the  
 370 measured and fitted quantities,  $(S_0 - \mathcal{F}_S)/\mathcal{F}_S$ , see Fig. 6. As it is clear from  
 371 this last figure, the points are homogeneously distributed around 0, and they do  
 372 not show any trend, which confirms the quality of fitting function and supports  
 373 also our choice of the fitting range, see comments at the end of Section 5.1. The  
 374 results for other gases are close to that measured for Argon.

375 From the fitting coefficients,  $\mathcal{A}_S$  and  $\mathcal{B}_S$ , the effective flow dimension of the  
 376 porous medium  $a$ , *i.e.* effective pore radius, can be found as

$$a = 4\sigma_p \frac{\mathcal{B}_S}{\mathcal{A}_S}. \quad (34)$$

377 To calculate the characteristic dimension of the porous medium,  $a$ , from the  
 378 previous expression, Eq. (34), we need only the information on the velocity slip  
 379 coefficient,  $\sigma_p$ , which characterizes the gas-surface interaction. In addition, Eq.  
 380 (34) is independent of the external geometrical parameters of a sample, so we are  
 381 not restricted to only cylindrical shape of the porous media. In the following, we  
 382 assume that all the gases interact with the wall of the porous medium diffusively  
 383 and the analytical value of this coefficient ( $\sigma_p = 1.018$ ) is used for further  
 384 calculations. To estimate the error, induced by this assumption, we calculated  
 385 the relative (compared to Nitrogen)  $\sigma_p$  value from following relation

$$\frac{\sigma_p}{\sigma_p^{N_2}} = \frac{\mathcal{A}_S/\mathcal{A}_S^{N_2}}{\mathcal{B}_S/\mathcal{B}_S^{N_2}}. \quad (35)$$

386 This relative value  $\sigma_p/\sigma_p^{N_2}$  of the velocity slip coefficient for Argon and the first  
 387 disc is of the order of

388 3%, which is less than the measurement accuracy. Therefore, the assumption  
 389 on the equality of  $\sigma_p$  coefficient for analyzed here gases is justified, so we continue  
 390 to use the same value of the velocity slip coefficient (analytical value 1.018 [26])  
 391 for all gases used in the experiments.

392 To obtain the characteristic flow dimension (effective pore size) we used  
 393 here the experimental data in the hydrodynamic and slip flow regimes. Another  
 394 possible approach to calculate the effective pore size from the measurements  
 395 is presented in [Appendix C](#). This methodology is based on the utilization of the  
 396 measurements in the free molecular and hydrodynamic flow regimes, but it was  
 397 not applied in this work.

## 398 6. Other characteristic parameters of porous sample

399 As it discussed in previous Section, from the mass flow rate fitting expression  
 400 we can extract: the characteristic dimension of porous medium,  $a$ , and also the  
 401 number  $N$  of the capillaries as

$$N = \frac{\mathcal{B}_S L_c}{\pi a^4}. \quad (36)$$

402 However, in Eq. (36) the capillary length,  $L_c$ , is still unknown, so we can make  
 403 two assumptions to obtain this value. One of possibilities is to assume that the  
 404 capillary length is equal to the porous disc thickness,  $L_c = L$ , so the tortuosity  
 405 factor,  $l_\tau$ , Eq. (10), is equal to 1. However, with this assumption the sample  
 406 porosity,  $\varepsilon = 2.2\%$ , is much smaller than that provided by the manufacturer,  
 407 15.9%.

408 The second possible choice is to assume that the capillary length,  $L_c$ , is equal  
 409 to  $l_\tau L$ . However, to calculate  $l_\tau$  we have to introduce new additional parameter,  
 410 the porosity,  $\varepsilon$ , which can be known either from the manufacturer or from the  
 411 tomography analysis (see Section 8), then the tortuosity is calculated as

$$l_\tau = \frac{a}{2} \sqrt{\frac{\varepsilon}{\mathcal{B}_S} \frac{S}{L}}. \quad (37)$$

412 Finally, to have the complete realistic description of a porous sample by using  
 413 the model of the bundle of the tortuous capillaries we need to use additionally  
 414 the information about the porosity.

415 The last important data, which can be extracted from the measurements,  
 416 also by using additional information about the porosity, is the value of the  
 417 surface-to-volume ratio, Eq. (13), which can be also calculated as

$$\mathcal{S}_A = \varepsilon \frac{2}{a}. \quad (38)$$

418 These results extracted from the measurements are compared with the results  
 419 of the computer tomography analysis and with that of the mercury porosimetry  
 420 in Section 9.

## 421 7. Permeability

422 In Section 2.3 we provided the definition of the permeability as it was pro-  
 423 posed by Darcy, *i.e.* for the incompressible fluid, and then its expression through  
 424 the mass flow rate, Eq. (8), more adapted for the gas flows, so the permeability  
 425 is calculated as

$$K = \dot{M} \frac{\mathcal{R}T}{p_m} \frac{\mu}{S} \frac{L}{\Delta p}. \quad (39)$$

426 By using the same model of the porous media as a bundle of  $N$  capillaries  
 427 with length  $L_c$  and replacing the mass flow rate in the previous expression by  
 428 its representation provided in Section 5.2, Eqs. (30), (31), we express the  
 429 permeability as

$$K = \dot{M}/M_{K0}, \quad M_{K0} = \frac{p_m \Delta p}{\mu v_0^2} \frac{2S}{L} = M_{S0} \frac{2S}{L}, \quad (40)$$

430 or

$$K = \frac{\pi a^4 N}{L_c} \frac{L}{2S} \left( \frac{1}{4} + \frac{\sigma_p}{\delta} \right). \quad (41)$$

431 The last expression can be rewritten in the form analogous to Eq. (32) and then  
 432 fitted according to the linear regression:

$$\mathcal{F}_K = \mathcal{A}_K X + \mathcal{B}_K, \quad (42)$$

433 where

$$\mathcal{A}_K = \sigma_p \frac{\pi a^3 N}{L_c} \frac{L}{2S}, \quad \mathcal{B}_K = \frac{\pi a^4 N}{4L_c} \frac{L}{2S}, \quad X = \ell, \quad (43)$$

434  $\mathcal{A}_K$  and  $\mathcal{B}_K$  are the fitting coefficients. By comparing the coefficients  $\mathcal{A}_K$  and  
 435  $\mathcal{B}_K$  of the permeability fit, Eq. (43), and coefficients  $\mathcal{A}_S$  and  $\mathcal{B}_S$ , Eq. (33), for  
 436 the fit of the mass flow rate, Eq. (32), one can see that they differ only in the  
 437 factor  $L/(2S)$  and the pore characteristic dimension can be also found from the  
 438 ratio of coefficients  $\mathcal{A}_K$  and  $\mathcal{B}_K$ , as it was done in Section 5.2 for  $\mathcal{A}_S$  and  $\mathcal{B}_S$   
 439 coefficients.

