Modelling gas storage in molecular nanosystems

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Contents

Signed Statement viii

Acknowledgements ix

Dedication x

Author’s publications xi

Abstract xii

1 Introduction 1

1.1 Overview ................................................................. 1
1.2 Adsorption of CH$_4$ on graphite ................................. 3
1.3 Adsorption of CH$_4$ on single and multi-walled carbon nanotubes ... 6
1.4 Adsorption of CH$_4$ on carbon nanotubes bundles and interstitial channels .................................................. 11
1.5 Adsorption of CH$_4$ on other nanostructures .................... 17
1.6 Thesis structure .......................................................... 22

2 Encapsulation of methane molecules into carbon nanotubes 24

2.1 Continuous approximation and Lennard-Jones potential ........ 26
2.2 Interaction of CH$_4$ with carbon nanotube ....................... 29
2.3 Results and discussions ................................................. 34
2.4 Conclusions ............................................................ 37
3 Packing configurations for methane storage in carbon nanotubes

3.1 Method

3.2 Zigzag configuration for CH$_4$@SWCNT

3.2.1 Numerical results for zigzag CH$_4$@SWCNT

3.3 Spiral configuration for CH$_4$@SWCNT

3.3.1 Numerical results for spiral CH$_4$@SWCNT

3.4 Conclusions

4 Modelling surface adsorption of methane on carbon nanostructures

4.1 Method

4.2 Interaction of CH$_4$ and graphite

4.3 Interaction of CH$_4$ and SWCNT groovesite

4.4 Results and discussions

4.5 Conclusions

5 Open carbon nanocones as candidates for gas storage

5.1 Method

5.2 Interaction of H$_2$, CH$_4$ and Ne with a single-walled carbon nanocone

5.3 Results and discussions

5.4 Conclusions

6 Encapsulation of methane in nanotube bundles

6.1 Method

6.2 Interaction of CH$_4$ with bundles

6.3 Suction of CH$_4$ into bundles

6.4 Results and discussions

6.5 Conclusion

7 Summary
A 109
A.1 Evaluation of integral $J_n$ defined by (2.2.3) .......................... 109
A.2 Derivation of equation (2.2.8) ........................................ 110
A.3 Evaluation of $K_{i,j}$ integral defined by (2.2.8) ................. 112
A.4 Evaluation of offset angle $\phi$ appearing in 2.2.8 ............... 113

B 115
B.1 Evaluation of equation (3.2.5) ........................................ 115
B.2 Evaluation of equation (3.2.6) ........................................ 117

C 119
C.1 Evaluation of $I_{cg}$ given by (4.2.2) .............................. 119
C.2 Evaluation of $I_{hg}$ given by (4.2.4) .............................. 119

Bibliography 121
List of Tables

2.0.1 Numerical values of constants used in this chapter (* denotes data from [1] and ** denotes data from [2]). 26

3.0.1 Numerical values of constants used in this chapter(* denotes data from [1], ** denotes data from [2], and *** denotes from [3]). 42

3.2.1 Average potential energy per CH$_4$ molecule (eV), equilibrium spacing $Z$(Å), offset position $\lambda$ (Å) and volume density $\eta_{vol}$ (g cm$^{-3}$) for the zigzag configuration of $(2m + 1)$ CH$_4$ molecules in three carbon nanotubes. 46

3.2.2 Average potential energy per CH$_4$ molecule (eV), angular spacing $\phi$ ($^\circ$), longitudinal spacing $Z$ (Å), offset position $\lambda$ (Å) and volume density $\eta_{vol}$ (g cm$^{-3}$) for the spiral configuration of $m$ CH$_4$ molecules in three carbon nanotubes. 51

4.0.1 Numerical values of constants used (* denotes data from [1] and ** denotes data from [2]). 62

4.4.1 Comparison of potentials for minimum energy (eV) and equilibrium location (Å) from existing data for the interaction of helium and argon with graphite. Lennard-Jones constants taken from [4] and [5] (* denotes from [4]). 68

4.4.2 Data (E - Experimental, T - Theoretical) on binding energy and equilibrium location for CH$_4$ adsorption on graphite. 69
5.0.1 Numerical values of constants used (* and ** denote data from [1] and [6] respectively). 80

5.1.1 Proposed base radii for carbon nanocones with $\Theta = 112.9^\circ$. 82

6.1.1 Numerical values of constants used (* denotes from [1], ** denotes from [2] and *** denotes from [7]). 96

6.3.1 Optimal bundle radii and total energies for CH$_4$-CNT and CH$_4$-SiNT bundles. 100
# List of Figures

1.5.1 Schematic representation for Mg-C$_{60}$@MOF showing a MOF cavity impregnated with magnesium-decorated C$_{60}$ [8] .......................... 17

2.1.1 CH$_4$ entering a carbon nanotube for models (I) and (II) ............ 28
2.1.2 Energy profile between CH$_4$ and carbon nanotube at $\phi \simeq 7\pi/18$ ........................... 29
2.2.1 Energy profile between CH$_4$ molecule and carbon nanotube for orientation 2.1.1(b) ................................................................. 34
2.3.1 Energy profile for CH$_4$ encapsulated into a (9,5) tube for orientation 1(a) ................................................................. 36

3.2.1 Zigzag configuration for $(2m+1)$ CH$_4$ molecules inside a carbon nanotube ................................................................. 45
3.3.1 Spiral configuration for $m$ CH$_4$ molecules inside a carbon nanotube ................................................................. 53
3.3.2 Volume for adsorption for CH$_4$ with zigzag and spiral packing ........ 56

4.2.1 CH$_4$ molecule interacting with graphite ........................................ 64
4.3.1 CH$_4$ molecule in SWCNT groove site ........................................ 66
4.4.1 Equilibrium location for CH$_4$ adsorption-graphite and groove site .... 69
4.4.2 Energy level curves for a CH$_4$ molecule in a single-walled carbon nanotube groove site starting from -0.4 eV (white) to 1.4 eV (darkest black) with an increment of 0.2 eV in colour strength .................. 70
4.4.3 Probability for CH$_4$ adsorption-graphite and groove surfaces ........ 70
4.4.4 CH$_4$ adsorption isotherms at 298 K ........................................ 71
5.0.1 Ne, H₂ and CH₄ interacting with a single-walled carbon nanocone of
length $L_2 - L_1$ and apex angle $\theta$ ........................................... 76
5.1.1 Binding energy and molecular force for CH₄ molecule, two H₂ molecules,
and four Ne atoms entering single-walled carbon nanocone ............. 79
5.1.2 Binding energy and molecular force for CH₄ molecule, two H₂ molecules,
and four Ne atoms entering single-walled carbon nanocone ............. 83
5.2.1 Binding energy and molecular force for CH₄ molecule, two H₂ molecules,
and four Ne atoms entering single-walled carbon nanocone ............. 84
5.2.2 Volume for adsorption for a CH₄ molecule, two H₂ molecules, and
four Ne atoms in a single-walled carbon nanocone for two distinct
nanocone radii ................................................................. 87
6.1.1 CH₄ molecule entering nanotube bundle ................................. 95
6.2.1 Total interaction energy between CH₄ molecule and sixfold symmetric
carbon and silicon nanotube bundles. ........................................ 98
6.3.1 Total molecular force for CH₄ molecule entering sixfold symmetric
carbon and silicon nanotube bundles. ....................................... 100
6.4.1 Suction energy for CH₄ molecule entering sixfold symmetric carbon
and silicon nanotube bundles ................................................. 101
6.4.2 Total interaction potential between an offset CH₄ molecule and sixfold
symmetric carbon and silicon nanotube bundles .......................... 102
6.4.3 Relationship between volume for CH₄ adsorption and temperature in
open cavity of sixfold symmetric carbon and silicon nanotube bundles 103
1.4.1 (a) Representation of molecule on unit cube with carbon at the center
of the cube; (b) Representation of offset angle on unit cube. .......... 113
Signed Statement

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no other material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide. I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968. The author acknowledges that copyright of the published works contained within this thesis resides with the copyright holder(s) of those works.

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Dedication

To the almighty Lord, Daddy, Mummy, Niyi&family, Bukola&family, Folake&family, Ayo, the Bamigboyes and to the memory of Samuel Okusanya.
Author’s publications


Abstract

In this thesis, we develop models for the adsorption of gases in various nanocontainers. We exploit the Lennard-Jones potential together with the continuous approximation, which assumes that discrete molecular structures may be approximated by replacement over the entire surface with a uniform atomic surface density. We first develop an entirely new model for a methane molecule which avoids needing to take into account the detailed atomic orientations and thus provides a major simplification to the numerical calculations, and which compares favourably with a detailed discrete formulation. This model is subsequently employed in a number of problems investigated throughout the thesis. Methane adsorption is examined in various molecular structures, which have been proposed as possible containers for methane storage; namely carbon nanotubes, carbon and silicon nanotube bundles (including interstitial and groove sites), graphite and carbon nanocones. Analytical expressions are obtained for the interaction energies and forces, the volume available for adsorption, the adsorption isotherms as well as for the probabilities for adsorption on the internal surfaces of these nanocontainers.

Computational simulation and mathematical modelling play important roles in predicting and verifying experimental outcomes which are often expensive and time consuming. Even though recent advances have greatly improved computations, due to the large number of atoms and force field calculations involved, computational simulations can still be time consuming as compared to the rapid evaluation of an analytic mathematical modelling solution. On the other hand, underlying an ideal mathematical model, there are many assumptions and approximations, but
such models often reveal the key physical parameters and optimal configurations. Here, we model the mechanics of gas storage and predict critical parameters such as the maximum and minimum geometric parameters for successful gas storage in these nanostructures, the presence or absence of energy barriers in the encapsulation process, as well as the total work done by the gas molecules during encapsulation. We determine the equilibrium distances in relation to the nanostructure surface, which are derived at the minimum energy configuration, for specific molecular structures such as graphite, a phenomenon which is essential to understanding the dynamics of the interaction. Storage in some of these molecular structures has already been investigated through either experiments or molecular dynamics simulations, and for those cases for which experimental data exists, the modelling presented in this thesis compares favourably. The major findings relate to gas encapsulation and packing in nanostructures, and the results presented here give, for the first time, accurate numerical values of minimum energies, equilibrium locations, gravimetric uptakes as well as volumes and probabilities for adsorption of gases onto these nanostructures.
Chapter 1

Introduction

1.1 Overview

Methane (CH$_4$), at room temperature is a colourless, odourless gas comprising four hydrogen atoms surrounding a centrally positioned carbon atom. It is the simplest alkane, and it is the main constituent of natural gas which typically comprises some concentration of other hydrocarbons (usually ethane) as well as small amounts of impurities such as carbon dioxide. In the form of natural gas, CH$_4$ may be used as a vehicle fuel, for the generation of electricity, and for the production of acetic acids and anhydrides. Nanotechnology promises to revolutionise the development of new materials for several industries, and in particular, the energy industry is poised to benefit from the development of these new materials. Storage of natural gas (predominantly, CH$_4$) in nanostructures is one innovation that could generate the widespread commercial use of environmentally clean and secure fuels, and gas storage using nanotechnology is emerging as a new, effective and efficient means of gas conservation. Nanoscale containers constructed from various nanostructures have been proposed as feasible, storage devices for gases such as CH$_4$, and in order to attain this, an improved understanding of its interaction with molecular structures is necessary. Compared to other hydrocarbon fuels, burning CH$_4$ produces less carbon
dioxide for each unit of heat that is released, so that it is regarded as a comparatively clean fuel which is abundant and naturally occurring. High daily levels of carbon emissions have increased research into CH$_4$ conservation. However, in addition to the technological and economical problems associated with CH$_4$ production or mining, efficient storage and transportation are the major bottlenecks associated with its widespread use as a clean source of energy, and these are problems which molecular modelling might resolve.

The major difference between conventional carbon nanostructures such as graphite, single and multi-walled carbon nanotubes, and carbon nanotube bundles is their geometric configuration. CH$_4$ adsorption on graphite arises primarily from the interactions between the sheet and the molecules, while for nanotubes and nanotube bundles, the adsorption process is also influenced by the interactions between neighbouring CH$_4$ molecules given the confined space in these nanostructures. Further, for carbon nanotubes, adsorption occurs at single sites in the internal space of the tube, while for nanotube bundles, the interstitial and groove spaces offer more available sites for CH$_4$ adsorption. Recently, other nanoscale containers have been proposed for CH$_4$ storage including nanocones [9], metal organic frameworks (MOFs) [8], covalent organic frameworks (COFs) [10] and nanocapsules [11]. In the continuing search for highly efficient storage materials, these new materials represent novel directions.

Studies on CH$_4$ storage in molecular containers have been carried out using three main approaches, namely experimental [12, 13, 14], molecular dynamics simulation [15, 16] and mathematical modelling [17, 8], and methods that combine more than one of these approaches [18, 19]. Experimental procedures are perhaps the closest to reality, but this approach is often expensive, time consuming and there is little control in terms of identifying important parameters in the procedure. Molecular computational techniques attempt to simulate an experimental procedure using mathematical force-field formulae, but these calculations can also be computationally expensive and time consuming with every case requiring a separate calculation.
In contrast, an applied mathematical modelling approach is based on many assumptions and approximations, but provides computationally efficient outcomes, identifies important physical parameters, makes predictions and general observations. In the following section, we present a summary of adsorption of CH$_4$ onto graphite. An examination of CH$_4$ adsorption on carbon nanotubes and nanotube bundles (including interstitial and groove sites) is given in sections 1.3 and 1.4. Some discussion of CH$_4$ adsorption on other non-conventional nanostructures is provided in section 1.5, and a brief summary is presented in the final paragraph of this chapter.

### 1.2 Adsorption of CH$_4$ on graphite

CH$_4$ adsorption on graphite has an extensive history [17, 20, 21, 22, 23, 24, 4, 25] largely due to its practical and theoretical significance which includes the production of carbon (graphite) through CH$_4$ pyrolysis [26], and since the recent discovery of fullerenes and carbon nanotubes, there has been a renewed interest in graphite. Vidali et al [23] present a review of over 250 gas-surface systems including the CH$_4$-graphite system. They tabulate van der Waals adsorption coefficients, equilibrium distances, well depths and binding energies for the laterally averaged interaction potential as deduced from the analyses of experimental data and calculations. Severin et al [22] carry out a molecular dynamics study of a CH$_4$ molecule adsorbed on a graphite surface utilizing pairwise potential calculations to predict the height of a CH$_4$ monolayer above the graphite surface, as well as the vibrational frequency against the surface, with the three objectives: (i) the development of molecular dynamics programs to model small rigid molecules adsorbed onto a graphite surface, (ii) determination of a CH$_4$-surface pairwise potential that will reproduce the available experimental thermodynamic and structural evidence, and (iii) the use of this effective pairwise potential to examine the behaviour of a single molecule diffusing across the surface. Their model comprises a unit cell of graphite as a rhombus of side 2.46 Å with an included angle of 120°, and a base containing 288 atoms. It is
shown that at 18.6 K and 53.4 K, the CH₄ molecule sits as a tripod above the surface but rotates freely around the C-H bond at the higher temperature. At 108 K, the CH₄ molecule tumbles and collides with the surface, but not as a free rotor. The average equilibrium height of the CH₄ molecule above the surface is also predicted to be 3.35 Å. Phillips et al [21, 27] use intermolecular potentials and lattice sums to investigate vibrational zero-point energies, equilibrium structure of a CH₄-graphite system, conditions for monolayer-bilayer and bilayer-trilayer coexistence. They calculate the potential energy, relative to the basal plane of a semi-infinite graphite crystal, of a CH₄ molecule whose center (C atom) at \( r \) is height \( z \) above a point \((x,y)\) on the graphite surface given by

\[
\phi_m(r; \theta, \phi) = \sum_i \sum_j \phi_{ij}(r_{ij}; \theta, \phi),
\]

where \( m = 1, 2 \). They determine the lowest-lying-energy configuration of a single CH₄ molecule as in a tripod position above a bridge site with two tripod legs straddling the graphite carbon-carbon bond with the CH₄ carbon at a vertical height of 3.32 Å above the graphite plane at the minimum potential energy. Rayment et al [12] employ neutron diffraction to study experimentally, the adsorption of CH₄ on graphitized carbon black. For their experimental work, they employ Vulcan III (2700) as their graphitized carbon black with a surface area of 71 m² g⁻¹, and give an equilibrium distance of CH₄ - graphite surface as 3.35 Å for a static CH₄ molecule, while for a freely rotating CH₄ molecule, an equilibrium distance of 3.2 Å is predicted.

Other theoretical contributions include for example, Yang et al [20], who employ a density-functional calculation for the adsorption of CH₄ on graphite. A plane-wave basis set and a projection-augmented-wave (PAW) method is adopted rather than the pseudopotentials for the carbon and hydrogen atoms of the system. The adsorption energy \( E_{ab} \) is taken to be
\[ E_{ab} = E(\text{CH}_4/\text{graphite}) - E(\text{graphite}) - E(\text{CH}_4), \] (1.2.2)

where \(E(\text{CH}_4/\text{graphite})\) is the energy of the total system, \(E(\text{graphite})\) is the energy of the graphite alone and \(E(\text{CH}_4)\) is the energy of the isolated (gas phase) \(\text{CH}_4\) molecule. At zero temperature, the \(\text{CH}_4\) carbon is predicted to be sitting on an atop site of the graphite substrate with the tripod legs oriented toward the open centers of the three adjacent graphite hexagons at an equilibrium distance of 3.21 Å for six layers of graphite. Sabzyan et al [28] employ semi-empirical quantum mechanical techniques to investigate \(\text{CH}_4\)-graphite interaction. A planar polyaromatic molecule that has chemical characteristics similar to graphite is chosen as a model for graphite, and the interaction potential energy curves for nine different relative \(\text{CH}_4\) orientations as functions of some inter-molecular distance \(R\) are calculated. The physical interaction energy at each distance \(R\), \(\Delta E(R)\) is calculated using a super-molecular method defined by:

\[ \Delta E(R) = E_b(G - M) - (E_b(G) + E_b(M)), \] (1.2.3)

where \(E_b(G - M)\), \(E_b(G)\) and \(E_b(M)\) are the calculated binding energies of the \(\text{CH}_4\)-graphite complex at distance \(R\), and the isolated graphite and \(\text{CH}_4\) molecules respectively. Based on parametrisation method 3 (PM3) potentials, for the first eight orientations in which the \(\text{CH}_4\) molecule approaches the graphite surface perpendicularly, the minima potential curves for the strongest orientations occur at an equilibrium distance of 3.82 Å and 3.90 Å. Ricca et al [29] examine \(\text{CH}_4\) physisorption on graphite using a second order Möller-Plesset perturbation theory, and two models for graphite namely, pyrene (\(\text{C}_{16}\text{H}_{10}\)) and circumpyrene (\(\text{C}_{42}\text{H}_{16}\)). The binding energy of \(\text{CH}_4\) on graphite is estimated to be 0.1518 ± 0.043 eV with an
equilibrium distance of 4.27 Å.

1.3 Adsorption of CH\textsubscript{4} on single and multi-walled carbon nanotubes

Carbon nanotubes, are the strongest material known to date [30] with unique physical properties such as low density, high flexibility, high thermal and electrical conductivities and miniature size [30, 31, 32, 33], and can be thought of as a rolled up graphene sheet which forms a cylinder with an sp\textsuperscript{2} electronic structure [33]. However, since their recent discovery, there has been a relative shift of interest from gas adsorption on graphite to gas adsorption in carbon nanotubes. Jakobtorweihen et al [15] employ molecular dynamics simulations for the self-diffusion of CH\textsubscript{4} inside single-walled carbon nanotubes (SWCNT) at zero-loading limit. Intermolecular interactions are modelled with the shifted and truncated Lennard-Jones 12 – 6 potential with a cut-off radius of 14 Å while the fluid molecules are modelled as united-atoms. The self-diffusion coefficient of CH\textsubscript{4} molecules are modelled employing a slightly modified version of the Stokes-Einstein-equation (SEE) given by

\[ D_s = \frac{T k_B}{\Gamma \mu}, \]

where \( D_s \) is the self-diffusion coefficient, \( T \) is the temperature, \( k_B \) is the Boltzmann constant, \( \Gamma \) is the collision frequency, \( \mu = m_f m_c / (m_f + m_c) \) is the reduced mass, \( m \) the mass of the particle, \( f \) stands for a fluid molecule and \( C \) a carbon atom. It is shown that for smaller radius CNTs, the potential minimum is located at the center of the tube while for larger radius CNTs the minimum is located near the tube walls. The authors also predict that for CNTs with radii greater than 0.56 nm, the diffusivity increases with temperature while for radii smaller than 0.56 nm, the reverse is the case. This phenomenon is explained by the influence of
temperature on collision frequency. If the influence of temperature is stronger on collision frequency, the self-diffusivity decreases but if the influence of temperature is weaker on collision frequency, self-diffusivity increases with temperature. This observation is highlighted quantitatively by calculating the probability to detect a molecule at a fluid-wall distance smaller than 0.35 nm. For example, for CH$_4$ inside a (20, 0) CNT at 300 K, a probability of 0.26 is found which diminishes to 0.24 for 700 K. In the case of the (11, 0) tube, this probability increases from 0.19 to 0.39 for the same temperature range. Ganji et al [34] investigate the interaction of SWCNT and a CH$_4$ molecule employing first principles calculations. The discussion of the role of structural defects and nanotube curvature on the adsorption capacity of SWCNT is presented in this study. Density functional based tight binding (DFTB) method calculations for the structural optimizations of carbon nanotubes and CH$_4$ molecule using a tabulated set of integrals derived from ab initio density functional theory (DFT) calculations are performed. The binding energy $E_b$ is assumed to be given by

$$E_b = E_{CNT+Methane} - E_{CNT} - E_{Methane},$$

(1.3.2)

where $E_{CNT+Methane}, E_{CNT}$ and $E_{Methane}$ are the total energies of the carbon nanotube with adsorbate, free carbon nanotube and single CH$_4$ molecule, respectively. After full structural optimization, a CH$_4$ molecule is predicted to prefer to be adsorbed on the hollow site of the hexagon ring of metallic (6, 6) CNT, and from the obtained binding energies, CH$_4$ molecule’s affinity to a metallic single-walled carbon nanotube is about 61% stronger than that of a semi-conducting one. The results also agree with [35] in proposing the interior surfaces of carbon nanotubes as favoured sites for CH$_4$ encapsulation. Further, it is found that there is considerable increase in the adsorption binding energy of the order of 156% for defected CNTs in comparison with defect-free CNTs due to the presence of structural defects in CNTs.
Some experiments include, for example, Lee et al. [36], who study CH$_4$ adsorption on multi-walled carbon nanotubes (MWCNT) at (303.15, 313.15 and 323.15) K. These authors adopt two zeolites and MWCNT for the adsorbent, and the MWCNT are made using chemical vapour deposition (CVD) which gives homogeneous lengths and well-defined parameters. The outer diameter of the multi-walled carbon nanotube is $70 - 100$ nm, the inner diameter is $15 - 20$ nm, the length is $20 - 30$ µm, and the bulk density is $0.005 - 0.006$ g cm$^{-3}$. CH$_4$ of high purity (99.9%) is used while the adsorption equilibrium data for CH$_4$ is obtained using the static volumetric method. The adsorption capacity is calculated using the mass balance on the basis of temperature and pressure measured before and after the adsorption equilibrium state given by

$$\frac{PV}{zRT}|_{L_1} + \frac{PV}{zRT}|_{A_1} = \frac{PV}{zRT}|_{L_2} + \frac{PV}{zRT}|_{A_2} + NM, \quad (1.3.3)$$

where $P$ is pressure, $T$ is temperature, $V$ is volume, $R$ is the gas constant, $M$ is the molecule mass, $z$ is the compressibility factor, and $N$ is the amount adsorbed, subscripts of 1 corresponds to the state prior to adsorption, and 2 denotes the final equilibrium state. Results for the adsorption of CH$_4$ on MWCNT is obtained at (303.15, 313.15 and 323.15) K and for pressures up to 3 MPa, and it is shown that CH$_4$ adsorption equilibrium for MWCNT and the two zeolites are significantly different on temperature. Unlike zeolites, CH$_4$ adsorption is weakly favourable at low pressures ($< 1.5$ MPa), while capillary condensation occurs at higher pressures. The pressure responsible for capillary condensation of CH$_4$ is seen to increase with temperature. Experimental results demonstrate that the isosteric enthalpies of adsorption with the surface loading varies in range from $-15$ kJ mol$^{-1}$ to $-50$ kJ mol$^{-1}$ for MWCNT and from $-10$ kJ mol$^{-1}$ to $-40$ kJ mol$^{-1}$ for the HSZ-320 zeolite and show almost a constant value of $-15$ kJ mol$^{-1}$ for the DAY zeolite. Finally, the multi-walled carbon nanotube adsorbents for the experiment are shown to have
energetically heterogeneous surfaces. Murris et al [13] carry out experiments to measure CH₄ adsorption on SWCNT at 78.7 and 77.3 K, employing SWCNT closed at both ends prepared by means of the yttrium-nickel catalyzed electric arc method in helium atmosphere with radius 6.85 ± 1 Å. Isotherms are measured in classical volumetric apparatus as well as the cryogenic system with a uniform and constant cell temperature of 0.05 K. For calorimetric measurements, the adsorbate is introduced in a continuous way at an extremely slow constant rate, around 2 cm³ h⁻¹ for which it is checked that the quasi-equilibrium conditions are fulfilled. The results show that CH₄ adsorption isotherms on SWCNT provide evidence of two types of comparatively uniform patches on the surface of the sample, giving rise to two distinct steps on the isotherms. Also, it is indicated that one type of patch is more attractive than a graphite surface and the other less attractive. A phase transition is predicted, evidence of which is given in the volumetric measurements to occur at 88 ± 2 K on the less attractive quasi-uniform fraction of the surface, illustrating the advantages and limits of adsorption volumetry for the characterization of nanotube surfaces.

