A novel experimental setup for simultaneous adsorption and induced deformation measurements in microporous materials
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A new experimental set-up is presented allowing the simultaneous measurement of adsorption isotherms and adsorption-induced deformations. It is composed of a manometric technique coupled with a digital image correlation set-up for full-field displacement measurements. The manometric part is validated by comparing adsorption isotherms with those obtained by a gravimetric method. The principles and methods of both adsorption isotherm and induced deformation measurements are presented in details. As a first application of this new apparatus, the coupling between adsorption and induced deformation is characterised for a microporous media (activated carbon) saturated by pure \( \text{CO}_2 \) (318.15K, \([0-60]\) bar) and pure \( \text{CH}_4 \) (303.15K, \([0-130]\) bar). For this very homogeneous porous material, the induced deformation is characteristic of a pure volumetric swelling but the full-field set up may allow the characterisation of localised pattern of deformation for heterogenous or cracked microporous media.

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Keywords: Adsorption; deformation; microporous materials; experiment; manometric technique; digital image correlation

I. INTRODUCTION

Following the IUPAC recommendation1,2, the pore space in porous materials is divided into three groups according to the pore size diameters: macropores of widths greater than 50 nm, mesopores of widths between 2 and 50 nm and micropores (or nanopores) of widths less than 2 nm. Zeolites, activated carbon, tight rocks, coal rocks, source rocks, cement paste or construction materials are among these materials. In recent years, a major attention has been paid on these microporous materials because the surface-to-volume ratio (i.e., the specific pore surface) increases with decreasing characteristic pore size. Consequently, these materials can trap an important quantity of fluid molecules as an adsorbed phase. This is important for applications in petroleum and oil recovery, gas storage, separation, catalysis or drug delivery.

For these microporous materials, a deviation from standard poromechanics, which was introduced by Biot 75 years ago3,4, is expected. In very small pores, the molecules of fluid are confined. Interaction between molecules is modified. This effect, denoted as molecular packing, includes fluid-fluid and fluid-solid interactions and has significant consequences at the macroscale, such as instantaneous swelling deformation. In different contexts, these deformations may be critical. For instance, in situ adsorption-induced coal swelling has been identified5,6 as the principal factor leading to a rapid decrease in \( \text{CO}_2 \) injectivity during coal bed methane production enhanced by \( \text{CO}_2 \) injection. Generally, natural and synthesised porous media are composed of a double porosity: the microporosity where the fluid is trapped as an adsorbed phase and a meso or a macro porosity required to ensure the transport of fluids to and from the smaller pores. If adsorption in nanopores induces instantaneous deformations at a higher scale, the matrix swelling may close the transport porosity, reducing the global permeability of the porous system or annihilating the functionality of synthesised materials. Conversely, gas desorption can lead to matrix shrinkage and microcracking, which may help oil and gas recovery in the context of unconventional petroleum engineering7. The effects of adsorbent deformation on physical adsorption has also been identified8 as the major challenge concerning gas porosimetry in nano-porous non-rigid materials (e.g. metal organic framework). In conclusion, there is now a consensus in the community that major attention has to be focused on the coupled effects appearing at the nanoscale within microporous media because they may have significant consequences at the macroscale.

Experimentally, different authors tried to combine gas adsorption results and volumetric swelling data. Pioneer works of Meehan9 showed the effect of carbon dioxide sorption on the expansion of charcoal but only mechanical deformations were reported and no adsorption quantities were measured. Later on, different authors7,10–15 performed tests on bituminous coal, because it is of utmost importance in the context of \( \text{CO}_2 \) geological sequestration and coal bed reservoirs exploitation. However, most results in the literature are not complete in a sense that adsorption and swelling experiments are not measured simultaneously15 or performed on the exact same coal samples12. Other authors presented simultaneous in situ adsorption and swelling results but the volumetric

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strain is extrapolated from a local measurement – using strain gauges\textsuperscript{7,17,18} or LVDT sensors\textsuperscript{15,19} – or by monitoring the silhouette expansion\textsuperscript{11}.

Recently, important efforts have been involved in molecular simulations\textsuperscript{20–23} or in poromechanical modeling\textsuperscript{24–26} in order to predict adsorption-induced deformation in nanoporous materials. However, there is still a need for detailed experimental data presenting simultaneous adsorption-induced deformation measurements for validation purpose, especially for heterogeneous materials.

