# Thermodynamics of Hydrogen Adsorption in Slit-like Carbon Nanopores at 77 K. Classical versus Path-Integral Monte Carlo Simulations

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Hydrogen in slit-like carbon nanopores at 77 K represents a quantum fluid in strong confinement. We have used path-integral grand canonical Monte Carlo and classical grand canonical Monte Carlo simulations for the investigation of the "quantumness" of hydrogen at 77 K adsorbed in slit-like carbon nanopores up to 1 MPa. We find that classical simulations overpredict the hydrogen uptake in carbon nanopores due to neglect of the quantum delocalization. Such disagreement of both simulation methods depends on the slit-like carbon pore size. However, the differences between the final uptakes of hydrogen computed from both classical and quantum simulations are not large due to a similar effective size of quantum/classical hydrogen molecules in carbon nanospaces. For both types of molecular simulations, the volumetric density of stored energy in optimal carbon nanopores exceeds 6.4 MJ dm$^{-3}$ (i.e., 45 kg m$^{-3}$; Department of Energy target for 2010). In contrast to the hydrogen adsorption isotherms, we found a large reduction of isosteric enthalpy of adsorption computed from the quantum Feynman's path-integral simulations in comparison to the classical values at 77 K and pressures up to 1 MPa. Depression of the quantum isosteric enthalpy of adsorption depends on the slit-like carbon pore size. For the narrow pores (pore width $H \in [0.59-0.7]$ nm), the reduction of the quantum isosteric enthalpy of adsorption at zero coverage is around 50% in comparison to the classical one. We observed new phenomena called, by us, the quantum confinement-inducing polymer shrinking. In carbon nanospaces, the quantum cyclic polymers shrink, in comparison to its bulk-phase counterpart, due to a strong confinement effect. At considered storage conditions, this complex phenomenon depends on the size of the slit-like carbon nanopore and the density of hydrogen volumetric energy. For the smallest nanopores and a low density of hydrogen volumetric energy, the reduction of the polymer effective size is the highest, whereas an increase of the pore size and the density of hydrogen volumetric energy causes the polymer swelling up to a value slightly below the one computed from the bulk phase. Quantum confinement-inducing polymer shrinking is of great importance for realizing the potential of quantum molecular sieves.

## Introduction

A precise knowledge of the structural and dynamic properties of hydrogen is even more desirable if one considers its growing importance as a proposed energy carrier for a not-far future of our planet.[1] In modern nanomaterials science, topics of high interest are quantum fluids in strong confinement on nanometer length.[2-7] Obviously, the static and dynamic properties of quantum fluids in pores of molecular dimensions are closely related to the timely problem of on-board hydrogen storage.[8-10]

Hydrogen seems to be the path for the future for clean energy consumption; however, the "Holy Grail" adsorbent for on-board hydrogen storage remains undiscovered.[1,8] Moreover, key to the success of adsorptive storage is not only the choice of suitable adsorbent but also optimal operating conditions.[8]

Even in the bulk phase, the experimental static and dynamic investigations of hydrogen fluid are difficult. As an example, the X-ray determination of the structure factor of the bulk hydrogen is difficult due to its small number of electrons. A neutron diffraction experiment, on the other hand, is equally difficult due to recoil effects whose sizes are determined by the ratio between the neutron and molecular mass. In 2002, Zoppi et al.[11] calculated the microscopic structure factor of *para*-hydrogen at 15.7 K according to Feynman's path-integral Monte Carlo simulations (PIMC). Moreover, Zoppi et al.[11] showed that the experimental structure factor for *para*-hydrogen at 15.7 K measured by Bermejo and co-workers[12] by neutron diffraction experiment did not quantitatively agree with the PIMC results. Not long ago, Celli et al.[13] obtained reasonable quantitative agreement of the microscopic structure factor for liquid *para*-hydrogen at low temperatures below 20.1 K measured by neutron

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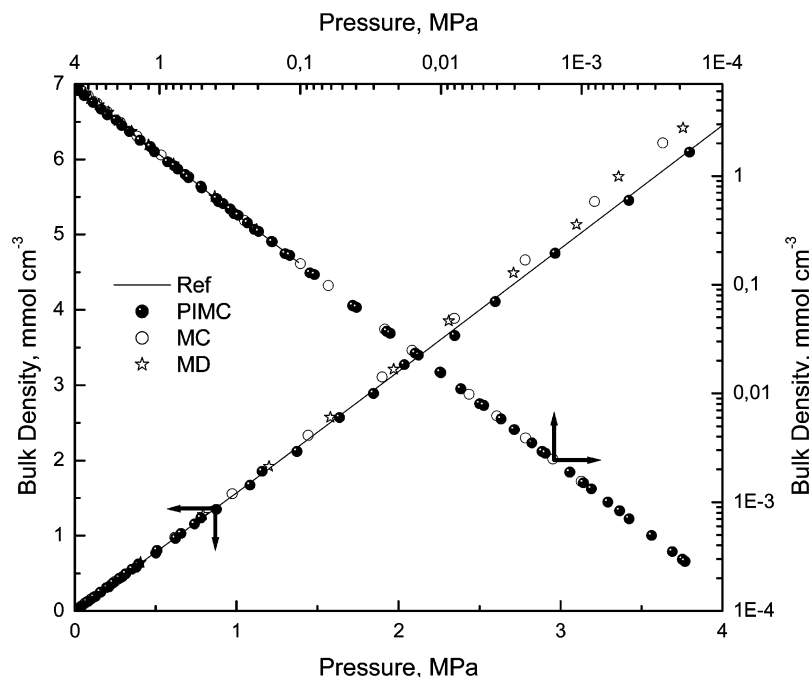
**Figure 1.** Comparison of the experimental equation-of-state for hydrogen at 77 K [Ref-39] with the ones computed from PIMC [path-integral (*N,V,T*) Monte Carlo simulation], MC [classical (*N,V,T*) Monte Carlo simulation], and MD [classical (*N,V,T*) molecular dynamics].

