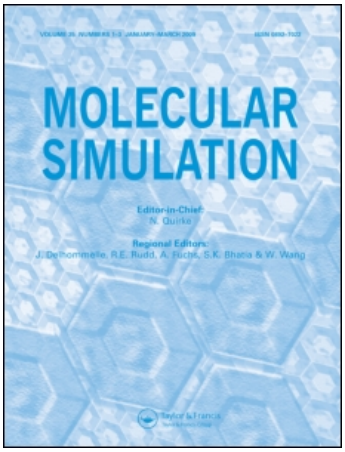


**Molecular Simulation**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

# Computer Simulation of Hydrogen Adsorption on Graphitic Materials

Roger F. Cracknell[a]
[a] Shell Global Solutions UK, Chester, UK

**To cite this Article** Cracknell, Roger F.(2001) 'Computer Simulation of Hydrogen Adsorption on Graphitic Materials', Molecular Simulation, 27: 5, 287 — 293
**To link to this Article: DOI:** 10.1080/08927020108031354
**URL:** http://dx.doi.org/10.1080/08927020108031354

*Molecular Simulation*, Vol. 27, pp. 287–293
Reprints available directly from the publisher
Photocopying permitted by license only



# COMPUTER SIMULATION OF HYDROGEN ADSORPTION ON GRAPHITIC MATERIALS

ROGER F. CRACKNELL

*Shell Global Solutions UK, Cheshire Innovation Park, PO Box 1, Chester CH13SH, UK*

*(Received May 2001)*



## 1. INTRODUCTION

I was delighted and honoured to have been asked to participate in the meeting organised by Nick Quirke to celebrate David Nicholson's achievements in the field of molecular simulation. I was a PhD student with David (and Neville Parsonage) between 1987 and 1990. The experience was sufficiently agreeable that I returned to do a further two years of postdoctoral research with David between 1992 and 1994.

I am sure that many other contributors to this volume will have commented on the seminal importance of "Computer Simulation and the Statistical Mechanics of Adsorption" which David co-authored with Neville Parsonage in 1982 [1]. At that time, no one could have guessed how influential, this work would become—it has been cited over 350 times. Advances in computer technology have meant that computer simulation has now become a vital part of the chemists toolkit, especially in the field of modelling of adsorption.

The purposes of this article are two-fold—firstly to recall my time working with David, and secondly to give an example of how the ability to model the adsorption properties of novel materials is of key industrial importance.

## 2. LIFE AT THE TOP OF THE 8TH FLOOR

The only lift going that high was the service lift. It could (and probably still does) take an age to reach its destination, especially if cylinders were being delivered to

the labs below. On reaching the top, you could probably smell the coffee machine with a black residue on the bottom because it had not been turned off from the previous brew. The group had coffee at 10.45 a.m. and I always tried to make sure that I was in by then, although to my shame, I did not always succeed. Sometimes, there were good excuses for a tardy arrival such as the 1987 great storm when fallen trees totally disrupted London's public transport. The same storm blew down David's garden wall onto his neighbours Porsche—I think he was secretly rather proud of this and I am sure he felt that he had contributed in a small way, albeit inadvertently to the downfall of the 1980s "Me" society.

Apart from discussing current affairs, those coffee times were wonderful for discussing why our simulations were not converging and how we could improve the algorithm whilst maintaining microscopic reversibility and the like. This was David's escape from the administrative burdens (such as organising all the undergraduate examinations) which he performed very conscientiously but did not particularly enjoy. It was clear that getting deeply involved in the tough fundamental scientific problems was and is David's joy. Those discussions over a whiteboard with David and Neville were among the most fulfilling and enjoyable times I have ever had, even though I usually lost the argument.

A new state of the art IBM PC AT had just been delivered for Steven Zara, the post-doc. Such things were like gold dust and it was not long before the thieves paid the lab a visit—a sure sign in David's eyes that Britain was going down the pan. Nevertheless, Steven and David showed that you could get as much number crunching done on a PC because you had exclusive use as you could on the Cray owned by the University of London in spite of Steven's best efforts to subvert the queuing system by splitting simulations into small chunks so that they would quickly get to the top of the job queue.