Tanaka et al [37] employ non-local DFT method to study CH₄ adsorption on SWCNT at 303 K, modelling the attractive part of the fluid-fluid interaction for their non-local DFT using the Lennard-Jones potential, while the repulsive part of the fluid-fluid interaction is modelled by an equivalent hard-sphere potential with an approximate hard-sphere diameter \( d \). The results show that total excess adsorptions on the internal and external surfaces of the tubes are almost independent of the pore size although adsorption on the external surface makes a significant contribution to the total amount of CH₄ adsorbed. The authors also report that interstitial adsorption constitutes a small fraction of the total amount adsorbed on the open-ended single-walled carbon nanotube. Zhao et al [16] perform an \textit{ab initio} study of the energetics, structural, electronic, and optical properties of the CH₄ -doped ultrathin 4 Å and larger diameter carbon nanotubes. They employ an \textit{ab initio} method that uses the pseudopotential and plane waves along with the DFT with
the wavefunctions determined in a fixed potential according to a state by state or band by band conjugate gradient algorithm. The number of atoms in a unit cell of the isolated (3, 3), (5, 0), (4, 2), and (10, 10) nanotubes are 12, 20, 56 and 40 respectively. For establishing the stability of a configuration, the chemical binding energy (CBE) of the system is defined by subtracting the optimized energy of the unit cell of the doped nanotube from the sum of the optimized energy of the unit cell of the undoped nanotube and the energy of the isolated chain or chains of the CH$_4$ molecules adsorbed in or on the doped tube and divide the difference by the number of the CH$_4$ molecules in the unit cell. For the physisorption of the CH$_4$ molecule on the carbon nanotubes, the attractive van der Waals interaction energy is included by employing the relation

$$E_{vdW} = -\sum_i \sum_j C_{ij} \left(\frac{1}{r_{ij}}\right)^6,$$  \hspace{1cm} (1.3.4)

where $C_{ij}$ is a parameter having the units as energy $\times$ (distance)$^6$ and the subscripts $i$ and $j$ stand for the CH$_4$ molecules and the C atoms, respectively.

Similarly, the zero-point vibrational energy (ZPVE) is given by

$$E_{zp} = \frac{1}{2} \sum_i \hbar \omega_i,$$  \hspace{1cm} (1.3.5)

where the sum is over all the phonon frequencies ($\omega_i$) for all the atoms in the unit cell. The most favoured site for the CH$_4$ molecule adsorption is shown to lie inside the large diameter tubes, and the adsorption of the CH$_4$ molecule is preferred on the mid-hexagonal sites of the achiral tubes except on the mid-bond sites of the (3, 3) tube. It is also observed that quite small changes in the radii of the nanotubes are induced by the adsorption of the CH$_4$ molecules, with large buckling occurring in the armchair tubes in contrast to the negligible or quite small changes in the zigzag tubes. The maximum admissible exohedral adsorption of the CH$_4$ molecules on all
the surface sites of all the tubes is quite small, while on the other hand, the maximal admissible endohedral adsorption in the large diameter (10, 0) and (10, 10) tubes is approximately 2.5% and 10%, respectively. The band gap of the semiconducting achiral zigzag nanotube is reduced by the adsorption of the CH$_4$ molecule while the reverse is observed in the case of a chiral semiconducting tube.

1.4 Adsorption of CH$_4$ on carbon nanotubes bundles and interstitial channels

In this section, we review CH$_4$ gas storage in nanotube bundles and in those regions of space in between constituent nanotubes forming a bundle. Kondratyuk et al [18] carry out experiments and simulations to observe the effects of molecular length for a one-dimensional adsorption site on carbon nanotubes. The SWCNTs employed in their experiments are produced using pulsed laser vaporization of graphite with a Ni-Co catalyst with the distribution of tube diameter centered near 13.6 Å and length $\approx 320$ nm, while the hybrid Monte-Carlo (HMC) method is used for the simulations on the nanotubes-CH$_4$ system. The nanotube bundle employed in the simulations consist of two (10, 10) nanotubes, each containing 20 unit cells (length 49 Å) and the gap between the walls of the adjacent tubes is set to 3.2 Å. The alkane-alkane potential is divided into nonbonded (eq 1.4.1), bond stretching and bond bending (eq 1.4.2) and torsion terms (eq 1.4.3) as follows

$$u(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right],$$  \hspace{1cm} (1.4.1)

$$u_{\text{stretch}} = \frac{1}{2}k_r(r - r_0)^2, \quad u_{\text{bend}} = \frac{1}{2}k_\theta(\theta - \theta_0)^2,$$  \hspace{1cm} (1.4.2)
$u_{t\text{orsion}} = c_0 + c_1[1 + \cos \phi] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)], \quad (1.4.3)$

where $\epsilon_{ij}$ is the depth of the potential well, $\sigma_{ij}$ is the finite distance at which the intermolecule potential is zero, and $r_{ij}$ is the distance between the interacting molecules. The Lorentz-Berthlot combining rules are used to calculate $\sigma_{ij}$ and $\epsilon_{ij}$. It is predicted from the results that there are three distinct adsorption sites on single-wall carbon nanotubes for CH$_4$ adsorption using temperature programmed desorption and on the basis of their molecular simulations (and earlier experiments), the highest binding energy adsorption site is inside the nanotubes, with the groove sites between adjacent tubes in bundles the second highest. The simulation work concludes that desorption from the exterior surface of the nanotubes occurs at the lowest temperature while desorption from the nanotube interior occurs at the highest temperature, and adsorbed molecules are packed in a one-dimensional manner in the grooves with the length of the molecule determining the capacity of the groove site.

A theoretical and experimental study is carried out by Albesa et al [19], who present the combined results of \textit{ab initio} and molecular mechanical calculations, computer simulations, and adsorption isotherm investigations of CH$_4$ adsorbed on SWCNT in a bundle. Using CH$_4$ gas with purity higher than 99% in the experiment, the isosteric heat of adsorption $Q_{st}$ of the gas adsorbed on the carbon nanotubes is calculated from two isotherms at close but different temperatures, $T_1$ and $T_2$, via the equation

$Q_{st} = \frac{RT^2}{(T_2 - T_1)} \log \left( \frac{p_2}{p_1} \right), \quad (1.4.4)$

where $p_1$ and $p_2$ are the equilibrium pressures at temperatures $T_1$ and $T_2$, respectively, when the amount of gas adsorbed is constant, and $T$ is the corresponding mean temperature. In the \textit{ab initio} and molecular mechanical calculations, three different carbon nanotube diameters are considered: 9.49, 16.28, and 20.34 Å corresponding to (7,7), (12,12), and (15,15) nanotubes in the armchair structure,
respectively, while the Lennard-Jones $12 - 6$ potential is employed to model the interaction between CH$_4$ molecules for the simulation section. Results from the ab initio and molecular mechanical calculations show that for nanotubes with small diameters, CH$_4$ binding energy is greater on the groove sites than on the surface of the nanotubes, and when the diameter is large enough (greater than 20 Å), the highest binding energy corresponds to the interstitial channel sites with the surface of the nanotubes having the lowest binding energy. The simulation study show that for closed tubes, the adsorption process starts as linear chains (1D process) at the strongest binding energy sites corresponding to the groove site for narrow tubes. After the groove sites are filled, the adsorption process then proceeds to the external surface of the bundles (2D process). From the experimental work, it is shown that the adsorption isotherm of CH$_4$ at 77.3 K predicts that as the temperature increases, the distinguishable stepwise adsorption behaviour is less pronounced, and above 103 K, the substeps disappear. Fernando et al [14] study the thermodynamics of adsorption of light alkanes and alkenes (including CH$_4$) in single-walled carbon nanotube bundles by configurational-bias Grand Canonical Monte Carlo (GCMC) simulation. The non-bonded interactions between pseudoatoms on different adsorbate molecules, as well as the interactions between carbon atoms of a nanotube and the pseudoatoms of adsorbate molecules, are governed by the Lennard-Jones 12-6 potential, and the force field adopted for the adsorbates is the transferrable potential for phase equilibria (TraPPE) where the adsorbate groups are treated as single interaction sites. For a pseudoatom of an adsorbate molecule located at a nearest distance $\delta$ from the central axis of a nanotube, the authors develop an effective potential, $U_{st}(\delta)$, by integrating the Lennard-Jones solid-fluid potential over the positions of all wall atoms of the nanotube (whose length is assumed to be infinite) given by

$$u_{st}(\delta) = 4\rho_s R \int_0^\pi u_{sf}(r) d\theta dz, \quad r^2 = R^2 + \delta^2 - 2\delta R \cos \theta, \quad (1.4.5)$$
where \( R = D/2 \) is the pore radius, \( z \) is the distance along the cylinder axis, \( \theta \) is the radial angle, and \( \rho_s = 0.382 \, \text{Å}^2 \) is the atomic surface density of the single-walled carbon nanotube wall and \( u_{sf}(r) \) is the Lennard-Jones solid-fluid potential. The results show external adsorption to be rather independent of the individual tube diameter and in the low-pressure region, adsorption into the grooves prevails over the other external surface sites. However, the calculated isosteric heat of adsorption at zero-loading \( q^0_{st} \) values for intrabundle confinement are very dependent on nanotube diameter, but the dependency tends to reach saturation and an asymptotic behaviour as the diameter increases. Also confinement in the internal volume of the bundle is predicted to be always more energetically favourable than external adsorption, over the whole pressure range, and that the difference increases with pressure and molecular weight.

Johnson et al [38] carry out neutron diffraction measurements on a powder sample of bundles of SWCNT to gain insight into adsorption sites for CH\(_4\) molecules. In parallel, numerical methods, based on empirical force-fields, are employed to calculate the adsorption of CH\(_4\) in bundles and neutron diffraction patterns based on these structures. The neutron diffraction experiment is performed on a 660 mg single-walled nanotube sample with deuterated CH\(_4\) (of 99.96% purity) used as adsorbate, while for the numerical modelling, three modules are employed. The force-field module allowing total energy calculations and energy minimizations to be performed as a function of structure, the sorption module is used to perform a Monte Carlo search of the binding sites as a function of adsorbate pressure and temperature for rigid gas molecules and nanotubes, and the amorphous diffraction module enables the diffraction pattern to be calculated for an “ordered” structure over limited spatial range, either by restricting the range to be smaller than the dimensions of the periodic model, or simply by removing the boundary conditions.
The total, spherically averaged scattering $I(Q)$ is given by

$$I(Q) = \sum_{i>j} \frac{\sigma_i \sigma_j \sin(Q r_{ij})}{Q r_{ij}},$$

where $Q = (4\pi/\lambda) \sin \theta$, $2\theta$ is the scattering angle, $\lambda$ is the neutron wavelength, $\sigma_i$ and $\sigma_j$ are the coherent scattering cross-sections of atoms $i$ and $j$ and $r_{ij}$ is the distance between atoms $i$ and $j$. Their experimental and numerical results show that adsorption on the groove and surface sites is straightforward, with the CH\textsubscript{4}-nanotube interaction found to be the predominant interaction, approximately twice as stable as the surface sites. Deformation from the cylindrical structure of isolated nanotubes is predicted to be an important factor in bundle structures, and when CH\textsubscript{4} is forced into the interstitial sites, the tubes deform but the nanotube carbon atoms furtherest from the CH\textsubscript{4} remain close to their original positions, thereby minimising lattice expansion. For bundles composed of larger diameter tubes ((11, 11) and (12, 12)), the binding energies, with deformation of the nanotubes, are comparable to the stabilities of the surface and groove sites. The diffraction data in their study supports the adsorption scenario in which a significant fraction of the interstitial sites are populated, followed by the groove and other interstitial sites, and finally the surface sites. Cao et al [39] investigate the adsorption of CH\textsubscript{4} on triangular arrays of SWCNT at room temperature using the GCMC method. The cut and shifted Lennard-Jones potential model is used to represent the interactions between CH\textsubscript{4} molecules, and the single-walled nanotube is arranged according to the $(m,m)$ armchair. In the simulation, the specified independent variables are temperature, the chemical potential and pore volume. The uncertainty of the final results for the simulation (ensemble averages of the number of adsorbate molecules in the box and the total potential energy) is estimated to be less than 2%. The (15, 15), (20, 20), (25, 25), and (30, 30) single-walled nanotube arrays with van der Waals gaps that are varied from 0.335 to 1.0 nm are used as adsorbents for CH\textsubscript{4} storage. It is indicated that the (15, 15) single-walled nanotube arrays with a vDW
CHAPTER 1. INTRO

A gap of $\triangle = 0.8$ nm is the optimal adsorbent among all of the cases studied for CH$_4$ storage at room temperature, while at 4.1 MPa, the total volumetric and gravimetric capacities (including endohedral and exohedral adsorption) of CH$_4$ on the (15, 15) single-walled nanotube arrays with $\triangle = 0.8$ nm reach 216 V/V and 215 g CH$_4$/kg of C, respectively, which not only exceeds the DoE target [40], but slightly greater than the CNG capacity (200 V/V) at 20 MPa.

Zhao et al [16] study gas adsorption on SWCNT and bundles using first principles methods. They perform the self-consistent field (SCF) electronic structure calculations based on DFT with either localised basis or plane-wave basis, studying both zigzag (10, 0), (17, 0) and armchair (5, 5), (10, 10) tubes with a one-dimensional periodic boundary condition applied along the tube axis. The results show that the adsorption energy in the interstitial and groove sites of the tube bundle is considerably larger than that on the surface sites. The internal pore site is also more favourable than the surface site and it is noted that the realistic possibility of adsorption of gases in the interstitial sites of nanotube bundles could be smaller if the kinetic radius of the gas molecule is taken into account. Talapatra et al [41] present the results of an adsorption isotherm investigation of CH$_4$ on closed-ended single-wall carbon nanotube bundles consisting of measurements conducted for temperatures in the range between 69 to 129 K. In their experiment, the authors employ nanotubes not subjected to any post-production treatment, while the CH$_4$ gas used in their measurements had 99.999% purity. The isosteric heat of adsorption is defined as

$$q_{st} = -k_B T^2 \frac{\partial}{\partial T} (\log P)_{n},$$

(1.4.7)

where $n$ is the amount of gas adsorbed on the nanotube substrate, $P$ is the pressure of the coexisting three-dimensional vapour, $k_B$ is the Boltzmann constant, and $T$ is the temperature at which the isotherm is measured. It is found that the isosteric heat is a decreasing function of coverage, and the binding energy values for CH$_4$ on single-walled nanotubes is larger by about 70% than the values on planar graphite.
They also predict that adsorption substep for groove sites will occur at pressures lower than those corresponding to mono-layer formation on planar graphite, at the same temperature due to the deeper energy wells present in groove sites.

### 1.5 Adsorption of CH₄ on other nanostructures

Danna \textit{et al} [42] synthesise carbon nanostructures using a typical floating catalyst chemical vapour deposition (FCCVD) in a horizontal tubular reactor. The temperatures for the synthesis is varied between 1173.15 to 1423.15 K to produce three distinct nanostructures, which are carbon nanotubes, nanofibers and carbon nanoporous balls. CH₄ adsorption experiments are then conducted at room temperature and pressure. The adsorption capacities are recorded continuously with a computer data acquisition system existing within the BET equipment until no further change is measured. Their results show successful fabrication of carbon nanofibers/nanotubes and carbon nanoporous balls using FCCVD. A remarkable storage capacity of CH₄ is achieved with the carbon nanoporous balls with specific surface, 5.0675 m²/g at low pressure and room temperature at maximum gravimetric
capacity of 20.8 wt%, compared to other nanoparticles, which showed no adsorption at atmospheric temperature and pressure. Bekyarova et al [43] compress single-wall carbon nanohorns (SWNHs) repeatedly at 50 Mpa to generate a nanocarbon material of high bulk density. In contrast to carbon nanotubes, which grow in a triangular lattice with narrow intertubular gaps, nanohorns self-assemble in spherical aggregates, with space between adjacent nanohorns that is large enough to accommodate small gas molecules. SWNHs are prepared by laser-ablating graphite without a catalyst at room temperature; the size and morphology of a given aggregate is controlled by the type and pressure of the buffer gas in the chamber. They predict CH$_4$ uptake of up to 160 cm$^3$/cm$^3$ of adsorbent at 303 K and 3.5 MPa, exceeding the DoE target [40] of 150 cm$^3$/cm$^3$ of adsorbent that has been set for practical use of storage media.

Shao et al [44] prepare activated microbeads (a-MCMBs) with high BET specific surface area of 3190 m$^2$/g for CH$_4$ and hydrogen adsorption, by first mixing the filtrated residue of petroleum and carbon black (2 wt%), then maintain the mixture in an autoclave with a nitrogen environment at 680 K for 4.5 hours (refer to [44] for full details). They find that the experimental isotherms for CH$_4$ is almost linear at ambient temperature, 298 K. In addition, the CH$_4$ adsorption can reach 14.73 wt% at the pressure of 0.99 MPa and capillary condensation and the hysteresis phenomenon are observed when the adsorption and desorption isotherms for CH$_4$ is measured at 77 K. The experimental result is then compared with a GCMC simulation using the Steele 10-4-3 potential to represent the interaction between the fluid molecule and the solid wall. There is good agreement between the experimental result and the simulation model, and the model is then used to predict adsorption of CH$_4$ over a wide range of pressure up to 12 MPa. The prediction shows that adsorption amount of CH$_4$ reaches 36 wt% at 289 K and 4 MPa, which is a relatively high score in comparison with other well-known carbon materials. Mendoza-Cortés et al [10] determine CH$_4$ uptake (at 298 K and 0.1 to 10 MPa pressure) for a variety of covalent organic frameworks (COFs), including both two-dimensional and
three-dimensional systems using GCMC simulations based of force fields (FF) developed to fit accurate second-order Møller-Plesset (MP2) pertubation theory. This FF is validated by comparison with the equation of state for CH$_4$ and by comparison with the experimental uptake isotherms at 298 K. Comparison of the results for the FF and simulation procedure with experiment show that the predicted excess CH$_4$ uptake in COF-5 is 11.3 wt% at 8 MPa is in good agreement with the experimental value of 11.1 wt% at 7.8 MPa. Similarly, the predicted excess uptake in COF-8 of 10.6 wt% at 8 MPa is very close to the experimental result of 10.3 wt% at 7.8 MPa. Further, the GCMC trajectory find that multilayer formations coexist with the pore filling mechanism, and a pore diameter ($\sim$ 12 Å), a large pore volume ($\sim$ 5 cm$^3$/g), and a high surface area ($>$ 5000 m$^2$/g) can lead to large volumetric CH$_4$ uptakes. They also show that the best COF in terms of total volume of CH$_4$ per unit volume COF absorbent is COF-1, which can store 195 v/v at 298 K and 3 MPa, exceeding the DoE target [40] for CH$_4$ storage of 180 v/v at 298 K and 3.5 MPa. Senkovska and Kaskel [45] evaluate three porous coordination polymers Cu$_3$(btc)$_2$, Zn$_2$(bdc)$_2$dabco, and Cr$_3$F(H$_2$O)$_2$O(bdc)$_3$ for potential CH$_4$ storage materials. Prior to measurements, the samples are outgassed by heating in vacuum at an elevated temperature until the weight is constant, while CH$_4$ is dosed into the adsorption vessel to a certain pressure and room temperature (303 K). Measurements of CH$_4$ adsorption isotherms in the pressure range up to 17.5 MPa show that a significant gain in storage is obtained in a broad region of pressure compared to the empty vessel. At pressures up to 10 MPa, Cu$_3$(btc)$_2$ is predicted to be one of the most promising MOF materials for CH$_4$ storage with a gravimetric uptake and an excess adsorption of 15.7 wt% at 303 K and a volumetric CH$_4$ uptake of 228 v/v at 15 MPa. It is concluded that the adsorption/desorption process is reversible, indicating that the frameworks are stable upon adsorption of CH$_4$ by high pressure. Loh et al [46] present the adsorption of CH$_4$ onto two different types of activated carbons, namely, Maxsorb III and ACF (A-20) at temperatures from (278.15 - 343.15) K and pressures up to 2.5 MPa, and the adsorption isotherms are measured
using the volumetric technique. In the experimental section, they employ \( \text{CH}_4 \) of purity grade 99.9995\% and the thermophysical properties of the adsorbent materials are measured using an Autosorb (Quantachrome gas sorption instrument) machine. The results show that the adsorbent materials are highly microporous and heterogeneous in surface structure from their pore size distribution, and measurement of the equilibrium uptake of \( \text{CH}_4 \) on both adsorbents are compared with another batch of Maxsorb III and the predicted values are about 10 to 15\% higher, making the proposed materials promising candidates for \( \text{CH}_4 \) storage. Thornton et al [8] propose a new direction (Fig. 1.5.1) for \( \text{CH}_4 \) and hydrogen storage materials involving the incorporation of magnesium-decorated fullerenes (\( \text{Mg-C}_{60}@\text{MOF} \)) within metal-organic frameworks (MOFs). The authors model the system using a novel approach underpinned by surface potential energies developed from Lennard-Jones parameters, beginning with the assumption that the isoreticular MOF (IRMOF) structure can be approximated by spherically shaped cavities such that the cavity surface, defined at a particular radius, consists of the framework atoms, namely zinc, oxygen, carbon and hydrogen. These results predict an exceptional performance for the \( \text{Mg-C}_{60}@\text{MOF} \) family of materials, including predictions for a volumetric \( \text{CH}_4 \) uptake of 265 v/v, which is the highest reported for any material, and significantly exceeding the DoE target [40]. Whitener et al [47] propose expanding the size of an opening on a \( \text{C}_{60} \) fullerene using successive cage scission so as to achieve the encapsulation of \( \text{CH}_4 \) in the chemically modified cage. The encapsulation experiment is performed at 473.15 K under 19.2 MPa of \( \text{CH}_4 \) gas using 1-methyl-naphthalene as a solvent. The experiment shows that not only is the encapsulation of \( \text{CH}_4 \) possible in an open cage of a \( \text{C}_{60} \), it is also demonstrated that \( \text{CH}_4 \) can rotate freely in the \( \text{C}_{60} \) cavity. Vakhrushev et al [11] investigate the possibility of \( \text{CH}_4 \) storage in bottle-like nanocapsules (a system of combined nanotubes forming bottle-like pores) with an added advantage of having a fill-and-lock mechanism for \( \text{CH}_4 \) storage. The simulation is carried out using the molecular dynamics method with a time step size of 1 fs. A nanocapsule consisting of nanotubes with three different diameters
is proposed: (20, 20), (10, 10), and (8, 8) which are combined by heptagonal rings. The nanocapsule also contains the endohedral complex K@C60, in which a charge of +1e is uniformly distributed over the C_{60} shell. Their results give the value of the electric intensity necessary to overcome the capillary forces, which hinders the K@C60 displacement from the region (10, 10) to the region (20, 20) to be $5.14 \times 10^9 \text{ V m}^{-1}$. In addition, it is shown that the nanocapsule can retain $\sim 17.5$ mass% of CH$_4$ at an internal pressure of 10 MPa and a temperature of 300 K.