direction experiments with that computed from PIMC simulations. In a series of papers, Johnson et al.[14−16] showed that Feynman PIMC simulations reproduce the thermodynamic properties and phase equilibrium of quantum fluids such as hydrogen, deuterium, tritium, neon, and others. The application of classical molecular simulations for the modeling of the both static and dynamics properties of bulk hydrogen is limited to high temperatures and low pressures. In contrast to the path-integral formalism, classical simulations cannot explain the experimentally observed differences in the bulk properties of hydrogen isotopes (i.e., equation of state, variation of heat capacity at constant volume and pressure upon temperature, surface tension, volatility, melting point, etc.).[6,7,17]

In nanopores, the geometrical constraints and additional molecule−surface interactions affect both structural and dynamics properties of hydrogen.[18−23] Many quantum effects appear at low temperatures due to the effect of quantum statistics. However, in nanopore confinement, quantum effects are enhanced in comparison with those in the bulk phase due to the very large potential gradients existing within objects of nanoscale dimensions, and as a consequence, the motion of quantum molecules is restricted in some directions.[19−24] Moreover, the delocalization effects due to the position−momentum uncertainty principle introduce quantum fluctuations in addition to the thermal ones.[7] This may result in a decrease of phase transition temperatures as compared to a purely classical system under otherwise

unchanged conditions.[6,7] Moreover, due to the "swelling effect", we can expect that quantum molecules interact weaker with the pore walls in comparison to the interaction of its classical counterpart.[19,23,24] This lowers the total adsorbed amount and isosteric enthalpy of adsorption of a quantum molecular system in comparison to that of the classical one under the same conditions.[23−25] The physical adsorption of hydrogen in novel nanoporous materials is now under wide investigation both experimentally and theoretically.[1−3,26,27] In the majority of published papers, the authors pay more attention to the determination of the absolute/excess adsorption isotherms of hydrogen.[23,24,26−31] The aim of these measurements or computations of the hydrogen weigh percent and density stored in nanoporous materials is to answer the key question: Can the nanomaterial be used as an efficient vessel for on-board storage of supercritical hydrogen? However, key to the success of adsorptive storage is the choice of suitable adsorbent and optimal operating conditions.[8] As shown by Bhatia and Myers[8] for a given adsorbent, the optimum operating conditions are determined by the enthalpy of hydrogen adsorption. We want to point out that calorimetric measurements are especially difficult for adsorption systems consisting of light, weakly interacted adsorbates (i.e., hydrogen, helium, deuterium, neon, etc.) below ambient temperature.[32,33] Computer simulations offer an alternative tool to use for the investigation of the storage of hydrogen in nanoporous systems. If the underlying physical situation and the intermolecular potentials are known, computer simulations are a convenient vehicle for extrapolating experimental results

