Adsorption-Induced Expansion of Graphene Oxide Frameworks: Observation by In Situ Neutron Diffraction

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ABSTRACT: We have investigated adsorption-induced deformation in graphene oxide framework materials (GOFs) using neutron diffraction at sample pressures up to 140 bar. GOFs, made by the solvothermal reaction of graphite oxide and benzene-1,4-diboronic acid, are a suitable candidate for deformation studies due to their narrow (~1 nm), monodispersed, slit-shaped pores whose width can be measured by diffraction techniques. We have observed, in situ, a monotonic expansion of the slit width with increasing pressure upon adsorption of xenon, methane, and hydrogen under supercritical conditions. The expansion of ~4% observed for xenon at a pressure of 48 bar is the largest deformation yet reported for supercritical adsorption on a carbonaceous material. We find that the expansion of the three gases can be mapped onto a common curve based solely on their Lennard-Jones parameters, in a manner similar to a law of corresponding states.

1. INTRODUCTION

The expansion of carbon-based materials upon molecular adsorption has been known for many years.1−3 Most thoroughly studied has been adsorption from the liquid state where the expansions observed are the largest.1−11 However, pore dynamics in response to supercritical adsorption has been subjected to much less experimental investigation. It is desirable to address this situation on two accounts. From a technological perspective, supercritical adsorption has a potential role in such areas of current interest as methane capture, hydrogen storage, battery materials, and gas separation.14−18 Also, from a fundamental perspective, supercritical adsorption allows the study of systems in which the dominant interactions are described by van der Waals potentials and hence are more tractable theoretically.19 Here, we report experimental investigation of the expansion induced by van der Waals gases in an adsorbent well described by “slit-shaped” pores, materials known as graphene oxide frameworks (GOFs).20

Early studies with liquid adsorbents on graphite oxide (GO)20−22 showed its interlayer spacing to increase by as much as 50% upon adsorption of polar solvents with as many as two layers of molecules intercalating between the GO sheets. Later results6 demonstrated a strong temperature dependence of the structure of these same graphite oxide/alcohol complexes. More recently, interest in exfoliating GO to produce graphene has revived research in these GO/solvent systems.23−25 The correlation between a solvent’s chemical properties and the degree of expansion has been investigated for a variety of solvents of different polarity, molecular size, and strength of interaction with the adsorbent.7,8 Remarkably, in the case of water adsorbed in graphite oxides, the system shows a negative thermal expansion coefficient12 and a negative compressibility at mechanical pressures up 1.5 GPa.21

An adsorbent response to the adsorption of a van der Waals gas has been observed for a few carbon-based materials including activated carbon and carbon xerogels. The most common experimental technique for studying adsorption-induced deformation has been dilatometry.1,22,25 We note that dilatometry measures the macroscopic length change of a bulk sample with a resolution typically on the order of micrometers and sample lengths on the order of centimeters. Balzer et al.23,24 used dilatometry to study the deformation of carbon xerogels caused by adsorption of gases N2, Ar, CO2, and H2O under subcritical conditions. For all four gases, they observed an initial contraction followed by an expansion as the gas approached the saturated vapor pressure. Shkolin and Fomkin25 measured the expansion of an activated carbon upon the adsorption of supercritical methane using a similar experimental setup. They also observed an initial contraction.
followed by an expansion with a maximal strain of $\sim 0.2\%$ at 60 bar.

In addition, small-angle neutron and X-ray scattering have also been used to study pore deformation upon adsorption$^{26,27}$ at subcritical temperatures. In contrast to dilatometry, these techniques offer the advantage of being able to probe on a length scale of $\sim 1-10$ nm. Bahadur et al.$^{26}$ observed an initial expansion of activated carbon upon adsorption of CO$_2$ followed by a contraction as the gas approached saturation, a strain isotherm that differs markedly from that observed by Balzer et al.$^{23}$ Detailed analysis of measurements on activated carbon is difficult due to the variety of pore shapes and sizes. For this reason, it is desirable to perform measurements on more uniform materials, that is, with a unimodal pore shape and a monodispersed pore size.