Recently, Vakifahmetoglu et al [48] investigate hydrogen and CH$_4$ storage in silicon oxycarbide (SiOC) derived carbon. The SiOC samples are prepared using commercially available preceramic polymers and have two different carbon contents. CH$_4$ uptake measurements are carried out at room temperature and excess CH$_4$ uptake values of 21.5 and 16.4 wt% are reported at 6 MPa for the two different carbon content SiOC examined. These authors comment that these values are higher than those previously cited for microporous carbide derived carbons with the largest CH$_4$ excess uptake prior to this study reported to be $\sim 15$ wt%. Xiang et al [49] synthesize MOF with incorporated carbon nanotubes and doped with lithium as storage devices for CH$_4$ and carbon dioxide. Using [Cu$_3$(btc)$_2$] for the metal organic frameworks, their results show that at 298 K and 1.8 MPa, the capacity of lithium-doped CNT@[Cu$_3$(btc)$_2$] for CH$_4$ adsorption reaches 120 mg g$^{-1}$. This is higher than the value of 72 mg g$^{-1}$ for lithium doped MOF without the incorporation of CNT, and shows that the CNT incorporation enhances the adsorption capacities of the MOF structure. Other studies such as [50] probe MOF-5 and activated carbons as adsorbents for gas storage. This study presents data on porosity, surface area and gas storage obtained under different temperatures and pressures. The adsorbents are selected because of their high and similar adsorption capacities (per unit of gram), their availability, and their high gas storage capacities. It is shown that the gravimetric uptake of CH$_4$ on those activated carbons examined can reach up to 14 wt%, which is slightly higher than the $\sim 13$ wt% recorded on MOF-5. However, the authors also conclude that when the crystal density is used, the MOF-5 structure
becomes the material with the best artificial performance.

In summary, molecular storage of CH$_4$ could occur in three conventional nanostructures namely, graphite, nanotubes and nanotube bundles (including interstitial and groove sites), as well as other molecular nanostructures. Computer simulations and mathematical modelling are important complements to experiments. Mathematical modelling is an effective and computationally efficient method to model gas storage in nanostructures, using the continuous approximation which assumes that intermolecular interactions can be approximated by average atomic surface densities. Molecular structures such as metal organic frameworks have very high storage capacity but are quite difficult to construct practically. Temperature and pressure effects on the gravimetric and volumetric uptake of CH$_4$ in these nanostructures are important for adsorption capacity, with high pressures and lower temperatures proving to be beneficial for effective higher uptakes of CH$_4$ in these nanostructures. In general, the theoretical work is in good agreement with experimental data, and which overall indicates a promising future for natural gas storage in molecular structures, and ultimately, clean energy for the environment.

1.6 Thesis structure

This thesis is presented in seven chapters. Chapter 1 provides an overview and the background to the modelling of natural gas storage in both conventional nanostructures namely graphite, single and multi-walled carbon nanotubes and nanotube bundles (including interstitial and groove sites) as well as other molecular structures such as metal organic frameworks (MOFs). In the following chapter, the interaction of a CH$_4$ molecule with a single-walled carbon nanotube is investigated with the aim of developing a simple mathematical model for the CH$_4$ molecule which avoids a detailed determination of each atomic orientation and significantly simplifies the calculations necessary when examining the interaction of CH$_4$ with nanostructures. In Chapter 3, this model for CH$_4$ is then extended to study the practical problem of
packing natural gas (CH$_4$) molecules in carbon nanotubes of varying sizes with the intention of predicting the system for which the energy is minimised. The volume available for CH$_4$ storage in these tubes is also investigated. Chapter 4 examines the problem of a CH$_4$ molecule interacting with graphite with a view to gaining a better understanding of its interaction with carbon nanostructures such as carbon nanotubes which can be thought of as rolled-up graphene sheets. Chapter 4 also examines CH$_4$ adsorption in the region of space between two carbon nanotubes (termed the “groove site”). Adsorption probabilities, isotherms and equilibrium locations of CH$_4$ for these surfaces are also determined. The adsorption and interaction of the gases CH$_4$, hydrogen (H$_2$) and neon (Ne) with open carbon nanocones is examined in Chapter 5. Analytical expressions for the interaction energies, the volume available for adsorption as well as the force profiles describing the encapsulation process in these structures are presented in this chapter. In Chapter 6, the interaction of CH$_4$ in an open cavity of a carbon and silicon nanotube bundle with the central tube absent is presented. This study provides considerable insight into the preferred location of a CH$_4$ molecule in a nanotube bundle, the bundle radii required for CH$_4$ encapsulation, as well as the recent emergence of nanostructures constructed from silicon materials as possible gas storage media. A concluding summary is presented in Chapter 7.
Chapter 2

Encapsulation of methane molecules into carbon nanotubes

Nanotechnology promises much for the world in terms of novel nanodevices and new technologies, and many advances stemming from it are already being implemented. Two sectors that nanotechnology has the potential to revolutionize are energy and the environment. The need for cleaner fuels has become critical due to the heavy demand for products made from natural gas, and CH\textsubscript{4}, which is the main constituent of natural gas, has been proposed as a possible source of clean energy. This idea is increasingly becoming more relevant in a world that requires sources of energy which are both renewable and environmentally sustainable. Many studies have examined the use of CH\textsubscript{4} as a source of energy, but more research is still needed. Most of the quantitative studies carried out deal with the storage and adsorption of CH\textsubscript{4} in nanotubes. The idea of expanding the size of an opening on a C\textsubscript{60} using successive cage scission so as to achieve the encapsulation of CH\textsubscript{4} in the chemically modified cage was first proposed by Whitener et al. [47]. High temperatures and pressures are essential in making the insertion of CH\textsubscript{4} into the cage possible. Lee et al. [36] investigate the adsorption equilibria for CH\textsubscript{4} on multi-walled carbon nanotubes using the static volumetric method at different temperatures and pressures. Other
studies on the adsorption of CH$_4$ on single-walled carbon nanotubes, for example Tanaka et al. [37], employ a functional density theory model for the adsorption of CH$_4$ on single-walled carbon nanotubes. They assume an homogenous cylindrical tube for the open-ended single-walled carbon nanotube and model an isolated single nanotube as opposed to aligned bundles of nanotubes which are usually found.

A more mathematical approach has been adopted by Thornton et al. [51] for which interactions between a gas molecule and a pore wall are investigated, in order to predict gas diffusion regimes for different pore sizes, shapes and compositions. Using the Lennard-Jones potential for the molecular interactions, the study also predicts transport of light gases, including CH$_4$, through carbon tubes and slits. Their novel approach suggests that gases can accelerate through the entrance of the pore opening due to the large molecular forces. Other novel studies include the possibility of storing CH$_4$ in bottle-like nanocapsules (a system of combined nanotubes forming bottle-like pores) with the added advantage of having a fill-and-lock mechanism for CH$_4$ storage [11]. These authors examine the effects of different tube radii and an applied electric field on the filling strengths of the nanocapsule with CH$_4$.

It is observed that very little work has been carried out on the mathematical modelling describing the encapsulation and interaction of CH$_4$ with carbon nanotubes. The work presented in this chapter is aimed at developing mathematical models using classical applied mathematics to describe different orientations of a CH$_4$ molecule and its interactions with an open-ended carbon nanotube. The Lennard-Jones potential for non-bonded atoms and the continuous approximation, which assumes that the interatomic interactions can be modelled by smearing the atoms uniformly across the surfaces, are used to determine the molecular interaction energy for each of the atoms of the CH$_4$ molecule and the smooth carbon nanotube. Carbon nanotubes of varying radii are investigated and the total interaction energy for the CH$_4$ molecule is obtained. We comment that this chapter assumes an ideal environment, but the storage of CH$_4$ in nanosystems is more complex however, and
should include a study of temperature dependence of adsorption capacity. These considerations are outside the scope of this study. The Lennard-Jones potential employed in calculating the energy potential is described in the following section, and the subsequent section gives a brief derivation of the basic results of this chapter. The final section provides a discussion of the results in this chapter.

<table>
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<td>Radius of (10, 10)</td>
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<td>Radius of hydrogen-sphere</td>
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<td>*Repulsive constant C-C</td>
<td>B = 29000 eV Å$^{12}$</td>
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<tr>
<td>**Attractive constant C-H</td>
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<td>Mean surface density of carbon nanotube</td>
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Table 2.0.1: Numerical values of constants used in this chapter (* denotes data from [1] and ** denotes data from [2]).

### 2.1 Continuous approximation and Lennard-Jones potential

In this section, we outline the techniques employed in calculating the total interaction energy between a CH$_4$ molecule and a carbon nanotube. We assume two different models (I) and (II) for the CH$_4$ molecule as shown in Fig. 2.1.1(a) and 2.1.1(b) respectively. The first model, which describes an orientation that is rotationally symmetric about the nanotube axis is subdivided into two configurations; one which describes a particular orientation as shown in Fig. 2.1.1(a), and the other an average of 100 distinct orientations. The CH$_4$ molecule is located such that the carbon atom and one of the hydrogen atoms are lying on the axis of the nanotube as...
shown in Fig. 2.1.1, with the other three hydrogen atoms located off the axis of the tube. We also assume that each atom of the CH$_4$ molecule is well defined by its co-ordinate position. We derive the total interaction energy as a sum of the individual interaction energies for all the atoms in the CH$_4$ molecule and the carbon nanotube. We then derive a rotational matrix $R$, to define a general co-ordinate position which we employ to calculate the average interaction energy for 100 different orientations of the CH$_4$ molecule. The second model assumes that the CH$_4$ molecule has the carbon atom on the axis of the carbon nanotube, while the four hydrogen atoms are smeared over a spherical surface of a certain radius $a$ ($a = 1.1$ Å, C-H bond length in CH$_4$) which is centered on the carbon atom.

The Lennard-Jones potential function for two non-bonded atoms is given by

$$\nu(\rho) = -A\rho^{-6} + B\rho^{-12},$$

(2.1.1)

where $A$ and $B$ denote the attractive and repulsive constants respectively, as given in Table 2.0.1, and $\rho$ is the distance between two typical surface elements. Using the continuous approximation which assumes that the carbon atoms on the carbon nanotube can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the total interaction energy is given by

$$E = \eta_1\eta_2 \int \int \nu(\rho)dS_1dS_2,$$

(2.1.2)

where $\eta_1$ and $\eta_2$ denotes the mean surface densities of the nanotube and the CH$_4$ molecule, respectively, and $\nu(\rho)$ is the Lennard-Jones potential function for two non-bonded atoms with typical surface elements $dS_1$ and $dS_2$. In summary, the calculation reduces to (i) calculating the interaction energy of an on axis carbon atom or hydrogen atom with a carbon nanotube, (ii) calculating the interaction energy of an offset hydrogen atom and a carbon nanotube, and this calculation may be used for the two other hydrogen atoms due to the assumption of symmetry for
the hydrogen atoms of the CH$_4$ molecule off the axis of the tube, (iii) calculating the average interaction energy for 100 CH$_4$ orientations by rotating the four hydrogen atoms around the axis, and (iv) calculating the interaction energy of an on axis hydrogen shell and a carbon nanotube. Finally, to facilitate the evaluation of the integrals, we assume that the carbon nanotube is semi-infinite in length, which is reasonable for a molecule entering one opening of a carbon nanotube, because the non-bonded interactions modeled here operate over very small distances, which are of the order of a few nanometers.

Figure 2.1.1: CH$_4$ entering a carbon nanotube for models (I) and (II)
2.2 Interaction of CH$_4$ with carbon nanotube

For the first model (see Fig. 2.1.1(a)), the total interaction energy between CH$_4$ and a carbon nanotube is given as the sum of the individual interaction energies. We define a Cartesian coordinate system with its origin located at the center of the open end of the carbon nanotube, and the nanotube axis co-linear with the positive z-axis, then an arbitrary point on the tube is given by $(b \cos \theta, b \sin \theta, z)$, and the distance between either a carbon or hydrogen atom located on the axis of the tube at $(0, 0, Z)$ and an arbitrary point on the tube is given by

$$\rho^2 = b^2 + (z - Z)^2,$$

where $Z$ is the distance between the open-end of the carbon nanotube and either of the atoms on the axis of the tube. According to the orientation of the molecule shown in Fig. 2.1.1(a), it can be seen that the distance $Z$ from the center of the carbon nanotube is slightly larger for the hydrogen atom on axis than that of the
carbon atom. Substituting (2.2.1) into (2.1.1) and (2.1.2), we derive the energy function between either a carbon or hydrogen atom, and a single-walled carbon nanotube as

\[ Q = b\eta_1 \int_0^\infty \int_0^{2\pi} \left( \frac{-A}{\rho^6} + \frac{B}{\rho^{12}} \right) d\theta dz. \]  

(2.2.2)

The integral can be re-written in terms of the integrals \( J_n \) defined by

\[ J_n = \int_0^\infty \int_0^{2\pi} \frac{1}{\rho^{2n}} d\theta dz, \]  

(2.2.3)

where \( n = 3 \) or \( 6 \). Substituting these values of \( n \) into (2.2.3) and (2.2.2), we derive the energy function as

\[ Q = b\eta_1 [-AJ_3 + BJ_6], \]

and upon evaluating the integrals, we find that

\[ J_3 = \pi b^{-5} \left[ \frac{3\pi}{8} + \frac{3}{4} \tan^{-1} \left( \frac{Z}{b} \right) + \frac{3Zb}{4(b^2 + Z^2)} + \frac{Zb^3}{2(b^2 + Z^2)^2} \right], \]  

(2.2.4)

and

\[ J_6 = \pi b^{-11} \left[ \frac{9\pi}{3840} + \frac{3}{640} \tan^{-1} \left( \frac{Z}{b} \right) + \frac{Zb^9}{5(b^2 + Z^2)^5} + \frac{9Zb^7}{40(b^2 + Z^2)^4} \right. \]

\[ + \frac{7Zb^5}{60(b^2 + Z^2)^3} + \frac{Zb^3}{16(b^2 + Z^2)^2} + \frac{3Zb}{80(b^2 + Z^2)} \]  

(2.2.5)

A brief derivation of the analytical evaluation given by (2.2.4) and (2.2.5) is given in Appendix A.

Using the same coordinate system for the center of the carbon nanotube, the distance between any of the three hydrogen atoms located off the axis of the tube and the carbon nanotube may be expressed as

\[ \rho^2 = (b \cos \theta - \epsilon \sin \phi)^2 + (b \sin \theta)^2 + (z - \epsilon \cos \phi)^2 \]
where \( \phi \) and \( \epsilon \) represents the offset angle and the offset distance from the axis of the tube respectively, and are shown in Fig 2.1(a). We comment that the offset angle is defined as the angle (in degrees) by which an hydrogen atom is away from the axis of the carbon nanotube.

On substituting (2.2.6) into (2.2.3), the interaction energy is given as

\[
E = b \eta \int_0^\infty \int_0^{2\pi} \frac{-A}{[(b + \epsilon \sin \phi)^2 - 4b \epsilon \sin \phi \cos^2 \frac{\theta}{2} + (z - \epsilon \cos \phi)^2]^3} + \frac{B}{[(b + \epsilon \sin \phi)^2 - 4b \epsilon \sin \phi \cos^2 \frac{\theta}{2} + (z - \epsilon \cos \phi)^2]^\alpha} d\theta dz,
\]

(2.2.7)

and following the method of [52], the interaction energy becomes

\[
E = 2\pi \eta b \left[ -A \left( \frac{K_{3,3}}{4} + \frac{3(K_{1,5} + K_{5,1})}{8} \right) + B \left( \frac{63(K_{1,11} + K_{11,1})}{256} + \frac{35(K_{3,9} + K_{9,3})}{256} + \frac{30(K_{5,7} + K_{7,5})}{256} \right) \right]
\]

(2.2.8)

where \( K_{i,j} \) are defined by

\[
K_{i,j} = \frac{(b^2 + 2b \epsilon \sin \phi + \epsilon^2)^{-I}}{i + j - 1} F_1(I; \frac{j}{2}, \frac{1}{2}; J; (1 - p^2)w_1, w_1),
\]

where \( I = (i + j - 1)/2, J = (i + j + 1)/2, p = (b - \epsilon \sin \phi)/(b + \epsilon \sin \phi), w_1 = (b + \epsilon \sin \phi)^2/(b^2 + 2b \epsilon \sin \phi + \epsilon^2) \) and \( F_1(a; b, b_1; c; x, y) \) denotes Appell’s hypergeometric function of two variables. The details of this evaluation are given in Appendix A.

Following similar calculations by Cox et al [53], the interaction energy for an offset
atom in a carbon nanotube which is infinite in length, is given by
\[
E_{\text{off}} = \frac{3\pi b\eta_1}{8} \left( -AJ_2 + \frac{21B}{32} J_5 \right),
\]
where \( J_n \) is defined in terms of an ordinary hypergeometric function given by
\[
J_n = \frac{2\pi}{(b-\epsilon)^{2n+1}} F\left(n + \frac{1}{2}, \frac{1}{2}; 1; \frac{-4b\epsilon}{(b-\epsilon)^2}\right),
\]
where \( \epsilon \) is the magnitude of the offset vector from the tube axis, which we rotate to derive the average interaction energy for 100 different orientations for a \( \text{CH}_4 \) molecule using the rotational matrix given by
\[
R = \begin{pmatrix}
\cos \theta \cos \phi & -\cos \theta \sin \phi & -\sin \theta \sin \phi \\
\cos \theta \sin \phi & \cos \theta \cos \phi & \sin \theta \cos \phi \\
-\sin \theta & -\sin \theta & \cos \theta
\end{pmatrix},
\]
where \( \phi \) is a planar angle analogous to that shown in Fig. 2.1.1(a) and \( \theta \) is a further rotational angle (see for example [54]).

For model II (see Fig. 2.1.1(b)), we determine the interaction energy between the four hydrogen atoms smeared over a spherical surface and a carbon nanotube by first evaluating the surface integral of the Lennard-Jones potential over the sphere. Following [55], for a typical point on the carbon nanotube, the interaction energy between the hydrogen shell of the \( \text{CH}_4 \) molecule and the nanotube is given by
\[
G(\rho) = 4\pi a^2 \eta_2 \left[ \frac{B}{5} \left( \frac{5}{(\rho^2 - a^2)^6} + \frac{80a^2}{(\rho^2 - a^2)^7} + \frac{336a^4}{(\rho^2 - a^2)^8} + \frac{512a^6}{(\rho^2 - a^2)^9} + \frac{256a^8}{(\rho^2 - a^2)^{10}} \right) - A \left( \frac{1}{(\rho^2 - a^2)^3} + \frac{2a^2}{(\rho^2 - a^2)^4} \right) \right],
\]
where \( \eta_2 \) is the mean atomic surface density of the hydrogen shell. With reference to the same rectangular Cartesian coordinate system used for the first model, which has its origin located at the center of one end of the carbon nanotube and the
CHAPTER 2. ENCAPSULATION OF CH₄ INTO SWCNT

nanotube axis co-linear with the positive z-axis, a typical point on the surface of the carbon nanotube has coordinates \((b \cos \theta, b \sin \theta, z)\), where \(b\) is the radius of the semi-infinite tube. Similarly, with reference to the Cartesian coordinate system, the center of the hydrogen shell has coordinates \((0, 0, Z)\), where \(Z\) is the distance in the \(z\) direction which can either be positive or negative. Therefore, the distance \(\rho\) between the center of the spherical molecule and a typical point on the carbon nanotube is given by (2.2.1). Using the Lennard-Jones potential function together with the continuous approximation, the interaction energy between the hydrogen shell and a single-walled carbon nanotube is given by

\[
E_t = b \eta_1 \int_{-\pi}^{\pi} \int_0^{\infty} G(\rho) dz d\theta,
\]

where \(G(\rho)\) is defined above. The integrals to be evaluated are all of the form

\[
H_n = \int_{-\pi}^{\pi} \int_0^{\infty} \frac{1}{(\rho^2 - a^2)^n} dz d\theta,
\]

\[
= \int_{-\pi}^{\pi} \int_0^{\infty} \frac{1}{[b^2 - a^2 + (z - Z)^2]^n} dz d\theta, \quad (2.2.9)
\]

where \(n\) is a positive integer. It can be seen that (2.2.9) is independent of \(\theta\), and therefore we may deduce

\[
H_n = 2\pi \int_0^{\infty} \frac{1}{[b^2 - a^2 + (z - Z)^2]^n} dz.
\]

The analytical expansion of the above can be deduced in a similar manner to that for \(J_n\) given in Appendix A by letting \(\lambda^2 = b^2 - a^2\), \(z_\ast = z - Z\) and expanding using the expression from [56] (\((\mathcal{J} 2.512(2))\) also given in the Appendix A of this thesis.
CHAPTER 2. ENCAPSULATION OF CH$_4$ INTO SWCNT

2.3 Results and discussions

The calculations are performed using the algebraic software package MAPLE and in this section we present the numerical results showing the relationship between the interaction energy for different sizes of carbon nanotubes and a single CH$_4$ molecule. We comment that the numerical results are derived from the analytical expressions given above for the interaction between a methane molecule and carbon nanotubes as given by the discrete and continuous models in Fig. 2.1.1.

