Requirements to Determine the Average Pore Size of Nanoporous Media Using Ultrasound

Klaus Schappert* and Rolf Pelster*
FR Physik, Universität des Saarlandes, 66123 Saarbrücken, Germany

ABSTRACT: Liquids in nanoporous media are exposed to an adsorption-induced pressure, a consequence of the interaction with the pore surface. The smaller the pore diameter, \(d_p\), the higher the pressure at saturation and thus the bulk modulus of the confined liquid. Therefore, it has been proposed to use ultrasonic measurements on saturated nanoporous media for the determination of the average pore size. Here, we discuss the requirements for such an analysis. Although predictions for the size-dependent pore pressure and the liquid’s modulus, \(K^{\text{iso}}(d_p)\), are based on isothermal simulations, an experimentalist studying the propagation of ultrasonic waves determines adiabatic moduli, \(K^{\text{ad}}(d_p)\). We show that the quantity relating adiabatic and isothermal moduli, the heat capacity ratio \(\gamma = c_p/c_v\), exhibits a strong pressure dependence for many bulk liquids. In nanopores, this translates into size-dependent \(\gamma(d_p)\), provided the confinement does not alter the heat capacity ratio. Disregarding this effect in the analysis of ultrasonic data would yield an underestimate of the isothermal modulus and thus an overestimate of the average pore size. For a correct analysis, an experimentalist thus needs to know the size dependence of three quantities: the isothermal modulus, adsorption-induced pressure, and heat capacity ratio.

1. INTRODUCTION

It is well known that the adsorption of a fluid in a porous material causes a pressure on the pore surface. This pressure induces a deformation of the porous matrix, which was observed for a multitude of porous materials during the adsorption of a gaseous, liquid, or supercritical fluid. The effect of sorption-induced deformation is a very common phenomenon in nature as a result of the great number of natural porous materials (e.g., shales, clays, coal gangue, charcoal, and sandstones). Several of these media possess pores with a diameter in the range of nanometers. The matrix’s reaction upon sorption of fluids can be exploited for several technical applications. Among others, porous matrices may be used as actuators.

In recent years, a further impact of the deforming pressure caused by adsorbed liquids was revealed by ultrasonic and theoretical studies: the change of the elasticity of the adsorbate. The deforming pressure, usually termed solvation pressure \(p_s\) or adsorption stress, has different contributions. For a given sample, the solvation pressure changes when the curvature of the liquid–vapor interface is modified, e.g., during the initial (isothermal) desorption process. Such a change of the so-called Laplace pressure causes an almost linear change of the longitudinal modulus of the adsorbate [shown for argon (see refs 29 and 36) and implicitly also for \(n\)-hexane (see ref 28)]. The strength of interaction between the adsorbate and pore surface might also modify the adsorption pressure. Thus, different adsorbates exhibit a varying deviation of their elastic moduli from the corresponding bulk values. For a fully saturated sample, the solvation pressure is inversely proportional to the pore radius. Accordingly, theoretical studies for argon in smooth silica pores showed that the isothermal bulk modulus of adsorbed argon, \(K^{\text{iso}}_{\text{ads}}\), is proportional to the inverse pore size \(1/d_p\) with the pore diameter \(d_p\).

These theoretical findings on the impact of the pore size on the elastic modulus of the adsorbate could be used for the determination of the pore size using ultrasound as proposed by Gor. In contrast to standard procedures, such a new method does not require the measurement of a complete sorption isotherm. For the extraction of the elastic properties of the confined fluid from measured effective moduli, only ultrasonic measurements on the empty and saturated sample are needed (see, e.g., refs 34, 43, and 44). Then, the average pore size can be found directly through a comparison with the theoretical calibration curve \([K^{\text{iso}}_{\text{ads}}(d_p)]\). However, the theoretical calculations and simulations yield the pore size dependence of the isothermal values of the moduli, whereas the ultrasonic experiments yield the adiabatic moduli. Thus, the experimental values have to be converted to the isothermal values or vice versa. Generally, the adiabatic and the isothermal moduli, \(K^{\text{ad}}\) and \(K^{\text{iso}}\), are related to each other via the heat capacity ratio \(\gamma = c_p/c_v = K^{\text{ad}}/K^{\text{iso}}\). Here, we study the pressure dependence of this ratio and its influence on the
dependence of the adiabatic modulus on the pore size. Our findings are relevant for the correct determination of the pore size using the combination of ultrasound and simulations.