440 From Eq. (41) we also obtain the well known Klinkenberg expression

$$K = K_D \left(1 + 4 \frac{\sigma_p}{\delta}\right) = K_D (1 + 4\sigma_p Kn), \quad (44)$$

441 where  $K_D$  is the hydrodynamic (Darcy or intrinsic) permeability

$$K_D = \frac{\pi a^4}{8} \frac{NL}{L_c S} = \frac{\varepsilon}{l_\tau^2} \frac{a^2}{8}, \quad (45)$$

442 which can be found from the fitting coefficient  $\mathcal{B}_K$  (or  $\mathcal{B}_S$ , obtained from the fit  
 443 of the mass flow rate) as

$$K_D = \mathcal{B}_K = \mathcal{B}_S \frac{L}{2S}. \quad (46)$$

444 As it is clear from Eq. (44), in the slip flow regime, the permeability becomes  
 445 inversely proportional to the rarefaction parameter, *i.e.* to the mean pressure.  
 446 Therefore, we can rewrite Eq. (44) in the following form, proposed initially by  
 447 Klinkenberg [16],

$$K = K_D \left(1 + \frac{b}{p_m}\right), \quad (47)$$

448 here  $b$  is a gas dependent coefficient. By identifying Eqs. (44) and (47) we can  
 449 deduce the expression for  $b$ :

$$b = 4\sigma_p \frac{\mu v_0}{a} \quad [\text{Pa}]. \quad (48)$$

450 It is clear that  $b$  coefficient depends not only from the gas nature through the gas  
 451 viscosity, the most probable molecular velocity and the velocity slip coefficient,  
 452 but also from the characteristic dimension  $a$  (effective pore radius) of the porous  
 453 medium, therefore, expression (47) is not at all universal.

454 It is worth to note that the Klinkenberg expression, Eq. (47), is derived  
 455 from the expression of the mass flow rate through a bundle of capillaries in  
 456 the slip flow regime, so, theoretically, expression (47) is valid only in the slip

457 flow regime. To find the limits of the validity of the Klinkenberg expression the  
458 model proposed in [30] for the mass flow rate through a single capillary for all  
459 flow regimes, Eq. (27), can be used:

$$K = G \frac{K_D}{4\delta}. \quad (49)$$

460 The limits of the validity of the Klinkenberg expression for the analyzed porous  
461 samples are discussed in Section 9.

## 462 8. Tomography analysis

463 To have additional information about the samples, a typical sample from  
464 the same batch was scanned with MicroXCT-400 tomograph at CEREGE,<sup>1</sup>  
465 which uses the linear attenuation method. The focal spot size of X-ray beam  
466 was 5-7  $\mu\text{m}$ . The geometrical voxel size is determined by the size and number  
467 of detector elements and the source-object-detector distances (magnification).  
468 The microXCT-400 is also equipped with many optical lenses that lead to an  
469 additional optical magnification. In this work, an x40 optical lens was used  
470 [31]. Finally, the geometrical voxel size is fixed to 1.8  $\mu\text{m}$ . The image stack  
471 corresponds to a cylinder of 1.8 mm of diameter and 1.8 mm thick composed  
472 of 1000 slices of  $1000 \times 1000$  voxels size. The porous morphological analysis was  
473 performed with the iMorph software [31], [9] on a cubic Region Of Interest (ROI)  
474 made of  $500 \times 500 \times 500$  voxels, see Fig. 7, which represents 0.35% of the total  
475 volume of the analyzed sample.

476 The pore network segmentation is a crucial step consisting to binarize the  
477 reconstructed volume from X-ray computed tomography acquisitions. Because  
478 our 3D images of porous sample are under resolved and weakly contrasted,  
479 hysteresis method is well adapted for the binarization compared to classical Otsu  
480 binarization method which results in our case to a mixing of phases (*i.e.* the solid  
481 and poral phases). The hysteresis function [32] performs a dual thresholding  
482 operation on the original grayscale image using two threshold values (lower  
483 and upper). For the specific application of membrane binarization, the lower  
484 threshold is chosen as the smaller threshold that allows the percolation of the  
485 poral network and the upper threshold is tuned to obtain the porosity given by  
486 the manufacturer [33].

487 The local thickness is computed for every voxel of the poral space by filling  
488 the pore space with spheres

489 [34], [35]. The volumetric distribution of the local thickness gives the mean  
490 pore size diameter equal to  $7.26 \pm 5.31 \mu\text{m}$ . Its cumulative distribution (Fig. 8)  
491 shows that 65% of the total pore volume is composed of structures with local  
492 thickness inferior to 5  $\mu\text{m}$ , and that 80% of the total pore volume is occupied  
493 by structures with local thickness inferior to 7  $\mu\text{m}$ .

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<sup>1</sup>Centre for Research and Teaching in Environmental Geoscience, Aix Marseille University, Aix-en-Provence, France, <https://www.cerege.fr>



494 To quantify the size of the constrictions in the vicinity of the pores, we use  
495 a watershed pore segmentation method based on the ultimates eroded. The  
496 watershed operator [36] that is used to individualize each pore surrounded by  
497 constrictions, relies on iterative erosion and dilation. The Euclidean distance  
498 of the pixel to the nearest background pixel is therefore called the Euclidean  
499 distance map. The erosion process (that consist in peeling the distance map  
500 successively) needs to be constrained such that the isolated pixels (*i.e.* pixels  
501 surrounded by eight neighbors in each and any erosion iteration) may not be  
502 eroded. These pixels coincide with the local maxima in the Euclidean distance  
503 map and are called ultimate eroded points [37], because further constrains eros-  
504 ions do not change the image of ultimate's points. The ultimate eroded points  
505 are now iteratively dilated through the watershed region growing process and  
506 following the distance map values (Fig. 9). The voxels that correspond to the  
507 meeting region coming from different ultimate's points labels are identified as  
508 throats. For every throat surface we compute the equivalent ellipsoid and we  
509 report here the distribution values of the major and the minor axis (Fig. 9).  
510 The minor axis length gives the diameter of the maximal inscribed disk into the  
511 throat. The mean values are  $7.7 \mu\text{m}$  and  $18.8 \mu\text{m}$  for the minor and major axis,  
512 respectively.