Firstly, in Fig. 2.1.2, we plot the relation between the axial distance and interaction energy for a CH$_4$ molecule encapsulated into a (9,5), (8,8) and (10,10) carbon nanotube from the open-end of the tube as given in Fig. 2.1.1(a) using an offset angle given approximately by $7\pi/18$. The reason behind this choice of offset angle is detailed in Appendix A. The total interaction energies are given by 0.42106 eV, 0.26735 eV and 0.10864 eV for the (9,5), (8,8) and (10,10) carbon nanotubes respectively. We observe that the lowest interaction energy for all the carbon nanotubes considered in this study occurs for the (9,5) tube. This observation is consistent
with [55] where the acceptance and suction energies between an atom, C$_{60}$ fullerenes and single-walled carbon nanotubes are investigated. Encapsulation of CH$_4$ is possible in all three cases above as the energetically most favorable location of the CH$_4$ molecule is inside the tube so that there are no energy barriers present at the open-end of the carbon nanotubes.

Bienfai et al [57] predict that CH$_4$ rotates almost freely even at relatively low temperatures (50 – 120 K) giving rise to the possibility of different CH$_4$ orientations when interacting with a single-walled carbon nanotube. Employing $E_{\text{off}}$ and the rotational matrix $R$ given above, we may rotate the offset vector of magnitude $\epsilon$ for the hydrogen atoms through the two rotational angles $\theta$ and $\phi$, and calculate the average interaction energy for 100 different orientations of a CH$_4$ molecule inside a single-walled carbon nanotube. The average interaction energies are found to be 0.41025 eV, 0.25059 eV and 0.10431 eV for the (9, 5), (8, 8) and (10, 10) carbon nanotubes respectively.

In Fig. 2.2.1, we plot the relation between the axial distance $Z$ and interaction energy for a CH$_4$ molecule encapsulated into a (9, 5), (8, 8) and (10, 10) carbon nanotube from the open-end of the tube as given by model (II). The total interaction energies for this model are given by 0.41464 eV, 0.25521 eV and 0.10396 eV for the (9, 5), (8, 8) and (10, 10) carbon nanotubes, respectively. As in the first model, we observe that the lowest interaction energy occurs for the case of the (9, 5) nanotube. Also, for all three cases, we observe that the energetically most favorable location for the CH$_4$ molecule is inside the tube in the positive $z$ direction given rise to the possibility of encapsulation of the CH$_4$ molecule in all three tubes. These observations are also consistent with [58] and [55].

We comment that for both models, the potential energies decrease as the tube size increases, an observation which can also be seen in the encapsulation of C$_{60}$ fullerenes in carbon nanotubes [58]. This can be explained as a consequence of the assumption that the CH$_4$ molecule remains on the nanotube axis. Furthermore, it is
observed that even though both models show energetically more favorable positions inside the tube, they also provide very accurate approximations for the interaction energies. For the discrete model, the interaction energy percentage differences are 1.5%, 4.8%, and 4.5% for the (9, 5), (8, 8) and (10, 10) single-walled carbon nanotubes respectively in comparison to the continuous model. These percentage differences are reduced to 1.1%, 1.8%, and 0.3% for the (9, 5), (8, 8) and (10, 10) single-walled carbon nanotubes respectively when the average energy of 100 CH$_4$ orientations are compared to the continuous model. Our results suggest that the continuous approximation is a valid model for the hydrogen atoms of the CH$_4$ molecule especially at temperatures when the CH$_4$ molecule is known to rotate almost without barriers. The smooth decrease in the energy profile coupled with the absence of an energy barrier at the open-end of the nanotube for both models suggests that the CH$_4$ molecule may be easily accepted into the nanotube. The energy profile as shown in Fig. 2.3.1 shows the interaction energy for a CH$_4$ molecule entering a (9, 5) carbon nanotube by varying the axial distance of the molecule and the offset distance for the hydrogen atoms as described by model (I). This figure shows that the CH$_4$ molecule
is easily sucked into the tube and that the energetically more favorable position for the molecule is inside the tube. We note that although chemical reactions and structural edge effects are not considered in this study, they may play a role in the total adsorption process for CH$_4$ on carbon nanotubes [34]. We further comment that although we assume the CH$_4$ molecule is centered on the axis, the equilibrium configuration might well have the CH$_4$ molecule closer to the tube wall on encapsulation, particularly for larger radius carbon nanotubes [15, 59]. The interaction between CH$_4$ and the wall of a carbon nanotube as the CH$_4$ molecule moves closer to the tube wall is examined further in Chapter 3.

2.4 Conclusions

In this chapter we investigate CH$_4$ storage in carbon nanotubes, by considering two different models of the CH$_4$ molecule in the calculations. The interaction energies for the encapsulation for CH$_4$ in carbon nanotubes are derived from the Lennard-Jones potential and the continuous approximation, resulting in double surface integrals giving the total potential energy between a CH$_4$ molecule interacting with a carbon nanotube as both a series expression and terms involving hypergeometric functions. For the first model considered, the total energy is calculated by summing individual energies for each atom in the CH$_4$ molecule and the entire carbon nanotube modeled with the continuous approximation, whereas for the second model, we assume that the four hydrogen atoms in the CH$_4$ molecule are smeared over a spherical surface. Various parameters such as nanotube radius, hydrogen sphere radius, offset and rotational angles for surrounding atoms, and distance between the CH$_4$ molecule and the carbon nanotube are considered in order to determine the energy variations, minimum and maximum energies required for CH$_4$ encapsulation in different carbon nanotubes for both models. Numerical evaluations are performed using the software package MAPLE to determine the different CH$_4$ encapsulation energies for (9, 5), (8, 8) and (10, 10) carbon nanotubes. The calculations presented in this
chapter could be extended to determine suction energies and acceptance conditions required for storage of several other gas molecules in carbon nanotubes. The major outcome of the chapter is the identification of the continuous approximation for the CH\textsubscript{4} molecule described in model (II), which is simple and is independent of the orientation of the molecule and gives comparable results to the discrete formulation even at relatively low temperatures.
Chapter 3

Packing configurations for methane storage in carbon nanotubes

In order for gas storage in nanostructures to be made practical, the nature of the intermolecular interactions must be properly understood at the nanoscale. \( \text{CH}_4 \) at room temperature is a colorless and odorless gas, with molecules comprising a carbon atom surrounded by four hydrogen atoms. The storage and preservation of \( \text{CH}_4 \) gas is an important global issue given the widespread occurrence of the gas. \( \text{CH}_4 \) is an essentially clean gas which is used in everyday life for fuel and energy, and research into an improved understanding of its preservation and storage has obvious practical benefits. The present rising levels of carbon emissions means that \( \text{CH}_4 \) provides a possible alternative source of clean and secure energy, since \( \text{CH}_4 \) is more environmentally friendly than most hydrocarbon fuels and it is also readily available. Many studies have examined \( \text{CH}_4 \) storage in various molecular containers [60, 43, 11, 61, 47, 62]. Bottle-like nanocapsules, which have the complementary advantage of a fill-and-lock system that is initiated from the displacement arising from an electric field, have been proposed as a possible novel means of \( \text{CH}_4 \) storage.
CHAPTER 3. PACKING CONFIG. OF CH$_4$ INTO CNT

[11]. Other studies show that the encapsulation of CH$_4$ in nanocapsules is also possible at normal temperature in the absence of an electric field, but with an elevated pressure, which has the benefit of a more efficient operation cycle for the nanocapsule [60]. Tanaka et al. [37] employ a functional density model for CH$_4$ adsorption on single-walled carbon nanotubes. They assume a cylindrical tube for the open-ended single-walled carbon nanotube and examine an isolated single nanotube as opposed to aligned bundles of nanotubes which are normally proposed. The idea of chemically modifying the size of an opening on a C$_{60}$ through successive cage scission for CH$_4$ storage was first proposed by Whitener et al., [47] but elevated temperatures and pressures are necessary to ensure insertion into the cage. Other studies show that idealized bundles of single-walled nanotubes and worm-like pores behave as an efficient storage media at low to moderate pressures, because of the availability to the CH$_4$ molecules of a high density of energetic centers located on the carbon surfaces [63]. Bekyarova et al. [43] were the first to report extremely high CH$_4$ adsorption in single-walled carbon nanoporous rigid structures and they predict single-walled carbon nanomaterials with a disordered structure as possible storage media for CH$_4$ and other supercritical gases. Cao et al. [39] employ a grand canonical Monte Carlo method to investigate adsorption storage of CH$_4$ on triangular arrays of single-walled nanotubes and show that the (15, 15) single-walled nanotube arrays with a van der Waals gap of 0.8 nm is an optimal adsorbent. Some studies on CH$_4$ storage and adsorption in multi-walled carbon nanotubes such as for example, Lee et al. [36] involve the static volumetric method at specific temperatures and pressures, and they argue that the adsorption of CH$_4$ on multi-walled carbon nanotubes is weakly favorable at low pressures, while capillary condensation occurs at higher temperatures. They also indicate that the pressure responsible for capillary condensation of CH$_4$ increases with temperature. Other studies examine storage of CH$_4$ in vessels other than nanotubes, and Comotti et al. [61] propose nanoporous dipeptides for adsorption, separation and storage of gases such as CH$_4$, carbon dioxide and hydrogen. Their novel proposal for using crystals of bimolecules
showing permanent porosity to capture relevant gases for energetic applications is the first such proposal.

A mathematical modeling approach is adopted by Adisa et al [64], where interactions between a CH$_4$ molecule and nanotube bundles are used to analyse CH$_4$ encapsulation in carbon and silicon nanotube bundles. They find that silicon nanostructures may be superior candidates for CH$_4$ storage at temperatures in the range 200 – 400 K. An approach motivated from classical applied mechanics is adopted by Thornton et al. [51] and they use interactions between a gas molecule and a pore wall to predict the various gas diffusion regimes for different pore sizes, shapes and compositions. Utilizing the Lennard-Jones potential for molecular interactions, they predict movement of light gases, including CH$_4$, through carbon slits and tubes, and their results show that due to the large molecular forces, gases can accelerate through the entrance of a pore opening. Other novel studies include CH$_4$ storage in a nanocapsule under normal conditions and with a certain mass of the CH$_4$ molecule retained after storage [62]. This study proposes nanocapsules of such structures as a new and effective way for CH$_4$ storage that may be used to store other gases.

To date there have been very few mathematical models used to describe the storage and interaction of CH$_4$ with carbon nanotubes. In this chapter, we adopt the Lennard-Jones potential and the continuous approximation to predict the packing configurations for a succession of CH$_4$ molecules inside a single-walled carbon nanotube (in the case of C$_{60}$ fullerenes, such packings are referred to as nanopeapods). We derive an analytical expression for the potential energy that when minimized, gives the structure of the molecules in the carbon nanotube. We investigate zigzag and spiral configurations inside a (9,5), (8,8) and (10,10) carbon nanotube. We comment that in this model, we account for physisorption of CH$_4$ molecules to CNTs and ignore the possible chemisorption of CH$_4$ molecules to CNTs. The Lennard-Jones potential and the continuous approximation employed in deriving the analytical expression for the interaction energy are described in the following section.
CHAPTER 3. PACKING CONFIG. OF CH₄ INTO CNT

Table 3.0.1: Numerical values of constants used in this chapter(* denotes data from [1], ** denotes data from [2], and *** denotes from [3]).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of (9, 5)</td>
<td>b = 4.813 Å</td>
</tr>
<tr>
<td>Radius of (8, 8)</td>
<td>b = 5.428 Å</td>
</tr>
<tr>
<td>Radius of (10, 10)</td>
<td>b = 6.784 Å</td>
</tr>
<tr>
<td>Radius of hydrogen-sphere</td>
<td>a = 1.1 Å</td>
</tr>
<tr>
<td>*Attractive constant C-C</td>
<td>A = 17.4 eV Å⁶</td>
</tr>
<tr>
<td>*Repulsive constant C-C</td>
<td>B = 29000 eV Å¹²</td>
</tr>
<tr>
<td>**Attractive constant C-H</td>
<td>A = 14.94 eV Å⁶</td>
</tr>
<tr>
<td>**Repulsive constant C-H</td>
<td>B = 14544 eV Å¹²</td>
</tr>
<tr>
<td>***Attractive constant H-H</td>
<td>A = 1.05 eV Å⁶</td>
</tr>
<tr>
<td>***Repulsive constant H-H</td>
<td>B = 210.11 eV Å¹²</td>
</tr>
<tr>
<td>Mean surface density of hydrogen-sphere</td>
<td>η₂ = 0.263Å⁻²</td>
</tr>
<tr>
<td>Mean surface density of carbon nanotube</td>
<td>η₁ = 0.3812Å⁻²</td>
</tr>
<tr>
<td>Mass of CH₄</td>
<td>M = 26.6391 × 10⁻²⁷ kg</td>
</tr>
</tbody>
</table>

The analysis and minimum energy values for the zigzag and spiral configurations comprising 2m + 1 and m CH₄ molecules are discussed in sections 3.2 and 3.3 respectively. Analytical expressions for both configurations are derived in section 3.2 and a concluding summary is presented in the final section.

3.1 Method

In this section we outline the procedure employed in the calculations. We model a single CH₄ molecule assuming that the four hydrogen atoms are smeared over a spherical surface of a certain radius a with the carbon atom assumed to be situated at the center of the sphere [65]. The major advantage of modelling the CH₄ molecule in this manner is that the particular orientations of the four hydrogen atoms becomes immaterial to the calculation, which is important in terms of providing a major simplification. For certain assumed packing configurations, we derive the total interaction energy for a succession of CH₄ molecules in a carbon nanotube using the Lennard-Jones potential together with the continuous approximation. Since the
van der Waals force is short range [66], and following the work of Baowan et al. [66] and Hodak et al. [67], nearest neighbor interactions are assumed to provide the main contribution to the total interaction energy. In particular, we assume that for CH$_4$ packing in a nanotube, only the nearest neighbour interactions and the nearest CH$_4$ molecule to the carbon nanotube wall and the carbon nanotube, contribute to the total potential energy of the system. The total energy between two interacting CH$_4$ molecules is calculated by summing the following four contributions:

(i) the interaction energy between the carbon atom of the first molecule and the hydrogen-sphere of the second molecule,
(ii) the interaction energy between the carbon atom of the second molecule molecule and the hydrogen-sphere of the first molecule,
(iii) the interaction energy between the hydrogen-sphere of the first and second molecules,
(iv) the interaction energy between the carbon atoms of both molecules.

Further, the total interaction energy between a CH$_4$ molecule and the carbon nanotube is assumed to comprise the interaction energy between the carbon atom and the carbon nanotube, and the interaction energy between the hydrogen-sphere and the carbon nanotube.

The Lennard-Jones potential for two non-bonded atoms is given by

$$\nu(\rho) = -A\rho^{-6} + B\rho^{-12},$$  \hspace{1cm} (3.1.1)

where $A$ and $B$ denote the attractive and repulsive constants respectively, and $\rho$ is the distance between two atoms. Using the continuous approximation which assumes that the carbon atoms on the carbon nanotube can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the total
potential energy is given by

\[ E = \eta_1 \eta_2 \int_{S_1} \int_{S_2} \nu(\rho)dS_1 dS_2, \tag{3.1.2} \]

where \( \eta_1 \) and \( \eta_2 \) represents the average atomic surface densities (namely, number of atoms/surface area) of the nanotube and a CH\(_4\) molecule, respectively, and \( \nu(\rho) \) is the Lennard-Jones potential function for two non-bonded atoms with typical surface elements \( dS_1 \) and \( dS_2 \) distance \( \rho \) apart. The numerical values of the constants used in this chapter are as given in Table (3.0.1). We comment that we employ the same Lennard-Jones parameters for C-C interactions for both the CH\(_4\) - nanotube interaction and the CH\(_4\) - CH\(_4\) interaction [65, 64, 1, 55]. In order to obtain the total (average) potential energy in a nanotube packed with CH\(_4\) molecules (CH\(_4\)@SWCNT), we need to examine the potential energy between two CH\(_4\) molecules and the potential energy between a CH\(_4\) molecule and a carbon nanotube. The potential energy of a multi-body system consisting of pairs of molecules, otherwise referred to as the pair potential approximation is given by

\[ Q = \frac{1}{2} \sum_{i,j=1, i \neq j}^{N} E(\rho_{ij}), \]

where \( \rho_{ij} \) represents the distance between surface element \( i \) and surface element \( j \) [68]. We note that for two structures where the pairwise interaction within each structure can be ignored, then the paired interaction is given by

\[ Q = \sum_{i=1}^{N} \sum_{j=1}^{M} E(\rho_{ij}), \]

where \( i \) and \( j \) sum for all atoms in each structure and the continuous approach replaces these double summations over the two molecules with a double surface integral as given by equation (3.1.2).
Following similar calculations by Thornton et al [8], the volume of CH$_4$ adsorption in the free-cavity of a carbon nanotube is given by

\[ V_{ad} = \int_{R_0}^{R_1} 4\pi R^2 \left[ 1 - e^{(-|E_{min}|/kT)} \right] dR, \]

where $E_{min}$ is the average potential energy per CH$_4$ molecule, $k$ is the Boltzmann constant and $T$ is the temperature in Kelvin. We note that the upper and lower limits of the above integral correspond to the maximum and minimum distance away from the tube axis for which the potential energy remains negative.

### 3.2 Zigzag configuration for CH$_4$@SWCNT

![Zigzag configuration for (2m + 1) CH$_4$ molecules inside a carbon nanotube](image)

**Figure 3.2.1:** Zigzag configuration for (2$m$ + 1) CH$_4$ molecules inside a carbon nanotube

In this section we assume a zigzag packing configuration of CH$_4$ molecules encapsulated inside a single-walled carbon nanotube infinite in length, and we now detail the determination of the interaction energy. A packing configuration as shown in Fig. 3.2.1, is assumed, comprising of (2$m$+1) CH$_4$ molecules inside the single-walled carbon nanotube. In addition we assume that the total potential energy of the configuration to comprise (2$m$ + 1) CH$_4$ molecules interacting with the entire carbon nanotube, (2$m$ − 1) type X interactions on both the upper and lower levels, and 2$m$ type Y interactions. As stated earlier, we only consider a single nearest neighbor
Table 3.2.1: Average potential energy per CH$_4$ molecule (eV), equilibrium spacing $Z$(Å), offset position $\lambda$ (Å) and volume density $\eta_{vol}$ (g cm$^{-3}$) for the zigzag configuration of $(2m+1)$ CH$_4$ molecules in three carbon nanotubes.
interaction for interaction types X and Y, as indicated in Fig. 3.2.1.

With reference to a rectangular Cartesian coordinate system \((x, y, z)\), a typical point on the surface of a carbon nanotube assumed to be infinite in length and symmetric, has coordinates \((b \cos \theta, b \sin \theta, z)\), where \(b\) denotes the tube radius. With reference to the same rectangular Cartesian coordinate system, and with the centre of the left-most molecule lying on the axis \((y = z = 0)\), the upper \(\text{CH}_4\) molecules have centers with coordinates \((\lambda, 0, 2iZ)\), \((i = 0, 1, ...m)\) and correspondingly, the lower \(\text{CH}_4\) molecules have centers with coordinates \((-\lambda, 0, Z(2j - 1))\), \((j = 1, 2, ...m)\) where \(\lambda\) is the offset distance from the tube axis to the center of the \(\text{CH}_4\) molecule in the \(x\)-direction as shown in Fig. 3.2.1. Further, we assume the lower \(\text{CH}_4\) molecules to be centrally located between two adjacent upper \(\text{CH}_4\) molecules in the \(z\)-direction.

Consequently, given the assumed symmetry of the tube, the total potential energy is given by

\[
E_{zz}^{tot} = (2m + 1)E_t + (2m - 1)E_X + 2mE_Y,
\]

where \(E_t\) represents the potential energy between the \(\text{CH}_4\) molecules and the carbon nanotube, \(E_X\) and \(E_Y\) denote interaction energies arising from interaction types X and Y respectively. Furthermore, the individual interaction energies given above are divided into two sub-interaction energies, namely, one for the carbon atom at the center of the hydrogen-sphere and the other for the hydrogen-sphere itself. The total interaction energy between a single \(\text{CH}_4\) molecule inside a carbon nanotube and a carbon nanotube is given by

\[
E_i = E_{tc} + E_{th},
\]

where \(E_{tc}\) denotes the total interaction energy between the carbon atom and the carbon nanotube and \(E_{th}\) denotes the total interaction energy between the hydrogen-sphere and the carbon nanotube. The distance \(\rho\) between the center of the \(\text{CH}_4\)
molecule to any point on the surface of the carbon nanotube is given by

\[ \rho^2 = (b - \lambda)^2 + 4b\lambda \sin^2(\theta/2) + [z - 2iZ]^2, \]  

(3.2.1)

where \( b \) is the radius of the carbon nanotube. We note that since the tube is assumed to be infinite, the \( z \)-coordinate is irrelevant to the calculations. Substituting (3.2.1) into (3.1.1) and (3.1.2), we obtain

\[ E_{tc} = b\eta_1 \int_{-\infty}^{\infty} \int_{-\pi}^{\pi} \left( \frac{-A}{\rho^6} + \frac{B}{\rho^{12}} \right) d\theta dz, \]

(3.2.2)

where \( \eta_1 \) denotes the atomic surface density of the carbon nanotube. The integral could generally be re-written as

\[ H_n = b \int_{-\infty}^{\infty} \int_{-\pi}^{\pi} \frac{1}{\rho^{2n}} d\theta dz, \]

(3.2.3)

where \( n = 3 \) or \( 6 \). The total interaction energy \( E_{th} \) between the hydrogen-sphere and the carbon nanotube is derived by performing a surface integral on the interaction energy between the carbon atom and the hydrogen-sphere over a nanotube. Following Cox et al.\[55\], the interaction energy between the carbon atom and the hydrogen-sphere is given by \( E_{ch}(\rho) = G(\rho) \) where the function \( G(\rho) \) is defined by

\[ G(\rho) = \frac{\pi a \eta_2}{\rho} \left[ \frac{-A}{2} \left( \frac{1}{(\rho - a)^4} - \frac{1}{(\rho + a)^4} \right) + \frac{B}{5} \left( \frac{1}{(\rho - a)^{10}} - \frac{1}{(\rho + a)^{10}} \right) \right], \]

where \( \eta_2 \) is atomic density of the hydrogen-sphere and \( a \) is the assumed radius of the hydrogen-sphere given by \( a = 1.1 \ \text{Å} \), being the C-H bond length for a CH\(_4\) molecule. Consequently, the total interaction energy \( E_{th} \) between the hydrogen-sphere and the carbon nanotube is given by

\[ E_{th} = b\eta_1 \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} G(\rho) dz d\theta. \]

(3.2.4)
Also following similar calculations by Cox et al. [55], the potential energy between
the carbon atom and the nanotube is given by

\[ E_{tc} = \pi^2 \eta_1 \frac{-A}{192} \sum_{m=0}^{\infty} \left( \frac{(2m + 4)! \lambda^m}{(m + 2)!m!(4b)^m} \right)^2 + \frac{B}{9676800b^{10}} \sum_{m=0}^{\infty} \left( \frac{(2m + 10)! \lambda^m}{(m + 5)!m!(4b)^m} \right)^2, \tag{3.2.5} \]

and the total interaction energy between the hydrogen-sphere and the carbon nanotube
is given by

\[ E_{th} = 8\pi^3 a^2 b \eta_1 \eta_2 \left[ \frac{-A}{2}(2J_3 + 4a^2 J_4) + \frac{B}{5}(5J_6 + 80a^2 J_7 + 336a^4 J_8 + 512a^6 J_9 + 256a^8 J_{10}) \right], \]

\[ J_n = \frac{(2n - 3)!!}{(2n - 2)!![(b - \lambda)^2 - a^2]^{n-1/2}} F \left( n - \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{-4b\lambda}{(b - \lambda)^2 - a^2} \right), \tag{3.2.6} \]

where \( F(a, b; c; z) \) is the usual hypergeometric function. Details of the evaluation
for \( E_{tc} \) and \( E_{th} \) are given in Appendix B. The interaction energy between two CH\(_4\) molecules \( E \) for the interaction types X and Y is given by

\[ E = E_{hh} + 2E_{ch} + E_{cc}, \]

where the subscripts \( ch, hh \) and \( cc \) denote the carbon atom - hydrogen-sphere interactions, hydrogen-sphere - hydrogen-sphere interactions and carbon atom - carbon atom interactions respectively. Following similar calculations by Baowan et al. [66] and Cox et al. [55], the carbon atom - hydrogen-sphere interaction is given by

\[ E_{ch} = G(\delta), \tag{3.2.7} \]
and the hydrogen-sphere - hydrogen-sphere interaction is given by

$$E_{hh} = \frac{4\pi^2 a^2 \eta^2 \delta^2}{\delta^3} \left[ -\frac{A}{6} \left( \frac{1}{(\delta + 2a)^3} + \frac{1}{(\delta - 2a)^3} - \frac{2}{\delta^3} \right) \right] + \frac{B}{45} \left( \frac{1}{(\delta + 2a)^9} + \frac{1}{(\delta - 2a)^9} - \frac{2}{\delta^9} \right),$$

(3.2.8)

where $\delta$ is the distance between the two centers of the interacting CH$_4$ molecules, $\delta_X = 2Z$, for type X interactions, and $\delta_Y = 2\lambda + Z$, for type Y interactions. The interaction energy $E_{cc}$ is given by the Lennard-Jones potential in (3.1.1) with the appropriate distances as given above.

