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MODELLING HYDROGEN STORAGE INSIDE FULLERENCES

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Abstract

Carbon-based nanomaterials such as fullerenes and nanotubes have been intensively studied due to the potential application for hydrogen storage materials. However, those recent studies have been carried out through experiments and computationally intensive molecular simulations. In this study, the storage of hydrogen molecules inside fullerenes has been investigated based on applied mathematical modelling using the basic principles of mechanics. The Lennard-Jones potential is employed to determine the total potential energy of the system. The encapsulation of hydrogen molecules inside fullerenes have been examined using the continuous approximation and an equation of state. The model is validated against the existing experimental data and molecular dynamics simulations. Furthermore, the effects of pressure and temperature on the encapsulation process have been studied. The main advantage of the approaches used in this study is that it provides analytical formulae which can generate important insights into encapsulation process and reveal optimal parameters or situations that might be otherwise almost impossible through experimentation.

Key words: hydrogen storage, fullerenes, Lennard-Jones potential, an equation of state, mathematical model.

1 Introduction

The Goldberg type I fullerene with I_n symmetries, namely C_{60}, C_{240}, C_{540}, C_{960} and C_{1500} are hallow clusters comprising of $60n^2$ carbon atoms on each shell [7]. Fullerenes are an extensively studied nanomaterial because of their unique physical and chemical properties such as their high flexibility and thermal conductivity. The use of fullerenes in hydrogen storage and delivery of energy is one of potential applications in nanotechnology. Recently, different experimental measurements have been reported on hydrogen storage ability of carbon-based nanomaterials such as fullerenes, carbon nanotubes. In the case of C_{60} fullerene, the storage capacity is only 0.28 wt.%. at 40°C [9]. It has been reported that hydrogen could be stored in open-end carbon nanotubes by using capillary action up to 5-10 wt.% [5]. These results reveal the excellent ability of hydrogen storage of carbon nanotubes.

Various computational techniques including molecular dynamic simulation [9], Monte Carlo techniques [1] and quantum-thermodynamical models [2] have been successfully applied to study hydrogen adsorption in carbon-based nanomaterials. However, those recent studies have been carried out through experiments and computationally intensive molecular simulations. In this study, the storage of hydrogen molecules inside Goldberg type I fullerenes has been investigated based on applied mathematical modelling using the basic principles of mechanics. The Lennard-Jones potential is employed to determine the total potential energy of the system. The encapsulation of hydrogen molecules inside fullerenes have been examined using the continuous approximation proposed by Cox *et al.* [4] and the methodology developed by Thornton *et al.* [10]. An equation of state from thermodynamic and kinetic principles is a key ingredient used in simulating hydrogen storage in the fullerenes. The model is validated against the existing experimental data and molecular dynamics simulations. Furthermore, the effects of pressure and temperature on the encapsulation process have been studied.

2 Theory and Mathematical Formulation

2.1 Lennard-Jones Function and Continuous Approximation

The interaction potential of a hydrogen molecule with a carbon surface of spherical shape is described by the Lennard-Jones potential energy function. The 6-12 Lennard-Jones potential is given by

$$\Phi(\rho) = 4\varepsilon\left[-\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12}\right] = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \qquad (1)$$

where ρ, ε and σ denote the distance between two atoms, the potential well depth of two atoms and the Lennard-Jones distance between two atoms, respectively. Furthermore, the constants A and B are attractive and repulsive Lennard-Jones constants respectively, which can be obtained from $A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$.

Using the continuous approach, where the atoms at discrete locations on the molecule are averaged over a surface, the total potential energy between a hydrogen molecule and fullerenes is obtained by calculating integral over the surface of fullerene

$$E(\rho) = \eta \int_S \Phi(\rho) dS, \tag{2}$$

where η, dS denote the mean surface density of the fullerene and the surface element of the fullerene, respectively. The analytical formulation for the total potential energy in (2) can be founded in Cox *et al.* [4] which is given by

$$E(\rho) = \frac{\pi\eta b}{\rho}\left(\frac{A}{2}\left(\frac{1}{(\rho+b)^4} - \frac{1}{(\rho-b)^4}\right) - \frac{B}{5}\left(\frac{1}{(\rho+b)^{10}} - \frac{1}{(\rho-b)^{10}}\right)\right), \tag{3}$$

where b is the radius of the fullerene.