As will be discussed below, a number of authors have attempted to compute the response of an adsorbent during sub- and supercritical adsorption.$^{13,28-31}$ In these studies, the adsorbent is typically modeled as containing uniform slit-shaped pores with walls connected by a linear spring. Such models have yielded an expansion for small pores, contraction for large pores, and nonmonotonic behavior for intermediate cases.

In this paper, we demonstrate that materials called graphene oxide frameworks (GOFs), which have well-defined slit-shaped pores, permit an in situ measurement of pore width by neutron diffraction. Such measurements can provide a valuable test of theoretical models and/or computer simulations of adsorption-induced expansion. GOFs have been recently investigated for applications in catalysis,$^{32}$ separation,$^{33}$ battery materials,$^{34}$ and gas storage.$^{20,35-37}$ In contrast to activated carbons, which have a disordered pore structure, GOFs are made with a rational design that provides a route to fabricating complex and functional carbon adsorbents. They contain a more ordered pore geometry than activated carbons, while still achieving surface areas up to 1000 m$^2$/g.$^{36}$ A synthesis using an intercalation procedure was originally proposed by Burress et al. in 2010.$^{20}$ It entailed dissolving benzene-1,4-diboronic acid (DBA) in methanol and then intercalating the DBA into graphite oxide. The authors proposed a reaction of DBA with the hydroxyl groups of the graphite oxide, resulting in a covalent cross-linking of the sheets as shown in Figure 1a. Mercier et al.$^{36}$ proposed an alternative model of GOFs in which the DBA molecules are physically adsorbed between oxidized areas of adjacent graphene sheets rather than covalently bonded to them (Figure 1b). They gave several reasons justifying their model, including the observation that GOFs swell by as much as 50% when wetted with methanol. Such swelling would be unlikely within the covalently cross-linked model with DBA molecules perpendicular to the GO layers. Presumably, these two models would also have markedly different strain isotherms. As discussed in the next sections, we have used volumetric adsorption isotherms and in situ neutron diffraction to investigate the gas pressure-induced expansion of GOFs and find that they can be mapped onto a common curve depending on the van der Waals parameters of the gas/solid interactions.

## 2. EXPERIMENTAL SECTION

### 2.1. GOF Synthesis and Characterization.

We made graphene oxide (GO) from a synthetic graphite powder (Alfa Aesar, 7–11 micron) using a modified Hummer’s method.$^{38}$ The quality of the GO was confirmed with Fourier transform infrared (FTIR) spectroscopy (Figure S1) and X-ray diffraction (XRD) (Figure 2). The interlayer spacing increased from 0.335 nm (graphite) to 0.811 nm (GO) consistent with previous values for well-oxidized carbon sheets.$^{36,39,40}$ Peaks in the FTIR spectrum at 725, 1400, and 1100 cm$^{-1}$ are attributed to the presence of carbonyl, hydroxyl, and epoxide groups, respectively,$^{39,41}$ and provide further confirmation of a

![Figure 1. Postulated models of GOFs: (a) Covalently cross-linked model of ref 20. (b) Parallel linker model of ref 36. Color scheme: H: gray; B: pink; C: cyan; O: red.](image)

![Figure 2. Comparison of the XRD scans for GO and GOF. An interlayer spacing of 1.03 nm is within the range of previously reported GOF samples20,36 (0.90–1.05 nm).](image)
standard GO composition (see the Supporting Information Figure S1).

To produce GOFs for the in situ neutron scattering measurements, we used the optimized synthesis parameters established by Mercier et al.\(^6\) including linker ratio and reaction temperature and time. A mass ratio of 1:3 GO:benzene-1,4-diboric acid (DBA) (Sigma-Aldrich) was added to methanol. The solution was placed on a vortex shaker to dissolve the acid and disperse the GO and then decanted into a metal-jacketed acid digestion vessel to facilitate a closed reaction at elevated temperatures. The vessel was placed in an oven at 90 °C for 24 h. After removal from the oven, the solution was transferred into a falcon tube and centrifuged to separate the GOF from solution with the excess methanol and DBA decanted off. The centrifugation step was repeated multiple times, adding methanol each time, to remove excess DBA. The samples were then dried in a vacuum oven at 60 °C for 24 h to remove residual methanol. GOFs were characterized with XRD, nitrogen sorption, and prompt gamma activation analysis (PGAA) to confirm the samples shared the same pore structure and linker concentration as those previously reported in the literature.