The original IBM PCs gave way to 286s with transputer arrays for a parallel processing and when I re-joined the group in 1992 as a post-doc, we had even got 486s and even though the office on the eighth floor was replaced by one on the ground floor of the extension, it still remained a stimulating place to work not least because all the members of the group who had joined while I was away (in particular Roland Pellenq) revelled in the scientific arguments with whiteboard, marker pens and overbrewed coffee.

## 3. HYDROGEN STORAGE IN CARBON MATERIALS

### 3.1. Introduction

David Nicholson has maintained an interest in porous materials throughout his career, from both the complementary standpoints of transport properties and

adsorption. Many of his insights into adsorption have been based on a careful analysis of the gas–solid intermolecular potential. My contribution to this festschrift contains a brief account of a piece of work where the strength of the gas–solid intermolecular forces is key to the potential usefulness of a class of materials for storage of hydrogen. For a fuller account of the methodology used, the reader is referred to Ref. [2].

The ability to store hydrogen on-board vehicles is the subject of considerable research effort. Advances in proton exchange membrane (PEM) fuel cell technology have stimulated this effort over the last decade. Compressed hydrogen storage at pressures between 250 and 350 bar is a relatively proven technology, however the lack of vehicle range is likely to make this problematic as a long term solution for passenger cars, although it may be an acceptable solution for buses where a tank can be accommodated on the roof space. Adsorptive storage of hydrogen in carbon based materials has been suggested as a possible alternative approach.

Rodriguez, Baker and co-workers [3,4] have reported uptake of hydrogen in GNFs of 40% by weight. If these results are confirmed, then this class of material could be a suitable storage medium for hydrogen for use in fuel cell vehicles. Other workers have reported more moderate levels of uptake (up to 10%) in carbon based systems [5–7]. In order to test whether these results are feasible, results are reported here for grand canonical Monte Carlo simulation of hydrogen adsorption in model slit-like pores. A classical technique was employed but the results obtained are shown to be consistent with previous path integral Monte Carlo calculations of Wang and Johnson [8,9].



### 3.2. Simulations

Hydrogen was modelled as a two-centre Lennard–Jones molecule with parameters for each site given by Table I.

The potential was based on a spherical model of hydrogen due to Buch [10] which has been reparameterised into a two centre model [2]. It was felt that an elongated model for hydrogen would be more appropriate for hydrogen given that

TABLE I Parameters for hydrogen model

| H–H *distance* (nm) | *Hard sphere diameter* $\sigma_{HH}$ (nm) | *Well depth* $\varepsilon_{HH}/(k)$ |
|---|---|---|
| 0.074 | 0.259 | 12.5 K |

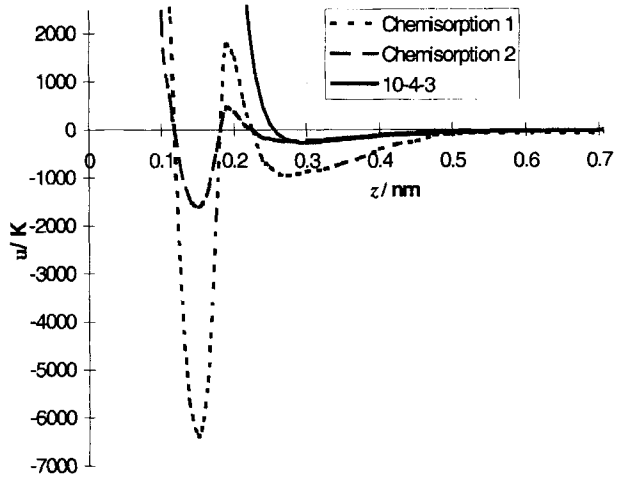


FIGURE 1 The interaction of a single hydrogen site with a graphitic surface and two hypothetical models for chemisorption. ($z$ = distance from wall).



it exists exclusively in the ortho form at room temperature, however it is shown in Ref. [2] that this makes a very small difference to the results.

The interaction between hydrogen and each graphitic surface was modelled on the basis of dispersion forces, using the "10–4–3" potential [11]. Although there is no theoretical basis to suggest a much stronger interaction between molecular hydrogen and the surface, we also investigated using two hypothetical potentials (Fig. 1) with "chemisorption" minima as well as dispersion minima in order to see how this would affect the uptake.