2. DATA, ANALYSIS, AND DISCUSSION

Recently, calculations of Gor\textsuperscript{30} showed that the isothermal modulus $K_{\text{ads}}^{\text{iso}}$ of argon in smooth nanopores exhibits a proportionality on the inverse pore size (see Figure 1a). This observation is a consequence of an increasing adsorption stress (or solvation pressure) with a decreasing pore size (see Figure 1b). For the determination of the quantities displayed in Figure 1, Gor used classical density functional theory (DFT) (see ref 30 for details). The data in Figure 1a show that the effect of an enhancement of the adsorbate’s modulus is significant. For the smallest pores with a diameter of 2 nm ($1/d_p = 0.5$), the modulus is increased by a factor of $\approx 1.9$ in comparison to the modulus of nonconfined argon, $K_{\text{bulk}}^{\text{iso}}$.

With the knowledge of the dependence of $K_{\text{ads}}^{\text{iso}}$ on the pore size, it is possible to determine an average pore size of a sample, if the isothermal modulus of adsorbed argon is known from measurements. Such a new method for the determination of the pore size was already indicated by Gor\textsuperscript{30} when he published the results shown in Figure 1 (see also ref 31). However, ultrasonic measurements yield the adiabatic values for the moduli, not the isothermal ones. Both quantities are related to each other via the ratio of specific heat, $\gamma$:

$$K^{\text{ad}} = \frac{\gamma p}{\bar{c}} K^{\text{iso}}$$

Generally, the heat capacity ratio depends on temperature. The corresponding $\gamma$-values for bulk argon at its vapor pressure $p_0$ (and at higher pressures) decrease with decreasing temperature, as shown in Figure 2a. The DFT calculations of Gor\textsuperscript{30} were performed for confined liquid argon at 80 K. In contrast to nonconfined argon,\textsuperscript{43,47} bulk argon solidifies already near 84 K.\textsuperscript{36} Thus, for the conversion of the moduli shown in Figure 1, it is necessary to extrapolate $\gamma$ to 80 K (see Figure 2a). The authors in refs 30, 31, and 36 argued that the "parameter $\gamma$ is not sensitive to pressure"\textsuperscript{31} and consequently a constant $\gamma$-value (at the bulk vapor pressure $\gamma = 1.979$ at 80 K) could be used for the conversion between isothermal and adiabatic moduli. However, a study of the literature values for $\gamma$ reveals a decrease of $\gamma$ with increasing pressure (see Figure 2a,b). This strong pressure dependence of the heat capacity ratio significantly influences the values for $K_{\text{ads}}^{\text{iso}}$ in particular for small nanopores. Due to the lack of data below the melting point of argon, we have approximated the pressure dependence of the heat capacity ratio at 80 K with a simple equation: $\gamma = \gamma(p_0) - ap/(bp + 1)$. For the determination of constants $a$ and $b$, we used the values of $\gamma$ at three pressures ($p_0$, $p = 24$ MPa, and $p = 65$ MPa; see Figure 2a). The resulting curve is shown in Figure 2b as a dotted line ($T = 80$ K). The dotted lines at higher temperatures were calculated via the same procedure. In the range where data is available, the agreement between fit and data is so good that the respective curves in Figure 2b...
coincide and cannot be distinguished. What is important in the following analysis is not the accuracy of the extrapolated data but the fact that $\gamma$ depends on pressure. This has an impact on the conversion between isothermal and adiabatic data and thus on the respective size dependence:

$$\frac{K_{ad}(d_P)}{K_{ad}^{bulk}} = \frac{\gamma(p)}{\gamma(p_0)} \frac{K_{iso}(d_P)}{K_{iso}^{bulk}}$$

(2)