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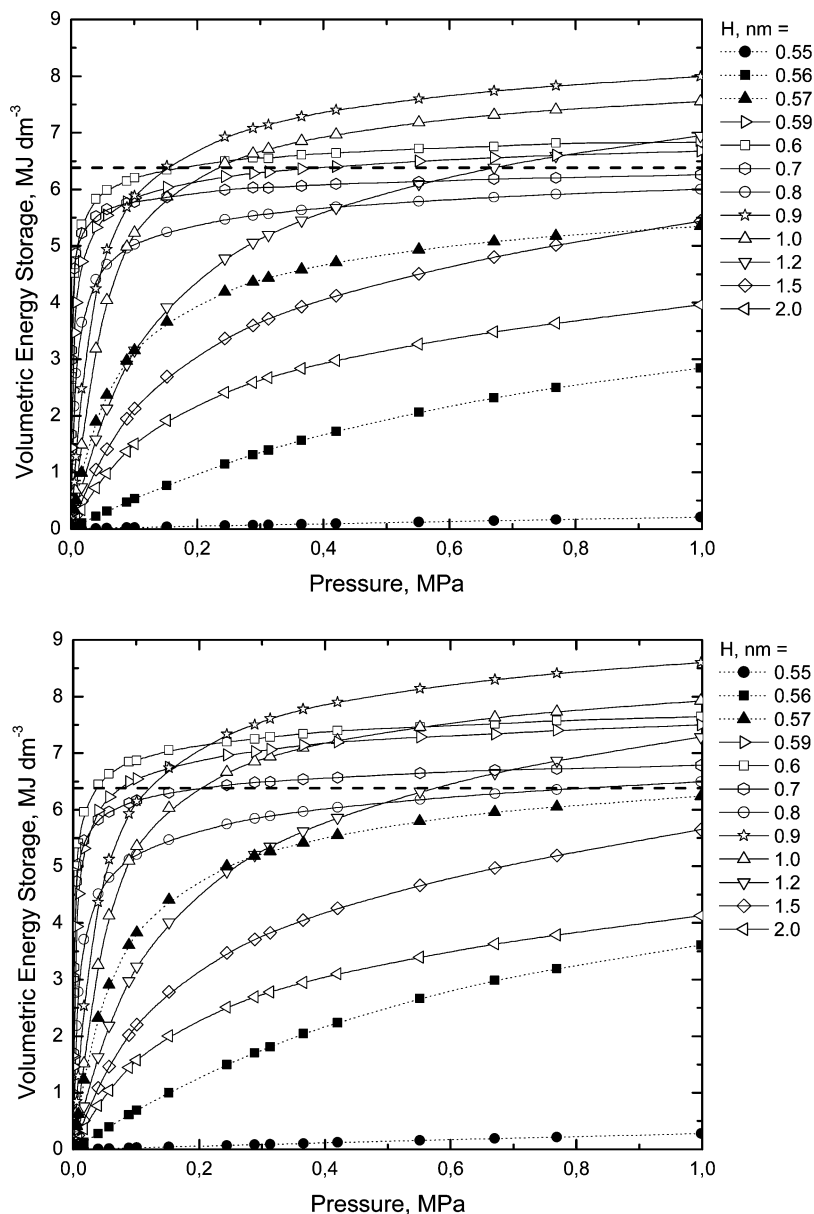
**Figure 2.** Selected hydrogen absolute adsorption isotherms simulated up to a pressure of 1 MPa by the PIGCMC (top panel) and the classical GCMC (bottom panel) methods in carbon slit-like pores of various sizes at 77 K. Dashed lines correspond to the Department of Energy target for 2010 (45 kg m$^{-3}$ = 6.38 MJ dm$^{-3}$).

to conditions of difficult experimental access. For instance, the thermodynamic functions of adsorption processes such as isosteric enthalpy of adsorption can be easily computed from molecular simulations.[34−38]

The current paper aims to develop a complete description of the physical adsorption of hydrogen in slit-like carbon nanopores at 77 K and pressures up to 1 MPa. For this purpose, we concentrated on both the volumetric content of the stored energy and the isosteric enthalpy of adsorption versus hydrogen loading at the mentioned conditions. We used path-integral grand canonical Monte Carlo simulations (PIGCMC) and classical grand canonical Monte Carlo (GCMC) simulations for the investigation of the "quantumness" of hydrogen physisorption in the mentioned

conditions. The paper consists of two parts. The first, included in the Supporting Information, contains a brief description of the simulation details showing potential models, simulation methodology, and thermodynamic quantities characterizing hydrogen adsorption in slit-like carbon nanopores. In the second part, we provide detailed comparison of hydrogen properties in the bulk phase and confinement computed from classical and quantum Monte Carlo simulations. Our studies are the first where the effect of "quantumness" on the physisorption of hydrogen in slit-like nanopores at 77 K and pressures up to 1 MPa is rigorously treated on such a scale. Finally, we summarize our computational study in conclusions.

## Results and Discussion

Let us consider the quantum spreading of hydrogen molecules at 77 K and pressures up to 4 MPa in the bulk phase. Here, we stress that the approximation of the diatomic hydrogen molecule by an effective Lennard-Jones sphere is justified by the relatively high temperature and low-density region. We now focus our

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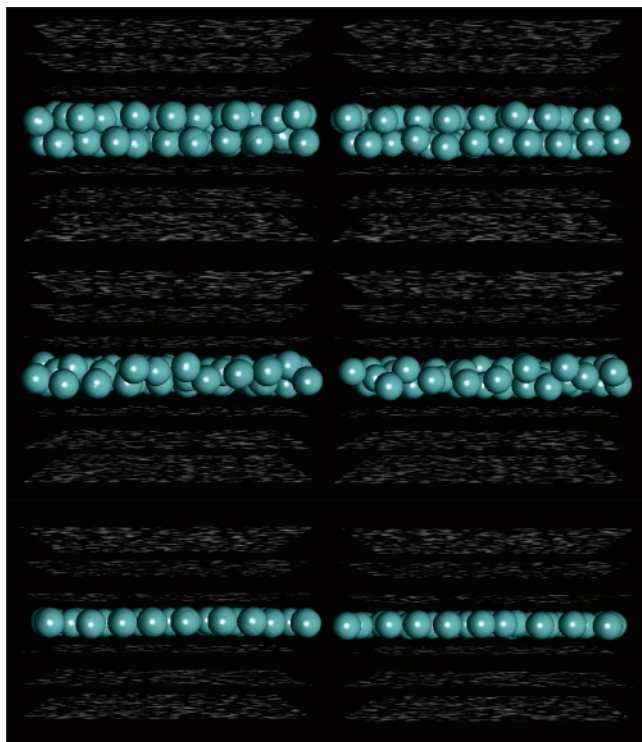
**Figure 3.** Snapshot of hydrogen adsorbed in a slit-like carbon pore of pore widths $H = 0.9$, 0.8, and 0.6 nm, respectively (1 MPa and 77 K), collected from the PIGCMC (left panels: 12 beads of size $\sigma_{ff}$ were placed within the mean gyration radius of the cyclic polymers) and classical GCMC (right panels: the sphere size is $\sigma_{ff}$).