The "Chemisorption 1" potential derives from DFT calculations of the interaction between *atomic* hydrogen and graphite [12]. Since we are in fact considering the interaction between an atom on a hydrogen *molecule* and the surface, the model sets an exaggerated upper bound on the interaction strength. Indeed the bond dissociation enthalpy of a H–H bond of 436 kJ mol$^{-1}$ ($\varepsilon/k$ = 52442 K) is greater in magnitude than the potential well of the atomic hydrogen–carbon interaction. The "Chemisorption 2" potential is scaled so as to give a dispersion minimum that coincides with that for the "10–4–3" potential and could be viewed as a more plausible model for chemisorption.

Grand canonical Monte Carlo simulations [1] were typically run for 5 million configurations and used up to 500 particles. The rate of acceptance for particle creations and deletions was typically in the range of 5–15%.

Previous work [13] has suggested that a pore which can contain between two and three molecular layers would be optimal for gas storage. Figure 2 shows

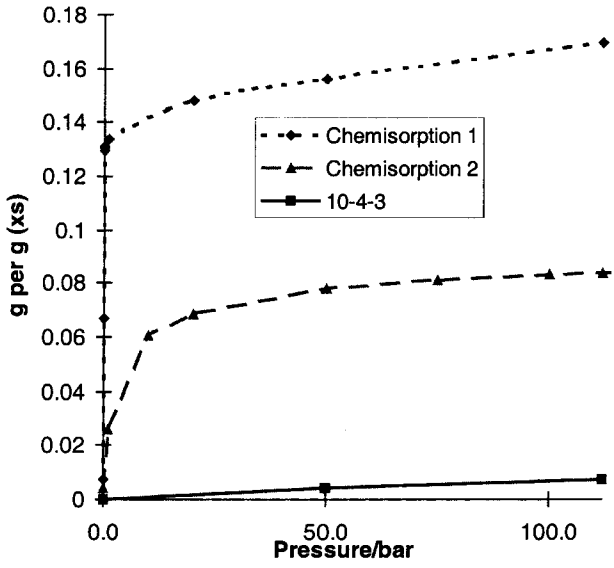


FIGURE 2 Simulated adsorption isotherms for hydrogen in a pore of width $H = 0.9$ nm for three models of the gas solid potential. $T = 298$ K.

simulation results for a pore of width $H = 0.9$ nm, where the uptake is expressed in grams adsorbed per gram of adsorbent. The conversion to these units has assumed a maximum graphite surface area of $2680\,m^2\,g^{-1}$ and hence represents an upper bound on what could be found in a real system. For the "10–4–3" potential, an excess hydrogen uptake of about $0.008\,g\,g^{-1}$ is predicted (corresponding to an absolute uptake of around $0.015\,g\,g^{-1}$–1.5 wt%) in agreement with the findings of Wang and Johnson [8,9].

The "Chemisorption 1" results imply that the material could store up to 17 wt %, however its practical use as a medium for storage of hydrogen in a pressurised system at ambient temperature would be limited by the fact that the hydrogen does not desorb to any extent at 1 bar. This is not surprising in view of the fact that the isosteric heat of adsorption (determined by Monte Carlo Integration) for hydrogen in the $H = 0.9$ nm pore is $105.9\,kJ\,mol^{-1}$—similar to values for chemisorption of molecular hydrogen on metal surfaces.

The adsorbent modelled with "Chemisorption 2" can store up to about 8 wt % of hydrogen at 112 bar. At atmospheric pressure and ambient temperature, the material would retain about 2.5 wt % of hydrogen. For a practical system operating between 1 and 20 bar, the system would yield approximately 4.5 wt % over the adsorption/desorption cycle. This is somewhat less than the US DOE Hydrogen plan for Fuel Cell Vehicles, although it might be possible to use waste

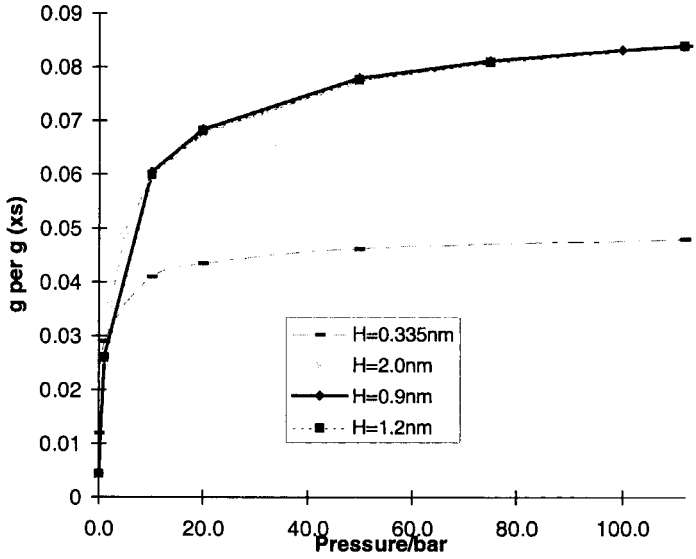


FIGURE 3 Simulated adsorption isotherms for hydrogen in a pores of various widths for "Chemisorption 2" model of the gas solid potential. $T = 298$ K.