In this context, this paper aims to present a novel apparatus allowing the simultaneous \textit{in situ} measurements for validation purpose, especially for heterogeneous materials.

In section II, the novel apparatus is described and the experimental method is fully detailed by presenting both the manometric technique and the digital image correlation set-up. In section III, this new apparatus is used to characterise \textit{in situ} adsorption-induced deformation on a nanoporous activated carbon saturated with pure methane and carbon dioxide.

\section{II. EXPERIMENTAL APPARATUS: PRINCIPLES AND METHODS}

\subsection{A. Device description}

A new experimental set-up is proposed to measure \textit{in situ} and simultaneous adsorption-induced deformation in microporous materials. The set-up couples a home-built manometric apparatus for gas adsorption measurements and a digital image correlation set-up for full-field displacement measurements.

Figure 1 shows a sketch of the experimental set-up. It is composed of:

- a manometric set-up for gas adsorption measurements:
  
  - a dosing volume \((V_D)\) composed of a dosing cell and a connecting network. The dosing volume is \((V_D \pm \Delta V_D) = (95.95 \pm 0.09) \text{ ml}\), with a relative error of \(\frac{\Delta V_D}{V_D} = 0.09\%\),
  
  - a measuring volume \((V_M)\) composed of a measuring cell where the sample takes place on a sapphire window. The volume cell is \((V_M^0 \pm \Delta V_M^0) = (188.8 \pm 0.3) \text{ ml}\) with a relative error of 0.2%,
  
  - a digital manometer (\textit{Wiika}, measuring range: \([0, 250]\text{ bar},\) precision: \(\pm 0.005\text{ bar}\)),
  
  - an electrical heat regulator (\textit{Horst GmbH HT31}) coupled with a PT100 temperature probe,
  
  - two \textit{in situ} thermocouples \textit{IEC}, type K, (\textit{RS thermocouple}, precision: \(\pm 0.1\text{ K}\)) ;
  
  - a digital image correlation set-up for full-field measurements:
    
    - a digital camera (\textit{PixeLINK, PL-B781U}),
    
    - an optical lens (\textit{Edmundoptics}, focal length : 25 mm),
    
    - a standard LED lighting unit,
    
    - a computer.

\subsection{B. Gas adsorption measurements}

Excess adsorption isotherms are built step by step from gas adsorption measurements performed using an home-built manometric set-up. The manometric technique has been widely used by the community for gas adsorption measurements and different studies may be found in the literature (see e.g. Rouquerol \textit{et al.}\textsuperscript{27}, Battistutta \textit{et al.}\textsuperscript{18}, Badalyan \textit{et al.}\textsuperscript{28}). The principle of the technique consists in balancing the gas quantities before and after adsorption thanks to temperature and pressure measurements at the equilibrium.

Carrying out an adsorption isotherm measurement at a given temperature requires different steps:

1. A porous sample, of a known mass \(m_i\), is introduced in the measuring cell.

2. The porous sample is purified under given vacuum and heating conditions (typically 24h at 343.15 K).

3. An accurate estimation of the measuring volume \(V_M\) is performed using a non adsorbing gas (typically helium is chosen).

4. The gas adsorption isotherm is finally built step by step by estimating the exceeding adsorbate moles of gas for incremental increasing pressure at thermal equilibrium. At each step, an amount of gas is introduced in the dosing volume \(V_D\). After equilibrium, pressure and temperature in \(V_D\) are measured. Then, the gas is allowed to fill the whole system \(V_D + V_M\) and a part of it is adsorbed on the adsorbent sample and a part of it remains non-adsorbed. When the new equilibrium is reached, the new pressure and temperature in the whole system \(V_D + V_M\) are measured and the amount of non-adsorbed gas is deduced. The amount of exceeding adsorbed gas is then estimated by difference following Eq. (1).

\begin{equation}
\begin{aligned}
\n_i^{\text{ex}} &= n_i^{\text{ex}} + \delta n_i^{\text{ex}} \\
\delta n_i^{\text{ex}} &= V_M \rho_i^{M} + V_D \rho_i^{D} - V_D + V_M \rho_i^{M+D}.
\end{aligned}
\end{equation}