Established properties of GOF include a relatively high specific surface area (∼400 m\(^2\)/g or greater), a high concentration of subnanometer pores, an expanded interlayer spacing of ∼9.5 Å (dry)/∼10.5 Å (in air), and an ∼3 at% concentration of boron (from DBA linker).\(^20,36\) We present characterization data of all synthesized batches in the Supporting Information (Figures S6–S12). The best batch, judged by the above criteria, was then selected for in situ neutron diffraction scattering measurements and is discussed here. Due to limited beam time at the neutron scattering facility, observations of adsorption induced expansion were limited to this batch.

PGAA measurements\(^42\) (Figure S2) revealed our GOF contained 3.4 wt % boron, equivalent to a C:DBA ratio of about 35:1. This DBA linker concentration is comparable to those observed by Mercier et al.\(^36\) (46:1) and Burress et al.\(^20\) (33:1 to 55:1). XRD measurements (Figure 2) were taken on a Scintag X2 diffractometer, using a Cu K\(\alpha\) source (0.154 nm wavelength). The interlayer spacing, \(d_{001}\) calculated from the sample’s (001) Bragg reflection, increased from 0.81 nm for the GO precursor to 1.03 nm for the GOF. This increase indicates successful incorporation of the DBA molecules between the GO sheets and is consistent with interlayer spacings previously observed for GOFs (0.9–1.1 nm).\(^20,36,43\)

The crystallite dimension, \(\kappa\lambda/(\beta\cos\theta)\), was also extracted from the XRD data (Figure 2) where \(\kappa\) is a shape factor chosen to be 0.9, \(\lambda\) is the X-ray wavelength, \(\beta\) is the full-width-at-half-maximum of the (001) Bragg reflection in radians, and \(\theta\) is the Bragg angle.\(^44\) The crystallite domain size normal to the graphene sheets of the GO sample in Figure 2 is ∼13.7 nm compared to ∼16.9 nm for the GOF. Interestingly, both dimensions correspond to about 17 stacked GO sheets, suggesting that incorporation of the DBA does not markedly change the stack size.

Subcritical nitrogen isotherms (Figure 3) were measured on a Quantachrome Autosorb 1-c. Samples were outgassed at 120 °C without exposure to air before nitrogen loading. The BET surface area was determined with a \(P/P_0\) range of 0.01 to 0.03 suitable for nanoporous materials.\(^45\) The measured specific BET surface area, \(\Sigma = 390 \text{ m}^2/\text{g}\), is within or close to the ranges reported for GOFs in the literature (410–1030 m\(^2\)/g\(^46\) and 70–470 m\(^2\)/g\(^20\)). We observed an extended hysteresis loop between the adsorption and desorption legs of the nitrogen isotherm. Such behavior is not one of the canonical subcritical nitrogen isotherms enumerated by the IUPAC.\(^45\) It was an early indication that the pore structure may be changing as a function of amount adsorbed.

We extracted the pore size distribution (Figure 4) from the nitrogen isotherm data using the QSDFT model for slit-shaped pores.\(^46\) As previously observed with GOFs, the majority of the pore volume comes from pores of width < 1.0 nm with the mode of the distribution at ∼0.7 nm. Some degree of caution must be observed when interpreting pore size distributions calculated from nitrogen adsorption isotherms. Quantitative conclusions are especially difficult for pores of width comparable to the size of the adsorbate molecules, as they are expected to be in our GOF samples, due to the long equilibration times for pore filling at \(P/P_0 < 10^{-4}\).\(^47\) With this...
caution in mind, the pore size distribution and the XRD data provide a consistent model of the pore structure of our GOF sample. Pore size distributions measure the void distance between the GO sheets defining the slit, whereas XRD measures \( d_{001} \), i.e., the center-of-carbon to center-of-carbon distance between GO sheets. The difference between these two measures of the pore width is approximately the diameter of a GO carbon atom (\( \sim 0.3 \) nm). Therefore, the peak in the XRD at 1.03 nm (Figure 2) is consistent with the slit-pore width of \( \sim 0.7 \) nm observed in the pore size distribution. The total pore volume, \( V_{\text{pore}} = 0.24 \text{ cm}^3/\text{g} \), was determined from the adsorbed volume at \( P/P_0 = 0.99 \).