513 We compute the penetration length of the porous sample for different particle  
514 diameters [38]. The results are presented on Figure 10. From this information  
515 we can the easily deduce the geometrical cutt-off size of the membrane. From  
516 Figure 10, it is clear that only the particles with a diameter of around  $3.5 \mu\text{m}$   
517 are able to cross the porous sample.

## 518 9. Results and comparison

519 In this Section we present the results obtained with the proposed method-  
520 ology on the effective pore size, tortuosity, surface-to-volume ratio and the per-  
521 meability. We compare these porous sample characteristics to the data obtained  
522 from the tomographic and porosimetry analyses, when they are available.

### 523 9.1. Pore size

524 We start by the analysis of the pore size with one porous sample from a  
525 batch, called previously first disc. Applying the presented here experimental  
526 methodology, explained in details in Section 5.2, the effective pore dimensions  
527 are extracted from the mass flow rate measurements,

528 see Table 4. By analyzing the data presented in Table 4, we can see that  
529 for this porous sample the effective pore diameters,  $2a$ , calculated with different  
530 gases, are very close one to another. The uncertainty in the estimation of the  
531 characteristic pore dimension is of the order of 16% for Nitrogen and decreases  
532 up to 13.9% for Argon. The average pore dimension, estimated with two gases,  
533  $2a = 3.6 \mu\text{m}$ , is obtained with an uncertainty of 13.9%.

534 The uncertainty of the effective pore dimension is calculated using the square  
535 root of the summation of the fitting coefficients uncertainty, which is calculated  
536 from the limits of a 95% confidence interval of the fitting parameters.

537 The iMorph computer analysis of the tomographic data, see Section 8, allows  
538 to obtain the representation of the porous structure of a sample as the system of  
539 the pores which are connected by the constrictions (throats). From the analysis  
540 of the aperture map distribution, Fig. 8, it was found that 65 % of total pore  
541 volume is composed of the structures with the local thickness smaller than  $5\mu\text{m}$ ,  
542 which is close to the results found for the first disc. From the distribution of  
543 the throat size dimensions, shown on Fig. 9, it is clear that 25% of the throats  
544 have the dimension equal to  $3.6\mu\text{m}$ . In addition, from the iMorph analysis it  
545 was also found that only the particles with diameter of around  $3.5\mu\text{m}$  are able  
546 to cross the sample, see Fig. 10.

547 All this information confirms our experimental finding for the first disc. From  
548 this analysis, we can conclude that the proposed gas flow methodology allows us  
549 to estimate the effective pore size which determines the flow through a porous  
550 medium. This dimension is also correlated to the throat size dimension and to  
551 the particle cut-off dimension, obtained from the tomography analysis.

### 552 9.2. Tortuosity and surface-to-volume ratio

553 The information about the effective pore dimension is extracted without  
554 any additional knowledge about the analyzed porous sample. However, if we  
555 assume that the sample porosity is equal to 13.6%, the value obtained from the  
556 tomographic analysis, then additional characteristics of the porous sample are  
557 obtained: the tortuosity, Eq. (37), the capillaries number,  $N$ , Eq. (36), and  
558 surface-to-volume ratio,  $\mathcal{S}_A$ , Eq. (38). All these values are presented in Table 4  
559 for the first disc. These characteristics can be compared with the data on the  
560 tortuosity and surface-to-volume ratio, obtained from the tomography analysis,  
561 see Table 5. The tortuosity in three directions is given in Table 5 and the  
562 gas permeation direction corresponds to the  $z$  axis. The computer tomography  
563 tortuosity in this direction is equal to 1.61, which is close to the tortuosity  
564 calculated for the first disc, 2.5, see Table 4.

565 The averaged over two gases value of the surface-to-volume ratio is equal to  
566  $15.0 \times 10^4 \text{ m}^2/\text{m}^3$  for the first disc, see Table 4. This value is of the same  
567 order of magnitude as that provided by the tomographic analysis,  $6.27 \times 10^4$   
568  $\text{m}^2/\text{m}^3$ , see Table 5.

569 Both data on the tortuosity and surface-to-volume ratio, found from the  
570 proposed methodology, are close to that obtained from the tomography analysis.

### 571 9.3. Non-destructive analysis

572 To check the repeatability of the determination of the effective pore size  
573 dimension, we have analyzed the second disc, which was provided by the same  
574 manufacturer, so supposed to be identical to the first disc.

575 The same analysis was carried out for this second disc and the effective  
576 pore diameters,  $2a$ , calculated with three gases are provided in Table 4. As for  
577 the first disc, the effective pore diameters obtained with different gases are very  
578 close one to another. The uncertainty in the estimation of the characteristic pore  
579 dimension is of the order of 16% for Argon and decreases up to 12% and 10%

580 for Helium and Nitrogen, respectively. The average pore dimension, estimated  
581 with three gases,  $2a = 22 \mu\text{m}$ , is obtained with an uncertainty of 13.6%. The  
582 much larger effective pore size,  $22 \mu\text{m}$ , found for the second disc, represents  
583 a possible sample imperfection: the largest pores are interconnected for this  
584 sample and so they determine the gas flow rate. This structural defect is also  
585 visible through the mercury porosimetry analysis of a sample from the second  
586 batch and it results in a peak between 20 and 30 microns, see Fig. 11.

587 This finding suggests that the proposed gas flow method could potentially  
588 be used as a method of the non-destructive analysis of a porous sample.