attention on the description of the experimental equation-of-state (EOS) for hydrogen at 77 K by classical MC and MD as well as quantum MC simulations, depicted in Figure 1. The first observation is that, at low pressures up to 2 MPa, both classical and quantum simulation techniques describe experimental EOS[39] reasonably well. It is not surprising if we take into account that, in such a range of pressures, hydrogen obeys the ideal gas law. Further increase in pressure causes a systematic increase in the deviations of classical simulations from experimental data. This result can be explained by basic physical arguments. Increasing the density of hydrogen causes enhancement of quantum fluctuations that cannot be captured from the classical point of view. In contrast, for pressures up to 4 MPa, the quantum curve merges with the experimental EOS. It is not surprisingly since the PIMC simulations yield exact results over the whole temperature range from the classical to the deep quantum regime. How large is the quantum dispersion in space? Following the Heisenberg uncertainty principle $(\Delta p)^2(\Delta x)^2 \approx h^2$, we can theoretically predict delocalization of a particle in space from the simple formula, $\lambda \equiv \langle(\Delta x)^2\rangle^{1/2} \approx h^2/\langle(\Delta p)^2\rangle^{1/2} \approx \sqrt{\beta\hbar^2/m}$ (cf. Figure 1S).[40,41] For hydrogen at 77 K, $\lambda = 0.56$ Å. It should be noted that such an estimate is qualitative and not accurate when the interactions among particles occur.[41] On the other hand, PIMC allows quantification of uncertainty spreading, that is, the average gyration radius of the ring polymer.[42–45] We found that the average

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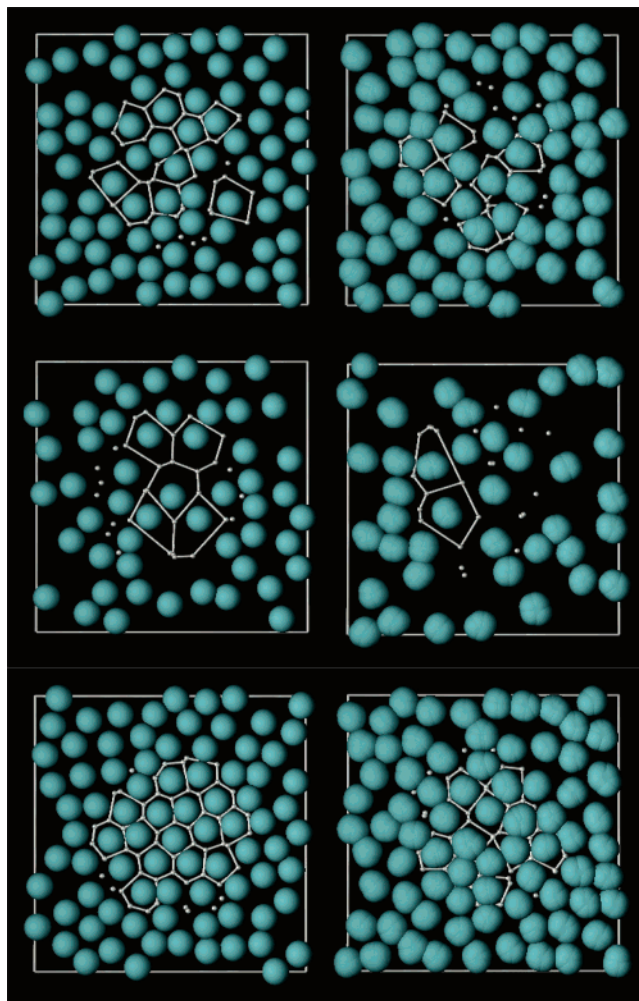(45) Sese, L. M. *Mol. Phys.* **1993**, *78*, 1167.



**Figure 4.** Snapshot of adsorbed layer of hydrogen adjacent to the carbon pore wall (i.e., contact layer; from the top, the slit-like carbon pore widths are $H = 0.9$, 0.8, and 0.6 nm) (1 MPa and 77 K), collected from the PIGCMC (right panels: 12 beads of size $\sigma_{ff}$ were placed within the mean gyration radius of cyclic polymers) and classical GCMC (left panels: the sphere size is $\sigma_{ff}$). We constructed two-dimensional Voronoi−Dirichlet polyhedra[47,48] within the circle with radius $R = 2.5\sigma_{ff}$.

gyration radius of the ring polymer at 77 K slightly depends on the pressure range, i.e., $R_g = 0.28 - 0.29$ Å (see Supporting Information). As expected, the average gyration radius of the ring polymer reproduces the wave nature of a light hydrogen molecule, i.e., $R_g \approx \lambda/2$.