2.2. Adsorption Experiments. We performed adsorption measurements with a custom-built volumetric gas adsorption apparatus capable of measurements up to 140 bar. The manifold is equipped with a digital temperature sensor and two transducers to measure pressures ranging from \( 10^{-9} \) to 245 bar. Sample temperature is regulated with a Lakeshore 336 temperature controller with a platinum resistance thermometer mounted on the cold finger of a bottom loading liquid nitrogen cryostat. For calculation of adsorbed quantities, pressure and temperature are mapped to densities through the NIST REFPROP database.

The instrument was checked for accuracy with a well-characterized commercial carbon sample, MSC-30 (Mead-Westvaco). High-purity gas has been used in all experiments (99.995% purity hydrogen, 99.99% purity methane and xenon). For all adsorption measurements, approximately 400 mg of the GOF sample was placed in an aluminum sample cell and outgassed under vacuum at 120 °C for 12 h.

2.3. Neutron Diffraction. Neutron diffraction is well-suited for the in situ structural investigation of GOF expansion in that neutrons can penetrate the high-pressure aluminum sample cell. Our neutron diffraction patterns in Figure 5 were obtained using a two-axis diffractometer equipped with a five-counter multidetector data acquisition system located at C-port of the University of Missouri Research Reactor.49 The measurements were performed in a transmission geometry and with a neutron wavelength of 0.433 nm, appropriate for the large interlayer distances of a GOF. Each diffraction pattern took \( \sim 20 \) h with a 0.25° step size in the arm position. Within the \( Q \)-range available, only the first GO/GOF reflection labeled \( (001) \) (see Figure 5a,b), corresponding to the interlayer separation \( d_{001} \), is observable. The small peak at \( \sim 16 \text{ nm}^{-1} \) is due to the presence of a glass wool filter in the sample cell. Each diffraction peak was fit with a Gaussian plus a linear background (Figure 5c) where the peak center is at the position \( Q_{001} = 2\pi/d_{001} \). While the background across the full \( Q \)-range in Figure 5a,b is clearly not linear, it is a satisfactory approximation in the region of the \( (001) \) peak (see Figure 5c).

3. RESULTS

3.1. Adsorption Isotherms. We measured adsorption isotherms of the following gases on GOFs at the temperature(s) indicated: hydrogen (78 K and 293 K), methane (293 K), and xenon (293 K) (see Figure 6). These van der Waals...
gases were selected based on two primary criteria: (1) the technological interest in hydrogen and methane as energy carriers and (2) the wide range of their critical temperatures: 33.2 K (H₂), 190.8 K (CH₄), and 289.8 K (Xe). As we shall see, the magnitude of the adsorption-induced expansion turns out to depend on the critical temperature. The measurement of hydrogen excess adsorption on a GOF at 78 K and 293 K has been reported by at least two other groups, whereas methane and xenon isotherms have not been reported previously. Further discussion of applications to hydrogen storage is in the Supporting Information.

In Figure 6a, we show the amount adsorbed in terms of the Gibbs excess, \( N_{\text{exc}} \), defined as the difference (normalized to the adsorbent mass) between the number of adsorbed gas molecules in the system and the number that would be present at the same temperature and pressure in the absence of the adsorbent. The Gibbs excess is the most direct experimental quantity available in that the only material parameter required in its calculation is the skeletal volume of the adsorbent (volume of sample inaccessible to gas). We also report (Figure 6b) the absolute adsorption, \( N_{\text{abs}} \), defined as the total number of adsorbed gas molecules per mass of the adsorbent, a more basic physical quantity than the Gibbs excess except that it requires introducing the total pore volume, \( V_{\text{pore}} \), of the adsorbent as a parameter (see section 2.1). The absolute adsorption \( N_{\text{abs}} \) may be calculated from the excess adsorption using

\[
N_{\text{abs}} = N_{\text{exc}} + \rho_{\text{bulk}} V_{\text{pore}}
\]

where \( \rho_{\text{bulk}} \) is the density of the bulk gas in the system.