heat in the vehicle to enable more hydrogen to desorb at ambient pressure. Figure 3 shows results for "Chemisorption 2" at various widths. Provided that there is enough room for a strongly adsorbed layer to form next to each graphitic surface, then the uptake (in wt %) is independent of pore width. It is noted that with this model for the potential, a single layer of hydrogen could intercalate between stacked graphitic sheets with spacing 0.335 nm.

### 3.3. Conclusions

Modelling the interaction between *molecular* hydrogen and graphitic surfaces using dispersion forces suggests that the uptake would not exceed 1.5%. There is no theoretical basis for the existence of significantly stronger forces, however two hypothetical chemisorption potentials have been investigated to answer the "what-if" question. The stronger potential gave adsorption of up to 17 wt % but with negligible desorption at ambient pressure, thereby making it impractical. Even with very strong gas–solid interactions, it is difficult to understand how hydrogen uptakes of 40 wt% could occur. The results suggest that some type of chemical interaction would be required to explain the uptakes in the 4–7 wt % range in various carbon systems reported by other workers [5–7].

## *References*


[1] Nicholson, D. and Parsonage, N.G. (1982) *Computer Simulation and the Statistical Mechanics of Adsorption* (Academic Press, London).

[2] Cracknell, R.F. (2001) "Molecular Simulation of Hydrogen Adsorption in Graphitic Nanofibers", *Phys. Chem. Chem. Phys.* **3**, 2091.

[3] Chambers, A., Park, C., Baker, R.T.K. and Rodriguez, N.M. (1998) "Hydrogen storage in graphitic nanofibers", *J. Phys. Chem. B* **102**, 4253.

[4] Park, C., Anderson, P.E., Chambers, A., Tan, C.D., Hidalgo, R. and Rodriguez, N.M. (1999) "Further studies of the interaction of hydrogen with graphitic nanofibers", *J. Phys. Chem. B* **103**, 10572.

[5] Turpin, M.C. (2000)."Hydrogen storage in carbon nanofibres", Presentation to British Carbon Group conference on Chemical and Physical Characterisation of Carbonaceous Materials, April 10–11, Leeds, UK.

[6] Dillon, A.C., Gennett,T., Allemann, J.L, Jones, K.M., Parilla, P.A. and Heben, M.J. (1999)."Carbon Nanotube Materials for Carbon Storage". Proceedings of the 1999 US DOE/NREL Hydrogen Program Review, "http://www.eren.doe.gov/hydrogen/docs/26938toc.html#storage".

[7] Dillon, A.C. and Heben, M.J. (2001) "Hydrogen storage using carbon adsorbents: past, present and future", *Appl. Phys. A-Mater.* **72**, 133.

[8] Wang, Q. and Johnson, J.K. (1999) "Molecular simulation of hydrogen adsorption of graphite nanofibers", *J. Chem. Phys.* **110**, 577.

[9] Wang, Q. and Johnson, J.K. (1999) "Molecular simulation of hydrogen adsorption in single walled carbon nanotubes and idealized carbon slit pores", *J. Phys. Chem. B* **103**, 277.

[10] Buch, V. (1994) "Path integral simulations of mixed para-D2 and ortho D2 clusters: the orientational effects", *J. Chem. Phys.* **100**, 7610.

[11] Steele, W.A. (1974) *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford).

[12] Jeloaica, L. and Sidis, V. (1999) "DFT investigation of the adsorption of atomic hydrogen on a cluster model graphitic surface", *Chem. Phys. Lett.* **300**, 157.

[13] Cracknell, R.F., Gordon, P. and Gubbins, K.E. (1993) "Influence of pore geometry on the design of microporous materials for methane storage", *J. Phys. Chem.* **97**, 494.