#### 589 9.4. Permeability

590 The hydrodynamic (intrinsic) permeability  $K_D$ , calculated from the mass  
591 flow rate measurements, is provided in Table 6, for the first and second discs,  
592 respectively. As it is clear from Table 6 the hydrodynamic permeability is gas  
593 independent within the experimental uncertainty and it is found to be much  
594 smaller for the second disc. It is also worth to underline that two parameters  
595 for description of the permeability in form of Eq. (44),  $a$  and  $K_D$ , are obtained  
596 directly from the fit of the measured mass flow rate or permeability data without  
597 any additional information about the sample porosity.

598 The intrinsic permeability is also provided by iMorph computer analysis,  
599 based on the analytical relation for the channel conductivity, and it is equal to  
600  $1.3 \times 10^{-14} \text{ m}^2$ . This value is close to that obtained for the first disc,  $0.9 \times 10^{-14}$   
601  $\text{m}^2$ , see Table 6.

602 The permeability for both discs is plotted on Fig. 12 as a function of the  
603 Knudsen number. The permeability increases in more than two orders of mag-  
604 nitude (first disc) when the mean pressure is decreasing.

605 In Table 6 the  $b$  coefficient is provided for two porous discs and it is two times  
606 smaller for the first disc compared to the second one which confirms that the  
607 Klinkenberg expression is not universal and the  $b$  coefficient is gas and porous  
608 sample dependent.

609 The measured and calculated from Eqs. (49), (27) permeabilities are shown  
610 on Fig. 13. Very good agreement between experimental and analytical data  
611 are found in the near hydrodynamic, slip and beginning of the transitional flow  
612 regimes, see Fig. 13. However, in the free molecular flow regime, the semi-  
613 analytical expression overestimate the experimental data. It can be explained  
614 by the fact that the experimental data are fitted only in the slip flow regime.  
615 Therefore, the deviation between measured and semi-analytical data is found  
616 for the large Knudsen number range. It also confirms that the Klinkenberg  
617 expression is valid in the slip regime only.

618 The implementation of Eqs. (49), (27) shows an interesting potential of  
619 extracting intrinsic permeability from apparent permeability in free molecular  
620 and transitional regimes.

## 621 10. Conclusion

622 The classical model of the porous media presentation as a bundle of capil-  
623 laries was revised. The original methodology was suggested to determine the  
624 characteristic flow dimension. The experimental procedure is developed to de-  
625 termine the effective pore size (characteristic flow dimension) and the number  
626 of capillaries, related to the model a bundle of capillaries. The experimentally  
627 obtained effective pore dimension is in very good agreement with the results of  
628 the mercury porosimetry and micro-computed tomography. The use of addi-  
629 tional information on the sample porosity allows to find the tortuosity and the  
630 surface-to-volume ratio, which were close to that calculated from the tomogra-  
631 phy analysis. The Klinkenberg formula was also analyzed, and it was shown that  
632 this expression is not general and  $b$  coefficient reveals gas and porous medium  
633 dependency. In addition, the Klinkenberg expression is valid only for the slip  
634 flow regime, which was shown experimentally. Therefore, this formula has to  
635 be used with precaution in the case of low porous structures. The intrinsic  
636 permeability obtained by tomography analysis is very close to the measured  
637 permeability, which is not surprising in the case of the homogeneous porous  
638 medium. The proposed approach is the first very promising stage to evolve  
639 towards measurements of even lower permeabilities and also the characteristic  
640 dimension (pore size) of membranes used for microfiltration ( $> 100$  nm) and  
641 ultrafiltration ( $> 10$  nm).

## 642 Acknowledgement

643 The project leading to this publication has received funding from Excellence  
644 Initiative of Aix-Marseille University - A\*MIDEX, a French "Investissements  
645 d'Avenir" programme. It has been carried out in the framework of the Labex  
646 MEC. The authors (M.V. Johansson, P. Perrier, and I. Graur) would like to  
647 acknowledge the financial support provided by the European Union network  
648 program H2020, MIGRATE project under Grant Agreement No.643095.

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	1st disc	2nd disc
Regime	$\ell$ [ $\mu\text{m}$ ]	$\ell$ [ $\mu\text{m}$ ]
HYDRO	$1.9 \times 10^{-3} < \ell$	$0.11 < \ell$
SLIP	$0.19 < \ell$	$1.1 < \ell$
FM	$19 > \ell$	$110 > \ell$

Table 2: Flow regimes identification.

GAS	1st disc		2nd disc	
	$A_S$ [ $10^{-9} \text{ m}^2$ ]	$B_S$ [ $10^{-16} \text{ m}^3$ ]	$A_S$ [ $10^{-9} \text{ m}^2$ ]	$B_S$ [ $10^{-15} \text{ m}^3$ ]
He			$2.4 \pm 0.2$	$7.1 \pm 0.1$
N <sub>2</sub>	$1.2 \pm 0.2$	$5.5 \pm 0.1$	$2.9 \pm 0.2$	$7.2 \pm 0.1$
Ar	$1.2 \pm 0.1$	$5.5 \pm 0.1$	$2.4 \pm 0.4$	$7.4 \pm 0.2$
AVR	$1.2 \pm 0.1$	$5.5 \pm 0.1$	$2.6 \pm 0.3$	$7.2 \pm 0.1$

Table 3: Fitting coefficients  $A_S$  and  $B_S$  with  $S$ -fit.

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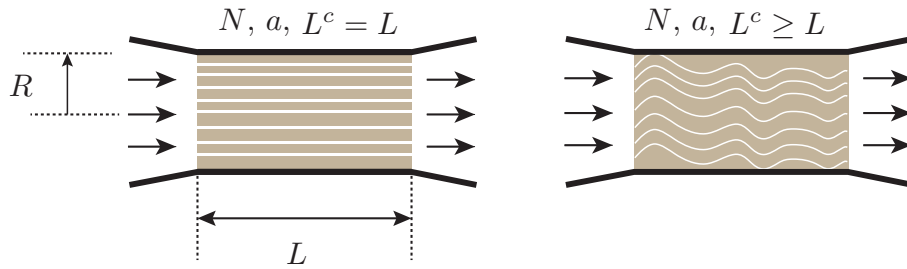


Figure 1: Models of the flat ceramic microporous membrane: bundle of  $N$  parallel capillaries of the same radius  $a$  (left) of the same length  $L_c$  equal to the membrane thickness  $L$ ; (right) of the capillary length  $L_c$  is greater than the membrane thickness  $L$ ,  $L_c = l_\tau L$ .