Quantum effects become important only when the thermal de Broglie wavelength of the particles becomes comparable to the characteristic interparticle distance.[41,46] Let us focus our attention to the absolute adsorption isotherms of hydrogen at 77 K and pressures up to 1 MPa computed from classical and quantum GCMC, displayed in Figure 2. First, the shape and variation of the volumetric energy stored with pore size in the considered range of storage pressures is close for both types of GCMC simulations. All of the absolute hydrogen adsorption isotherms shown in Figure 2 are supercritical, and we did not observe the symmetry breaking due to first-order phase transition. We recognized that, for narrow nanopores, classical simulation overpredicts the volumetric energy storage at 1 MPa, in contrast to the quantum path-integral method (cf. Figure 2). This disagreement results from the zero-point motion of quantum

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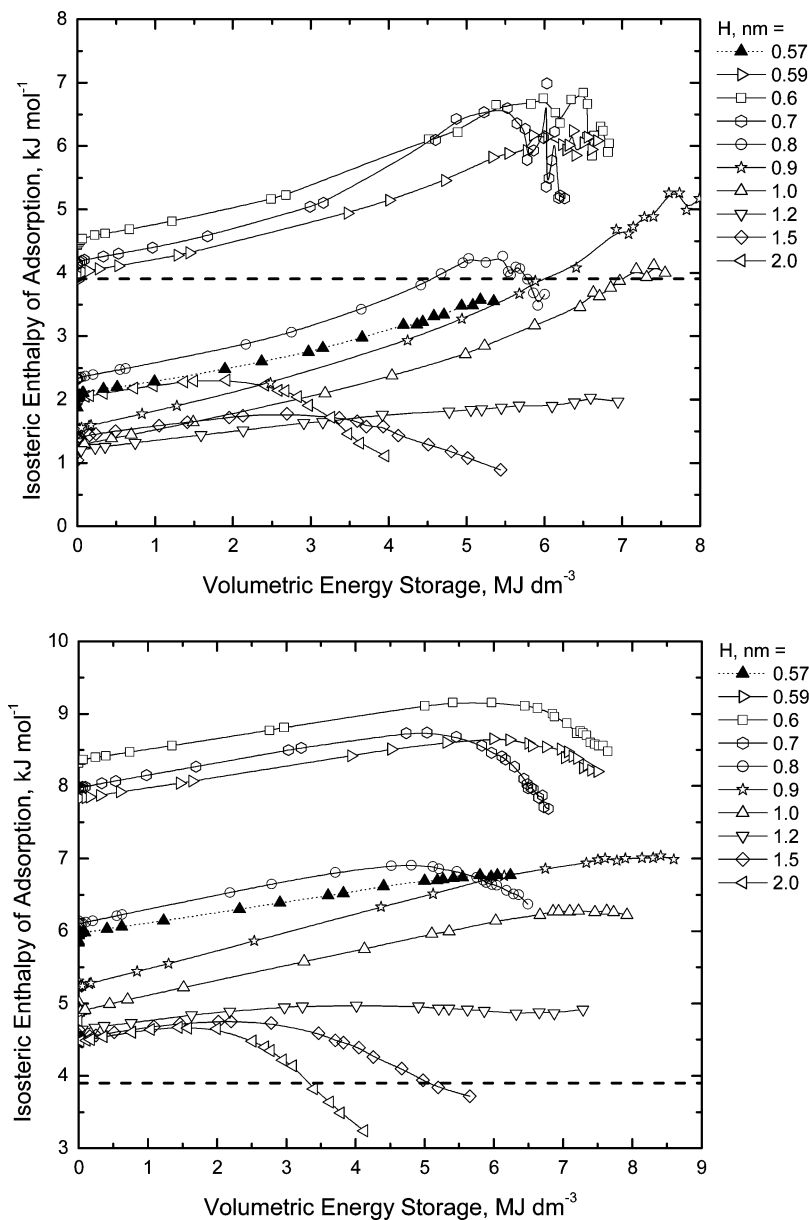
**Figure 5.** Selected hydrogen isosteric enthalpy of adsorption simulated up to a pressure of 1 MPa by the PIGCMC (top panel) and the classical GCMC (bottom panel) methods in carbon slit-like pores of various sizes at 77 K. Dashed lines correspond to an optimal enthalpy change (i.e., 3.9 kJ mol$^{-1}$) at 77 K during the delivery cycle calculated according to the Bhatia and Myers criteria.[8]