The Lennard-Jones parameters used for non-bonding interaction between carbon and hydrogen molecule are taken from the work of Chan *et al.* [3], which are given by $A = 13.531$ eV $\times$Å^6 and $B = 1.2493 \times 10^4$ eV $\times$Å^{12}.

We assume that fullerene molecules can be modelled a spherical shape, and the mean surface density for the spherical molecule can be evaluated by $\eta = N/(4\pi b^2)$. The numerical values of the constants used in our model are as given in Table 1. The radii of fullerenes are taken from the work by Dunlap and Zope [6].

Table 1: Numerical values for constants used in this model

Radius of C_{60}	3.5481 Å
Radius of C_{240}	7.0728 Å
Radius of C_{540}	10.5528 Å
Radius of C_{960}	14.0342 Å
Mean surface density of C_{60}	0.3793 Å^{-2}
Mean surface density of C_{240}	0.3818 Å^{-2}
Mean surface density of C_{540}	0.3859 Å^{-2}
Mean surface density of C_{960}	0.3879 Å^{-2}

2.2 Thermodynamic and Kinetic Principles

Thermodynamic and kinetic principles are employed to determine the hydrogen storage capacities of various fullerenes, at a given temperature and external pressure. The methodology used here has been developed by Thornton *et al.* [10]. The stored hydrogen is composed of two phases including adsorbed hydrogen phase and a non-adsorbed gas phase (or bulk phase). Due to the kinetic theory, the probability of adsorption $P_{ad}(\rho)$ that a H_2 molecule will be adsorbed inside a fullerene can be approximated by

$$P_{ad}(\rho) = 1 - \exp\left(-\frac{|E(\rho)|}{RT}\right), \tag{4}$$

where R is the universal gas constant and T is the temperature in Kelvin. The total free molar volume V_f within fullerene can be divided into two volumes, the volume for gas molecules in the adsorbed phase and the volume for gas in the bulk phase:

$$V_{ad} = \int_0^{\rho_0} 4\pi\rho^2 P_{ad}(\rho)d\rho, \quad V_{bulk} = \int_0^{\rho_0} 4\pi\rho^2(1 - P_{ad}(\rho))d\rho, \tag{5}$$

where the radial boundary of the cavity ρ_0 is located where the total potential energy for adsorption is equal to the average kinetic energy, i.e. $E(\rho_0) = RT$. Hence, the total free volume V_f is equal to the sum $V_f = V_{ad} + V_{bulk}$.

A key ingredient in kinetic theory is the van der Waals equation of state, which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or potential energy. The equation of state can be directly applied to bulk gas phase, namely

$$p\left(\frac{V_{bulk}}{n_{bulk}} - \nu_0\right) = RT \tag{6}$$

where p is the pressure, n_{bulk} is the number of moles of gas molecules in the bulk phase and ν_0 is the van der Waals constant. In addition, an appropriate equation of state for gas molecules in the adsorbed phase proposed in [10] is given by

$$p\left(\frac{V_{ad}}{n_{ad}} - \nu_0\right) = RT\exp[-Q/(RT)], \tag{7}$$

where n_{ad} is the number of moles of gas molecules in the adsorbed phase and the heat of adsorption Q is given by $Q = |\bar{E}| + RT/2$. Here, $\bar{E}$ is the mean potential energy between gas molecules and the fullerene.

Finally, the total gravimetric uptake can be calculated as the weight percentage in the following way,

$$wt.\% = \frac{n_{tot}m}{n_{tot}m + M} \times 100,$$

where $n_{tot} = n_{ad} + n_{bulk}$ is the total number of molecules within the cavity, m is the mass of a gas molecule and M is the mass of container. We refer the reader to [10, 8] for the full calculation details of the percent by weight for the gas molecules adsorbed on nanostructures.

3 Results and Discussion

In this study, the hydrogen storage capacities are calculated at temperatures of 77 K and 300 K, and a pressure of 10 Mpa. As shown in Figs 1(a) and 1(b), the total gravimetric uptake for H_2 molecules encapsulated into Goldberg type I fullerenes of various sizes are calculated and compared with the existing theoretical studies from Cabria *et al.* [2]. They have used a quantum-thermodynamical model to calculate the gravimetric hydrogen uptake in spherical porous carbons using three different hydrogen-carbon surface interaction potentials based on Lennard-Jones (LJ), Mϕller-Plesset (MP2) and Density Functional Theory (DFT) calculations.