3.2. Diffraction. At each point along the adsorption isotherms of the three gases adsorbed on our GOF sample (Figure 6), we obtained an in situ neutron diffraction pattern (Figures S3, S4, and S5). Unfortunately, time constraints did not allow tandem isotherm/diffraction measurements with adsorbed \( N_2 \). In the time available, we felt that extending the range of critical temperatures down to 33 K as offered by H₂ as well as investigating the expansion of the adsorbate (such as capillary condensation). However, the isotherm of each of our gases is measured at supercritical conditions; thus, no phase change of the bulk fluid occurs.

Xenon shows the largest increase in \( d_{001} \) with pressure. To our knowledge, the 4% increase in \( d_{001} \) that we have observed at a maximum bottle pressure of 48 bar is the largest expansion reported for supercritical adsorption. Furthermore, the interlayer spacing is still increasing at this pressure.

4. DISCUSSION

Given that at supercritical temperatures, the interaction of methane, hydrogen, and xenon with the GO sheets of GOFs is well described by van der Waals interactions, we seek a more general understanding of the expansion observed. In Figure 7, the dependence of \( d_{001} \) on pressure changes significantly with gas and temperature. In all cases, however, the expansion begins rapidly and then slows down as the pressure increases in a way that is reminiscent of the absolute adsorption isotherms \( N_{\text{abs}}(P) \) shown in Figure 6. This behavior suggested plotting the interlayer spacing \( d_{001} \) as a function of the absolute amount of adsorbed gas \( N_{\text{abs}} \) in the pores as shown in Figure 8. Now, the observed expansion of the GOF under the pressure of Xe and CH₄ does not level off at high adsorption. This dependence of \( d_{001} \) on \( N_{\text{abs}} \) motivated us to consider whether the expansion could be explained in terms of the interaction strength of the gases with the GO sheets.

Figure 7. Expansion of \( d_{001} \) of GOF as a function of pressure for Xe, CH₄, and H₂ at temperature above their critical temperature. In the case of H₂, data is presented at two temperatures, 79 and 293 K.

Figure 8. Interlayer spacing \( d_{001} \) as a function of the absolute amount of gas adsorbed in the pores \( N_{\text{abs}} \) (cf. Figures 6 and 7). The expansion versus the amount adsorbed does not level off at high \( N_{\text{abs}} \) for Xe and CH₄.
During the past decade, a theoretical basis for adsorption-induced deformation of porous materials has been investigated by several authors.\textsuperscript{28,31} A model of carbonaceous slit-shaped pores connected by a linear spring showed them to deform during adsorption with an expansion observed for small pores \( d_{001} < 0.84 \text{ nm} \) and contraction for larger ones \( d_{001} > 1.23 \text{ nm} \). A nonmonotonic pore response was found for intermediate widths. For slit pores with a \( d_{001} \approx 0.94 \text{ nm} \), which dominate our GOF sample, the dependence of interlayer spacing on pressure was predicted to contract initially before expanding above a certain pressure,\textsuperscript{28} whereas we observe a monotonic expansion in our system. These results suggest that the assumption of slit pores spanned by a linear spring as in refs 17 and 20 may not adequately represent the response of a GOF for which a more complex linker/spacer framework may suppress contraction.