molecules. Extending the slit-like pore size causes fast reduction of quantum effects. As a result, for wider slit-like carbon nanopores, the excluded volumes (i.e., the ratio of the pore width and the size of adsorbed hydrogen) are very close for both classical and quantum adsorbed hydrogen. For a better understanding of the obtained results, we compare the equilibrium configurations obtained from classical and quantum GCMC. For both kinds of Monte Carlo simulations, the highest stored volumetric energy was obtained for $H = 0.9$ nm (cf. Figure 2). As one can see from Figures 3 and 4 and from the Monte Carlo simulation movie in the Supporting Information, in both cases, two dense molecular layers of adsorbed hydrogen are formed. The solid−fluid potential exerts a strong effect on the contact, adsorbed hydrogen layers (i.e., layers adjacent to the pore walls). The two-dimensional Voronoi−Dirichlet polyhedra[47,48] are primarily composed of irregular hexagons, as shown in Figure 4. Slightly below this pore size, that is, for $H = 0.8$ nm, both methods predicted

imperfect packing of hydrogen molecules (cf. Figure 3 and Supporting Information, zigzag-type arrangement of hydrogen molecules in nanopore). For this size of the slit-like pore, the two-dimensional Voronoi−Dirichlet polyhedra constructed for the contact hydrogen layers are characterized by complex, partially ordered structures (i.e., irregular wider hexagons and polyhedra of higher degree). This imperfect packing of hydrogen molecules in nanospaces results in lower volumetric energy storage. Finally, for $H = 0.6$ nm, both classical and quantum GCMC methods predicted formation of a dense, one molecular hydrogen layer highly localized in the overlapped solid−fluid potential minims generated by the pore walls (cf. Figure 3 and Supporting Information). The two-dimensional Voronoi−Dirichlet polyhedra constructed for the contact hydrogen layers are primarily composed of regular and compact hexagons (cf. Figure 4). Summing up, we showed that both classical and quantum GCMC predicted similar packing and structures of adsorbed hydrogen molecules at 77 K and pressures up to 1 MPa in slit-like carbon nanopores. Moreover, both classical and quantum

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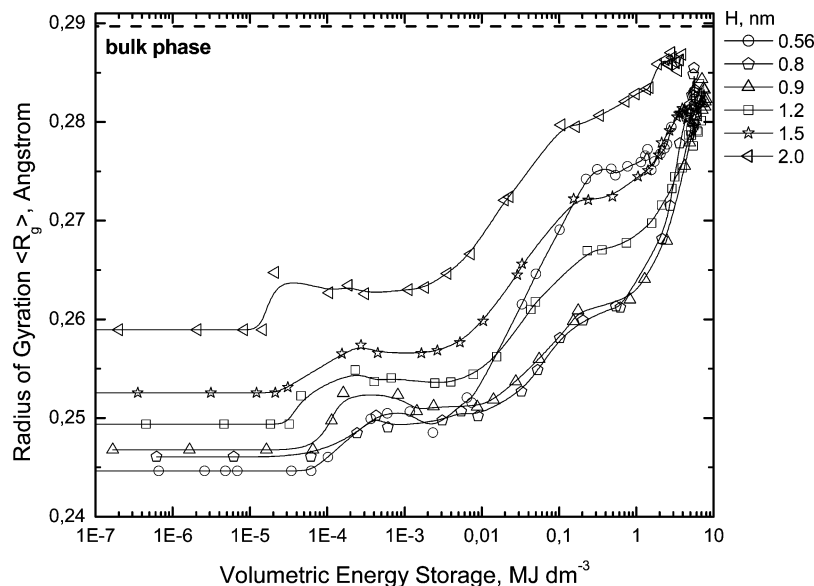
**Figure 6.** Dependence of the average gyration radius of the ring polymer upon volumetric energy storage for selected slit-like pore sizes computed from PIGCMC at 77 K. The average gyration radius of the ring polymer in the bulk phase is $R_g = 0.29$ Å.

GCMC simulations predicted that the ordering of adsorbed hydrogen and stored volumetric energy is predominantly determined by the slit-like carbon pore width (i.e., pore geometry and size).

On the contrary, the enthalpy released during hydrogen physisorption computed from classical and quantum simulation differs significantly (cf. Figure 5). Compared to purely classical systems, the quantum delocalization introduces fluctuations in addition to the thermal ones. The isosteric enthalpy of adsorption computed from quantum simulations is reduced in comparison to that of classical simulations for all slit-like carbon nanopores. On the other hand, the shape of the isosteric enthalpy of adsorption versus hydrogen loading for both quantum and classical simulations is similar. According to classical simulation, the highest isosteric enthalpy of hydrogen adsorption in slit-like carbon nanopores at 77 K and zero pressure is around 8−8.5 kJ mol$^{-1}$ (for $H = 0.6$ nm). This value is close to the isosteric enthalpy of adsorption for the best metal−organic framework reported by Garberoglio et al.[49] (MOF-3; 8.8 kJ mol$^{-1}$ at 77 K and zero pressure). Clearly, the huge value of the released enthalpy during the adsorption of hydrogen in slit-like carbon nanopores computed from classical GCMC is unrealistic due to the stronger molecular interactions of hydrogen in MOF-type nanomaterials. On the contrary, the isosteric enthalpy of hydrogen adsorption in slit-like carbon nanopores reported by Bénard and Chahine[50] or Bhatia and Myers[8] is, on average, <6 kJ mol$^{-1}$. These experimental and simulation results coincide with our isosteric data computed from the quantum PIGCMC simulations (cf. Figure 5). It may be noted that the enthalpy at 77 K and zero pressure for a series of isoreticular metal−organic frameworks reported by Garberoglio et al.[49] is around 4 kJ mol$^{-1}$. For slit-like carbon nanopores, we found comparable isosteric enthalpy at zero pressure for pore width $H \in [0.59−0.7]$ nm. For wider slit-like carbon pores, the enthalpy extrapolated to zero pressure is decreased (cf. Figure 5). We note here that Chakravarty[25] observed 25% depression of the quantum isosteric enthalpy of helium adsorbed in silicate in the temperature range of 10−20 K. In conclusion, reduction of the quantum isosteric enthalpy of