### 3.2.1 Numerical results for zigzag CH$_4$@SWCNT

In this section the numerical results for the zigzag packing configuration formed by CH$_4$ molecules in different carbon nanotube sizes are presented. By minimizing the energy of the system (this minimization is done by employing the Optimization package in MAPLE on the analytic expression for the total interaction energy), we obtain the offset position $\lambda$ between the center of the CH$_4$ molecule and the axis of the carbon nanotube, and the equilibrium spacing $Z$ between the centers of two nearest neighboring CH$_4$ molecules. We investigate (9,5), (8,8) and (10,10) carbon nanotubes assumed to be infinite in length and comprising $(2m + 1)$ CH$_4$ molecules. Using the computational algebraic package MAPLE, the optimum potential energy for a zigzag system of CH$_4$ molecules encapsulated in different sized carbon nanotubes are presented in Table 3.2.1. In order to ensure a genuine optimal potential energy, the total energy function was first graphed before utilizing the optimization package in MAPLE. For a (9,5) carbon nanotube, the offset position $\lambda = 0$, with an equilibrium distance $Z = 4.4964$ Å between three CH$_4$ molecules inside the tube is found. This means that inside a (9,5) carbon nanotube, CH$_4$ molecules are more likely to align and form a linear chain along the tube axis. This observation is consistent with Baowan et al. [66] where the same situation arises.
\begin{table}
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{m} & \multicolumn{4}{c|}{\textbf{(9,5)}} & \multicolumn{4}{c|}{\textbf{(8,8)}} \\
\hline
 & \textbf{\(\phi\)} & \textbf{\(Z\)} & \textbf{\(\lambda\)} & \textbf{\(E_{sr}\)} & \textbf{\(\eta_{vol}\)} & \textbf{\(\phi\)} & \textbf{\(Z\)} & \textbf{\(\lambda\)} & \textbf{\(E_{sr}\)} & \textbf{\(\eta_{vol}\)} \\
\hline
3 & 180.0004 & 3.9900 & 0.7592 & -0.4677 & 0.0014 & 3 & 180.0004 & 2.9861 & 1.5075 & -0.3817 & 0.0019 \\
4 & 180.0004 & 3.9757 & 0.7599 & -0.4737 & 0.0013 & 4 & 180.0004 & 2.9267 & 1.5193 & -0.3890 & 0.0025 \\
5 & 180.0004 & 3.9687 & 0.7604 & -0.4773 & 0.0023 & 5 & 180.0004 & 2.8889 & 1.5281 & -0.3935 & 0.0031 \\
10 & 180.0004 & 3.9573 & 0.7613 & -0.4846 & 0.0042 & 10 & 180.0004 & 2.7950 & 1.5525 & -0.4027 & 0.0063 \\
15 & 180.0004 & 3.9541 & 0.7616 & -0.4871 & 0.0070 & 15 & 180.0004 & 2.7489 & 1.5651 & -0.4059 & 0.0094 \\
20 & 180.0004 & 3.9526 & 0.7618 & -0.4883 & 0.0093 & 20 & 180.0004 & 2.7175 & 1.5737 & -0.4075 & 0.0126 \\
25 & 180.0004 & 3.9517 & 0.7619 & -0.4890 & 0.0116 & 25 & 180.0004 & 2.6924 & 1.5806 & -0.4085 & 0.0157 \\
50 & 180.0004 & 3.9500 & 0.7620 & -0.4905 & 0.0232 & 50 & 180.0004 & 2.3020 & 1.6810 & -0.4111 & 0.0315 \\
100 & 180.0004 & 3.9492 & 0.7622 & -0.4912 & 0.0463 & 100 & 180.0004 & 2.2897 & 1.6842 & -0.4125 & 0.0629 \\
200 & 180.0004 & 3.9488 & 0.7622 & -0.4916 & 0.0927 & 200 & 180.0004 & 2.2846 & 1.6856 & -0.4132 & 0.1259 \\
\hline
\end{tabular}
\end{table}

Table 3.2.2: Average potential energy per CH\(_4\) molecule (eV), angular spacing \(\phi\) (\(^\circ\)), longitudinal spacing \(Z\) (\(\text{Å}\)), offset position \(\lambda\) (\(\text{Å}\)) and volume density \(\eta_{vol}\) (g cm\(^{-3}\)) for the spiral configuration of \(m\) CH\(_4\) molecules in three carbon nanotubes.
for a (10, 10) tube packed with C_{60} fullerenes. In addition, the equilibrium distance between the molecules decreases as the number of molecules in the tube increases, which is a consequence of the packing of the molecules. However, as the tube size increases, the CH\textsubscript{4} molecules move closer to the tube wall owing to the larger available space inside the tube. Offset locations 1.42 Å and 2.91 Å are obtained for three interacting CH\textsubscript{4} molecules inside (8, 8) and (10, 10) carbon nanotubes respectively, while the equilibrium spacing 2.10 Å and 2.13 Å are obtained for the same three interacting molecules inside (8, 8) and (10, 10) carbon nanotubes respectively. We also comment that the interactions between CH\textsubscript{4} molecules contributes more to the chain formation than the interactions between CH\textsubscript{4} and the tube wall. We further comment that for the problem of putting spheres into cylinders as a function of the diameter of the two, a linear chain is formed if \( D/d = 1 \) while genuine zigzag patterns are formed if \( 1 \leq D/d \leq 1.995 \), where \( D \) is the cylindrical diameter and \( d \) is the spherical diameter [69]. The values for the constants employed for evaluating the average potential energy can be found in Table 3.0.1, and detailed numerical values for the energy and the parameters involved in this configuration can be found in Table 3.2.1. Finally we comment that the volume density \( \eta_\text{vol} \) reported in Table 3.2.1 is calculated for a fixed length of nanotube based on the minimum volume capable of adsorbing the maximum number of CH\textsubscript{4} molecules considered here (201 molecules for \( m = 100 \)). Hence the density reported for \( m = 100 \) can be considered a maximum density for adsorbed CH\textsubscript{4} in each of the nanotubes we investigate.

3.3 Spiral configuration for CH\textsubscript{4}@SWCNT

In this section we examine an assumed spiral configuration as shown in Fig. 3.3.1 for \( m \) CH\textsubscript{4} molecules inside a carbon nanotube. We derive the minimum energy and the corresponding angular spacing \( \phi \), longitudinal spacing \( Z \) and the offset location \( \lambda \) for this configuration. The total interaction energy for this configuration is derived by assuming that there are \((m - 1)\) type X interactions, \((m - 2)\) type Y interactions,
Figure 3.3.1: Spiral configuration for $m$ CH$_4$ molecules inside a carbon nanotube

$(m - 3)$ type V interactions, $(m - 4)$ type U interactions and that all of the $m$ CH$_4$ molecules inside the carbon nanotube are interacting with the tube. For this configuration, we also assume four nearest neighbor interactions of types U, V, X, Y as shown in Fig. 3.3.1, and that the tube is axially symmetric.

With reference to the same Cartesian coordinate system $(x, y, z)$, a typical point on the surface of a carbon nanotube has coordinates $(b \sin \theta, b \cos \theta, z)$ where $b$ denotes the radius of the carbon nanotube. Also, the tube is again assumed to be infinite in length. Using the same Cartesian coordinate system $(x, y, z)$ with the origin at the center of the tube axis and aligned with the left-most CH$_4$ molecule, the centers of the CH$_4$ molecules have coordinates $(\lambda \cos(j \phi), \lambda \sin(j \phi), jZ)$. It is worth noting that a special case of the zigzag pattern arises from $\phi = \pi$. Using (3.1.2), the total potential energy of the system is given by

$$E_{sr}^{tot} = mE_t + (m - 1)E(\delta_1) + (m - 2)E(\delta_2)$$
$$+ (m - 3)E(\delta_3) + (m - 4)E(\delta_4),$$

where $E$ and $E_t$ denote the interaction energy between two CH$_4$ molecules and interaction energy between $m$ CH$_4$ molecules and the carbon nanotube respectively.
The distances between the centers of the neighboring CH$_4$ molecules are given by

$$\delta_p^2 = 4\lambda^2 \sin^2(p\phi/2) + (pZ)^2, \quad p \in \{1, 2, 3, 4\}. \quad (3.3.1)$$

Similarly the total potential energy for interaction types U, V, X, Y is given by

$$E = E_{hh} + 2E_{ch} + E_{cc},$$

where the subscripts $ch, hh$ and $cc$ denote the carbon atom-hydrogen-sphere interactions, hydrogen-sphere-hydrogen-sphere interactions and carbon atom-carbon atom interactions respectively. The analytical expressions for the interaction energies above are given by (3.2.7), (3.2.8) and (3.1.1) respectively, with the appropriate distance for each interaction type given by (3.3.1). We note that the distance between the center of a CH$_4$ molecule and any point on the surface of the carbon nanotube is given by

$$\rho^2 = (b - \lambda)^2 + 4b\lambda \sin^2[(\theta - (j\phi))/2] + (z - jZ)^2.$$  

Given the assumption of axial symmetry of the tube, we note that the term $(j\phi)$ has no effect on the values of the integrals (3.2.2) and (3.2.3) and therefore we may let $(j\phi) = 0$, so that the distance between the center of a CH$_4$ molecule and any point on the surface of the carbon nanotube becomes

$$\rho^2 = (b - \lambda)^2 + 4b\lambda \sin^2\theta/2 + (z - jZ)^2.$$  

Since the tube is assumed to be infinite, this distance is analogous to (3.2.1). The total interaction energy between a CH$_4$ molecule inside the carbon nanotube and the carbon nanotube for the spiral configuration is given by

$$E_t = E_{tc} + E_{th},$$
and the analytical expressions for the above energy functions are given by (3.2.5) and (3.2.6).

### 3.3.1 Numerical results for spiral CH₄@SWCNT

In this section, we present the numerical results for the spiral packing configuration formed by CH₄ molecules in carbon nanotubes. By minimizing the energy of the system, we may obtain the offset position \( \lambda \) between the center of the CH₄ molecule and the axis of the carbon nanotube, the equilibrium spacing \( Z \) between the centers of two nearest neighboring CH₄ molecules as well as the angular spacing \( \phi \). The carbon nanotube is assumed to be infinite in length and we examine \( m \) CH₄ molecules in (9,5), (8,8) and (10,10) carbon nanotubes. Using the computational algebraic package MAPLE, the optimum potential energy for a spiral system of CH₄ molecules encapsulated in different radii carbon nanotubes are presented in Table 3.2.2. In this configuration, spiral patterns are obtained in all three tubes and the angular spacing \( \phi \simeq \pi \) in the (9,5) and (8,8) carbon nanotubes may be viewed as a special case of the zigzag configuration. For the present problem, the angular spacing \( \phi \) is approximately equal to \( \pi/2 \) in the (10,10) tube. Also the equilibrium spacing \( Z \) decreases as the tube is packed with more CH₄ molecules. This is a consistent phenomena apparent in both configurations, as is the increase in the offset distance as the tube size increases. These observations are consistent with results from simulations where an increase in tube size causes an increase in CH₄ self-diffusivity [29, 15, 70], where Skoulidas et al [70] employ a fully atomistic technique in their study. The values for the constants employed for evaluating the average potential energy can be found in Table 3.0.1, detailed numerical values for the energy and the parameters involved in this configuration are given in Table 3.2.2. As before, the volume density \( \eta_{vol} \) reported in Table 3.2.2, is for a fixed length and hence the last row gives what can be considered a maximum density of adsorbed CH₄.
CHAPTER 3. PACKING CONFIG. OF CH$_4$ INTO CNT

Figure 3.3.2: Volume for adsorption for CH$_4$ with zigzag and spiral packing

(a) Volume for adsorption for CH$_4$ - (9, 5) CNTs

(b) Volume for adsorption for CH$_4$ - (8, 8) CNTs

(c) Volume for adsorption for CH$_4$ - (10, 10) CNTs
In Fig. 3.3.2, we plot the relation between the total volume for adsorption and temperature for CH$_4$ packed inside (9, 5), (8, 8) and (10, 10) CNTs. We employ the average minimum potential energy per CH$_4$ molecule as $m \to \infty$ from tables 3.2.1 and 3.2.2, to approximate the free-cavity volume available for CH$_4$ adsorption with increasing temperature. As expected, the available free-cavity volume increases as the tube size increases with the (10, 10) tube having the largest free-cavity volume. We also comment that in a (9, 5) and (10, 10) CNT, CH$_4$ molecules stay adsorbed with a spiral packing configuration in the cavity of a CNT at higher temperatures in the range $570 - 600$ K and $500 - 650$ K, respectively, as opposed to a zigzag packing configuration. Furthermore, the volume of adsorption decreases as temperature increases due to CH$_4$ molecules having a higher mean kinetic energy and therefore less likely to adsorb onto the CNT walls. This observation is in good agreement with Adisa et al [64], where CH$_4$ physisorption onto nanotube bundles is studied, Thornton et al [51], where interactions between a gas molecule and a pore opening are used to predict various gas diffusion regimes and Jakobtorweihen et al [15], where molecular dynamics simulations are used to predict self-diffusivity of CH$_4$ molecules with increasing temperature. The optimal average potential energy for both spiral and zigzag packing configurations is found in the (10, 10) CNT, confirming the results of Agrawal et al [59] in proposing larger diameter tubes as the most favoured site for CH$_4$ molecule adsorption in nanotubes.

### 3.4 Conclusions

With a view to modeling CH$_4$ gas storage in carbon nanotubes, we investigate two different packing configurations for CH$_4$ molecules inside single-walled carbon nanotubes of varying radii. The zigzag configuration involves two parameters which are the offset distance $\lambda$ between the center of the CH$_4$ molecule and the axis of the tube, and the distance $Z$ between the centers of two interacting CH$_4$ molecules. The spiral configuration has three parameters which are the angular spacing $\phi$ be-
between CH$_4$ molecules, the offset distance $\lambda$ between the center of the CH$_4$ molecule and the axis of the tube, and the distance $Z$ between the centers of interacting CH$_4$ molecules. Analytical expressions involving hypergeometric functions for both configurations are obtained. CH$_4$ molecules inside a (9, 5) carbon nanotube form a linear chain along the axis of the tube but a genuine zigzag pattern occurs for the (8, 8) and (10, 10) carbon nanotubes, both of which have larger radii than a (9, 5). For the spiral configuration, the angular spacing between CH$_4$ molecules is $\phi \simeq \pi$ for (9, 5) and (8, 8) carbon nanotubes, and $\phi \simeq \pi/2$ for a (10, 10) carbon nanotube. Both configurations show similar features such as the equilibrium distance between CH$_4$ molecules decreases as the number of molecules increases; the offset distance of CH$_4$ molecules increases with increasing tube radius; the available free-cavity volume increases as the tube size increases; and the volume of adsorption decreases as temperature increases. The results presented are shown to be in excellent agreement with results from experiments and molecular dynamics and moreover, can be obtained without the need to run computationally intensive simulations. Hence, they may be used to predict the effects of temperature and tube size on CH$_4$ packing in nanostructures. Our results might serve to provide a proper understanding of gas storage inside carbon nanotubes, and the approach adopted here might be extended to storage of other gases in other nanostructures.
Chapter 4

Modelling surface adsorption of methane on carbon nanostructures

In order to comprehensively fulfil the need for molecular CH$_4$ storage in carbon nanostructures, it is necessary to understand the adsorption properties between CH$_4$ and graphitic materials. The study of CH$_4$ adsorption on graphite has an extensive history [20, 21, 22, 23, 24, 4, 25] largely due to its practical and theoretical significance which includes the production of carbon (graphite) through CH$_4$ pyrolysis [26]. However, since the recent discovery of fullerenes and carbon nanotubes, there has been increased interest in graphite. Vidali et al [23] present a review of over 250 gas-surface systems including the CH$_4$-graphite system. They tabulate van der Waals adsorption coefficients, equilibrium distances, well depths and binding energies for the laterally averaged interaction potential as deduced from the analyses of experimental data and calculations. Severin et al [22] carry out a molecular dynamics study of a CH$_4$ molecule adsorbed on a graphite surface by utilizing pairwise potential calculations to predict the height of a CH$_4$ monolayer above the graphite surface, as well as the vibrational frequency against the surface. Phillips et
al [21, 27] use intermolecular potentials and lattice sums to investigate vibrational zero-point energies, equilibrium structure of a CH$_4$-graphite system, conditions for monolayer-bilayer and bilayer-trilayer coexistence. Their results show that the bilayer and trilayer films are significantly compressed at coexistence. A second order Möller-Plesset perturbation theory study of CH$_4$ physisorption on graphite estimates the binding energy of CH$_4$ on graphite as 0.1518 ± 0.043 eV [29], while a density-functional study predicts an adsorption energy of 0.118 eV with a 3.21 Å equilibrium distance above the graphite carbon [20].

Thornton et al [8] propose metal-organic frameworks impregnated with magnesium-decorated fullerenes as possible storage media for CH$_4$. Their volumetric CH$_4$ uptake of 265 v/v is the highest reported value for any material and exceeds the DoE target of 180 v/v. Johnson et al [38] employ neutron diffraction and numerical modelling to investigate CH$_4$ adsorption on bundles of carbon nanotubes, and they find that although nanotube deformation is an important factor in limiting the size of interstitial channels, these channels allow for the stabilisation of adsorbed CH$_4$ molecules. Adisa et al [64] investigate CH$_4$ encapsulation in the open cavities of silicon and carbon nanotube bundles. These open cavities are assumed to arise due to the absence of a central nanotube in a six-fold nanotube bundle geometry. The study shows excellent agreement with other computational studies [71, 8, 51] especially in proposing silicon nanostructures as promising candidates for storage of gas fuels. Several studies have examined possible gas storage in interstitial channels of carbon nanotube bundles and groove sites between two aligned interacting nanotubes [14, 29]. Here we use the term “groove site” to mean the region of space between two aligned nanotubes, and by groove surface we mean the surface surrounding the groove site. Ricca et al [29] employ density functional theory and the MP2 model to predict that CH$_4$ adsorption in bundle interstitial channels and at groove sites is stronger than that on individual nanotubes, proposing a 0.6 kcal/mol difference in the binding energy. Adsorption in groove sites and interstitial channels is reported to be a significant contribution to the total adsorption capacity of a carbon nanostructure [43].
In this chapter, we employ classical applied mathematical modelling using the basic principles of mechanics to exploit the Lennard-Jones potential and the continuous approximation, to investigate CH$_4$ adsorption on graphite and in the groove site between two aligned single-walled carbon nanotubes. We derive analytical expressions for the binding energy between a CH$_4$ molecule adsorbing onto a graphitic surface, and further develop the approach in a previous work [64] to derive an analytical expression for the binding energy of a CH$_4$ molecule adsorbed in the groove site of two single-walled carbon nanotubes. In proposing the system of CH$_4$ adsorption in groove sites, we have in mind CH$_4$ storage in the interstitial channels between the individual single-walled carbon nanotubes that comprise a bundle. When minimized, these binding energies give the precise preferred structure and location of the molecule in the respective systems. In addition, we determine a relation between the probability for CH$_4$ adsorption onto a graphitic surface and groove surface under different temperature regimes, and we determine the adsorption isotherms using gravimetric methods at room temperature. Finally, we carry out a comparative study between our results and those from experimental and simulation studies. We comment that our model accounts for the physisorption of CH$_4$ molecules onto graphite and SWCNT groove sites but we assume no chemisorption of CH$_4$ onto these surfaces. In the following section, we discuss in detail, the method used in deriving the binding energies for the CH$_4$-graphite and CH$_4$-SWCNT groove site system. The analyses and derivation of the binding energies, equilibrium distances and adsorption probability of CH$_4$ onto graphite and SWCNT groove site are discussed in sections 4.3 and 4.4. Some discussion of the results is provided in section 4.5 and a brief summary is given in the final section of the chapter. Some analytical details are provided in Appendix C.
### Parameters and Values

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of (9, 0)</td>
<td>( b = 3.523 \text{ Å} )</td>
</tr>
<tr>
<td>Radius of hydrogen sphere</td>
<td>( a = 1.1 \text{ Å} )</td>
</tr>
<tr>
<td>*Attractive constant C-C</td>
<td>( A = 17.4 \text{ eV Å}^6 )</td>
</tr>
<tr>
<td>*Repulsive constant C-C</td>
<td>( B = 29000 \text{ eV Å}^{12} )</td>
</tr>
<tr>
<td>**Attractive constant C-H</td>
<td>( A = 14.94 \text{ eV Å}^6 )</td>
</tr>
<tr>
<td>**Repulsive constant C-H</td>
<td>( B = 14544 \text{ eV Å}^{12} )</td>
</tr>
<tr>
<td>Mean surface density of hydrogen sphere</td>
<td>( \eta_2 = 0.263 \text{Å}^{-2} )</td>
</tr>
<tr>
<td>Mean surface density of graphite</td>
<td>( \eta_1 = 0.3812 \text{Å}^{-2} )</td>
</tr>
<tr>
<td>Mean surface density of SWCNT</td>
<td>( \eta_1 = 0.3812 \text{Å}^{-2} )</td>
</tr>
</tbody>
</table>

Table 4.0.1: Numerical values of constants used (* denotes data from [1] and ** denotes data from [2]).

