

State of Hydrogen in Idealized Carbon Slitlike Nanopores at 77 K

Piotr Kowalczyk,^{*,†} Robert Hołyst,[†] Artur P. Terzyk,^{*,‡} and Piotr A. Gauden[‡]

Department III, Institute of Physical Chemistry, Polish Academy of Science, Kasprzaka Str. 44/52, 01-224 Warsaw, Poland, and Physicochemistry of Carbon Materials Research Group, Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarina Str., 87-100 Toruń, Poland

Received November 11, 2005. In Final Form: December 24, 2005

The purpose of this letter is to clarify recent findings and answer to the question: “What is the state of hydrogen in carbon slitlike pores at 77 K?” For this purpose, we determined the volumetric density of hydrogen in idealized carbon pores of molecular dimension at 77 K and pressure up to 1 MPa. We used quantum corrected grand canonical Monte Carlo simulation. We recognized the highest volumetric density of confined hydrogen (around 71% of hydrogen liquid at boiling point) for effective pore width 5.6 Å ($H^* = 3.04$) in the considered pressure range. Our computational results are in agreement with the calculations performed by Wang and Johnson and Rzepka et al. In contrast, we did not observe the high volumetric density of hydrogen in slitlike carbon pores exceeding the density of hydrogen liquid at the boiling point as was reported by Jagiello and Thommes. Moreover, we obtained qualitative agreement between the simulation results and some experimental findings reported by Nijkamp.

In light of the recent growing interest in hydrogen storage and fuel cell applications, it is necessary to develop deep understanding of the mechanism of hydrogen adsorption on carbonaceous materials treated as an effective and potential storage medium.

The purpose of this letter is to determine the volumetric density of hydrogen in idealized carbon slitlike pores of molecular dimensions at 77 K and pressure up to 1 MPa. This property of confined hydrogen is critical for adoption of carbonaceous materials composed of slitlike nanopores (i.e., activated carbons, activated carbon fibers, and others) as an efficient adsorbent for hydrogen storage. The high volumetric density of hydrogen in porous material reduces the size of tank and favorable physical adsorption overcompression method. The recent experimental and computational results show a scatter. This scatter brings us to the current study. Since the volumetric density of hydrogen fluid in nanopores is not directly measured by experiment, we concentrate on the theoretical reports. Rzepka et al.¹ reported volumetric density of hydrogen in idealized carbon slitlike nanopores at 77 K and pressures up to 30 MPa. The authors used standard grand canonical Monte Carlo simulation (GCMC) neglecting the quantum effects for fluid–fluid and solid–fluid interactions. For idealized carbon slitlike pores of width 10 and 7 Å and at 1 MPa, the values of the volumetric density of hydrogen fluid were around 52 and 45 g L⁻¹, respectively (see Figure 7 in ref 1). Wang and Johnson² performed the path integral grand canonical Monte Carlo simulations (PIGCMC) of hydrogen in idealized carbon slitlike pores at 77 K up to 10 MPa. The authors reported the volumetric density of hydrogen fluid 41, 62, 59, and 50 g L⁻¹ at 10 MPa for pore widths 6.2, 9.2, 12.3, and 20.5 Å, respectively (see Figure 2 in ref 2). In another study, Jagiello and Thommes³ reported the density of hydrogen at 77 K up to 0.1 MPa in carbon micropores of different sizes. The authors adopted nonlocal density functional theory (NDFT) for classical fluids neglecting quantum effects for fluid–fluid and solid–fluid interactions. Moreover, the authors used nonoptimized Lennard–Jones parameters without their numerical values.³ According to

this work, the highest volumetric density of hydrogen at 77 K and 0.1 MPa equal to 40 mmol cm⁻³ (i.e., 80.6 g L⁻¹) was observed for the pore having the effective width 3 Å (see Figure 1 in ref 3). *This value exceeds density of hydrogen liquid at the boiling point ($T = 20.268$ K and $\rho = 71$ g L⁻¹).* In other words, the supercritical hydrogen fluid is in liquid state in the smallest carbon slitlike nanopores at 77 K.

From this short summary of recent reports we see that the answer to the question “What is the state of hydrogen in carbon slitlike pores at 77 K?” is a timely and controversial problem. In a series of works by Levesque,^{4,5} Johnson et al.,^{2,6–8} Tanaka et al.,^{9–13} Kowalczyk et al.,¹⁴ and others, the importance of the quantum effects at 77 K and room temperature were recognized. Generally, the adsorption of quantum molecules is smaller than the classical ones due to Heisenberg’s uncertainty principle. The quantum correction enlarges an effective diameter of a molecule in comparison to its classical counterpart and therefore reduces adsorption in nanopores.