Under the simplifying assumption of a constant (pressure-independent) heat capacity ratio $\gamma(p) = \gamma(p_0)$, the relative change of the adiabatic modulus is of course the same as for the isothermal modulus (see also Figure 1a and red symbols in Figure 3b,c). The decrease of $\gamma$ with increasing pressure (see Figure 2b) results in a decrease of $\gamma$ with decreasing pore size (see Figure 3a), as the adsorption pressure increases with the inverse pore size (see Figure 1b). For example, for argon at 80 K in pores with a diameter of $d_P = 2$ nm, the adsorption stress takes the value of 63 MPa (see Figure 1b). At this pressure, $\gamma = 1.653 < \gamma(p_0) = 1.979$ (see Figures 2b and 3a for $1/d_P = 0.5$ nm and $1/d_P = 0$) and thus $\gamma(p)/\gamma(p_0) = 0.835$ holds. Consequently, for argon, the effect of an enhancement of the adsorbate’s modulus is weaker for the adiabatic modulus than that for the isothermal modulus. This becomes noticeable in Figure 3b, which shows the adiabatic modulus as a function of the inverse pore diameter for both a constant heat capacity ratio [red symbols denote simplification $\gamma(p) = \gamma(p_0)$] and the pressure-dependent $\gamma$ (blue symbols). Remarkably, also the adiabatic modulus calculated for the pressure-dependent heat capacity ratio exhibits a proportionality to the inverse pore diameter $d_P$. However, the effect of the pressure dependence of $\gamma$ on the pore size dependence of the adiabatic modulus is considerable, and as expected, it is particularly strong for the smallest pores. The adiabatic modulus for a pore diameter of 2 nm is increased by about 60% compared to its bulk value (instead of 90% for the isothermal modulus). Accordingly, the application of ultrasonic measurements for the determination of the average pore size requires the use of the actual pressure dependence of the heat capacity ratio. Otherwise, the pore size would be considerably overestimated from a measured value for $K_{ad}^{bulk}$ because the calculated value of $K_{ad}^{iso} = K_{ad}^{iso}/\gamma(p_0)$ instead of $K_{ad}^{iso} = K_{ad}/\gamma(p)$ would be too small.

Note that the pressure dependence of the heat capacity ratio significantly complicates the conversion between isothermal and adiabatic moduli in the sense that it requires more data. Under the assumption of a constant $\gamma$, it is necessary to know the dependence of only the isothermal modulus on the pore size: the dependence of the adsorption stress on the pore size is not necessary for the analysis. However, as a result of the existing pressure dependence of $\gamma$, also the knowledge of the pore size dependence of the adsorption stress is indispensable.

We can generalize our finding to other liquids. An analysis of data from the NIST45 reveals that for many liquids (nitrogen, alkanes, and water) the heat capacity ratio decreases with increasing pressure (see Figure 4). Thus, the relative enhancement of the adiabatic modulus of nonconfined liquids is weaker than the enhancement of the isothermal modulus. For alkanes, the pressure dependence of the heat capacity ratio decreases with increasing chain length (see Figure 4b) and thus also the extent of the effect of pressure on the conversion between adiabatic and isothermal moduli. For water, the effect is very weak and the difference is probably almost negligible.

Theoretical analyses (DFT calculations and simulations) must still show whether the dependence of the adsorbate’s modulus on the inverse pore size can be generalized to other adsorbates. However, our above statements are independent of the actual pore size dependence of the isothermal modulus for the different adsorbates.
Simulations and theoretical calculations generally supply the isothermal moduli of the nanoconfined material, whereas ultrasonic measurements yield the adiabatic values. Here, we have shown that it is essential to take the pressure dependence of the heat capacity ratio \( \gamma \) into account for the conversion between isothermal and adiabatic moduli of liquids confined in nanopores. The pressure acting in nanopores is rather high (up to \( \approx 63 \) MPa for argon in a pore with a diameter of 2 nm; see Figure 1b), which results in a considerable reduction of \( \gamma \). Disregarding this fact would cause a significant overestimation of the adiabatic modulus of the confined argon (e.g., by \( \approx 20\% \) for \( d_p = 2 \) nm). For the determination of the pore size from measurements of the adiabatic modulus, the effect is even greater. The actual pore size can be overestimated by more than 50%. As a result of the pressure dependence of the heat capacity ratio, it is also necessary to know the pore size dependence of the adsorption stress for the conversion between isothermal and adiabatic moduli. In summary, for the determination of an average pore size, the experimentalist needs to know the pore size dependence of both the isothermal modulus and the adsorption stress as well as the pressure dependence of the heat capacity ratio. Ideally, simulations could directly supply the adiabatic values of the elastic moduli, which would supersede the conversion between isothermal and adiabatic values. However, currently, such data is not available and a reliable method for the theoretical prediction of the adiabatic modulus of nanoconfinement fluids still has to be found.

As discussed above, the decrease of \( \gamma \) for argon with increasing pressure causes a weaker size dependence of the adiabatic modulus (in comparison to that of the isothermal modulus). Nevertheless, the adiabatic modulus also exhibits a linear dependence on the inverse pore size. (A weaker size dependence of the adsorbate’s modulus lowers, of course, the resolution of adiabatic measurements used to determine an average pore diameter.) Even without knowing the actual pore size dependence of the isothermal modulus for other confined fluids, we can generalize our observation that the pore size dependence of the adiabatic modulus is weaker than that for the isothermal modulus to other fluids, including liquid nitrogen, alkanes, and water. Similar to argon, these fluids exhibit a decreasing heat capacity ratio with increasing pressure (of considerably varying strength). The pressure dependence of the heat capacity ratio for water is rather weak. Thus, the magnitude of the effect will be minor, if the adsorption stress for water is of the same order as that for argon.