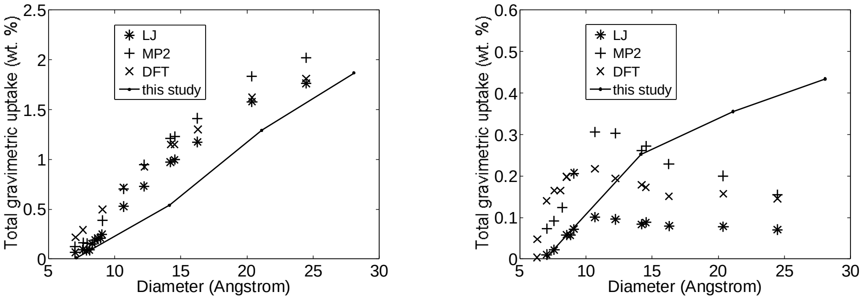
The qualitative behaviour of the storage capacities at 77 K as a function of fullerene diameters is the same for the simulation data from Cabria *et al.* [2] (Fig 1(a)). The simulations for C_{240}, C_{540} and C_{960} from this study slightly underestimate the simulation data from LJ, MP2 and DFT potentials

As shown in Fig 1(b), there are substantial qualitative differences at 300 K. However, the hydrogen storage capacities for C_{60} and C_{240} (of diameter 7.0962 Å and 14.1456 Å, respectively) at 300 K are in good agreement with the simulation for LJ potentials and MP2 potentials, respectively. The simulations for C_{540} and C_{960} from this study overestimate the simulation data from LJ, MP2 and DFT potentials (Fig 1(b)). The results also reveal that the accuracy of the models used depend strongly on interaction potentials used. Cabria *et al.* [2] have concluded that the MP2 method provides more realistic storage capacities because the MP2 potential considers a more reliable account of the dispersion interaction than the other two potentials.

The effect of pressure on hydrogen storage capacities has been shown in Figs 2(a) and 2(b). Pressures are varied from 10 MPa up to 10^3 MPa. The results reveal that the total gravimetric uptake at the temperature of 300 K increase monotonically from 0.34% to 0.57% for C_{240} and from 0.46% to 1.40% for C_{540}. Similarly, the simulation data for C_{540} at 77 K display a similar behavior. It should be noted that pressure does not affect the hydrogen storage capacities in other remaining cases.

We employ an algebraic package Maple to determine the relation between the distance Z and the total potential energy as graphically shown in Fig. ??. Further, the equilibrium distances Z at the minimum energy level for five cases of fullerenes are presented in Table 2.

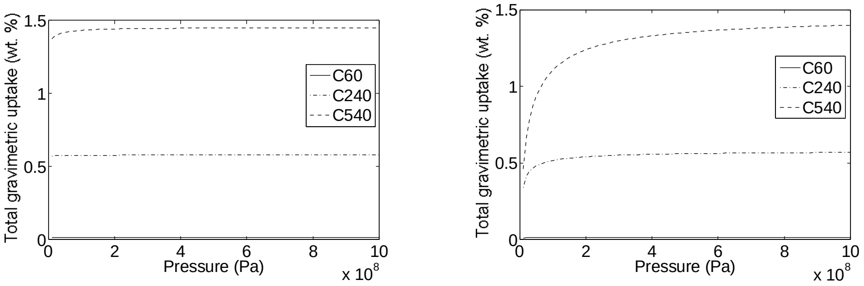
Following similar calculations by Thornton *et al.* [10], the probability P_{ad}



(a) at 77 K

(b) at 300 K

Figure 1: The total gravimetric uptake, obtained using LJ, MP2, DFT potentials and this study. Simulation data from Cabria *et al.* [2].



(a) at 77 K

(b) at 300 K

Figure 2: Effect of pressure on the total gravimetric uptake for C_{60}, C_{240} and C_{540}.