hydrogen adsorption has great impact on the optimal operating conditions. According to the thermodynamic criteria due to Bhatia and Myers[8], the optimal pore width for hydrogen storage at 77 K is around 0.6 nm (i.e., slit-like carbon pores that can accommodate one adsorbed layer of hydrogen), as shown in Figure 5.

To complete the picture of the quantum hydrogen adsorption in slit-like nanopores at 77 K and pressures up to 1 MPa, we collected the average gyration radius of the ring polymers as a function of volumetric energy storage and pore size (cf. Figure 6). At first glance, it is tempting to consider that the effective size of the ring polymer does not depend on the slit-like carbon pore size. However, we found shrinkage of the average gyration radius of hydrogen ring polymers in carbon nanopores. Moreover, this quantum confinement-inducing polymer shrinkage changed regularly with the pore size and the density of hydrogen volumetric energy. For the smallest nanopores and a low density of hydrogen volumetric energy, the reduction of the polymer effective size is the highest, whereas increasing the pore size of the slit-like nanopore and density of hydrogen volumetric energy causes the polymer swelling up to a value slightly below the one computed from the bulk phase. It seems reasonable that both solid−fluid and fluid−fluid interactions influence the quantum delocalization (i.e., wave function in Schrödinger's formulation of quantum mechanics) of confined hydrogen. For all of the investigated slit-like carbon pore sizes, the enhancement of density of adsorbed hydrogen (i.e., fluid−fluid interactions) leads to the enlargement of the average gyration radius of the hydrogen cyclic polymer at the considered storage conditions. To explore the impact of attraction of the pore walls on the quantum delocalization of hydrogen at 77 K, we performed a series of PIGCMC simulations for slit-like pores of different solid−fluid Lennard-Jones well depths. At a very low density of hydrogen volumetric energy (i.e., very low surface coverage), the average gyration radius of hydrogen does not depend on the solid−fluid Lennard-Jones well depth, as displayed in Figures 7 and 2S−5S. In other words, in this region, the quantum delocalization depends on the pure geometry constraints (i.e., size of nanopore). Increasing the loading of the hydrogen in slit-like pore leads to the swelling of quantum cyclic polymers due to stronger fluid−fluid interactions. However, the packing effect in perfect nanopores can drastically

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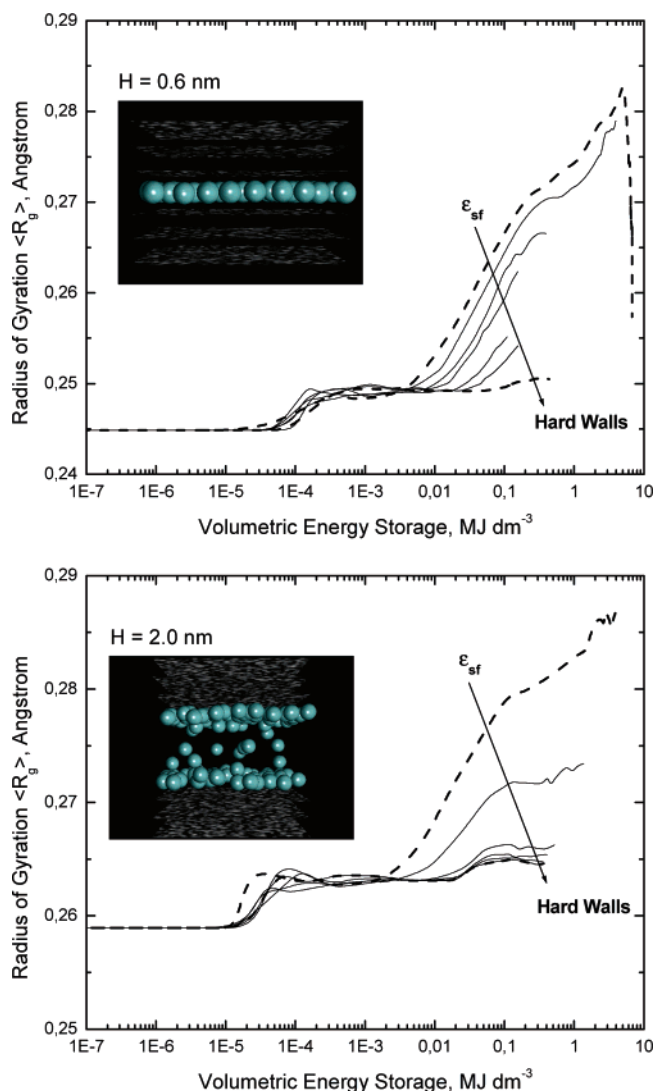(50) Bénard, P.; Chahine, R. *Langmuir* **2001**, *17*, 1950.