In Eq. (1), \(V_M \rho_i^{M}\) is the amount of remaining non-adsorbed gas in the measuring volume \(V_M\) at the
end of step \((i-1)\), \(\frac{V_D}{M} \rho_i^D\) is the amount of gas introduced in the dosing volume \(V_D\) at the beginning of step \(i\), \(\frac{V_M + V_{M+D}}{M+D} \rho_i^M\) is the amount of non-adsorbed gas in the whole system at the end of step \(i\), \(M\) is the gas molar mass and \(\rho\) is the gas density. The subscript represents the pressure step and the superscript represents the volume from which the gas density is estimated through an equation of state for given pressure and temperature. Typically, the equations developed by Span and Wagner\(^{29}\), Setzmann and Wagner\(^{30}\) and Arp and McCarty\(^{31}\) are used to estimate respectively the densities of CO\(_2\), CH\(_4\) and He.

Since the excess adsorption isotherm is built in an incremental way through Eq. (1), the relative errors accumulate step by step.

Typically, for one excess adsorption amount, the measurement uncertainty is given by Eq. (2).

\[
\Delta n_i^{ex} = \Delta n_i^{ex1} \left[ \frac{M}{M+D} \rho_i^M - \frac{M+D}{M} \rho_i^M \right] + \Delta V_M + \left[ \frac{M}{M+D} \rho_i^M - \frac{M+D}{M} \rho_i^D \right] \frac{\Delta V_D}{M} + \left( \Delta \rho_i^M + \Delta \rho_i^{M+D} \right) V_M + \left( \Delta \rho_i^D + \Delta \rho_i^{M+D} \right) V_D.
\]

In Eq. (2), \(\Delta \alpha\) is the measurement uncertainty of the quantity \(\alpha\).

The manometric part of the device has been validated by comparing the excess adsorption quantities measured on an \(Ecosorb\) activated carbon with the ones obtained with a reference gravimetric technique\(^{32}\). Figure 2 shows the comparison in term of excess adsorption isotherms \((T = 303.15\, \text{K})\) obtained for pure CH\(_4\) \((P \in [0-130]\, \text{bar})\) and pure CO\(_2\) \((P \in [0-60]\, \text{bar})\). A good agreement is clearly observed between the two set of data which validates the manometric technique for adsorption measurements.

Note that different test have been performed to ensure that the temperature is properly stabilised during the whole measurement duration. A typical temperature shift of 0.1 K is observed after 12 hours (which corresponds to the thermocouple sensor uncertainty) and the typical duration of a full adsorption isotherm measurement is 6 hours for the material tested here.

### C. Swelling measurement by digital image correlation

Swelling strain is estimated by full-field displacement measurements performed by digital image correlation (DIC) using Icasoft software\(^{33}\). The general framework of the digital image correlation (DIC) algorithm used in this paper is based on the formulation presented by Grégoire.
et al. \(^{34}\). The general principle is briefly recalled in Appendix A. Details may be found in Grégoire et al. \(^{34}\).

After purification, a reference image of the surface sample is acquired. At each pressure step, a deformed image is acquired. The two digital images corresponding to the reference and the deformed state are described by a discrete function representing the grey level of each pixel (Eq. A1). The optimal displacement field determination consists in the minimization of a cross-correlation coefficient on a set of image pixels (Eq. A2). The use of a cross-correlation allows to correct a possible difference in brightness between the two images\(^{34}\). Thanks to this technique, the full-field displacement is estimated with a typical resolution of 1/100 of a pixel\(^{33}\).

Fig. 3 presents a typical result of the full-field displacement estimation performed by the DIC technique for an activated carbon saturated with pure CO\(_2\) at \(P_b = 50.8\) bar. Fig. 3.a, 3.b and 3.c present respectively the reference image and the full-field displacements in the horizontal and vertical directions. A typical adsorption-induced swelling displacement field is obtained.

From the DIC estimation of the displacement field \((u = U_x \xi_x + U_y \xi_y)\), the deformation field is calculated based on a continuum mechanics framework with small displacement-gradient assumption \((\varepsilon = \frac{1}{2}(\nabla u + \nabla^T u))\) as well as the volumetric swelling strain \((\varepsilon_v = \text{tr}(\varepsilon))\), where \(\text{tr}()\) is the trace of the matrix). For an isotropic homogeneous materials, the volumetric swelling strain is directly equal to three times the ortho-radial strain \((\varepsilon_v = 3 \times \varepsilon_{99})\). See Appendix B for details on the volumetric swelling strain estimation. For an anisotropic, heterogeneous or cracked material, the volumetric swelling strain is not the measurable quantity of interest and the DIC-based method provides the full displacement field on the surface of the material from which the local deformation can be estimated. Figure 4 presents a typical result of the full-field ortho-radial strain estimation for an isotropic and homogeneous activated carbon saturated with pure CO\(_2\) at \(P_b = 50.8\) bar. A typical adsorption-induced homogeneous swelling strain field is obtained.