1st disc				
GAS	$2a$ [ $\mu\text{m}$ ]	$N$ [ $10^5$ ]	$\mathcal{S}_A$ [ $10^5 \text{ m}^2/\text{m}^3$ ]	$l_\tau$
N <sub>2</sub>	$3.7 \pm 0.6$	$3.4 \pm 1.0$	$1.5 \pm 0.6$	$2.6 \pm 0.4$
Ar	$3.6 \pm 0.5$	$3.8 \pm 1.0$	$1.5 \pm 0.6$	$2.5 \pm 0.4$
AVR	$3.6 \pm 0.5$	$3.8 \pm 0.9$	$1.5 \pm 0.6$	$2.5 \pm 0.4$
2nd disc				
GAS	$2a$ [ $\mu\text{m}$ ]	$N$	$\mathcal{S}_A$ [ $10^4 \text{ m}^2/\text{m}^3$ ]	$l_\tau$
He	$25 \pm 3$	$4300 \pm 900$	$2.2 \pm 0.7$	$4.7 \pm 0.6$
N <sub>2</sub>	$20 \pm 2$	$8000 \pm 1000$	$2.7 \pm 0.6$	$3.8 \pm 0.4$
Ar	$25 \pm 4$	$4000 \pm 1000$	$2.0 \pm 1$	$4.7 \pm 0.9$
AVR	$22 \pm 3$	$6000 \pm 1000$	$2.4 \pm 0.9$	$4.3 \pm 0.6$

Table 4: Estimation of the porous media characteristic dimension,  $a$ , the number of capillaries  $N$ , and the surface to volume ratio,  $\mathcal{S}_A$ , by using S-type fit and the porosity obtained from the micro-computed tomography,  $\varepsilon = 13.6\%$ . The tortuosity is calculated from Eq. (37).

$\varepsilon$	$\mathcal{S} \times 10^4$ [ $\text{m}^2/\text{m}^3$ ]	$l_\tau$		
		$x$	$y$	$z$
13.6%	6.27	$2.7 \pm 1.5$	$2.8 \pm 1.6$	$1.6 \pm 0.5$

Table 5: Results from iMorph analysis of the one part of the first porous disc, obtained with  $1.8 \mu\text{m}$  space resolution: porosity,  $\varepsilon$ , specific surface area,  $\mathcal{S}_A$ , and tortuosity,  $l_\tau$ , in three directions ( $x$ ,  $y$  and  $z$ ).

GAS	1st disc		2nd disc	
	$K_D$ [ $10^{-15} \text{ m}^2$ ]	$b$ [kPa]	$K_D$ [ $10^{-13} \text{ m}^2$ ]	$b$ [kPa]
He			$1.16 \pm 0.02$	$7.3 \pm 0.8$
N <sub>2</sub>	$8.9 \pm 0.2$	$17 \pm 2$	$1.16 \pm 0.02$	$3 \pm 0.2$
Ar	$9.0 \pm 0.2$	$18 \pm 3$	$1.20 \pm 0.03$	$2.6 \pm 0.5$
AVR	$9.0 \pm 0.2$	$18 \pm 3$	$1.18 \pm 0.02$	$4.3 \pm 0.5$

Table 6: Klinkenberg coefficients.

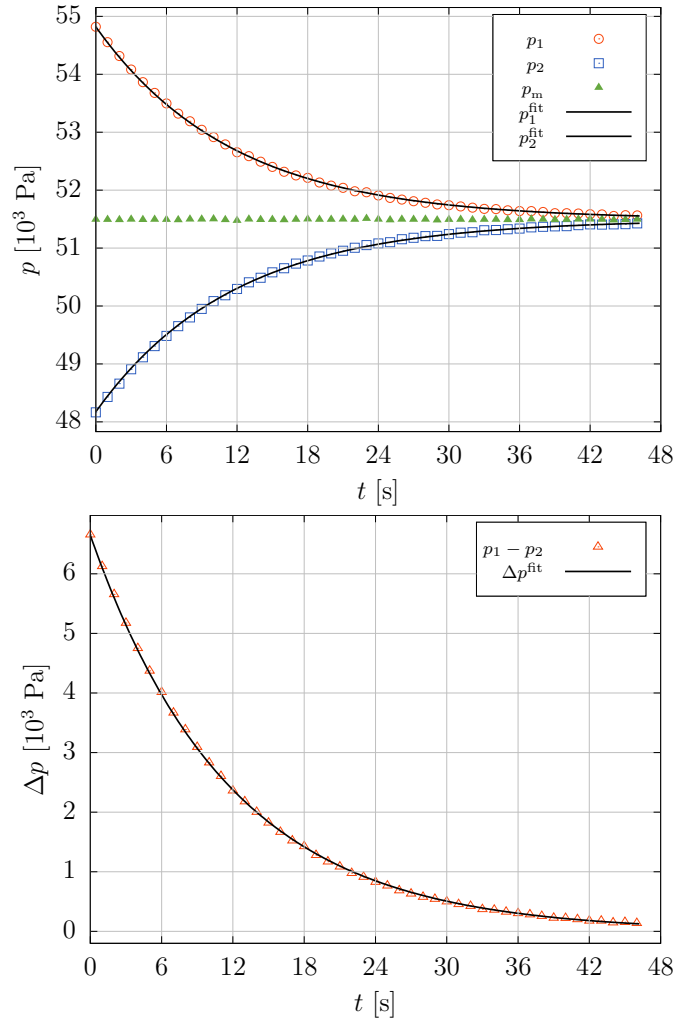


Figure 2: Upper figure: Pressure evolution in time, where the upstream tank pressure,  $p_1$ , is red and the downstream tank pressure,  $p_2$ , is blue, together with the respective fitting curves of the pressure evolution, in black, and the mean pressure  $p_m$  in grey. Lower figure shows the evolution of the pressure difference and the exponential fitting of the measurements.