### 4.1 Method

In this section we outline the mathematical modelling employed in our calculations. We model a single \( \text{CH}_4 \) molecule assuming that the four hydrogen atoms are smeared over a spherical surface of radius \( a = 1.1 \text{ Å} \) (C-H bond length in \( \text{CH}_4 \)) with the carbon atom assumed to be situated at the center of the sphere. A major advantage of this \( \text{CH}_4 \) model is that the particular orientation of the hydrogen atoms becomes immaterial, providing a significant simplification to the calculation [65].

The Lennard-Jones interaction potential for two atoms on two non-bonded molecules is given by

\[
\nu(\rho) = -A\rho^{-6} + B\rho^{-12},
\]

where \( A \) and \( B \) denote the attractive and repulsive constants respectively, and \( \rho \) is the distance between the two atoms. Using the continuous approximation which assumes that the carbon atoms on the carbon surface can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the
total potential energy is given by

\[ E = \eta_1 \eta_2 \int_{S_1} \int_{S_2} \nu(\rho) dS_1 dS_2, \]  

(4.1.2)

where \( \eta_1 \) and \( \eta_2 \) represent the average atomic surface densities (namely, number of atoms/surface area) of graphite (and SWCNT) and a CH\(_4\) molecule, respectively, and \( \nu(\rho) \) is the Lennard-Jones potential function for two non-bonded atoms with typical surface elements \( dS_1 \) and \( dS_2 \) at a distance \( \rho \) apart. The original sources and the numerical values of the constants used in this chapter are as given in Table 4.0.1.

Following similar calculations by Thornton et al [8], the probability \( Pr_{ad} \) that a CH\(_4\) molecule will be adsorbed on the open surface of a graphite sheet or in the free-cavity of SWCNT groove site is assumed to be given by

\[ Pr_{ad} = 1 - \exp(-|E_{min}|/RT), \]

(4.1.3)

where \( E_{min} \) is the CH\(_4\)-graphite and CH\(_4\)-groove site minimum binding energy, \( R \) is the universal gas constant and \( T \) is the temperature in Kelvin.

### 4.2 Interaction of CH\(_4\) and graphite

In this section, we examine the surface binding energy between a CH\(_4\) molecule interacting with graphite as shown in Fig. 4.2.1. We assume a graphitic configuration which is infinite in extent, and comprising four layers of graphene sheets, each at a distance \( \simeq 3.35 \) Å apart [22]. The CH\(_4\) molecule is assumed to interact with all four layers in the graphitic surface. We model a graphene sheet as a planar sheet consisting of a tessellation of hexagonal rings of carbon atoms to comprise a honeycomb lattice with hybridised \( sp^2 \) bonds [33]. Since the van der Waals interactions between interlaying graphene sheets are extremely weak [72], we assume the graphene-graphene layer interactions do not contribute towards the total binding
energy of the CH$_4$-graphite system. The total energy of the CH$_4$-graphite system is calculated by summing the following two contributions: (i) the interaction energy between the CH$_4$ carbon atom and graphite, and (ii) the interaction energy between the CH$_4$ hydrogen sphere and graphite.

We assume that the CH$_4$ carbon is a distance $\delta$ above the graphitic surface and therefore we define a three-dimensional Cartesian coordinate system, in which we locate the top graphitic plane $(p, q, 0)$ and the carbon atom located at $(0, 0, \delta)$. The distance $\rho$ between the CH$_4$ carbon to any point on the graphite surface is therefore given by

$$\rho_{cg}^2 = p^2 + q^2 + \delta^2, \quad (4.2.1)$$

substituting (4.2.1) into (4.1.1) and (4.1.2), we obtain an integral of the general form

$$I_{cg} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (p^2 + q^2 + \delta^2)^{-n} dp dq, \quad (4.2.2)$$

for $n = 3$ and 6. On evaluating the above integrals, we may derive the binding
energy between the CH$_4$ carbon and graphite to be given by

$$E_{cg}(\delta) = \eta_1 \left( -\frac{\pi A}{2\delta^4} + \frac{\pi B}{5\delta^{10}} \right), \quad (4.2.3)$$

where $\eta_1$ is the atomic density of graphite.

We now define a hydrogen sphere in spherical coordinates $(a, \theta, \phi)$ with its center a distance $\delta$ above the graphite surface. Since the graphite plane is infinite in extent, we can adopt the perpendicular distance from any of the CH$_4$ hydrogen atoms to the graphite surface as simply $\rho_{hg} = \delta + a \cos \phi$. We can therefore calculate the binding energy by integrating the expression $E_{cg}(\delta)$ given in (4.2.3) using this value for $\rho$ as the distance above the surface of graphite, and integrating over the hydrogen sphere. Substituting $\rho_{hg}$ into (4.1.1) and (4.1.2), the general integral of interest becomes

$$I_{hg} = \frac{\pi a^2}{n-1} \int_0^\pi \int_{-\pi}^\pi \frac{\sin \phi}{(\delta + a \cos \phi)^{2n-2}} d\theta d\phi, \quad (4.2.4)$$

for $n = 3$ and 6. On evaluating $I_{hg}$, we find that the binding energy between the hydrogen sphere and the graphite is given by

$$E_{hg}(\delta) = 2\pi^2 a n \eta_1 \eta_2 \left[ -\frac{A}{6} \left( \frac{1}{(\delta-a)^3} - \frac{1}{(\delta+a)^3} \right) + \frac{B}{45} \left( \frac{1}{(\delta-a)^9} - \frac{1}{(\delta+a)^9} \right) \right], \quad (4.2.5)$$

where $\eta_2$ is atomic density of the hydrogen sphere. Details for the derivation of (4.2.3) and (4.2.5) are given in Appendix C.

### 4.3 Interaction of CH$_4$ and SWCNT groovesite

In this section, we consider the binding energy of a CH$_4$ molecule in the groove site of two aligned (9, 0) single-walled carbon nanotubes. With reference to Fig. 4.3.1, we assume that the constituent nanotubes are each of the same radius $b$, and that they
lie on axis in the $xz$-plane which are parallel to and equidistant from the $z$-axis such that the distance $\rho$ between the CH$_4$ carbon and the two aligned carbon nanotubes is the same. With the groove geometry so defined, any of the two aligned single-walled carbon nanotubes in the groove has a surface in Cartesian coordinates which is given by $(\pm \sigma + b \cos \theta_i, b \sin \theta_i, z_i)$, where $i \in \{1, 2\}$, $0 \leq \theta_i \leq 2\pi$ and $-L \leq z_i \leq L$. We comment that for the analysis presented, we assume an infinite tube, with $-\infty \leq z_i \leq \infty$. With reference to the same Cartesian coordinates, we locate the CH$_4$ carbon at $(0, \delta, 0)$ and the hydrogen sphere at $(a \cos \theta_3 \sin \phi, \delta + a \sin \theta_3 \sin \phi, a \cos \theta)$.

The total energy between the CH$_4$-groove site system is calculated by summing the following two contributions: (i) the interaction energy between the CH$_4$ carbon atom and the groove site, and (ii) CH$_4$ hydrogen sphere and the groove site. The total binding energy for a CH$_4$ molecule in the groove site of two single-walled carbon nanotubes is given by

$$E_{bind} = -2E_{mt}(\delta),$$
where \( E_{mt} \) is the interaction energy between the \( \text{CH}_4 \) molecule and a single SWCNT calculated by summing the interaction energy between the \( \text{CH}_4 \) carbon and a single SWCNT with the interaction energy between the \( \text{CH}_4 \) hydrogen sphere and a single SWCNT [64]. The interaction energy between the \( \text{CH}_4 \) carbon and a SWCNT is derived by Cox et al [53] given by

\[
E_{mc}(\delta) = 2\pi^2 \eta_1 b \left( -\frac{3A}{8\delta^4} + \frac{63B}{256\delta^{10}} \right),
\]

where \( \eta_1 \) is the atomic density of the SWCNT. Similar to calculations by Cox et al [53] the binding energy between \( \text{CH}_4 \) hydrogen sphere and a SWCNT can be given by

\[
E_{mh}(\delta) = 4\pi^2 a^2 b \eta_1 \eta_2 \left[ \frac{-A}{8}(3J_2 + 5a^2J_3) + \frac{B}{5} \left( \frac{315}{256}J_5 \right. \right. \\
+ \left. \left. \frac{1155}{64}a^2J_6 + \frac{9009}{128}a^4J_7 + \frac{6435}{64}a^6J_8 + \frac{12155}{256}a^8J_9 \right) \right],
\]

where \( J_n \) is defined in terms of an ordinary hypergeometric function as

\[
J_n = \frac{2\pi}{[(b - \delta)^2 - a^2]^{n+1/2}} F \left( n + \frac{1}{2}, \frac{1}{2}, 1; \frac{-4b\delta}{(b - \delta)^2 - a^2} \right),
\]

for \( n = 3 \) or \( 6 \).

Further, the volume for \( \text{CH}_4 \) adsorption \( V_{ad} \) and the bulk volume \( V_{bulk} \) can be obtained by the volume integrals given by

\[
V_{ad} = \int_{r_1}^{r_2} 4\pi r^2 Pr_{ad} dr, \quad V_{bulk} = \int_{r_1}^{r_2} 4\pi r^2 (1 - Pr_{ad}) dr,
\]

where \( Pr_{ad} \) is the probability that a \( \text{CH}_4 \) molecule would stay in the bulk phase or become adsorbed onto the surface as given in (4.1.3). We comment that the upper and lower limits of the above integrals correspond to the maximum and minimum values respectively, of the distance \( \delta_{eq} \) for which the energy profiles in Fig. 4.4.1 remains negative. The heat of adsorption is therefore given by \( Q = |E_{av}| + k_B T/2, \)
Table 4.4.1: Comparison of potentials for minimum energy (eV) and equilibrium location (Å) from existing data for the interaction of helium and argon with graphite. Lennard-Jones constants taken from [4] and [5] (* denotes from [4]).

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{eq}$</td>
<td>$E_{min}$</td>
<td>$\delta_{eq}$</td>
</tr>
<tr>
<td>3.0193</td>
<td>-0.0209</td>
<td>3.4156</td>
</tr>
<tr>
<td>2.9833</td>
<td>-0.0207*</td>
<td>3.3692</td>
</tr>
</tbody>
</table>

where $E_{av} = (\int_{r_1}^{r_2} 4\pi r^2 E_{bind} \, dr)/V_f$, $E_{bind}$ is the total binding energy from Fig. 4.4.2, $V_f$ is the total free volume and the factor of 1/2 arises from assuming one degree of freedom.

The equations of state for the adsorbed phase and bulk phase are given respectively by (see for example [8])

$$P \left( \frac{V_{ad}}{n_{ad}} - v \right) = RT \exp \left( -\frac{Q}{RT} \right), \quad P \left( \frac{V_{bulk}}{n_{bulk}} - v \right) = RT,$$

(4.3.1)

where $P$, $n_{ad}$, $n_{bulk}$ and $v$ denote the external pressure, number density in the adsorbed phase, number density in the bulk phase and the occupied volume of densely packed gas molecules, respectively.

4.4 Results and discussions

In this section we present the results showing the binding energies and equilibrium distances for a CH$_4$ molecule interacting with graphite and a single-walled carbon nanotube groove site. Firstly, we compare our method with the 10-4-3 potential employed by Steele [4] for an atom of helium and argon interacting with graphite. As shown in table 4.4.1, our values for the minimum energy $E_{min}$ and equilibrium distance $\delta_{eq}$ are in excellent agreement with those obtained in [4]. For a helium atom interacting with graphite, 0.97% and 1.21% differences are observed respectively, for the minimum energy and equilibrium distance, while for an argon atom, 2.74% and 1.38% differences are observed respectively for the minimum energy and equilibrium
Table 4.4.2: Data (E - Experimental, T - Theoretical) on binding energy and equilibrium location for CH$_4$ adsorption on graphite.

<table>
<thead>
<tr>
<th>Minimum Energy (eV)</th>
<th>Equilibrium distance $\delta_{eq}$ (Å)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1400</td>
<td>3.45</td>
<td>E[23]</td>
</tr>
<tr>
<td>0.1544</td>
<td>3.45</td>
<td>E[73]</td>
</tr>
<tr>
<td>0.1721</td>
<td>3.35</td>
<td>E-T[74]</td>
</tr>
<tr>
<td>0.1824</td>
<td>3.27</td>
<td>E-T[75]</td>
</tr>
<tr>
<td>0.1814</td>
<td>3.35</td>
<td>E-T[76]</td>
</tr>
<tr>
<td>0.1180</td>
<td>3.21</td>
<td>T[20]</td>
</tr>
<tr>
<td>0.1400</td>
<td>3.45</td>
<td>T[22]</td>
</tr>
<tr>
<td>0.1443</td>
<td>3.92</td>
<td>T[77]</td>
</tr>
<tr>
<td>0.1672</td>
<td>3.32</td>
<td>T[21]</td>
</tr>
<tr>
<td>0.1948</td>
<td>4.27</td>
<td>T[29]</td>
</tr>
<tr>
<td>0.1987</td>
<td>3.83</td>
<td>This Study</td>
</tr>
</tbody>
</table>

Figure 4.4.1: Equilibrium location for CH$_4$ adsorption-graphite and groove site distance. We comment that the numerical results given in this study are however computationally instantaneous, in comparison to the truncated Fourier series expansion used in [4]. Moreover, our model produces accurate results without the need to take into account the actual position of the carbon atoms on the graphitic surface. In [24], the method used in [4] has been modified to deal with polar molecules.

The equilibrium distance $\delta_{eq}$ for CH$_4$-graphite is obtained by minimizing the
Figure 4.4.2: Energy level curves for a CH$_4$ molecule in a single-walled carbon nanotube groove site starting from -0.4 eV (white) to 1.4 eV (darkest black) with an increment of 0.2 eV in colour strength.

Figure 4.4.3: Probability for CH$_4$ adsorption-graphite and groove surfaces.

binding energy as shown in Fig. 4.4.1. Our results show that the equilibrium location for the CH$_4$ carbon - graphite carbon is 3.83 Å with a corresponding energy of 0.1987 eV. Our energy value is less than 9% above the experimental value of Kitaigorodskii et al [75] and about 2% above the value of Ricca et al [29] from MP2 perturbation theory. The equilibrium distance $\delta_{eq}$ obtained in this chapter is less
Figure 4.4.4: CH₄ adorption isotherms at 298 K

than 12% above the experimental values of Kitaigorodskii et al [75] and Vidali et al [23], and less than 3% below Albesa et al [77] derived from PM3 semi-empirical and density functional theory (DFT) calculations. Overall, our obtained values show good agreement in comparison with both experimental [23, 73, 74, 75, 76] and theoretical results [20, 21, 22, 77, 29] (see table 4.4.2) and are well within the spectrum of results in the literature. We comment that as the number of graphene sheets increases, the significance of the interaction of the CH₄ molecule with the newly added sheets towards the total interaction energy of CH₄-graphite decreases. This is apparent from the value of the interaction energy of 0.0002 eV between the CH₄ molecule and the fourth graphene sheet.

On minimizing the binding energy between the CH₄ molecule and the groove site, we obtain the equilibrium location (δₑₒ) for CH₄ away from the common axis. As shown in Fig. 4.4.1, the equilibrium location for CH₄ is 5.17 Å away from the common axis with a corresponding energy value of 0.2570 eV. This energy value is in good agreement with the experimental study by Talapatra et al [41] with a 2.8% difference and well within the range of 0.2428 ± 0.043 eV reported by Ricca et al [29]. Our estimated CH₄ equilibrium position in the groove confirms the current
view that CH$_4$ molecules initially fill the groove site and then move towards the outer surfaces of the single-walled carbon nanotubes [29, 41]. We also project the energy profile in the groove site onto the $\delta$ - $\sigma$ plane in Fig. 4.4.2, with the white region showing the minimum energy location. As shown in the figure, the minimum energy region agrees with that in Fig. 4.4.1 for the preferred location of the CH$_4$ molecule in the groove site. We plot the probability for CH$_4$ adsorption onto graphite and the open-cavity of the SWCNT groove site with different temperatures in Fig. 4.4.3. As shown in the figure, at lower temperatures, CH$_4$ molecules are more likely to stay adsorbed on the graphitic and groove surfaces than at higher temperatures, particularly above 200 K for graphite and 250 K for groove site. This observation is in excellent agreement with experimental studies in the literature [22, 23]. We further comment that this observation confirms Kondratyuk et al [18] whose study predicts desorption from groove sites at high temperatures.

Knowledge of the potential profiles between a CH$_4$ molecule interacting with graphite and single-walled carbon nanotubes groove site, enables us to determine the heat of adsorption $Q$, which is an important parameter in calculating the adsorption behaviour between a CH$_4$ molecule and these surfaces. We then employ Eq. (4.3.1) to determine the total gravimetric uptake of CH$_4$ on graphite and single-walled carbon nanotube groove site. The numerical results for CH$_4$ uptake are in good agreement with experimental and theoretical studies in the literature [44, 8]. As shown in Fig. 4.4.4, CH$_4$ adsorption isotherms are determined at a temperature of 298 K for pressures up to 1 Mpa. The total gravimetric CH$_4$ uptake on the graphitic surface is 2.67 wt.% and 7.45 wt.% for the groove surface. We comment that this difference in gravimetric uptakes could be a consequence of the higher binding energy that is evident in the interaction between CH$_4$ and the groove surface. However, our predicted CH$_4$ uptake on graphite is in agreement with the reported value of about 2.7 wt.% from experimental studies and GCMC calculations [10] for the same adsorption isotherm of 298 K. We further comment that the CH$_4$ uptake amount
in the groove surface compares favourably with the uptake amount of 7.9 wt.% reported by [8] for a standard MOF structure measured at the same temperature and pressure. This result however, is slightly lower than the predicted values for a MOF structure impregnated with magnesium decorated C$_{60}$ fullerenes [8] although structures such as impregnated MOFs are very complicated and not quite practical. However, we comment that an increase in temperature will certainly reduce the total gravimetric uptake of CH$_4$ as this would result in higher mean kinetic energy for the CH$_4$ molecules, to reduce the probability for adsorption onto the graphite and groove surfaces. Finally, as shown in Fig. 4.4.4 and the recent experimental studies [25, 44, 45, 10], we comment that higher pressures are critically important for increased CH$_4$ uptake in molecular structures.

### 4.5 Conclusions

With a view to modelling natural gas storage in carbon nanostructures, we investigate the binding energies of CH$_4$ with two different carbon materials namely, graphite and the groove site of two aligned single-walled carbon nanotubes. By the groove site, we mean the region occurring between two aligned single-walled carbon nanotubes. The binding energy for the CH$_4$-graphite system is derived as a function of the distance between the CH$_4$ carbon and the graphite carbon, while that of the CH$_4$-groove site system is obtained as a function of both the equilibrium distance to the outer-tube wall and the aligned single-walled carbon nanotubes radii. We obtain the equilibrium distance between CH$_4$ carbon-graphite, and CH$_4$ carbon-groove site by minimizing their respective binding energies. Our results show that the binding energy for CH$_4$-graphite is minimized when the CH$_4$ carbon is 3.83 Å above graphite, and 5.17 Å away from the common axis shared by the two aligned single-walled carbon nanotubes in the case of CH$_4$-single-walled carbon nanotubes groove site. We also investigate the relationship between probable CH$_4$ adsorption and gravimetric uptake onto graphite and the open-cavity of a groove site with temperature and
pressure, and our results predict reduced CH$_4$ adsorption onto graphite and groove surfaces at higher temperatures and lower pressures. Our results also show overall good agreement with other experimental and theoretical results in the literature. At first sight, this average modelling approach might appear to be drastic, but in those situations for which there exists computational data, the approach presented here generally yields accurate predictions, which are moreover computationally instantaneous. These results might serve to provide a deeper understanding of gas storage inside carbon nanostructures.
Chapter 5

Open carbon nanocones as candidates for gas storage

Carbon nanostructures have attracted considerable attention [78] due to their potential use in many applications including energy storage, gas sensors, biosensors, nanoelectronic devices and chemical probes. Carbon allotropes such as carbon nanocones and carbon nanotubes have been proposed as possible molecular gas storage devices [64, 65, 16, 19, 8, 22, 35, 9]. More recently, carbon nanocones have gained increased scientific interest due to their unique properties and promising uses in many novel applications such as energy and gas storage [79, 80, 81, 82, 83]. Studies on the structural properties of carbon nanocones include Yudasaka et al. [80], who predict that pentagonal defects in carbon nanocones perturb the low-energy electronic structure both locally and globally, defining both a local region of enhanced reactivity and a global phase relation which has consequences for electron transport around the apex. Shenderova et al. [81] employ analytical potentials to show that carbon nanocones can exhibit conventional cone shapes or can form concentric wave-like metastable structures. Their study also predicts that a pentagon in the centre of a cone is the most probable spot for emitting tunnelling electrons in the presence of an external field, implying that nanocone assemblies, if practically accessible, could be used as
Figure 5.0.1: Ne, H$_2$, and CH$_4$ interacting with a single-walled carbon nanocone of length $L_2 - L_1$ and apex angle $\theta$
highly localized electron sources for templating at length scales below traditional lithography techniques. Baowan and Hill [84] find that the equilibrium location for two distinct and identical cones moves further away from the vertex as the number of pentagons increases. They also observe that the equilibrium configuration is such that one cone is always inside another, and therefore predicting the existence of nested double-cones. Yu et al. [83] employ thermal desorption and photoemission to study the adsorption capacity of H$_2$ on carbon nanocones and they show that the maximum desorption peak is located near 250 K. They also predict that the desorption process is influenced by site geometry and adsorbate-adsorbate interactions. Fullerene interaction with carbon nanocones is investigated theoretically by Suarez-Martinez et al. [79] who conclude that fullerenes weakly bind to the external nanocone wall with an equilibrium spacing of 2.9 Å and binding energy in the range 0.5 − 0.9 eV, and also conclude that the binding energy increases with the number of pentagons at the tip. Majidi et al. [82] investigate Ne adsorption on carbon nanocones using molecular dynamics simulation and they find that saturation coverage and saturation pressure both depend on temperature, and at saturation conditions, the maximum values of the interior and exterior coverages are 0.17 and 0.39 Ne per carbon, respectively. They conclude that adsorption coverages on carbon nanocones are greater than those on carbon nanotubes, making carbon nanocones a desirable adsorbent.