### III. APPLICATION TO THE DETERMINATION OF ADSORPTION-INDUCED SWELLING ON ACTIVATED CARBON.

#### A. Adsorbent and adsorbates description

An activated carbon (Chemviron) is used as adsorbent material in this study. The sample is a cylinder and its main characteristics are collected in Table I. The geometrical dimensions have been measured with a caliper, the mass has been measured with a Precisa scale (XT 2220 M-DR), the specific pore surface has been measured with a gas porosimeter (Micromeretics ASAP 2020) according to the BET theory\(^{35}\). The specific micropore volume has been estimated according to the IUPAC classification\(^2\) (pore diameter down to 2 nm) based on a pore size distribution deduced from a low-pressure adsorption isotherm \((N_2 \text{ at } 77\text{ K from } 8 \times 10^{-8} \text{ to } 0.99 \text{ P/P}_0 \text{ in relative pressure range measured with the same gas porosimeter according to the HK theory}^{36}\).

The adsorbates, CO\(_2\) and CH\(_4\), as well as the calibrating gas, He, are provided by Linde Gas with a minimum purity of 99.995%, 99.995% and 99.999% respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>(cm)</td>
<td>(h = 1.922 \pm 0.004)</td>
</tr>
<tr>
<td>Diameter</td>
<td>(cm)</td>
<td>(d = 2.087 \pm 0.002)</td>
</tr>
<tr>
<td>Volume</td>
<td>(ml)</td>
<td>(V_{ech} = 6.57 \pm 0.03)</td>
</tr>
<tr>
<td>Mass</td>
<td>(g)</td>
<td>(m = 4.137 \pm 0.001)</td>
</tr>
<tr>
<td>Specific pore surface</td>
<td>(m(^2).g(^{-1}))</td>
<td>(S_{BET} = 1090 \pm 10)</td>
</tr>
<tr>
<td>Specific micropore volume</td>
<td>(cm(^3).g(^{-1}))</td>
<td>(v_{\mu} = 0.51)</td>
</tr>
<tr>
<td>Total micropore volume</td>
<td>(ml)</td>
<td>(V_{\mu} = 2.11)</td>
</tr>
<tr>
<td>Microporosity</td>
<td>(%)</td>
<td>(\phi_{\mu} = \frac{v_{\mu}}{V_{ech}} = 32.1)</td>
</tr>
</tbody>
</table>

#### B. Equilibration time, adsorption kinetics and deformation kinetics

Fig. 5 presents a typical result of the kinetics of sorption and deformation for an activated carbon saturated with pure CO\(_2\) at \(T = 303.15\) K for both adsorption (Fig. 5.a) and desorption (Fig. 5.b) for a bulk pressure varying respectively from \(P_b = 0\) bar to \(P_b = 20\) bar and from \(P_b = 20\) bar to \(P_b = 15\) bar. The thermodynamical equilibrium is reached after a time duration, which is identified equal to 15 min. This duration represents the minimum time increment between two constitutive experimental acquisitions for this material.

#### C. Simultaneous adsorption and induced deformation measurements

The main advantage of the proposed method is to provide simultaneous in situ measurements of both adsorption and deformation for the same sample in the exact same conditions.

Fig. 6 presents the results of these simultaneous measurements for an activated carbon filled with pure CO\(_2\) and pure CH\(_4\) at \(T = 318.15\) K and \(T = 303.15\) K respectively. Full-field deformation maps are presented as supplementary material (see section V). Collected experimental data are reported in appendix D.