**Figure 7.** Impact of the strength of solid−fluid Lennard-Jones well depth on the average size of adsorbed hydrogen ring polymers at 77 K. The average gyration radius of the ring polymer in the bulk phase is $R_g = 0.29$ Å. The calculations were performed for $\epsilon_{sf}$, $\epsilon_{sf}/2$, $\epsilon_{sf}/5$, $\epsilon_{sf}/10$, $\epsilon_{sf}/100$, $\epsilon_{sf}/1000$, the and hard wall.

reduce the quantum delocalization, as shown in Figures 7 and 2S (i.e., for $H = 0.6$ nm). Summing up, the impact of the type of nanomaterial, pore geometry and size, storage pressure, and temperature for the quantum confinement-inducing delocalization effects due to the position−momentum uncertainty principle is the complex phenomenon. Although the polymer shrinkage is not very large, it should play an important role in the quantum sieving of hydrogen isotopes by nanoporous materials since the idea of quantum separation is delocalization of quantum molecules in nanopores. Adjustment of the mentioned factors can be used for enhancement of the isotope separation in porous systems.

From the current rigorous investigations, we concluded that the description of the hydrogen adsorption isotherm by theoretical/simulation models is not enough for complete modeling of hydrogen adsorption phenomena at 77 K and pressures up to 1 MPa. We observe that classical and quantum simulations predict a similar uptake and shape of hydrogen absolute adsorption isotherms in slit-like carbon nanopores at the mentioned storage conditions. On the contrary, the isosteric enthalpy of adsorption differs significantly from classical to quantum theory. As a result, the optimum operation conditions for hydrogen storage can only be predicted from quantum simulations. The disagreement of

classical and quantum computations can be explained by simple physical arguments. The uptake of hydrogen in slit-like pores primarily depends on the effective size of classical and quantum hydrogen. This effective size of classical and quantum hydrogen adsorbed in slit-like carbon nanopores at 77 K and pressures up to 1 MPa is similar, as shown in Figures 3, 4, and the Supporting Information. On the other hand, the enthalpy released during hydrogen loading in nanopores is governed by geometrical constraints and fluctuations (thermal and quantum). Neglecting the quantum fluctuations causes artificially stronger interactions of classical hydrogen with the carbon pore walls. The obtained results have impact on the timely problem of on-board hydrogen storage and the quantum-sieving effect.

## Conclusions

In the current paper, we discussed the adsorption of hydrogen in slit-like carbon nanopores at 77 K and pressure up to 1 MPa. We have used path-integral grand canonical Monte Carlo and classical grand canonical Monte Carlo simulations for the investigation of the "quantumness" of hydrogen physisorption at the mentioned conditions. In agreement with previous simulation reports, we found that the density of hydrogen in carbon slit-like nanopores exceeds 6.4 MJ dm$^{-3}$ (i.e., 45 kg m$^{-3}$; Department of Energy target for 2010). We found that classical simulations overpredict the hydrogen uptake in carbon nanopores due to neglect of the quantum delocalization. Such disagreement of both simulation methods depends on the slit-like carbon pore size. However, the differences between the final uptakes of hydrogen computed from both classical and quantum simulations are not large due to the similar effective size of quantum/classical hydrogen molecules in carbon nanospaces. In great contrast to the hydrogen adsorption isotherms, we found a large reduction of isosteric enthalpy of adsorption computed from the quantum Feynman's path-integral simulations in comparison to the classical values at 77 K and pressures up to 1 MPa. As we have shown, depression of the quantum isosteric enthalpy of adsorption depends on the slit-like carbon pore size. For narrow slit-like carbon nanopores of pore width $H \in [0.59-0.7]$ nm, the reduction of the quantum isosteric enthalpy of adsorption at zero coverage is around 50%, in comparison to the classical one. We observed new phenomena called quantum confinement-inducing polymer shrinking. In carbon nanospaces, the quantum cyclic polymers shrink in comparison to its bulk-phase counterpart due to a strong confinement effect. At the considered storage conditions, this complex phenomenon depends on the size of the slit-like carbon nanopore and the density of hydrogen volumetric energy. For the smallest nanopores and a low density of hydrogen volumetric energy, the reduction of the polymer effective size is the highest, whereas increasing the pore size of the slit-like nanopore and the density of hydrogen volumetric energy causes the polymer swelling up to a value slightly below the one computed from the bulk phase. Quantum confinement-inducing polymer shrinking is of great importance for the realizing the potential of quantum molecular sieves.