H$_2$ and CH$_4$, gases at room temperature, hold much promise as sources of clean and affordable energy, since they are more environmentally friendly than most hydrocarbon fuels and they are also readily available [40]. However, due to the current difficulties of storage, the widespread commercial use of H$_2$ and CH$_4$ as vehicle fuels has not been achieved. Ne, unlike other inert gases, discharges electricity even at normal currents and voltages, and has major applications in the advertising industry. Using nanotechnology, potentially H$_2$, CH$_4$ and Ne could be stored more efficiently [8, 82], and thereby increasing their everyday commercial use. Experimental work suggests, at least at lower temperatures, that there is a highly organized packing
arrangement of \( \text{H}_2 \) inside carbon nanocones [85, 82], and that \( \text{CH}_4 \) molecules are not freely spinning but somehow self-organized into a confined structure in which there is a local order [86]. However, despite the potential use of carbon nanocones as gas storage devices, there is very little available literature on gas storage in carbon nanocones in comparison with that for carbon nanotubes.

In this chapter, we employ the 6 – 12 Lennard-Jones potential together with the continuous approximation to investigate the encapsulation of \( \text{H}_2 \), \( \text{CH}_4 \) and Ne in carbon nanocones. In proposing this study, we have in mind gas storage in carbon nanocones. We derive analytical expressions for the binding energies and molecular forces between a single \( \text{H}_2 \) and \( \text{CH}_4 \) molecule, and a single Ne atom for carbon nanocones of varying apex angle and length. Finally, we determine the volume available for \( \text{H}_2 \), \( \text{CH}_4 \) and Ne adsorption in carbon nanocones of varying radii. We comment that in these models, we account for the physisorption of \( \text{H}_2 \), \( \text{CH}_4 \) and Ne to carbon nanocones and we assume no chemisorption of these gases onto carbon nanocones. In addition, we comment that this chapter provides a new analytical expression for gas encapsulation and adsorption in open carbon nanocones, from which numerical values can be readily deduced to provide an extensive numerical landscape of the problem, that will facilitate new physical insight into this problem. For example, we may readily demonstrate the particular physical dimensions of open carbon nanocones that will readily encapsulate different gases, and which describes an entirely new physical phenomena but which is inherent in the formulae presented here. The Lennard-Jones potential and the continuous approximation employed in deriving the analytical expressions for the binding energies are described in the following section, a discussion of the derivation of the basic results of this study is given in section 5.2, while section 5.3 provides a discussion of the results. A brief conclusion is presented in the final section of the chapter.
CHAPTER 5. OPEN CARBON NANOCONES FOR GAS STORAGE

(a) Binding energy for $L_1 = 1.1782$ Å

(b) Molecular force for $L_1 = 1.1782$ Å

Figure 5.1.1: Binding energy and molecular force for CH$_4$ molecule, two H$_2$ molecules, and four Ne atoms entering single-walled carbon nanocone
Table 5.0.1: Numerical values of constants used (* and ** denote data from [1] and [6] respectively).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of hydrogen sphere</td>
<td>(a = 1.1 \text{ Å} )</td>
</tr>
<tr>
<td>*Attractive constant C-C</td>
<td>(A_{CC} = 17.4 \text{ eV Å}^6)</td>
</tr>
<tr>
<td>*Repulsive constant C-C</td>
<td>(B_{CC} = 29000 \text{ eV Å}^{12})</td>
</tr>
<tr>
<td>**Attractive constant C-H</td>
<td>(A_{CH} = 17.9 \text{ eV Å}^6)</td>
</tr>
<tr>
<td>**Repulsive constant C-H</td>
<td>(B_{CH} = 17483.5 \text{ eV Å}^{12})</td>
</tr>
<tr>
<td>**Attractive constant C-Ne</td>
<td>(A_{CNe} = 13.2 \text{ eV Å}^6)</td>
</tr>
<tr>
<td>**Repulsive constant C-Ne</td>
<td>(B_{CNe} = 12794.6 \text{ eV Å}^{12})</td>
</tr>
<tr>
<td>Mean surface density of hydrogen sphere</td>
<td>(\eta_h = 0.263\text{Å}^{-2})</td>
</tr>
<tr>
<td>Mean surface density of carbon nanocone</td>
<td>(\eta_c = 0.3812\text{Å}^{-2})</td>
</tr>
</tbody>
</table>

5.1 Method

In this section we outline the procedure employed in our calculations. We begin by defining a complete nanocone with a vertex present as a closed nanocone while a nanocone with no vertex is termed an open nanocone. For closed nanocones, the apex angle is given by \(\sin(\Theta/2) = 1 - (N_p/6)\), where \(N_p = 1, 2, 3, 4, 5\), is the number of pentagons, giving rise to five possible closed nanocone structures [87]. Open nanocones however may have more flexible structures with more than five different apex angles [88, 89] although Eksioglu et al. [90] argue that open nanocones should have exactly the same apex angles as those of closed nanocones. We model an open nanocone with base radius \(R = (3K\sigma_c\sin\theta)/2\) and height \(H = (3K\sigma_c\cos\theta)/2\), where \(\sigma_c\) is the C-C bond length, \(K\) is the number of hexagons as measured from vertex to vertex along the slant and \(\theta = \Theta/2\) is the half-angle of the carbon nanocone apex angle \(\Theta\) as shown in Fig. 5.0.1. Employing the formulae for \(R\) and \(H\) given above, the proposed base radii for the nanocones examined in this study are given in Table 5.1.1, using 1.421 Å [55] for the C-C bond length \(\sigma_c\), and \(L_1\) is obtained from the above expression for \(H\) and is employed in the analytical expression in Section 5.2. In addition, we model a single CH\(_4\) molecule assuming that the four hydrogen atoms are smeared over a spherical surface of radius \(a = 1.1 \text{ Å} \) (C-H bond...
length in CH$_4$) with the carbon atom assumed to be situated at the center of the sphere. A major advantage of this CH$_4$ model is that the particular orientation of the hydrogen atoms becomes immaterial thus, providing a significant simplification to the calculation [65]. The total energy calculation for the H$_2$, CH$_4$ and Ne to carbon nanocone system is therefore reduced to (i) calculating the interaction energy between the H$_2$, Ne, and CH$_4$ carbon atoms and nanocone, and (ii) calculating the interaction energy between the CH$_4$ hydrogen sphere and nanocone.

The Lennard-Jones interaction potential for two atoms on two non-bonded molecules is given by

$$\nu(\rho) = -A\rho^{-6} + B\rho^{-12},$$  \hspace{1cm} (5.1.1)

where $A$ and $B$ denote the attractive and repulsive constants respectively, and $\rho$ is the distance between the two atoms. Using the continuous approximation which assumes that the carbon atoms on the carbon surface can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the total potential energy is given by

$$E = \eta_1 \eta_2 \int_{S_1} \int_{S_2} \nu(\rho) dS_1 dS_2,$$  \hspace{1cm} (5.1.2)

where $\eta_1$ and $\eta_2$ represent the average atomic surface densities (namely, number of atoms/surface area) of a carbon nanocone and a CH$_4$ molecule, respectively, and $\nu(\rho)$ is the Lennard-Jones potential function for two non-bonded atoms with typical surface elements $dS_1$ and $dS_2$ at a distance $\rho$ apart. The original sources and the numerical values of the constants used in this study are as given in Table 5.0.1. We comment that the numerical data taken is from two different sources [1, 6] since there is no single source currently available. We further comment that the present modelling does not take into account quantum effects for H$_2$ binding into carbon nanocones, which is an issue that is not fully understood in the literature [91, 92, 93].

Following a similar calculation to that given by Thornton et al [8], the volume available for H$_2$, CH$_4$ or Ne adsorption in the free cavity of a single-walled carbon
Table 5.1.1: Proposed base radii for carbon nanocones with $\Theta = 112.9^\circ$

<table>
<thead>
<tr>
<th>$K$ Integer number of hexagons</th>
<th>$R$ (Å) Radius of carbon nanocone</th>
<th>$L_1$ (Å) Corresponding point along height $H$ of nanocone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7763</td>
<td>1.1782</td>
</tr>
<tr>
<td>2</td>
<td>3.5526</td>
<td>2.3563</td>
</tr>
<tr>
<td>3</td>
<td>5.3289</td>
<td>3.5345</td>
</tr>
<tr>
<td>4</td>
<td>7.1052</td>
<td>4.7126</td>
</tr>
</tbody>
</table>

The binding energy between $H_2$, CH$_4$ or Ne and a single-walled carbon nanocone is assumed to be given by

$$V_{ad} = \int_{L_1^*}^{L_2^*} \frac{1}{\pi r^2} (1 - e^{-|E_{min}|/kT}) \, dz,$$

where $E_{min}$ is the minimum binding energy of $H_2$, CH$_4$ or Ne to a single-walled carbon nanocone, $r = z \tan \theta$ is the variable cone radius, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin. We note that the upper and lower limits of the above integral $L_2^*$ and $L_1^*$ correspond to the maximum and minimum points along the single-walled nanocone axis for which the binding energy remains negative.

### 5.2 Interaction of $H_2$, CH$_4$ and Ne with a single-walled carbon nanocone

In this section, we examine the binding energy between $H_2$, CH$_4$, and Ne interacting with a single-walled carbon nanocone for interactions as shown in Fig. 5.0.1. We assume that the $H_2$ and CH$_4$ molecule, and Ne atom, are centered along the axis of the single-walled carbon nanocone and with the origin situated at the vertex of the extended carbon nanocone. Thus we locate a point on the nanocone surface in Cartesian coordinates at $(r \cos \phi, r \sin \phi, z)$, where $\phi$ is the angle in the $xy$-plane measured anti-clockwise from the $x$-axis, and $r = z \tan \theta$, is the surface radius. Similarly, the coordinates of the $H_2$, CH$_4$ carbon and Ne atom can be located in
CHAPTER 5. OPEN CARBON NANOCONES FOR GAS STORAGE

(a) Binding energy for $L_1 = 3.5345 \text{ Å}$

(b) Molecular force for $L_1 = 3.5345 \text{ Å}$

Figure 5.1.2: Binding energy and molecular force for CH$_4$ molecule, two H$_2$ molecules, and four Ne atoms entering single-walled carbon nanocone
CHAPTER 5. OPEN CARBON NANOCONES FOR GAS STORAGE

(a) Binding energy for $L_1 = 4.7126$ Å

(b) Molecular force for $L_1 = 4.7126$ Å

Figure 5.2.1: Binding energy and molecular force for CH$_4$ molecule, two H$_2$ molecules, and four Ne atoms entering single-walled carbon nanocone
Cartesian coordinates at \((0, 0, Z)\), where \(Z\) is the horizontal location of the \(H_2\), \(CH_4\) carbon or Ne atom along the \(z\) axis as shown in Fig. 5.0.1. The distance \(\rho\) between the centre of the \(H_2\), or \(CH_4\) molecule, or Ne atom to any point on the nanocone surface is therefore given by

\[
\rho_{\text{atom}}^2 = z^2 \tan^2 \theta + (z - Z)^2.
\]  

(5.2.1)

We comment that for the open nanocone, the positions of the two edges are \(z = L_1\) for the smaller open-end and \(z = L_2\) for the larger open-end as shown in Fig. 5.0.1. The numerical values for \(L_1\) employed in this study are as given in Table 5.1.1 and \(L_2\) is assumed to be infinite in length. Substituting (5.2.1) into (5.1.1) and (5.1.2), we obtain the total binding energy for a single atom with a carbon nanocone as given by

\[
E_{\text{tot}}^{\text{atom}} = 2\pi \eta_c \tan \theta \sec \theta \int_{L_1}^{L_2} z(-A\rho^{-6} + B\rho^{-12})dz,
\]

(5.2.2)

where \(\eta_c\) is the atomic surface density of the carbon nanocone. Following a similar calculation by Lee et al [94], the total binding energy \(E_{\text{tot}}^{\text{atom}}\) can be evaluated analytically and is given by

\[
E_{\text{tot}}^{\text{atom}} = -2A\pi \eta_c J_3 + 2B\pi \eta_c J_6,
\]

(5.2.3)

where \(J_m\) is defined as

\[
J_m = \sin \theta \left[ \frac{(z^2 - 2zZ \cos^2 \theta + Z^2 \cos^2 \theta)^{1-m}}{2(\sec^2 \theta)^{m-1}(1 - m)} \right]^{z=L_2}_{z=L_1} + \frac{\sin \theta \cos \theta}{Z^{2m-2}(\sin \theta)^{2m-1}} \int_{z=L_1}^{z=L_2} (\cos^2 \omega)^{m-1} d\omega.
\]

(5.2.4)

where \(L_1\) and \(L_2\) are the extremities of the carbon nanocone defined earlier, and \(\omega = \arctan(z - Z \cos^2 \theta / Z \sin \theta \cos \theta)\).

As previously described, we now locate a hydrogen sphere at \((0, 0, Z)\). The interaction energy for an atom interacting with the hydrogen sphere is derived in
Cox et al. [55] and is given by
\[
G(\rho) = \frac{\pi a \eta_h}{\rho} \left[ \frac{-A}{2} \left( \frac{1}{(\rho - a)^4} - \frac{1}{(\rho + a)^4} \right) + \frac{B}{5} \left( \frac{1}{(\rho - a)^{10}} - \frac{1}{(\rho + a)^{10}} \right) \right],
\]
where \(\eta_h\) is the atomic surface density of the hydrogen sphere. Therefore, the total interaction energy can be found by integrating (5.2.5) over the surface of a carbon nanocone and is given by
\[
E_{\text{hsphere}}^{\text{tot}} = 2b \eta_h \eta_c \pi^2 \sin \theta \left[ \frac{A}{2} (Q_{4+} - Q_{4-}) - \frac{B}{5} (Q_{10+} - Q_{10-}) \right],
\]
where \(Q_{n\pm}(n = 4, 10)\) are given by
\[
Q_{n\pm} = \left[ \cos^2 \theta (\rho \pm a) (1 - n) \right]^{z=L_2}_{z=L_1} + Z \cos^3 \theta \int_{z=L_1}^{z=L_2} \frac{d\lambda}{(Z \sin \theta \cosh \lambda \pm a)^n}, (5.2.6)
\]
where \(\rho\) as a function of \(z\) is defined by (5.2.1).

### 5.3 Results and discussions

In this section, we present the results showing the binding energy and molecular force for \(\text{H}_2\), \(\text{CH}_4\) and \(\text{Ne}\) entering carbon nanocones of varying apex angle and size. The numerical calculations are performed using the algebraic software package MAPLE and we give specific results for an apex angle of 112.9°[82] and \(L_2\) is assumed to be infinite. The numerical values for \(L_1\), the corresponding radii \(R\) and the integer number of hexagons \(K\), employed in this study are derived from Section 5.1 and are as given in Table 5.1.1 using 1.421 Å [55] for the C-C bond length \(\sigma_c\). Describing an encapsulation process from the smaller end of the nanocone, as shown in Fig. 5.1.1(a), the positive energy profile for the \(\text{CH}_4\) molecule indicates that the molecule may not pass through the smaller open-end of the cone due to the presence of an energy barrier at the cone entrance, while the \(\text{H}_2\) molecules and \(\text{Ne}\) atoms will be attracted inside the cone due to the negative energy profile, as the energetically
Figure 5.2.2: Volume for adsorption for a CH$_4$ molecule, two H$_2$ molecules, and four Ne atoms in a single-walled carbon nanocone for two distinct nanocone radii
most favourable position for the H$_2$ molecules and Ne atoms is inside the cone even though they are slightly repulsed after entering the cone. The molecular force that is calculated by differentiating the total binding energy with respect to the horizontal distance $Z$, is shown in Fig. 5.1.1(b). The molecular force profile shows that the H$_2$ molecules and Ne atoms experience an acceleration on entering the cone resulting in H$_2$ and Ne encapsulation. The gas molecules however, decelerate after entering as indicated by the negative force, while the CH$_4$ molecule experiences a large energy barrier at the entrance of the cone resulting in repulsion. We comment that the initial minimum energy well of 0.0278 eV at the entrance of the cone for a Ne atom during encapsulation in Fig. 5.1.1(a) is in agreement with the binding energy value of 0.02073 eV for exohedral adsorption derived from atomistic molecular dynamics simulation by Majidi et al. [82]. We further comment that although the force plot gives only the slope of the energy plot, it does allow for the visualization of phenomenon such as the magnitude of the maximum force, which is more easily obtained than the mere measurement of the gradient of the energy profile. Figures 5.1.2 and 5.1.2 describe the binding energies and molecular forces as H$_2$, CH$_4$ and Ne are being encapsulated inside carbon nanocones of lengths $L_1 = 3.5345$ Å and $L_1 = 4.7126$ Å respectively. As shown in these figures, the three gases experience a slight repulsive force just at the entrance of the cones but they are then attracted inside the cone as indicated by the positive force gradients in these figures. After encapsulation, they then decelerate again similar to the motion paths of the H$_2$ molecules and Ne atoms in Fig. 5.1.1(b). The presence of a slight energy barrier coupled with the minimum energy configuration inside the cone suggests that if the attractive force is high enough, the gases would overcome the repulsive force at the cone entrance and would be encapsulated as the energetically most favourable position for the gases is inside the cone, an observation which is consistent with CH$_4$ encapsulation inside carbon nanotubes [65]. For a carbon nanocone of length $L_1 = 3.5345$ Å, the average minimum energy for a H$_2$ molecule encapsulated inside the nanocone is 0.0048 eV, 0.0131 eV for a CH$_4$ molecule, and 0.00175 eV for a Ne
atom. We comment that encapsulation from the larger open-end is in the opposite direction to the encapsulation process from the smaller open-end. For example, for a carbon nanocone of length $L_1 = 3.5345 \, \text{Å}$, the gases would accelerate to the entrance of the cone, experience a deceleration by the cone entrance, accelerate again and then become encapsulated before decelerating. We comment that as the size of the carbon nanocones increases, the minimum binding energy and molecular force decreases, an observation seen in CH$_4$ encapsulation in varying sized carbon nanotubes [65].

In Fig. 5.2.2, we plot the relationship between the volume available for H$_2$, CH$_4$ and Ne adsorption and temperature. It can be seen from the figure that desorption occurs and increases with an increase in temperature. As shown in Fig. 5.2.2(a), at lower temperatures, the volume available for Ne adsorption decreases quicker than for H$_2$ and CH$_4$, whose volume available for adsorption starts to decrease at slightly higher temperatures, for a cone of radius 5.3289 Å. Similarly, for a cone of radius 7.1052 Å, desorption commences and increases as the temperature increases. This observation is in good agreement with Yu et al. [83], who employ thermal desorption and photoemission to predict gas desorption from carbon nanocones at higher temperatures. We further comment that as might be expected, an increase in the cone radius results in an increase in the volume available for adsorption.

5.4 Conclusions

With a view to modelling gas storage in carbon nanostructures, we investigate the encapsulation of three different gases inside single-walled carbon nanocones of varying vertex angle and size. We model these systems in terms of the parameters such as the nanocone base radius, the nanocone length, the initial distance between the carbon nanocone and the gas molecules and the nanocone apex angle. The interaction binding energies and molecular forces for the encapsulation of H$_2$, CH$_4$ and Ne
in carbon nanocones are derived from the 6 – 12 Lennard-Jones potential and the continuous approximation, resulting in surface integrals and giving rise to analytical expressions for the total binding energy between either H\textsubscript{2}, CH\textsubscript{4} or Ne interacting with a single-walled carbon nanocone. Our results suggest that a H\textsubscript{2} molecule or a Ne atom will experience a positive force resulting in the gas being accelerated inside the cone during encapsulation and then it will come to rest inside the cone. For larger cones, a CH\textsubscript{4} molecule will experience a similar motion during encapsulation while for smaller cones, there is a high energy barrier at the cone entrance resulting in a repulsive force which in the absence of any additional kinetic energy imparted to the molecule, does not allow the CH\textsubscript{4} molecule to enter the cone. Further, the volume available for H\textsubscript{2}, CH\textsubscript{4} and Ne adsorption also decreases with an increase in temperature, and the larger cones have more available free-cavity volume for adsorption. The analytical expressions resulting from this study are important to readily access the dominant features of the interaction, even though quantum effects are not included in this study. In particular, the question as to whether or not a gas molecule will be forced towards the interior of the cone may be addressed. Also, the effect of temperature on the volume available for encapsulation can be easily investigated. The results presented here are shown to be in excellent agreement with other theoretical results and molecular dynamics simulations, and moreover, they are obtained without the need to run computationally intensive simulations. Hence, they may be used to predict the effects of temperature and cone size on gas packing in nanocones. Our results might also serve to provide a proper understanding of gas storage inside carbon nanocones, and the approach adopted here can be extended to the storage of gases in other nanostructures.
Chapter 6

Encapsulation of methane in nanotube bundles

Nano-scale containers constructed from nanostructures have been proposed as feasible storage devices for critical gases such as CH$_4$ and in order to achieve this, an improved understanding of its interaction with other molecular structures is necessary. The idea of gas storage devices using nanotechnology is emerging as a new, effective and efficient means of gas conservation. Compared to other hydrocarbon fuels, burning CH$_4$ produces less carbon dioxide for each unit of heat that is released. Accordingly, CH$_4$ is referred to as a clean fuel which is abundant and naturally occurring. Rising levels of carbon emissions have increased research into CH$_4$ conservation, and the advent of nanotechnology offers the prospect of molecular containers as possible storage devices. CH$_4$ at room temperature is a colorless, odorless gas consisting of four hydrogen atoms surrounding a carbon atom. CH$_4$ is the simplest alkane and also the main constituent of natural gas. When in the form of natural gas, CH$_4$ may be used as a fuel for vehicles and other uses of CH$_4$ include generation of electricity and the production of acetic acids as well as acetic anhydrides. Due to the major use of CH$_4$ as a source of clean energy, its conservation is highly desirable. CH$_4$ storage in nanovessels has been proposed in many studies.
Whitener et al. [47], propose open-cage fullerenes as possible containers for CH$_4$ storage by modifying the size of an opening on a C$_{60}$ fullerene by successive cage scission for CH$_4$ insertion. Their study shows that certain temperatures and pressures are necessary for CH$_4$ insertion. Vakhrushev and Suyetin [11] show that bottle-like nanocapsules with a fill-and-lock mechanism initiated from the displacement arising from an electric field can be used as possible containers for CH$_4$ storage. Research on CH$_4$ storage in carbon nanotubes include [37], where a functional density theory model for the adsorption of CH$_4$ on single-walled carbon nanotubes is employed. They assume a homogenous cylindrical tube for an open-ended single-walled carbon nanotube and model an isolated single nanotube as opposed to aligned bundles of nanotubes which are more usually found. Several studies [96] [95] [14] [97] have examined gas storage in nanotube bundles. Cao et al. [95] investigate hydrogen storage in single-walled nanotube bundles, and their findings predict that the discharging gravimetric capacity of hydrogen in a bundle of single-walled carbon nanotubes at room temperature can reach 2.5wt%. Cruz et al. [14], investigate the thermodynamics of CH$_4$ adsorption in single-walled carbon nanotube bundles employing configurational-bias grand canonical Monte Carlo simulation and show that the confinement in the internal volume of the bundle is energetically more favorable than physisorption on the external surface.