Fig. 6.a presents the results in term of excess adsorption/desorption isotherms. CO\(_2\) and CH\(_4\) gas sorption in activated carbon is a reversible phenomenon and no hysteresis is observed between adsorption and desorption paths as previously reported in the literature\(^{32}\). Noting that adsorbed quantity amount increases when temperature decreases, Fig. 6.a shows that CO\(_2\) is preferentially
FIG. 3. Typical result of the full-field displacement estimation preformed by the DIC technique for an activated carbon saturated with pure CO$_2$ ($T = 303.15$ K, $P_b = 50.8$ bar, pixel size: 17.9 $\mu$m): (a) reference image; (b) full-field displacement in the horizontal direction; (c) full-field displacement in the vertical direction.

FIG. 4. Typical result of the full-field ortho-radial strain estimation for an activated carbon saturated with pure CO$_2$ ($T = 303.15$ K, $P_b = 50.8$ bar, pixel size: 17.9 $\mu$m). Adsorbed in carbon compare to CH$_4$ as previously reported in the literature.$^{12,18}$ This is the reason why CO$_2$ injection is used to increase CH$_4$ recovery in Enhanced Coal Bed Methane production.

Fig. 6.b presents the results in term of adsorption-induced volumetric strain. CO$_2$ and CH$_4$ gas adsorption-induced deformation is a reversible phenomenon but a small hysteresis is observed between the adsorption and the desorption paths. This hysteresis is not linked to the adsorption-deformation couplings but is due to an elastic compaction of the carbon matrix grains.$^{37}$ Cycling effect and material compaction are detailed in appendix C. For a given pressure, CO$_2$ adsorption produces more volumetric deformation than CH$_4$ adsorption, which is the source of the rapid decrease in CO$_2$ injectivity during coal bed methane production enhanced by CO$_2$ injection.

Fig. 7 presents the evolution of the volumetric strain versus the excess adsorbed quantity for both CO$_2$ and CH$_4$ at $T = 318.15$ K and $T = 303.15$ K respectively. The two evolutions for the two different gases are close together showing that the volumetric swelling is directly linked to the excess adsorbed quantity.

IV. CONCLUDING REMARKS

A new experimental set-up for the study of adsorption-induced deformation has been presented. The main advantage of the proposed method is to provide simultaneous in situ measurements of both adsorption and deformation for the same sample in the exact same conditions, which can be directly used for model validation. Gas adsorption measurements are performed using an home-built manometric apparatus and deformation measurements are performed using a digital image correlation set-up. This set-up allows full-field displacement measurements, which may be crucial for heterogeneous, anisotropic or cracked samples. For homogeneous and isotropic samples, homogeneous swelling strain deformation fields are observed and the volumetric swelling strain may be deduced. For an anisotropic, heterogeneous or cracked material, the volumetric swelling strain is not the measurable quantity of interest but the DIC-based method still provides the full displacement field on the surface of the material from which the local deformation can be estimated.

The novel apparatus and the experimental method have been fully detailed and used to characterise in situ adsorption-induced deformation on a nanoporous acti-
FIG. 5. Typical kinetics of sorption and deformation for an activated carbon saturated with pure CO$_2$ at $T = 303.15$ K: (a) adsorption from $P_b = 0$ bar to $P_b = 20$ bar; (b) desorption from $P_b = 20$ bar to $P_b = 15$ bar.

FIG. 6. Simultaneous adsorption and induced swelling measurements for an activated carbon filled with pure CO$_2$ and pure CH$_4$ at $T = 318.15$ K and $T = 303.15$ K respectively: (a) excess adsorption isotherm; (b) volumetric induced swelling.

FIG. 7. Swelling versus the excess amount of adsorbed gas (CO$_2$ and CH$_4$).

vated carbon saturated with pure methane and carbon dioxide. For a given pressure, CO$_2$ is preferentially adsorbed in this activated carbon compare to CH$_4$ and CO$_2$ adsorption produces more volumetric deformation than CH$_4$ adsorption. However, the simultaneous measurements of both adsorption and strain show that for a given amount of excess adsorbed quantity, a similar induced deformation is observed for CH$_4$ and CO$_2$ showing that the macroscopic swelling is intrinsically linked to the amount of excess adsorbed quantities within the nanopores.