In our analysis, we begin by hypothesizing that the expansion of the adsorbent results from the energy deposited into the system in the adsorption process. In other words, we make the ansatz that \( d_{001} \) has the functional dependence

\[
d_{001} = F(N_{abs} \epsilon_{abs})
\]

where \( N_{abs} \) is the number of adsorbed molecules (absolute adsorption) and \( \epsilon_{abs} \) is the depth of the holding potential for adsorption on a GO sheet. As will be discussed further below, we note that \( N_{abs} \) includes molecules in the sample that are not between the graphene sheets; however, we make the simplifying assumption that the number of molecules between the sheets is proportional to \( N_{abs} \). A reasonable approximation for the holding potential of a GO sheet is given by Steele’s potential: \textsuperscript{53,54}

\[
V_{10-4}(z) = 4\pi \rho \sigma^2 \epsilon_{sd} \left( \frac{1}{4} \left( \frac{\sigma_{sd}}{z} \right)^4 - \frac{1}{2} \left( \frac{\sigma_{sd}}{z} \right)^6 \right)
\]

(3)

Here, \( \rho = 38.2 \text{ nm}^{-2} \) is the areal density of carbon atoms in a graphene sheet and \( \sigma_{sd} \) and \( \epsilon_{sd} \) are the Lennard-Jones solid–fluid interaction parameters calculated using the Lorentz–Berthelot combination rules: \textsuperscript{55}

\[
\sigma_{sd} = \frac{\sigma_s + \sigma_f}{2}, \quad \epsilon_{sd} = \sqrt{\epsilon_s \epsilon_f}
\]

(4)

\( \sigma_s \) and \( \epsilon_{sd} \) and \( \sigma_f \) and \( \epsilon_{ff} \) are the solid and fluid parameters, respectively. In assuming this holding potential, we are neglecting the contribution from functional groups attached to the graphene. The potential depth is the minimum of \( V_{10-4} \) (eq 3):

\[
\epsilon_{abs} = \left( \frac{6\pi}{5} \right) \rho \sigma^2 \epsilon_{sd}
\]

(5)

For the carbon atoms in a GO sheet, we take \( \sigma_s = 0.34 \text{ nm} \) and \( \epsilon_{sd}/k_B = 28 \text{ K} \). Additionally, we take \( \sigma_{sd,H_2} = 0.305 \text{ nm} \), \( \sigma_{CH_4,H_2} = 0.373 \text{ nm} \), \( \epsilon_{Xe,Xe}/k_B = 0.407 \text{ nm} \), \( \epsilon_{sd,H_2}/k_B = 37 \text{ K} \), \( \epsilon_{CH_4,H_2}/k_B = 148 \text{ K} \), and \( \epsilon_{Xe,H_2}/k_B = 226 \text{ K} \). With these values, we obtain \( \epsilon_{abs}(H_2)/k_B = 482 \text{ K} \), \( \epsilon_{abs}(CH_4)/k_B = 1180 \text{ K} \), and \( \epsilon_{abs}(Xe)/k_B = 1600 \text{ K} \). For the gases considered here, there is, to a good approximation, a direct proportionality between \( \epsilon_f \) and the square root of their critical temperature \( T_c \). Using eq 4, \( \epsilon_f \propto T_c^{1/2} \), and eq 5, we rewrite eq 2 as

\[
d_{001} = F(N_{abs} \sqrt{T_c} (\sigma_{ss} + \sigma_{ff}))
\]

(6)

Figure 9 shows the dependence of the \( d_{001} \) spacing on \( N_{abs} \) after scaling with respect to the critical temperature of the adsorbed gas and its Lennard-Jones sigma parameter \( \sigma_{sd} \) (normalized to the values for Xe), according to eq 6. Here, we have assumed that the number of gas molecules between the GO sheets is proportional to \( N_{abs} \). After scaling, the methane and xenon data points nearly superimpose. Overall, the overlap indicates that our ansatz was a good starting point; the interlayer expansion does appear to be a function of \( N_{abs}\epsilon_{abs} \) (we also obtain a posteriori justification for the assumption of the holding potential in eq 3).