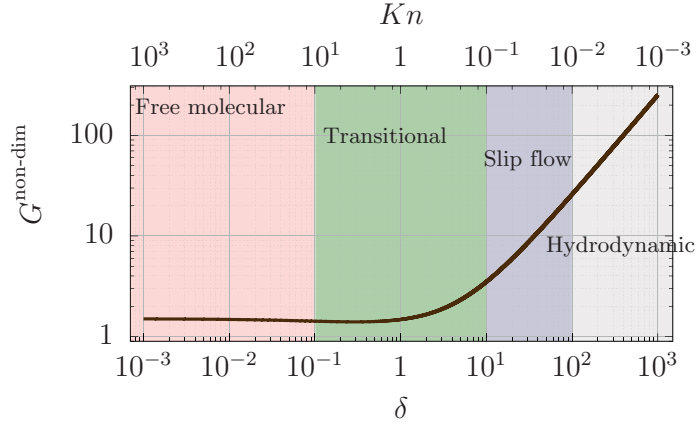


Figure 3: Dimensionless mass flow rate  $G$  for a single circular tube, Eq.(27), as a function of rarefaction parameter and Knudsen number.

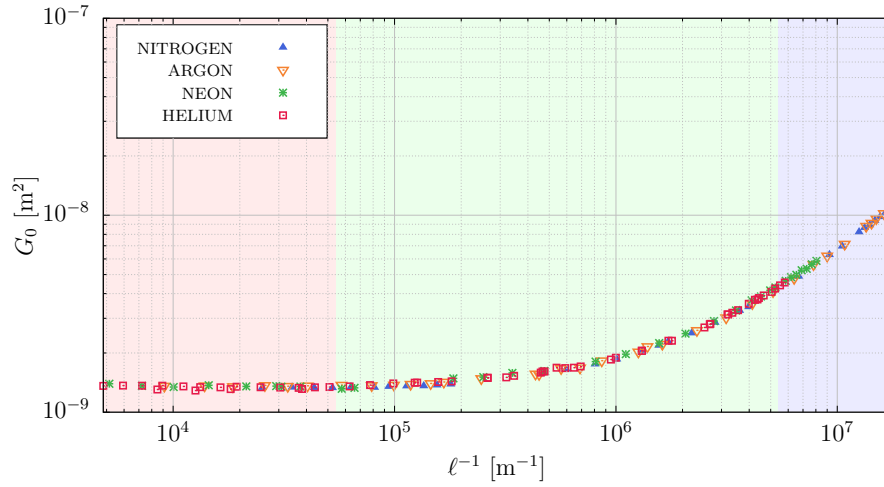


Figure 4: Experimental points for the first disc in normalized form of  $G_0$  function,  $G_0 = \dot{M}/(\Delta p/v_0)$  as a function of the inverse molecular mean free path,  $\ell^{-1}$ .

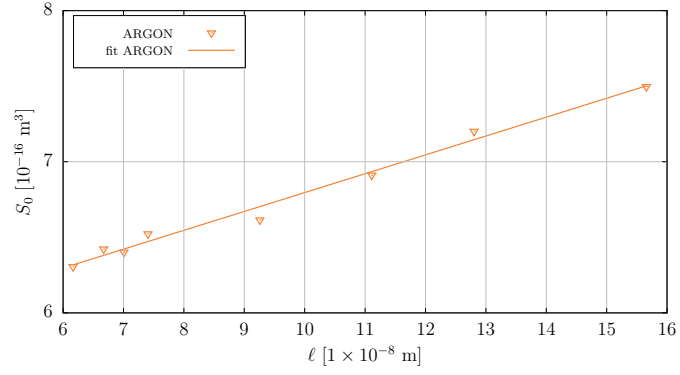


Figure 5: Experimental points of normalized mass flow rate,  $S_0$ , Eq. (31), and the corresponding fitting function, Eq. (32), as a function of the mean free path,  $\ell$ .

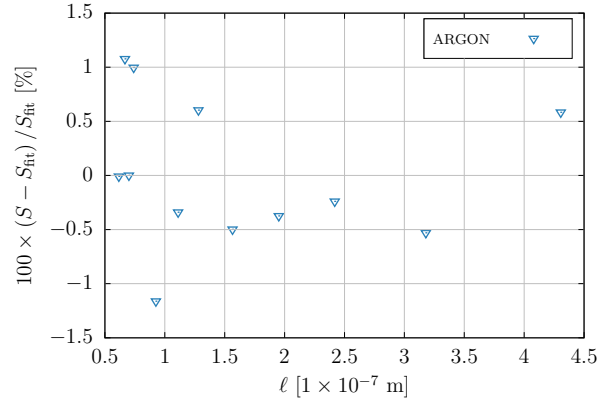


Figure 6: Difference between the experimental points for normalized mass flow rate, Eq. (31), and the fitting curve, Eq. (32), in form  $(S_0 - \mathcal{F}_S) / \mathcal{F}_S$  as a function of molecular mean free path,  $\ell$ .

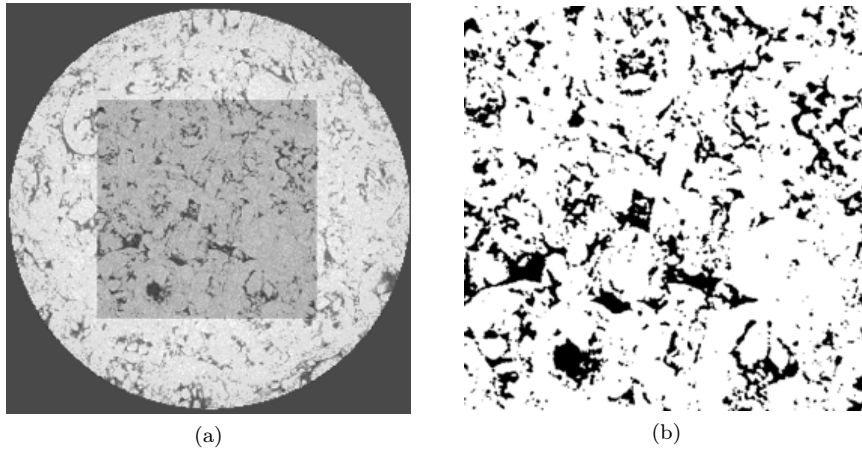


Figure 7: (a) X-ray reconstructed slice (1000x1000 voxels) and centered cubic Region Of Interest ( $500 \times 500$  voxels) use for the analysis (voxel size  $1.8 \mu\text{m}$ ); (b) binarization of the Region Of Interest.