For atomic systems, a simple test of the classical hypothesis is obtained by computing the de Broglie thermal wavelength Λ , defined as¹⁵

$$\Lambda = (2\pi\beta\hbar^2/m)^{1/2} \quad (1)$$

here $\beta = (k_b T)^{-1}$, $\hbar = h/2\pi$, m is the mass of an atom, h denotes the Planck’s constant, k_b is the Boltzmann’s constant, and T is

(4) Levesque, D.; Gicquel, A.; Darkrim, F. L.; Kayiran, S. B. *J. Phys.: Condens. Matter* **2002**, *14*, 9285.

(5) Darkrim, F.; Levesque, D. *J. Phys. Chem. B* **2000**, *104*, 6773.

(6) Wang, Q.; Johnson, J. K. *J. Phys. Chem. B* **1999**, *103*, 277.

(7) Wang, Q.; Johnson, J. K. *Mol. Phys.* **1998**, *95*, 299.

(8) Wang, Q.; Challa, S. R.; Sholl, D. S.; Johnson, J. K. *Phys. Rev. Lett.* **1999**, *82*, 956.

(9) Tanaka, H.; Fan, J.; Kanoh, H.; Yudasaka, Y.; Iijima, S.; Kaneko, K. *Mol. Simul.* **2005**, *31*, 465.

(10) Tanaka, H.; El-Merraoui, M.; Kodaira, T.; Kaneko, K. *Chem. Phys. Lett.* **2002**, *351*, 417.

(11) Tanaka, H.; El-Merraoui, M.; Kanoh, H.; Steele, W. A.; Yudasaka, M.; Iijima, S.; Kaneko, K. *J. Phys. Chem. B* **2004**, *108*, 17457.

(12) Tanaka, H.; Kanoh, H.; Yudasaka, M.; Iijima, S.; Kaneko, K. *J. Am. Chem. Soc.* **2005**, *127*, 7511.

(13) Tanaka, H.; Murata, K.; Miyawaki, J.; Kaneko, K.; Kokai, F.; Takahashi, K.; Kasuya, D.; Yudasaka, M.; Iijima, S. *Mol. Cryst. Liq. Cryst.* **2002**, *388*, 429.

(14) Kowalczyk, P.; Tanaka, H.; Hołyst, R.; Kaneko, K.; Ohmori, T.; Miyamoto, J. *J. Phys. Chem. B* **2005**, *109*, 17174.

(15) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1990; p 1.

* Corresponding author.

† Polish Academy of Science.

‡ Nicolaus Copernicus University.

(1) Rzepka, M.; Lamp, P.; de la Casa-Lillo, M. A. *J. Phys. Chem. B* **1998**, *102*, 10894.

(2) Wang, Q.; Johnson, J. K. *J. Chem. Phys.* **1999**, *110*, 577.

(3) Jagiello, J.; Thommes, M. *Carbon* **2004**, *42*, 1227.

the temperature. To justify a classical treatment of static properties, it is necessary that $\Lambda/a \ll 1$, where $a \cong \rho^{-1/3}$ is the mean nearest-neighbor separation and ρ is the number density. For hydrogen at the triple point ($T = 13.8$ K, $\rho = 0.077$ g cm $^{-3}$) $\Lambda = 0.33$ nm and $\Lambda/a = 0.94$. On the basis of the computations on hydrogen storage in the idealized bundle of single-walled carbon nanotubes, published by Levesque et al.,⁴ one can easily show that for hydrogen at 77 K and selected pressures in the bulk phase $p = 0.1, 0.5,$ and 1.0 MPa the de Broglie thermal wavelength is equal to $\Lambda = 0.14$ nm and $\Lambda/a = 0.06, 0.11,$ and 0.14 . Obviously, for hydrogen confined in an external strong potential field the dimensionless quantity Λ/a is different in comparison to the bulk phase due to enhancement of fluid density. For example, for hydrogen adsorbed in open single-walled carbon nanotubes at 77 K and selected pressures given above $\Lambda/a = 0.30, 0.32,$ and 0.33 . On the basis of the values of the density of hydrogen fluid in slitlike carbon nanopores at 77 K and 10 MPa reported by Wang and Johnson² $\rho = 41, 50, 59,$ and 62 gL $^{-1}$, we obtain $\Lambda/a = 0.32, 0.35, 0.36,$ and 0.37 . As one can see on average $\Lambda/a \cong 0.32$ and the condition $\Lambda/a \ll 1$ does not hold. Moreover, quantum behavior of hydrogen adsorbed in narrow pores manifests itself in the quantum sieving effects,^{8,12} which persist up to 300 K.¹⁶