Although scaling according to eq 6 allows Xe and CH\textsubscript{4} to share a common curve, it is evident that the fit for H\textsubscript{2}, which shows the smallest expansion, is poor. This situation is similar to the law of corresponding states where gas and liquid adsorption curves for many atoms and molecules can be cast into a common curve,\textsuperscript{57,58} while light H\textsubscript{2} and He deviate from this common curve due to quantum effects. However, it is difficult to make a quantitative estimate of quantum effects on the GOF expansion for H\textsubscript{2}. Another possible explanation that we have considered for the poorer fit of H\textsubscript{2} to the curve shared by Xe and CH\textsubscript{4} in Figure 9 is a change in the GOF structure on increasing pressure. In the case of H\textsubscript{2}, we observed the slope of the linear background on which the Bragg peak rides to increase at pressures in a range of 20–60 bar and an increase in the width of the Bragg peak in a range of 80–100 bar (see Figure 5 and Figure S5). These changes are consistent with a decrease in the GOF average grain size and occur at pressures where the deviation of H\textsubscript{2} from the common curve is the largest. In the case of our measurements on CH\textsubscript{4}, at pressures up to 100 bar, which followed those on H\textsubscript{2}, these effects decreased in magnitude and do not appear to have had an effect on the determination of \( d_{001} \). Our subsequent measurements on Xe were confined to pressures below 40 bar and showed no evidence of a decrease in the GOF grain size. Therefore, although we cannot rule out the presence of quantum effects in the GOF expansion observed for H\textsubscript{2}, its deviation from the curve common to Xe and CH\textsubscript{4} appears to be consistent with a decrease in the GOF grain size at high
pressures. In future measurements, it would probably be desirable to subject a GOF sample to several pressure cycles before beginning the diffraction measurements.

As shown in Figure 7, we have observed a significant expansion of the interlayer spacing of GOF for all three gases (~1.5% for H₂, ~3% for CH₄, and ~4% for Xe). Presumably, the Xe expansion would continue to increase at higher pressure. It is significant that the largest expansion occurs for Xe. With the largest polarizability and ε₆ of the three gases, it has the strongest van der Waals interaction with the GO sheets.

Next, we note in Figure 9 that the expansion of the interlayer spacing of Xe increases more rapidly above an inflection point at ~1.5 mol/kg. We suggest that this change in the expansion rate may be related to the completion of a fully compressed monolayer within the dominant slit-shaped pores of width of ~0.7 nm. The inflection point in the expansion might then represent the absolute adsorption at which the gas reaches liquid densities and it becomes easier to separate the GO sheets of the GOF than to compress the gas further. We can estimate the adsorbed density from the relation $\rho_{ads} = M_{ads}/V_{pore}$ where $M_{ads} = N_{ads}M$, $M$ is the molecular weight of the gas, and, from section 2.1, $V_{pore} = 0.242$ cm$^3$/g. In Figure 10, we have plotted the interlayer spacing $d_{001}$ versus the adsorbed density of Xe. We see that the inflection point falls close to the liquid density of Xe at its critical point, 1.16 g/cm$^3$, consistent with the scenario that we have described above.

5. CONCLUSIONS

In summary, we have observed a reproducible monotonic pore expansion in GOFs on increasing gas pressure, the largest such expansion yet observed for supercritical adsorption. Thus, we believe that GOFs provide useful model systems for studying the effect of adsorption on deformable slit-shaped pores. In addition, we have shown that the expansion observed for H₂, CH₄, and Xe can be scaled onto a single curve based on the gas critical temperature and molecular diameter in a way similar to the law of corresponding states. Future investigations of other van der Waals gases would be desirable to corroborate this scaling behavior. Nitrogen, whose subcritical adsorption isotherm showed hysteresis indicative of a pore structure changing with the amount adsorbed (Figure 3), would be of particular interest. With a critical temperature of 126 K and a molecular size comparable to CH₄, we would expect N₂ to yield an expansion intermediate between CH₄ and H₂. We estimate argon to have an expansion similar to N₂ based on its critical temperature (151 K) and smaller size. The scaling analysis used to interpret our measurements should also provide guidance to molecular dynamics simulations of supercritical adsorption of van der Waals gases on GOFs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02589.

FTIR and PGAA spectra; all neutron diffraction patterns for each gas and pressure; XRD and nitrogen sorption data for each batch of GOF synthesized; discussion of another figure of merit for our GOF sample (PDF)

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Notes
The authors declare no competing financial interest.

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