Table 2: The equilibrium distances Z and ϵ at the minimum interaction energy between H_2 and fullerenes

	C_{60}	C_{240}	C_{540}	C_{960}	C_{1500}
Z (Å)	0	4.1132	7.6197	11.1102	14.6030
ϵ (Å)	3.1781	2.5896	2.5631	2.5540	2.5495

that a H_2 molecule will be adsorbed inside a fullerene is assumed to be given by

$$P_{ad} = 1 - \exp(-|E_{min}|/RT),$$

where E_{min} is the binding energy, R is the universal gas constant which is 8.6471×10^{-5} and T is the temperature in Kelvin. Further, the number of H_2 molecules adsorbed inside a fullerene, n_{ad}, and the number of H_2 molecules in bulk phase, n_{bulk}, can be determined. The total uptake can be calculated as the weight percentage in the following way,

$$wt.\% = \frac{n_{tot}m}{n_{tot}m + M} \times 100,$$

where $n_{tot} = n_{ad} + n_{bulk}$ is the total number of molecules within the cavity, m is the mass of a gas molecule and M is the mass of container. We refer reader to [10, 8] for the full calculation details of the percent by weight for the gas molecules adsorbed on nanostructures.

Here, we determine the H_2 adsorption isotherms at a temperature of 77 K for pressures at 1 Mpa. The total number of H_2 molecules n_{tot} within the cavity and the total uptake calculated as the weight percentage $wt.\%$ for H_2 molecules encapsulated into five capsules of Goldberg type I fullerenes are present in Table 3.

Table 3: The total number n_{tot} and the total uptake by weight percentage $wt.\%$ for H_2 molecules encapsulated into five capsules of Goldberg type I fullerenes

	C_{60}	C_{240}	C_{540}	C_{960}	C_{1500}
n_{tot}	20	1,864	9,940	27,929	58,910
$wt.\%$	2.67	39.51	60.75	70.99	76.76

4 Conclusions

In this study, the hydrogen storage capacities of the Goldberg type I fullerenes have been simulated. The Lennard-Jones potential is employed to determine the total potential energy of the system. The encapsulation of hydrogen molecules inside fullerenes have been examined using the continuous approximation and an equation of state. The model has been used to study the effects of temperature and pressure on the encapsulation process. In comparison to other simulation techniques such as molecular dynamic simulation and Monte Carlo simulation, the main advantage of the approaches used in this study is that it provides analytical formulae which can generate important insights into encapsulation process and reveal optimal parameters or situations that might be otherwise almost impossible through experimentation. The model should also be able to apply to study the hydrogen or other gases storage in other nanostructures.

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References

[1] S. K. Bhatia and A. L. Myers, *Optimum Conditions for Adsorptive Storage,* Langmuir, **22** (4) (2006), 1688-1700.

[2] I. Cabria and M.J. Lopez and J. A. Alonso, *Simulation of the hydrogen storage in nanoporous carbons with different pore shapes,* Int J Hydrogen Energy, **36** (2011), 10748-10759.

[3] Y. Chan and J.M. Hill, *Hydrogen storage inside graphene-oxide frameworks,* Nanotechnology, **22**(30), (2011).

[4] B. J. Cox, N. Thamwattana and J. M. Hill, *Mechanics of atoms and fullerenes in single-walled carbon nanotubes. I. Acceptance and suction energies,* Proc. R. Soc. A **463** (2007), 461-476.

[5] A. C. Dillon, K. M. Jones, T. A. Bekkdahl, C. H. Kiang, D. S. Bethune and M. J. Heben, *Storage of hydrogen in single-walled carbon nanotubes,* Nature **386** (1997), 377-379.

[6] B. I. Dunlap and R. R. Zope, *Efficient quantum-chemical geometry optimization and the structure of large icosahedral fullerenes,* Chem. Phys. Lett., **422** (2006), 451-454.

[7] H. W. Kroto and K. Mckay, *The formation of quasi-icosahedral spiral shell carbon particles,* Nature **331** (1988), 328-331.

[8] O. O. Adisa, B. J. Cox and J. M. Hill, *Modelling the surface adsorption of methane on carbon nanostructures,* Carbon, doi: 10.1016/j.carbon.2011.03.046, 2011, xx.

[9] S. Riahi, P. Pourhossein, A. Zolfaghari, M. R. Ganjali and H. Z. Jooya, *Encapsulation Hydrogen Molecule in Fullerene (C_{60}),* Fullerenes, Nanotubes and Carbon Nanostructures, **17** (2009), 159-170.

[10] A. W. Thornton, K. M. Nairn, J. M. Hill, A. J. Hill and M. R. Hill, *Metal-Organic Frameworks Impregnated with Magnesium-Decorated Fullerenes for Methane and Hydrogen Storage,* J. Am. Chem. Soc., **131** (2009), 10662-10669.