To estimate the volumetric density of hydrogen fluid in idealized slitlike carbon nanopores at 77 K, we performed the GCMC of hydrogen, including quantum corrections in the potentials.^{9,11,12,14} In the GCMC, the single slab of graphite wall consists of four single lattice planes of graphite separated by a uniform spacing $\Delta = 0.335$ nm.¹⁴ All remaining simulation details can be found in the Supporting Information and ref 14. In all simulations, quantum effects were included for both hydrogen–hydrogen and hydrogen–carbon interactions through the Feynman and Hibbs effective potential (FH-GCMC). According to Sesé^{17,18} path integral Monte Carlo studies the second-order Feynman–Hibbs effective potential can be used when the reduced de Broglie thermal wavelength $\Lambda^* \equiv h/(2\pi mk_b T \sigma_{\text{ff}}^2)^{1/2} \leq 0.5$. The Λ^* value for hydrogen at 77 K is 0.47. So, at the considered temperature the Feynman and Hibbs approximation should reproduce the results obtained from the rigorous path integral simulation in the grand canonical ensemble. Detailed description of the intermolecular potentials adopted for the current study is attached to the Supporting Information.

Figure 1 presents the total quantum corrected solid–fluid interaction potential, classical contribution calculated from 10–4 Steele’s potential,¹⁹ and quantum contribution computed from the Feynman–Hibbs method at 77 K. As one can suspect, the classical solid–fluid interaction potential overestimates the solid–fluid interaction energy. Those effects strongly depend on the pore size. They are the highest for the smallest slitlike carbon pores. An increasing pore size causes the reduction of the quantum effects. Note that for the smallest pores quantum effects are very large and should reduce the uptake of hydrogen in comparison to classical treatment of the solid–fluid interactions. Moreover, some of the smallest slitlike pores can accommodate classical hydrogen molecules but they are closed if the quantum contribution is taken into account.

In Figure 2, we display the adsorption isotherms of hydrogen converted to volumetric density in idealized carbon nanopores at 77 K and pressure up to 1 MPa. Note that volumetric density of hydrogen in carbon slitlike pores of various sizes does not

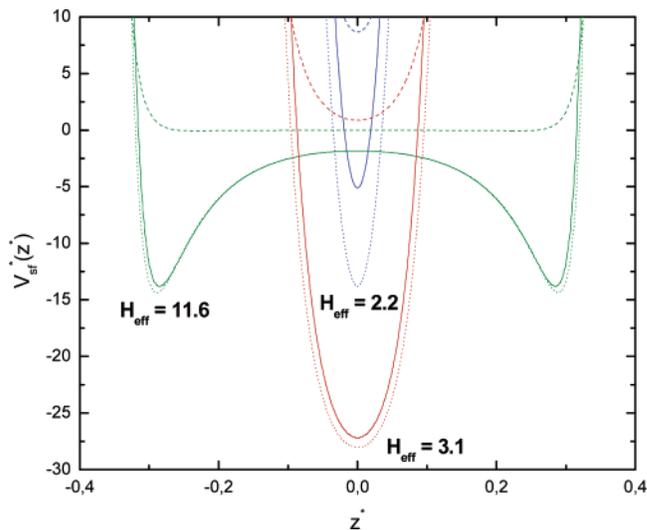


Figure 1. Reduced solid–fluid interaction potential, $V_{\text{sf}}(z)/\epsilon_{\text{ff}}$ (for hydrogen we used $\sigma_{\text{ff}} = 0.2958$ nm and $\epsilon_{\text{ff}}/k = 36.7$ K 4 , k is the Boltzmann’s constant) for the selected effective pore widths, $H_{\text{eff}} = H - 3.4$ Å, at 77 K: solid lines, total reduced solid–fluid interaction potential; dashed lines, the reduced quantum contribution; dotted lines, the reduced classical contributions.