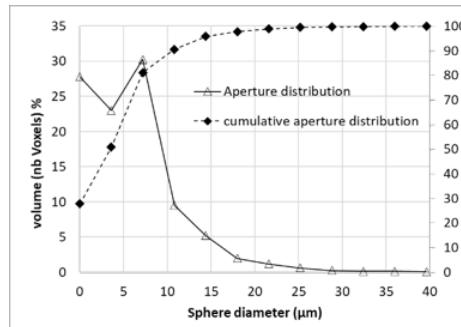


Figure 8: Aperture map distribution (65% of the voxels belong to as sphere with diameter inferior or equal to  $5 \mu\text{m}$  (blue voxels)).

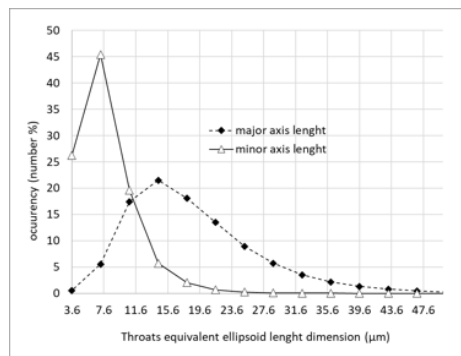


Figure 9: Throats size dimension and shape (70 % of the throats present an inner circle diameter equal to 7.6 μm, and 25 % equal to 3.6 μm).

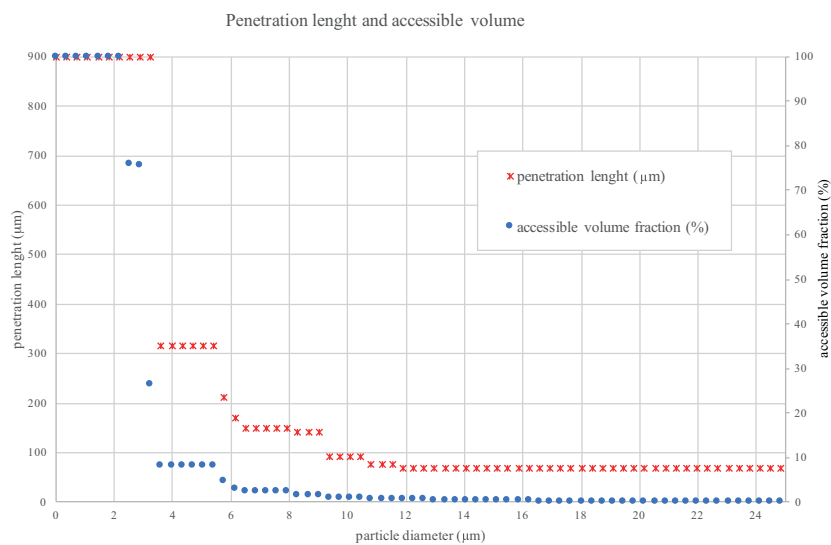


Figure 10: Microtomographic analysis: penetration length as a function of a particle diameter.

Mercury porosimetry

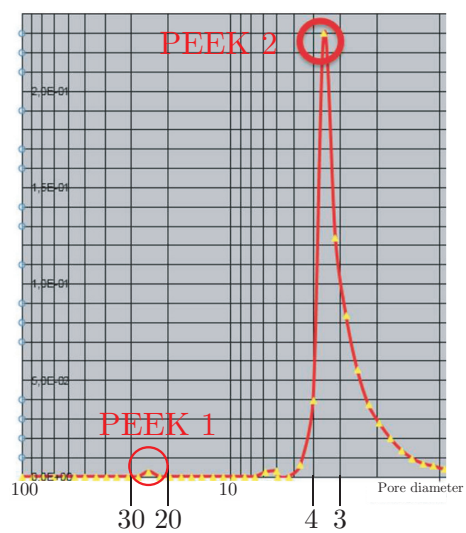
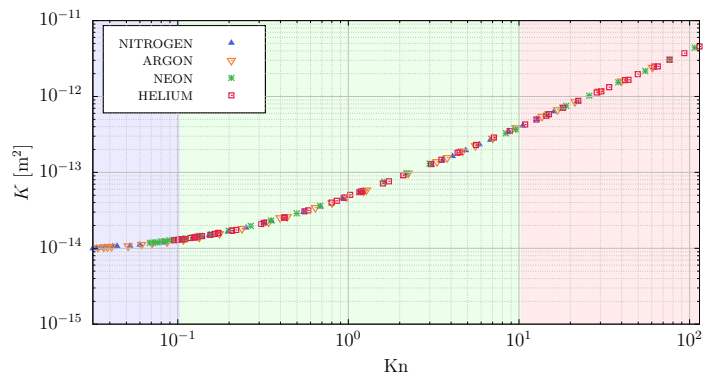
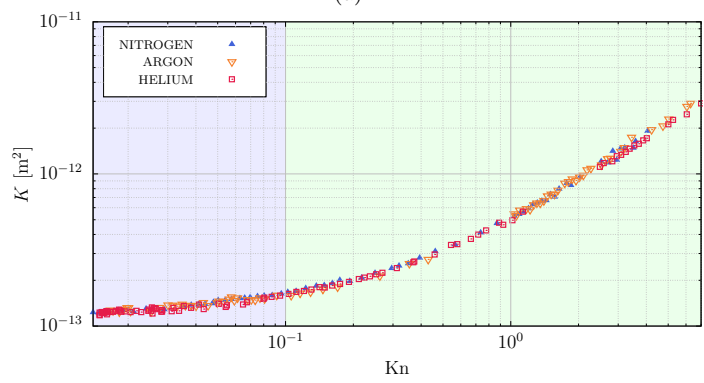


Figure 11: Mercury porosimetry. The pore size at  $x$  axis is given in  $\mu\text{m}$ .