V. SUPPLEMENTARY MATERIAL

See supplemental material at [URL will be inserted by AIP] for the full-field deformation maps used to estimated the volumetric swelling evolution presented in Figure 6 based on the procedure presented in appendix B.
ACKNOWLEDGMENTS

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Appendix A: General framework for digital image correlation

The general framework of the digital image correlation (DIC) algorithm used in this paper is based on the formulation presented by Grégoire et al. Here it is now applied for adsorption-induced deformation measurements. The principle of DIC was advanced in the context of experimental mechanics by Sutton et al.. Two digital images corresponding to a reference and a deformed state are described by discrete functions representing the grey level of each pixel and related by:

\[ f^*(x^*) = f(x + d(x)) \]  

where \( f \) and \( f^* \) are the discrete functions of the reference and the deformed state respectively, and \( d(x) \) is the displacement field vector (Fig. 8).

![FIG. 8. Reference and deformed images (Grégoire et al.)](image)

The optimal displacement field determination consists of the minimization of a cross-correlation coefficient on a set of initial image pixels, called a subset:

\[ C = 1 - \frac{\int_{\Delta M} f(x)f(x + d(x))dx}{\sqrt{\int_{\Delta M} f^2(x)dx} \sqrt{\int_{\Delta M} f^2(x + d(x))dx}} \]  

where \( \Delta M \) is the surface of the subset in the reference image (see Fig. 9).

The displacement field is typically decomposed on an appropriate functional basis on a subset:

\[ d(P) = \sum_j n_j(P)u_j \]  

where \( u_j \) are the unknown displacement vectors, \( P \) is a point of the subset, \( d(P) \) is its displacement vector given by the minimization of Eq. (A2) and \( n_j \) are interpolating functions to be chosen.

According to the numbers of unknowns introduced in the decomposition, Eq. (A3) is written as many times as needed to have a problem well-posed. Finally, the problem consists of inverting a matrix given by:

\[ D = [M]U \]  

where \( D \) is the vector of the optimal displacement obtained by the minimization of Eq. (A3), \( [M] \) is the matrix of the functional basis and \( U \) is the vector of the unknown displacements.

Typically, a bilinear continuous displacement field decomposition \( \{n_j\} = \{x, y, xy, 1\} \) and a cubic spline interpolation are used as in Touchal Mguil. Figure 9 shows a subset before \( (ABCD \) centered on \( P \)) and after \( (A^*B^*C^*D^* \) centered on \( P^* \)) deformation on the same coordinate system. The displacement field is estimated on each point by means of:

\[
\begin{align*}
    \{d_x(x,y) &= u_1 \hat{x} + u_2 \hat{y} + u_3 \hat{x}\hat{y} + u_4 \\
    d_y(x,y) &= u_5 \hat{x} + u_6 \hat{y} + u_7 \hat{x}\hat{y} + u_8
\end{align*}
\]  

where \( \hat{x} = \frac{x-x^*}{L} \) and \( \hat{y} = \frac{y-y^*}{L} \) are the homogeneous coordinates and \( L \) is the subset length. There are eight unknown \( u_j \) so Eq. (A5) are written at each point \( A, B, C, \) and \( D \). The solution is obtained by inverting the 8-dimensional matrix \([M]\) in Eq. (A4).

Finally, the algorithm is carried out on each subset of the initial image in order to obtain the full field displacement \( u(x,y) = \begin{pmatrix} U_x(x,y) \\ U_y(x,y) \end{pmatrix} \) with a resolution of 1/100 of a pixel.
Appendix B: Full-field deformation estimation and swelling calculation

1. Theoretical background

Traditionally, the deformation field is calculated based on a continuum mechanics framework with small displacement-gradient assumption \((\varepsilon = \frac{1}{2} (\nabla u + \nabla u^T))\). For adsorption-induced deformation in an isotropic homogeneous medium, we expect a swelling displacement field and cylindrical coordinates \((\varepsilon_r, \varepsilon_\theta, \varepsilon_z)\) are more appropriate to estimate the volumetric swelling. One gets:

\[
\varepsilon = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{yy} \end{pmatrix} = \begin{pmatrix} \varepsilon_{rr} & \varepsilon_{r\theta} \\ \varepsilon_{r\theta} & \varepsilon_{\theta\theta} \end{pmatrix} = \begin{pmatrix} \varepsilon_u & \varepsilon_\theta \\ \varepsilon_\theta & \varepsilon_v \end{pmatrix} (\varepsilon_u, \varepsilon_\theta)
\]

where:

\[
\begin{align*}
\varepsilon_{rr} &= \varepsilon_{xx} \cos^2 \theta + \varepsilon_{yy} \sin^2 \theta + 2 \varepsilon_{xy} \cos \theta \sin \theta \\
\varepsilon_{r\theta} &= (\varepsilon_{yy} - \varepsilon_{xx}) \sin \theta \cos \theta + \varepsilon_{xy} (\cos^2 \theta - \sin^2 \theta) \\
\varepsilon_{\theta\theta} &= \varepsilon_{xx} \sin^2 \theta + \varepsilon_{yy} \cos^2 \theta + 2 \varepsilon_{xy} \cos \theta \sin \theta
\end{align*}
\]

and:

\[
\varepsilon_{xx} = \frac{\partial U_x}{\partial x}; \quad \varepsilon_{xy} = \frac{1}{2} \left( \frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x} \right); \quad \varepsilon_{yy} = \frac{\partial U_y}{\partial y} \tag{B3}
\]

For a perfect swelling deformation field in an isotropic homogeneous medium, one may obtain:

\[
\begin{align*}
U_r(r) \\
U_\theta = 0
\end{align*}
\]

\[
\begin{align*}
\varepsilon_{rr} &= \text{constant} \\
\varepsilon_{\theta\theta} &= \frac{U_r(r)}{r} = \text{constant} = \varepsilon_{rr} \\
\varepsilon_{r\theta} &= 0 \\
\varepsilon_{zz} &= \varepsilon_{rr} = \varepsilon_{\theta\theta}
\end{align*} \tag{B4}
\]

Numerical errors may be introduced during the estimation of a radial strain field based on the numerical differentiation of a discrete radial displacement field (Eq. B4). Therefore, the ortho-radial strain field is directly linked to the norm of the displacement field assuming that the ortho-radial displacement field is negligible \((||u|| = \sqrt{U_r^2 + U_\theta^2} \approx U_r)\):

\[
\varepsilon_{\theta\theta} = \frac{U_r(r)}{r} = \frac{||u||}{\sqrt{(x-x_0)^2 + (y-y_0)^2}} \tag{B5}
\]

where \((x_0; y_0)\) is the origin of the cylindrical coordinate system.

Therefore the volumetric swelling is given by:

\[
\varepsilon_v = tr(\varepsilon) = 3 \varepsilon_{\theta\theta} = 3 \times \frac{||u||}{\sqrt{(x-x_0)^2 + (y-y_0)^2}} \tag{B6}
\]

2. Example and validation

The method proposed for the estimation of the adsorption-induced volumetric swelling is applied on an activated carbon saturated with pure CO\(_2\) at \(T = 303.15 \text{ K}, P_b = 50.8 \text{ bar}\). The resulting full-field deformation estimation performed by the DIC technique is presented in Figure 3.a.

In order to estimate the volumetric swelling through Eq. B5, the origin of the cylindrical coordinate system has to be identified. For this purpose, the norm of the displacement field is interpolated by cubic spline using Scilab software (the interpolation area is represented by a red square in Figure 3.a) and the origin is defined as the point \((x_0 = 563.5 \text{ px}; y_0 = 577.2 \text{ px})\) where the interpolated field reaches its minimum. Figure 10.b presents the ortho-radial strain estimated in the interpolation area by Eq. B5. A typical constant ortho-radial strain field is obtained in all the interpolation area except in the vicinity of the cylindrical coordinate origin point where a peak artefact is observed. Finally, the volumetric strain is estimated by averaging the ortho-radial strain field in the interpolation area where a mask (represented in white in Figure 10.b) is applied in the vicinity of the cylindrical coordinate origin point to minimize the influence of the artefact peak. The mask dimensions are \(150 \times 150 \text{ pixels}\), which represents \(5.6 \%\) of the interpolation area. A volumetric swelling of \(\varepsilon_v = 2.766 \pm 0.003 \%\) is obtained.

The validation of the proposed method is performed by comparing the strain field estimated based on classical continuum mechanics (Eq. B2-B3).

Based on continuum mechanics (Eq. B2-B3), one obtains:

\[
\begin{align*}
\varepsilon_{rr} &= 0.947 \% \quad ; \quad \varepsilon_{\theta\theta} = 0.920 \% \quad ; \quad \varepsilon_{r\theta} = 0.003 \%
\end{align*}
\]

Therefore, one indeed observes that \(\varepsilon_{rr} \approx \varepsilon_{\theta\theta}, \varepsilon_{r\theta} \approx 0\) and \(\varepsilon_v \approx 3 \times \varepsilon_{\theta\theta}\).