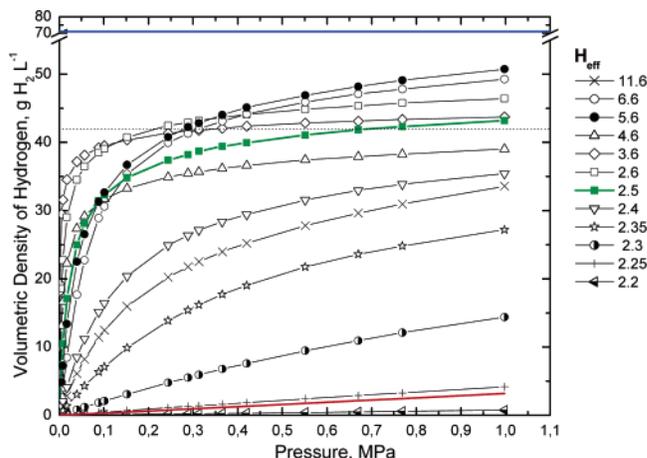


Figure 2. Selected hydrogen absolute adsorption isotherms simulated up to pressure 1 MPa by the quantum corrected GCMC method in carbon slitlike pores of various effective widths, $H_{\text{eff}} = H - 3.4$ Å, at 77 K. Solid red line corresponds to the bulk density of hydrogen at 77 K, whereas blue one is the density of hydrogen liquid at the boiling point. Solid green line corresponds to $H^* = H/\sigma_{\text{ff}} = 2$ is compared with the results taken from Wang and Johnson² (parallel dotted line, corresponding to the volumetric density of hydrogen 42 g of H $_2$ L $^{-1}$ at 77 K and 1 MPa).

approach the density of hydrogen liquid at the boiling point. We observe the highest volumetric density of confined hydrogen (around 71% of hydrogen liquid at boiling point) for the effective pore width 5.6 Å ($H^* = 3.04$). This result is in close agreement with the prediction of Wang and Johnson² ($H^* = 3.0$ for storage pressure up to 10 MPa). The results reported by Rzepka et al. slightly overestimated the volumetric density of hydrogen. For example, for $H = 7$ Å (note that $H_{\text{eff}} = H - 3.4$) and at 1 MPa, the authors obtained 45 g L $^{-1}$. According to the present FH-GCMC simulation for $H = 7$ Å and 1 MPa, the volumetric density is 43.7 g L $^{-1}$. It is clear since the quantum effects greatly lower the solid–fluid potential in the smallest idealized carbon slitlike pores (see Figure 2). Moreover, quantum effects increase extending the range of pressure and lowering the temperature.¹⁴ Here, we considered the moderate range of pressure up to 1 MPa and the temperature far from the boiling point of hydrogen.

(16) Trasa, R. A.; Kostom, M. K.; Cole, M. W. *Phys. Rev. B* **2003**, *67*, 035410.

(17) Sesé, L. M. *Mol. Phys.* **1994**, *81*, 1297.

(18) Sesé, L. M. *Mol. Phys.* **1995**, *85*, 931.

(19) Steele, W. A. *The Interaction of Gases with Solid Surfaces*; Pergamon Press: Oxford, 1974.

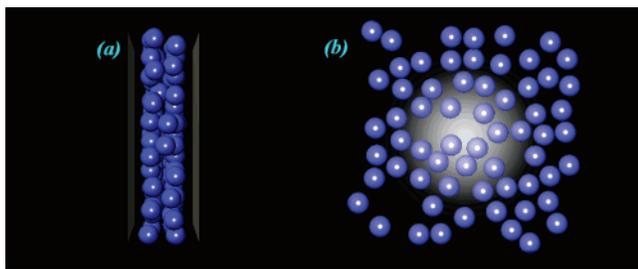


Figure 3. Snapshot of hydrogen adsorbed in the slitlike carbon pore of $H_{\text{eff}} = 6.6 \text{ \AA}$ at 1.0 MPa and 77 K collected from the simulation. Panel b presents the arrangement of the hydrogen molecules whose centers are placed in the first adsorbed layer.

For any size of carbon slitlike pore, we do not observe the high volumetric density of hydrogen exceeding 40 mmol cm^{-3} (80.6 g L^{-1}) as reported by Jagiello and Thommes.³ The efficiency of storage of hydrogen by physisorption, using porous materials composed of slitlike carbon nanopores overcompression is very large in the whole range of considered bulk pressure of hydrogen (see Figure 2).

Figure 3 presents the equilibrium snapshot of hydrogen molecules adsorbed in the slitlike carbon pore of $H_{\text{eff}} = 6.6 \text{ \AA}$ at 1.0 MPa and 77 K collected from the simulation. As one can see from Figure 3 and from the movie attached to the Supporting Information, the density of adsorbed hydrogen is lower than the liquid state. We do not observe the high-packed hexagonal structure characteristic of condensed fluid. We can see many vacant spaces in the first layer at 1.0 MPa and 77 K. The particles tend to form clusters due to densification. As mentioned by Do and Do,²⁰ this is the characteristics of supercritical fluid, that is, no condensation in either two dimensions or three dimensions.