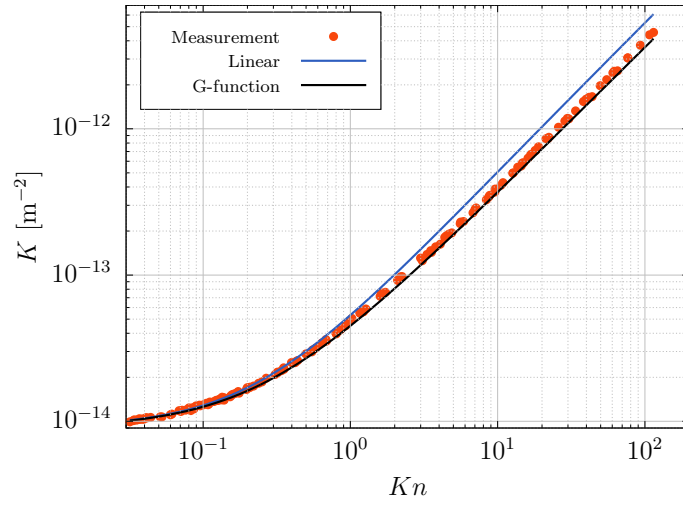
(a)



(b)

Figure 12: Permeability: (a) fist disc, (b) second disc.





(a)

Figure 13: Measured points, presented in dimensionless form,  $K/\frac{p_m \Delta p}{\mu v_0^2} \frac{2S}{L}$ , Eq. (25), and analytical form of  $K$  function, Eq. (27), (49).

767 **AppendixA. Real gas effects**

768 The ideal gas law assumes that gas molecules do not occupy any space and  
769 that there is no molecular potential for attraction and repulsion. Under high  
770 pressure, the first assumption breaks down as the volume occupied by the gas  
771 molecules cannot be neglected. When the temperature is low, the molecular  
772 potential cannot be neglected, otherwise, if there is no attraction condensation  
773 cannot occur. The ideal gas law is considered accurate when the temperature is  
774 significantly larger than the boiling point, *i.e.* at least two times greater than the  
775 critical temperature. Additionally, the pressure needs to be not much greater  
776 than atmospheric pressure, it has to be much lower than critical pressure.

777 To quantify the deviation from ideal gas law conditions, it is useful to intro-  
778 duce the compressibility factor [39]

$$Z = \frac{pV}{MRT}, \tag{A.1}$$

779 which assumes unity when the ideal gas law assumption is valid. In Table  
780 A.7 the measured compressibility factors is provided for the gases used in our  
study and for the maximal measured pressure (131kPa). All the gases have the

Gas	$Z$
He	1.0005
Ne	1.0005
N <sub>2</sub>	0.9998
Ar	0.99937
Kr	0.99793
Xe	0.99471

Table A.7: Measured compressibility factor [39].

781 compressibility factor close to unity. To extend the presented mass flow rate  
782 measurement method for real gases Eq. A.1 can be used to relate the gas mass  
783 and the compressibility factor to pressure.  
784

785 **AppendixB. Quasi-stationary assumption**

786 To derive the mass flow rate we have to consider the mass variation in time  
787 as a quasi-steady process. We assume that there are infinitesimal unbalanced  
788 forces which modify the state of the system slower than the system reaches  
789 its local equilibrium. In this case, we can approximate the thermodynamic  
790 processes as a succession of equilibrium states. This approximation can be  
791 considered as an accurate one when the average time needed for a gas molecule  
792 to travel through the porous medium is much greater than the time between  
793 two successive intermolecular collisions in the reservoir [40]. To quantitatively

794 estimate this time, we introduce a measure of the average time between two  
 795 successive collisions, the Mean Free Time,  $MFT$ , as

$$MFT = \ell/v_0, \quad (\text{B.1})$$

796 where the mean free path,  $\ell$ , and the most probable molecular velocity,  $v_0$ , are  
 797 defined by Eqs. (15) and (16), respectively. To estimate the average time for a  
 798 gas molecule to travel through the porous media we introduce the Fluid Travel  
 799 Time,  $FTT$ , as

$$FTT = \frac{\ell_\tau L}{u}, \quad (\text{B.2})$$

800 where  $\ell_\tau$  is the tortuosity, Eq. (10),  $L$  is the thickness of the porous sample and  
 801  $u$  is the fluid velocity. In the hydrodynamic flow regime we have

$$\Delta p = 0.5\rho u^2, \quad (\text{B.3})$$

802 where  $\rho$  is the gas density. Under typical experimental conditions, for the sam-  
 803 ple thickness  $L = 2$  mm, and assuming  $\ell_\tau = 2$ , the mean free time,  $MFT$ , is  
 804 five orders of magnitude less than the average fluid travel time,  $FTT$ , through  
 805 the porous media, therefore, we are well within the quasi-stationary state as-  
 806 sumption.

### 807 Appendix C. Two limits approximation

808 Additional possibility to obtain the porous medium characteristic dimension  
 809 can be done by using two limits of the flow regimes, which can be easily dis-  
 810 tinguished. The first limit is the free molecular regime (or Knudsen diffusion  
 811 regime), where the molecule-molecule collisions can be neglected because they  
 812 are a few numerous comparing to molecule-surface collisions. In this regime, the  
 813 mass flow rate is proportional to  $a^3$ . For the second limit regime, hydrodynamic  
 814 regime (Poiseuille flow), the opposite situation is realized: molecule-surface col-  
 815 lisions are very few numerous compared to molecule-molecule collisions. The  
 816 mass flow rate is proportional to  $a^4$ . Therefore, we can use the ratio of the nor-  
 817 malized mass flow rates, measured in these two regimes to find the characteristic  
 818 dimension of the porous media as following

$$\frac{\dot{M}_P/M_{S0}}{\dot{M}_{FM}/M_{G0}} = \frac{a}{4} \frac{3\sqrt{\pi}}{8} \frac{2 - \alpha}{\alpha}. \quad (\text{C.1})$$

819 However, two problems are related to the realization of this approach. First,  
 820 the value of the accommodation coefficient  $\alpha$  is unknown *a priori*. The second  
 821 curtail point is the correct determination of the flow regime, *i.e.* the correct  
 822 choice of the pressure range. From the theoretical point of view we know that the  
 823 both normalized mass flow rates  $\dot{M}_P/M_{S0}$  and  $\dot{M}_{FM}/M_{G0}$  have to be constant.  
 824 If this is not the case, the hydrodynamic (or free molecular) regime has not  
 825 been reached yet, and the determination of the characteristic dimension can  
 826 be affected by the essential error. Under our experimental conditions and for  
 827 the porous samples used here, we did not arrive to reach both regimes, so this  
 828 theoretically possible approach was not realized here.