Appendix C: Cycling effect and material compaction

This appendix and Figure 11 present the influence of three different loading cycles on both adsorption/desorption isotherms and volumetric swelling strain for an active carbon firstly saturated with pure CH\(_4\) at \(T = 303.15 \text{ K} \pm 0.1 \text{ K}\) and then saturated with pure CO\(_2\) at \(T = 318.15 \text{ K} \pm 0.1 \text{ K}\). The process to produce the active carbon composes three phases: first the carbon is grinded, then it is activated and finally it is compacted to obtain a cylindrical sample. During the first cycle of gas adsorption, there is a competition between a grain compaction shrinkage and the adsorption-induced volumetric swelling and a large hysteresis is observed because of the material compaction. This compaction is mostly irreversible and after the first cycle, the second and the third cycles are superimposed. Note that a small hysteresis remains because a small part of the compaction...
phenomenon is elastic. In Figure 6 are presented the data acquired during the third cycle for both CH$_4$ and CO$_2$ gas adsorption.

**Appendix D: Collected experimental data**

This appendix collects the experimental data presented in Figure 6.

### TABLE II. Collected experimental data in term of relative bulk pressure ($P_b$), excess adsorbed quantities ($n^{ex}$) and swelling strain ($\varepsilon_{sw}$) for an activated carbon saturated with pure CH$_4$ at $T = 303.15$ K $\pm 0.1$ K.

<table>
<thead>
<tr>
<th>$P_b$ (bar)</th>
<th>$n^{ex}$ (mmol.g$^{-1}$)</th>
<th>$\varepsilon_{sw}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.850±0.005</td>
<td>0.846±0.003</td>
<td>0.046±0.006</td>
</tr>
<tr>
<td>11.280±0.005</td>
<td>2.316±0.011</td>
<td>0.174±0.022</td>
</tr>
<tr>
<td>24.045±0.005</td>
<td>3.485±0.025</td>
<td>0.404±0.029</td>
</tr>
<tr>
<td>39.285±0.005</td>
<td>4.338±0.045</td>
<td>0.673±0.063</td>
</tr>
<tr>
<td>55.915±0.005</td>
<td>4.886±0.071</td>
<td>0.909±0.083</td>
</tr>
<tr>
<td>74.190±0.005</td>
<td>5.333±0.104</td>
<td>1.145±0.073</td>
</tr>
<tr>
<td>92.870±0.005</td>
<td>5.627±0.144</td>
<td>1.365±0.036</td>
</tr>
<tr>
<td>105.230±0.005</td>
<td>5.853±0.185</td>
<td>1.503±0.064</td>
</tr>
<tr>
<td>72.140±0.005</td>
<td>5.301±0.215</td>
<td>1.226±0.077</td>
</tr>
<tr>
<td>49.090±0.005</td>
<td>4.635±0.235</td>
<td>0.953±0.089</td>
</tr>
<tr>
<td>32.930±0.005</td>
<td>3.931±0.248</td>
<td>0.712±0.100</td>
</tr>
<tr>
<td>21.810±0.005</td>
<td>3.156±0.257</td>
<td>0.542±0.094</td>
</tr>
<tr>
<td>14.090±0.005</td>
<td>2.474±0.263</td>
<td>0.376±0.074</td>
</tr>
<tr>
<td>8.805±0.005</td>
<td>1.815±0.267</td>
<td>0.254±0.056</td>
</tr>
<tr>
<td>5.230±0.005</td>
<td>1.201±0.269</td>
<td>0.185±0.045</td>
</tr>
<tr>
<td>2.795±0.005</td>
<td>0.643±0.271</td>
<td>0.098±0.026</td>
</tr>
<tr>
<td>1.115±0.005</td>
<td>0.200±0.272</td>
<td>0.079±0.016</td>
</tr>
</tbody>
</table>

### BIBLIOGRAPHY

FIG. 11. Simultaneous adsorption and induced swelling measurements (three cycles) for an activated carbon filled with pure CO$_2$ and pure CH$_4$ at $T = 318.15$ K and $T = 303.15$ K respectively: (a) excess adsorption isotherm; (b) volumetric induced swelling.