To confirm our simulation results, we plotted the volumetric density of hydrogen at 77 K and 0.1 MPa and experimental density of hydrogen at 77 K and 0.1 MPa for different carbon materials reported by Nijkamp.²¹ Here, we must point out that the calculation of the volumetric density of hydrogen due to Nijkamp should be treated as a first approximation. Nijkamp assumed that the total pore volume available for hydrogen is equal to this computed from nitrogen adsorption data measured at 77 K. Next, the author did not take into account the structural heterogeneity of the various carbonaceous materials in rigorous fashion (see ref 14). Besides these simplifications, we obtain qualitative agreement between simulation results and experimental observations (see Figure 4). Only the volumetric density of hydrogen in the sample of activated carbon fiber ACF 1200 exceeds our predictions for 0.1 MPa. For all of the remaining samples of carbonaceous materials, the volumetric density of hydrogen reported by Nijkamp is in the range predicted by our simulations. Here, we point out that the experimental value of the hydrogen adsorption is the Gibbs excess isotherm. We compared the absolute value of adsorption (i.e., the sum of the Gibbs excess of adsorption and bulk part) obtained from simulations with the experimental Gibbs excess one because the density of the bulk fluid is considerably lower than the density

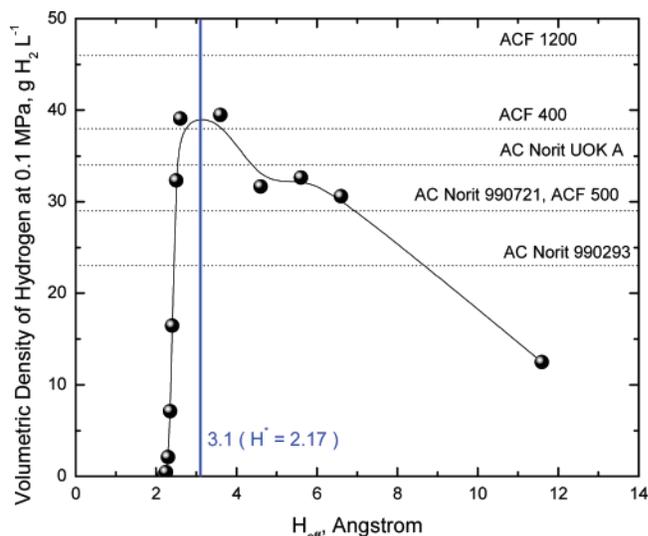


Figure 4. Volumetric density of hydrogen at 77 and 0.1 MPa in carbon slitlike pores of various sizes calculated in this study from the FH-GCMC simulation (solid line + circles). Dotted lines correspond to the experimental volumetric density of hydrogen at 77 K and 0.1 MPa for several carbon materials reported by Nijkamp.²¹

in the small carbon slitlike nanopores (see Figure 2). For the quantitative comparison of the experimental results with the simulation ones, the distribution of pore sizes should be taken into account (see ref 14).

In summary, we determined the volumetric density of hydrogen in idealized slitlike carbon nanopores at 77 K and pressures up to 1 MPa by using FH-GCMC simulations. We confirmed the results published by Wang and Johnson² and Rzepka et al.¹ We did not observe the high volumetric density of hydrogen in slitlike carbon pores exceeding the density of hydrogen liquid at the boiling point reported by Jagiello and Thommes.³ We recognized the highest volumetric density of confined hydrogen (around 71% of hydrogen liquid at boiling point) for the effective pore width 5.6 \AA ($H^* = 3.04$) in the considered pressure range. Moreover, we obtained the qualitative agreement between the simulation results and experimental findings. The efficiency of storage of hydrogen by physisorption using porous materials composed of slitlike carbon pores overcompression is very large in the whole range of considered bulk pressure of hydrogen. The presented calculations encourage further experimental research connected with the application of carbonaceous materials as an efficient medium for hydrogen storage at 77 K and at moderate pressures.

Acknowledgment. P.K. gratefully acknowledges Prof. Katsumi Kaneko and Dr Hideki Tanaka (Faculty of Science, Chiba University, Chiba, Japan) for discussions connected with the problem of hydrogen storage in nanoporous materials. P.K. also thanks Prof. Luis M. Sesè for providing the reprints of the papers.

Supporting Information Available: All remaining simulation details and a detailed description of the intermolecular potentials adopted for the current study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA053041N

(20) Do, D. D.; Do, H. D. *J. Chem. Phys.* **2005**, *123*, 084701.

(21) Nijkamp, M. G. Hydrogen Storage Using Physisorption. Modified Carbon Nanofibers and Related Materials. Thesis, Utrecht University: Utrecht, The Netherlands, 2002.