Besides the known pressure effects, additional factors (like the pore size, the structure of the pore surface, and the interaction strength between the adsorbate and pore surface) could influence the pressure dependence of the heat capacity ratio in nanoconfined as well as the size dependence of K. In this respect, further theoretical studies (e.g., simulations) and experiments with other adsorbates and porous materials might give some new insights.

3. CONCLUSIONS AND OUTLOOK

Simulations and theoretical calculations generally supply the isothermal moduli of the nanoconfined material, whereas ultrasonic measurements yield the adiabatic values. Here, we have shown that it is essential to take the pressure dependence of the heat capacity ratio \( \gamma \) into account for the conversion between isothermal and adiabatic moduli of liquids confined in nanopores. The pressure acting in nanopores is rather high (up to \( \approx 63 \) MPa for argon in a pore with a diameter of 2 nm; see Figure 1b), which results in a considerable reduction of \( \gamma \). Disregarding this fact would cause a significant overestimation of the adiabatic modulus of the confined argon (e.g., by \( \approx 20\% \) for \( d_p = 2 \) nm). For the determination of the pore size from measurements of the adiabatic modulus, the effect is even greater. The actual pore size can be overestimated by more than 50%. As a result of the pressure dependence of the heat capacity ratio, it is also necessary to know the pore size dependence of the adsorption stress for the conversion between isothermal and adiabatic moduli. In summary, for the determination of an average pore size, the experimentalist needs to know the pore size dependence of both the isothermal modulus and the adsorption stress as well as the pressure dependence of the heat capacity ratio. Ideally, simulations could directly supply the adiabatic values of the elastic moduli, which would supersede the conversion between isothermal and adiabatic values. However, currently, such data is not available and a reliable method for the theoretical prediction of the adiabatic modulus of nanoconfinement fluids still has to be found.

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■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: k.schappert@mx.uni-saarland.de (K.S.).
*E-mail: rolf.pelster@mx.uni-saarland.de (R.P.).

ORCID
Klaus Schappert: 0000-0002-0518-6081
Rolf Pelster: 0000-0001-7235-755X

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Bangham, D. H. The Gibbs Adsorption Equation and Adsorption on Solids. Trans. Faraday Soc. 1937, 33, 805–811.
(2) Gor, G. Y.; Huber, P.; Bernstein, N. Adsorption-Induced Deformation of Nanoporous Materials—A Review. Appl. Phys. Rev. 2017, 4, No. 011303.
(3) Gor, G. Y.; Neimark, A. V. Adsorption-Induced Deformation of Mesoporous Solids. Langmuir 2010, 26, 13021–13027.
(4) Gor, G. Y.; Neimark, A. V. Adsorption-Induced Deformation of Mesoporous Solids: Macroscopic Approach and Density Functional Theory. Langmuir 2011, 27, 6926–6931.
(5) Meehan, F. T. The Expansion of Charcoal on Sorption of Carbon Dioxide. Proc. R. Soc. A 1927, 115, 199–207.
(6) Bangham, D. H.; Fakhoury, N. The Swelling of Charcoal. Part I.-Preliminary Experiments with Water Vapour, Carbon Dioxide, Ammonia, and Sulphur Dioxide. Proc. R. Soc. A 1930, 130, 81–89.
(7) Bangham, D. H.; Fakhoury, N.; Mohamed, A. F. The Swelling of Charcoal. Part II.-Some Factors Controlling the Expansion Caused by Water, Benzene and Pyridine Vapours. Proc. R. Soc. A 1932, 138, 162–183.
(8) Amberg, C. H.; McIntosh, R. A Study of Adsorption Hysteresis by Means of Length Changes of a Rod of Porous Glass. Can. J. Chem. 1952, 30, 1012–1032.
(9) Yates, D. J. C. The Influence of the Polar Nature of the Adsorbate on Adsorption Expansion. *J. Phys. Chem.* 1956, 60, 543–549.

(10) Gor, G. Y.; Huber, P.; Weissmüller, J. Elastocapillarity in Nanopores: Sorption Strain From the Actions of Surface Tension and Surface Stress. *Phys. Rev. Mater.* 2018, 2, No. 086002.

(11) Gor, G. Y.; Bertinetti, L.; Bernstein, N.; Hofmann, T.; Fratzl, P.; Huber, P. Elastic Response of Mesoporous Silicon to Capillary Pressures in the Pores. *Appl. Phys. Lett.* 2015, 106, No. 261901.

(12) Gor, G. Y.; Paris, O.; Prass, J.; Russo, P. A.; Carrott, M. M. L. R.; Neimark, A. V. Adsorption of n-Pentane on Mesoporous Silica and Adsorbed Deformation. *Langmuir* 2013, 29, 8601–8608.

(13) Coudert, F.-X.; Boutin, A.; Fuchs, A. H.; Neimark, A. V. Adsorption Deformation and Structural Transitions in Metal-Organic Frameworks: From the Unit Cell to the Crystal. *J. Phys. Chem. Lett.* 2013, 4, 3198–3205.

(14) Balzer, C.; Waag, A. M.; Gehret, S.; Reichenauer, G.; Putz, F.; Hüsing, N.; Paris, O.; Bernstein, N.; Gor, G. Y.; Neimark, A. V. Adsorption-Induced Deformation of Hierarchically Structured Mesoporous Silica—Effect of Pore-Level Anisotropy. *Langmuir* 2017, 33, 5592–5602.

(15) Balzer, C.; Braxmeier, S.; Neimark, A. V.; Reichenauer, G. Deformation of Microporous Carbon during Adsorption of Nitrogen, Argon, Carbon Dioxide, and Water Studied by in Situ Dilatometry. *Langmuir* 2015, 31, 12512–12519.

(16) Balzer, C.; Wildhage, T.; Braxmeier, S.; Reichenauer, G.; Olivier, J. P. Deformation of Porous Carbons upon Adsorption. *Langmuir* 2011, 27, 2553–2560.

(17) Morak, R.; Braxmeier, S.; Ludescher, L.; Putz, F.; Busch, S.; Hüsing, N.; Reichenauer, G.; Paris, O. Quantifying Adsorption-Induced Deformation of Nanoporous Materials on Different Length Scales. *J. Appl. Crystallogr.* 2017, 50, 1404–1410.

(18) Prass, J.; Mütter, D.; Fratzl, P.; Paris, O. Capillarity-Driven Deformation of Ordered Nanoporous Silica. *Appl. Phys. Lett.* 2009, 95, No. 083121.

(19) Brochard, L.; Vandamme, M.; Pelleng, R. J.-M.; Fen-Chong, T. Adsorption-Induced Deformation of Microporous Materials: Coal Swelling Induced by CO₂−CH₄ Competitive Adsorption. *Langmuir* 2012, 28, 2659–2670.

(20) Vandamme, M.; Brochard, L.; Lecampion, B.; Coussy, O. Adsorption and Strain: The CO₂-Induced Swelling of Coal. *J. Mech. Phys. Solids* 2010, 58, 1489–1505.

(21) Schappert, K.; Pelster, R. Unexpected Sorption-Induced Deformation of Nanoporous Glass: Evidence for Spatial Rearrangement of Adsorbed Argon. *Langmuir* 2014, 30, 14004–14103.

(22) Schappert, K.; Reiplinger, N.; Pelster, R. Correlation between the Sorption-Induced Deformation of Nanoporous Glass and the Continuous Freezing of Adsorbed Argon. *Langmuir* 2016, 32, 7741–7746.

(23) Herman, T.; Day, J.; Beamish, J. Deformation of Silica Aerogel During Fluid Adsorption. *Phys. Rev. B* 2006, 73, No. 094127.

(24) Dolino, G.; Bellet, D.; Faivre, C. Adsorption Strains in Porous Silicon. *Phys. Rev. B* 1996, 54, 17919–17929.

(25) Kuila, U.; Prasad, M. Specific Surface Area and Pore-Size Distribution in Clays and Shales. *Geophys. Prospect.* 2013, 61, 341–362.

(26) Jabłońska, B.; Kityk, A. V.; Busch, M.; Huber, P. The Structural and Surface Properties of Natural and Modified Coal Gangue. *J. Environ. Manage.* 2017, 190, 80–90.

(27) Sharti, P.; Marmiroli, B.; Sartori, B.; Cacho-Nerin, F.; Keckes, J.; Amenitsch, H.; Paris, O. Humidity-Driven Deformation ofOrdered Mesoporous Silica Films. *Bioinspired, Biomimetic Nanoionobionics.* 2014, 3, 183–190.

(28) Page, J. H.; Liu, J.; Abeles, B.; Herbolzheimer, E.; Deckman, H. W.; Weitz, D. A. Adsorption and Desorption of a Wetting Fluid in Vycor Studied by Acoustic and Optical Techniques. *Phys. Rev. E* 1995, 52, 2763–2777.

(29) Schappert, K.; Pelster, R. Influence of the Laplace Pressure on the Elasticity of Argon in Nanopores. *Europhys. Lett.* 2014, 105, No. 56001.

(30) Gor, G. Y. Adsorption Stress Changes the Elasticity of Liquid Argon Confined in a Nanopore. *Langmuir* 2014, 30, 13564–13569.

(31) Gor, G. Y.; Siderius, D. W.; Rasmussen, C. J.; Krekelberg, W. P.; Bernstein, N. Relation Between Pore Size and the Compressibility of a Confined Fluid. *J. Chem. Phys.* 2015, 143, No. 194506.

(32) Dobrzanski, C. D.; Maximov, M. A.; Gor, G. Y. Effect of Pore Geometry on the Compressibility of a Confined Simple Fluid. *J. Chem. Phys.* 2018, 148, No. 054503.

(33) Schappert, K.; Pelster, R. Liquid Argon in Nanopores: The Impact of Confinement on the Pressure Dependence of the Adiabatic Longitudinal Modulus. *J. Phys. Chem. C* 2018, 122, 27425–27432.

(34) Schappert, K.; Pelster, R. Temperature Dependence of the Longitudinal Modulus of Liquid Argon in Nanopores. *J. Phys. Chem. C* 2018, 122, 5537–5544.

(35) Schappert, K.; Pelster, R. Experimental Method for the Determination of Adsorption-Induced Changes of Pressure and Surface Stress in Nanopores. *J. Phys.: Condens. Matter* 2017, 29, No. 06LT01.

(36) Gor, G. Y.; Siderius, D. W.; Shen, V. K.; Bernstein, N. Modulus—Pressure Equation for Confined Fluids. *J. Chem. Phys.* 2016, 145, No. 164505.

(37) Schappert, K.; Naydenov, V.; Pelster, R. Oxygen in Nanopores: A Study on the Elastic Behavior of Its Solid Phases. *J. Phys. Chem. C* 2016, 120, 25989–25995.

(38) Schappert, K.; Pelster, R. Strongly Enhanced Elastic Modulus of Solid Nitrogen in Nanopores. *Phys. Rev. B* 2013, 88, No. 245443.

(39) Schappert, K.; Gemmel, L.; Meisberger, D.; Pelster, R. Elasticity and Phase Behaviour of n-Heptane and n-Nonane in Nanopores. *Europhys. Lett.* 2015, 111, No. 56003.

(40) Lowell, S.; Shields, J. E.; Thomas, M. A.; Thommes, M. Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density; Kluwer Academic: Dordrecht, The Netherlands, 2004.

(41) Rouquerol, F.; Rouquerol, J.; Sing, K. Adsorption by Powders and Porous Solids; Academic Press: London, 1999.

(42) Landers, J.; Gor, G. Y.; Neimark, A. V. Density Functional Theory Methods for Characterization of Porous Materials. *Colloids Surf., A* 2013, 437, 3–32.

(43) Schappert, K.; Pelster, R. Continuous Freezing of Argon in Completely Filled Mesopores. *Phys. Rev. Lett.* 2013, 110, No. 135701.

(44) Makvo, G.; Mulerji, T.; Dvorin, J. The Rock Physics Handbook—Tools for Seismic Analysis of Porous Media, 2nd ed.; Cambridge University Press: Cambridge, U.K., 2009.

(45) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. Thermophysical Properties of Fluid Systems. In NIST Chemistry WebBook; Linstrom, P. J., Mallard, W. G., Eds; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD. https://webbook.nist.gov (retrieved September 16, between October 24 and November 2, and December 3, 2018).

(46) Tecgel, C.; Span, R.; Wagner, W. A New Equation of State for Argon Covering the Fluid Region for Temperatures From the Melting Line to 700 K at Pressures up to 1000 MPa. *J. Phys. Chem. Ref. Data* 1999, 28, 779–850.

(47) Schappert, K.; Pelster, R. Freezing Behavior of Argon Layers Confined in Mesopores. *Phys. Rev. B* 2011, 83, No. 164110.