After powering the micro-electronics revolution, silicon on the other hand, could also play an important new role in gas storage for ultra-clean fuels as silicon nanostuctures have recently been proposed as promising candidates for gas storage [71]. Other recent studies reveal that silicon nanostructures possess some special properties which could make them ideal containers for gas storage [94] [98]. Lan et al. [71] propose silicon nanotubes as candidates for hydrogen storage using a first principles calculation and grand canonical Monte Carlo simulations. They show that silicon nanotube arrays present significant improvements in the gravimetric adsorption capacity of hydrogen as compared to the isodiameter carbon nanotubes. However
there is presently no available literature on CH$_4$ storage in silicon nanotubes and silicon nanotube bundles, even though silicon nanostructures have been proposed as possible storage devices for clean-fuel producing gases.

In this chapter, we examine CH$_4$ storage and encapsulation in carbon and silicon nanotube bundles. Here we envisage a nanotube bundle comprising six-fold symmetry and having the central nanotube absent. We then calculate the interaction between a CH$_4$ molecule in the cavity left by the absent nanotube and the six surrounding nanotubes. We justify this configuration by the two considerations that nanotube bundles tend to aggregate in a triangular lattice to maximize the packing density and from such a configuration, the absence of a single tube, either by defect in packing or by design is the most applicable for study. In addition, the shown configuration follows accepted practice for representing nanotube bundles [99, 100, 101, 102, 103]. We develop mathematical models using classical applied mathematics to describe a CH$_4$ molecule interacting with carbon and silicon nanotube bundles. The Lennard-Jones potential for non-bonded atoms and the continuous approximation, which assumes that the interatomic interactions can be modeled by smearing the atoms uniformly across the surfaces, are used to determine the interaction energies, molecular forces and suction energies between a CH$_4$ molecule, with carbon and silicon nanotube bundles. We comment that in our model we account for physisorption of gas molecules to defect-free nanotubes. We do not model the possible effects of tube defects or chemisorption of gas molecules to nanotubes or defect sites. We also ignore possible storage in the smaller interstitial areas in bundles. The Lennard-Jones potential and the continuous approximation are described in the following section, while the analysis for the interaction of CH$_4$ with bundles and suction of CH$_4$ into bundles, are carried out in sections 6.2 and 6.3 respectively. Some discussion of the results in this chapter is provided in section 6.4 and a brief summary is given in the subsequent section.
6.1 Method

In this section, the Lennard-Jones potential and the continuous approximation employed to determine the interaction energies and forces between CH$_4$ and nanotube bundles are outlined. The model for the CH$_4$ molecule assumes that the four hydrogen atoms are smeared over a spherical surface of a certain radius $a$ centered on the carbon atom [65]. The Lennard-Jones potential for two non-bonded atoms is given by

$$\nu(\rho) = -A\rho^{-6} + B\rho^{-12},$$

where $A$ and $B$ are the attractive and repulsive constants respectively, and $\rho$ is the distance between two typical surface elements. Using the continuous approximation which assumes that the carbon atoms on the carbon nanotube can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density, the total potential energy is given by

$$E = \eta_1\eta_2 \int \int \nu(\rho)dS_1dS_2,$$

where $\eta_1$ and $\eta_2$ represents the mean atomic surface densities of the nanotube and the hydrogen sphere, respectively, and $\nu(\rho)$ is the Lennard-Jones potential function for two non-bonded atoms and $dS_1$ and $dS_2$ are typical surface elements on the surfaces $S_1$ and $S_2$ respectively. The values of the constants used in this study are given in Table 6.1.

Following [99] and [100], we assume a nanotube bundle to comprise an integral number $N$ of nanotubes aligned parallel to and equidistant from a common axis, and henceforth termed the bundle axis. In proposing this system, we have in mind a nanotube bundle with the central nanotube absent from the bundle. The perpendicular distance from the axis of the bundle to the axis of each constituent nanotube is referred to as the bundle radius $R$. We also assume that the constituent nanotubes
are each of equal length $2L$ and radius $b$ and that they are evenly distributed around the bundle axis so that the angle subtended at the bundle axis by two adjacent nanotubes is $2\pi/N$. With the bundle geometry as described above, the $ith$ tube in the nanotube bundle has a surface in rectangular Cartesian coordinates $(x, y, z)$ which is given by

$$
\left( R \cos \left( \frac{2\pi(i-1)}{N} \right) + b \cos \theta_i, R \sin \left( \frac{2\pi(i-1)}{N} \right) + b \sin \theta_i, z_i \right),
$$

where $i \in \{1, ..., N\}, 0 \leq \Theta_i \leq 2\pi$ and $-L \leq z_i \leq L$. Moreover, for some of the analysis presented, it is convenient to assume a semi-infinite tube, with $0 \leq z_i \leq \infty$, or a completely infinite tube, with $-\infty \leq z_i \leq \infty$. We comment that the geometry of the nanotube bundles employed is readily analyzed in [100] and [99], with the assumption that the inter-surface spacing for two parallel aligned cylinders is virtually a constant which is independent of the tube radii. Furthermore, since molecular interactions are short range, only the nearest neighbor interactions are considered when deriving the interaction energy for such bundles.
Table 6.1.1: Numerical values of constants used (* denotes from [1], ** denotes from [2] and *** denotes from [7])

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius of (10, 10) SiNT</td>
<td>(b = 5.289 \text{ Å} )</td>
</tr>
<tr>
<td>Radius of (8, 8) CNT</td>
<td>(b = 5.428 \text{ Å} )</td>
</tr>
<tr>
<td>Radius of hydrogen sphere</td>
<td>(a = 1.1 \text{ Å} )</td>
</tr>
<tr>
<td>Mass of (\text{CH}_4)</td>
<td>(M = 26.6391 \times 10^{-27} \text{ kg} )</td>
</tr>
<tr>
<td>*Attractive constant C-C</td>
<td>(A_{CC} = 17.4 \text{ eV } \text{Å}^6 )</td>
</tr>
<tr>
<td>*Repulsive constant C-C</td>
<td>(B_{CC} = 29000 \text{ eV } \text{Å}^{12} )</td>
</tr>
<tr>
<td>**Attractive constant C-H</td>
<td>(A_{CH} = 14.94 \text{ eV } \text{Å}^6 )</td>
</tr>
<tr>
<td>**Repulsive constant C-H</td>
<td>(B_{CH} = 14544 \text{ eV } \text{Å}^{12} )</td>
</tr>
<tr>
<td>***Attractive constant C-Si</td>
<td>(A_{CSi} = 95.53 \text{ eV } \text{Å}^6 )</td>
</tr>
<tr>
<td>***Repulsive constant C-Si</td>
<td>(B_{CSi} = 325940.81 \text{ eV } \text{Å}^{12} )</td>
</tr>
<tr>
<td>***Attractive constant H-Si</td>
<td>(A_{HSi} = 73.28 \text{ eV } \text{Å}^6 )</td>
</tr>
<tr>
<td>***Repulsive Constant H-Si</td>
<td>(B_{HSi} = 149177 \text{ eV } \text{Å}^{12} )</td>
</tr>
<tr>
<td>Mean surface density of hydrogen sphere</td>
<td>(\eta_h = 0.263 \text{ Å}^{-2} )</td>
</tr>
<tr>
<td>Mean surface density of CNT</td>
<td>(\eta_c = 0.3812 \text{ Å}^{-2} )</td>
</tr>
<tr>
<td>Mean surface density for SiNT</td>
<td>(\eta_s = 0.3260 \text{ Å}^{-2} )</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>(k = 8.6173 \times 10^{-5} \text{ eV } \text{K}^{-1} )</td>
</tr>
</tbody>
</table>

### 6.2 Interaction of \(\text{CH}_4\) with bundles

In this section, we examine the interaction energy between a \(\text{CH}_4\) molecule and a bundle of nanotubes. The total interaction energy for a \(\text{CH}_4\) molecule located at the center of a nanotube bundle, assumed to be infinite in length, and as shown in Fig. 6.1.1, is given by

\[
E_{\text{tot}}^{\text{int}} = -NE_{\text{mt}}(R),
\]

where \(R\) the bundle radius is the distance from the center of the \(\text{CH}_4\) molecule to the axis of the nanotubes in the bundle and \(E_{\text{mt}}\) is the interaction energy between the \(\text{CH}_4\) molecule and a single nanotube which is obtained by summing the interaction energy between the carbon atom at the center of the hydrogen sphere and a single nanotube, with the interaction energy between the hydrogen sphere and a single nanotube. Following similar calculations to [53], the interaction energy between the carbon atom at the center of the hydrogen sphere and a single nanotube may be
CHAPTER 6. ENCAP. OF CH$_4$ IN NANOTUBE BUNDLES

given by

$$E_{ct} = 2\pi^2 \eta_1 b \left(- \frac{3A}{8R^4} + \frac{63B}{256R^{10}}\right),$$

where $\eta_1$ is the mean atomic density of the nanotube. Also the interaction between the hydrogen sphere and a single nanotube is given by

$$E_{ht} = 4\pi^2 a^2 b \eta_1 \eta_2 \left[\frac{-A}{8} (3J_2 + 5a^2 J_3) + \frac{B}{5} \left(\frac{315}{256} J_5 + \frac{1155}{64} a^2 J_6 + \frac{9009}{128} a^4 J_7\right)ight. + \left. \frac{6435}{64} a^6 J_8 + \frac{12155}{256} a^8 J_9 \right],$$

where $a$ and $\eta_2$ are the radius and atomic surface density of the hydrogen sphere, respectively and $J_n$ is defined in terms of an ordinary hypergeometric function given by

$$J_n = \frac{2\pi}{[(b - R)^2 - a^2]^{n+1/2}} F\left(n + \frac{1}{2}, \frac{1}{2}; 1; \frac{-4bR}{(b - R)^2 - a^2}\right).$$

The total energy for CH$_4$-CNT bundle and CH$_4$-SiNT bundle is therefore respectively given by

$$E_{tot}^{int} = -N[E_{ct}(\eta_1 = \eta_c, A = A_{CC}, B = B_{CC}) + E_{ht}(\eta_1 = \eta_c, \eta_2 = \eta_h, A = A_{CH}, B = B_{CH})],$$

and

$$E_{tot}^{int} = -N[E_{ct}(\eta_1 = \eta_s, A = A_{CSi}, B = B_{CSi}) + E_{ht}(\eta_1 = \eta_s, \eta_2 = \eta_h, A = A_{HSi}, B = B_{HSi})],$$

where the mean atomic densities $\eta_c, \eta_s, \eta_h$, the attractive and repulsive constants $A$ and $B$, are as given in Table 6.1.1 (see caption for information source).
6.3 Suction of CH\textsubscript{4} into bundles

In this section, we discuss the suction of a CH\textsubscript{4} molecule into a nanotube bundle using the molecular interaction force between a CH\textsubscript{4} molecule and a nanotube bundle. The total molecular interaction force for a CH\textsubscript{4} molecule interacting with a nanotube bundle, as shown in Fig. 6.1.1, can similarly be given by

\[ F_{total} = -NF_{mt}, \]  

(6.3.1)

where \( F_{mt} \) is the molecular force for a CH\textsubscript{4} molecule interacting with a single nanotube which we obtain by summing the interaction force between the carbon atom at the center of the hydrogen sphere and a single nanotube, with the interaction force between the hydrogen sphere and a single nanotube. As derived in [55], the interaction force between the carbon atom at the center of the hydrogen sphere and
a single nanotube is given by

$$F_{ct} = 2\pi b\eta_1 \left[ \frac{A}{(R^2 + Z^2)^3} - \frac{B}{(R^2 + Z^2)^6} \right],$$

where $Z$ is the position of the CH$_4$ molecule along the bundle axis. In addition, the interaction force between the hydrogen sphere and a single nanotube is derived in [99], and is given by

$$F_{ht} = 4\pi a^2 b\eta_1\eta_2 \left[ \frac{A}{2} (2I_3 + 4a^2I_4) - \frac{B}{5} (5I_6 + 80a^2I_7 + 336a^4I_8 + 512a^6I_9 + 256a^8I_{10}) \right],$$

where the integrals $I_n$ can be given in terms of the hypergeometric function by

$$I_n = 2\pi \gamma^{-1/2} (\gamma + 4bR)^{1/2-n} F \left( 1, \frac{1}{2}; 1; \frac{-4bR}{\gamma} \right),$$

where $\gamma = (R - b)^2 - a^2 + Z^2$ and $Z$ denotes the axial position of the CH$_4$ molecule with respect to the nanotube bundle as noted earlier. Employing equation (6.3.1) and the same approach as for equation (6.2.1), we obtain the molecular interaction force for the CH$_4$-CNT bundle and the CH$_4$-SiNT bundle, respectively. Moreover, the total suction energy $E_{suc}^{tot}$ is the total work done by the molecular interactions, and can be readily calculated as the integral of $F_{total}$ from $-\infty$ to $\infty$. This is a good approximation, when the molecule starts more than 10 Å outside of the bundle and moves to a point more than 10 Å within the bundle.

Following similar calculations by [8], the volume for CH$_4$ adsorption in the open cavity of the bundle is given by

$$V_{ad} = \int_{R_0}^{R_1} 4\pi R^2 \exp[-|E_{min}|/kT]dR,$$
<table>
<thead>
<tr>
<th>Interaction Type</th>
<th>$R_{\text{min}}$ (Å)</th>
<th>$E_{\text{tot}}^{\text{int}}$ (eV)</th>
<th>$R_{\text{max}}$ (Å)</th>
<th>$E_{\text{tot}}^{\text{suc}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-CNT bundle</td>
<td>9.2578</td>
<td>0.6507</td>
<td>9.2533</td>
<td>0.6741</td>
</tr>
<tr>
<td>CH$_4$-SiNT bundle</td>
<td>9.4858</td>
<td>1.7523</td>
<td>9.4800</td>
<td>2.6343</td>
</tr>
</tbody>
</table>

Table 6.3.1: Optimal bundle radii and total energies for CH$_4$-CNT and CH$_4$-SiNT bundles

Figure 6.3.1: Total molecular force for CH$_4$ molecule entering sixfold symmetric carbon and silicon nanotube bundles.

where $E_{\text{min}}$ is the minimum energy as derived from Fig. 6.4.2, $k$ is the Boltzman constant and $T$ is the temperature. We note that the upper and lower limits of the above integral correspond to the maximum and minimum values respectively, of the bundle radii for which the energy profiles in Fig. 6.4.2 remains negative.
CHAPTER 6. ENCAP. OF CH$_4$ IN NANOTUBE BUNDLES

6.4 Results and discussions

In this section, we present the results showing the interaction energies, suction energies, and molecular forces, for a CH$_4$ molecule entering carbon and silicon nanotube bundles. In Fig. 6.2.1, we plot the relation between the total interaction energy $E_{tot}^{int}$ and the bundle radius $R$ for each interaction type, assuming that the nanotube bundles are of sixfold symmetry and are formed from (8,8) and (10,10) carbon and silicon nanotubes of equal length $2L$, respectively. As shown in Fig. 6.2.1, there is an optimal bundle radius $R_{min}$ that minimizes the total interaction energy $E_{tot}^{int}$, and the values for these radii for the two types of bundles considered are given in Table 6.3.1. We further comment that the interaction energy and the optimal bundle radius $R_{min}$ for CH$_4$-SiNT bundle is higher than that for the CH$_4$-CNT bundle. By substituting the values of $R_{min}$ for each interaction into equation (6.3.1), we obtain the force profiles for (8,8) and (10,10) carbon and silicon bundles as shown in Fig. 6.3.1. We comment that the CH$_4$ molecule is easily sucked into the bundle given the positive force in Fig. 6.3.1. We also note that since the force is an impulse acting
on the extremity of the bundle, and as predicted, the strength of the impulsive force is higher for the CH$_4$-SiNT bundle. In Fig. 6.4.1, we plot the relation between the total suction energy $E_{suc}^{tot}$ and the bundle radius. We also determine and adopt the optimal bundle radius $R_{max}$ as given in Table 6.3.1, which give rise to the maximum suction energy for encapsulation into the bundle. We find that CH$_4$-SiNT bundle has a higher suction energy than the CH$_4$-CNT bundle as the SiNT bundle is more energetically favorable for encapsulation of CH$_4$ than the CNT bundle.

In Fig. 6.4.2, we employ the optimal bundle radius $R_{max}$, which gives rise to the maximum suction energies to plot the interaction between a CH$_4$ molecule offset from the common bundle axis with carbon and silicon nanotube bundles. As shown in the figure, the preferred location of the CH$_4$ molecule inside the nanotube bundles is 5.416 Å offset from the CNT bundle axis and 5.251 Å offset from the SiNT bundle.
axis. These results are equivalent to the distance between the center of the CH\textsubscript{4} molecule and the bundle wall formed around the bundle radius $R$.

Figure 6.4.3: Relationship between volume for CH\textsubscript{4} adsorption and temperature in open cavity of sixfold symmetric carbon and silicon nanotube bundles

As shown in Fig. 6.4.3, at higher temperatures, SiNT bundles possess more volume for adsorption than their CNT counterparts. The volume for CH\textsubscript{4} adsorption in the bundles decreases as the temperature increases. This is as expected since an increase in temperature would result in the CH\textsubscript{4} molecules having a higher mean kinetic energy and therefore less likely to adsorb onto the nanotube walls. This observation is consistent with Thornton et al [51], where interactions between a gas molecule and a pore opening are used to predict various gas diffusion regimes.

### 6.5 Conclusion

With a view to the development of CH\textsubscript{4} storage in molecular containers, we examine the interaction of a CH\textsubscript{4} molecule with two different nanotube bundles, namely, (8,8) carbon nanotube bundle and (10,10) silicon nanotube bundle. Our results give the optimal bundle radii for maximum interaction and suction energies for CH\textsubscript{4} encapsulation in carbon and silicon nanotube bundles. The silicon nanotube
bundle is observed to have a higher optimal interaction and suction energy than that of the carbon nanotube bundle, for example in the CH$_4$-CNT bundle, the optimal suction energy is 0.6741 eV while in the CH$_4$-SiNT bundle, the optimal suction energy is 2.6343 eV. This is due to the fact that the silicon nanotube bundle has a greater optimal interaction energy than the carbon nanotube bundle. In addition, CH$_4$ stays adsorbed in the SiNT bundle for higher temperatures in the range 200 - 400 K. Overall, our results confirm those of [71], who propose silicon nanotubes as promising candidates for gas storage. Our emphasis here is the use of elementary mechanics and classical applied mathematics to formulate novel behavior in a scientific context previously only elucidated through experiments and molecular dynamics simulations. Finally, the results presented in this chapter might serve to properly understand gas storage inside nanotube bundles and the approach adopted here can be extended for the storage of other gases in similar nanostructures.
Chapter 7

Summary

In this thesis, we present applied mathematical models for a range of nanostructures which might serve as molecular storage devices for methane as well as other gases. Given the global need for alternative energy sources which are both sustainable and friendly to the environment, more research into better ways of storing natural gas is desirable. To avoid the existing storage bottlenecks that are hindering the widespread commercial use of methane as a clean source of energy, nanotechnology is emerging as a new area in energy research. In order to fulfil the need for widespread green energy sources, we might exploit the exceptional superior properties of nanomaterials in comparison to their micro and macro counterparts. The main objective of the applied mathematical approach adopted here is to characterise the dominant features for gas storage mechanics in molecular structures in the form of a mathematical model. Such mathematical modelling generates important insights into complex processes, and reveals optimal parameters or situations that might be otherwise almost impossible to discern either through trial-and-error experimentation or time-consuming computer simulations. The geometries of some conventional nanostructures are exploited in conjunction with the continuous approximation, which assumes that individual atoms on a molecular surface can be replaced by smearing the atoms over the entire surface and using a uniform atomic surface density to formulate analytical expressions for the interaction of methane
We investigate the interaction energy between a methane molecule and a carbon nanotube using two different models for the methane molecule, the first is a discrete model and the second is a continuous one. In the first model, we consider the total interaction as the sum of the individual interactions between each atom of the molecule and the entire nanotube, for which we employ the continuous approximation. We first determine the interaction energy by assuming that the carbon atom and one of the hydrogen atoms lie on the axis of the tube with the other three hydrogen atoms offset from the axis. Symmetry is assumed with regard to the arrangement of the three hydrogen atoms surrounding the carbon atom on the axis. We then rotate the atomic position into 100 discrete orientations and determine the average interaction energy from all orientations. In the second model, we approximate the methane molecule by assuming that the four hydrogen atoms are smeared over a spherical surface of a certain radius with the carbon atom located at the center of the sphere. The total interaction energy between the methane molecule and the carbon nanotube for this model is calculated as the sum of the individual interaction energies between both the carbon atom and the spherical surface and the carbon nanotube. These models are analyzed to determine the dimensions of the particular nanotubes which will readily suck-up methane molecules. The results determine the minimum and maximum interaction energies required for methane encapsulation in different tube sizes, and validate the second model for the methane molecule as a simple model which will later be exploited for the subsequent chapters, for example in Chapter 3, where we investigate methane packing in single-walled carbon nanotubes using the continuous model for methane developed in Chapter 2. We employ classical applied mathematical modelling using the basic principles of mechanics to exploit the Lennard-Jones potential function and the continuous approximation.

We consider both zigzag and spiral configurations formed by packing methane molecules into \((9, 5)\), \((8, 8)\) and \((10, 10)\) carbon nanotubes, and derive analytical expressions for the interaction potential energy of these configurations. The results
indicate that for the zigzag configuration for a (9,5) tube, the potential energy of the system is minimized when the methane molecules form a simple linear chain along the tube axis, but the methane molecules adopting genuine zigzag patterns as the tube size increases such as for the (8,8) and (10,10) tubes. For the spiral configuration, the potential energy of the system is minimized when the angular spacing is approximately equal to $\pi$ for the (9,5) and (8,8) tubes, and $\pi/2$ for the (10,10) tube. Overall, the results are in good agreement with molecular dynamics simulations in the literature and show that the most energetically efficient packing configuration of the three tubes studied, occurs for a (10,10) tube with a zigzag packing, while a (10,10) tube with a spiral packing configuration has the largest free-cavity volume for methane adsorption at higher temperatures.

The adsorption of methane on nanostructures other than a single-walled carbon nanotube is examined in Chapter 4, where methane adsorption is investigated on both graphite and in the region between two aligned single-walled carbon nanotubes, which we refer to as the groove site. We exploit the Lennard-Jones potential function and the continuous approximation to determine surface binding energies between a single methane molecule and graphite and between a single methane and two aligned single-walled carbon nanotubes. The modelling indicates that for a methane molecule interacting with graphite, the binding energy of the system is minimized when the centre of the methane molecule is 3.83 Å above the graphitic surface, while the binding energy of the methane-groove site system is minimized when the methane carbon is 5.17 Å away from the common axis shared by the two aligned single-walled carbon nanotubes. The results confirm the current view that for larger groove sites, methane molecules in grooves are likely to move towards the outer surfaces of one of the single-walled carbon nanotubes. Our results are computationally efficient and are in good agreement with experiments and molecular dynamics simulations, and show that methane adsorption on graphite and groove surfaces is more favourable at lower temperatures and higher pressures. Nanotube bundles tend to aggregate in a triangular lattice to maximize the packing density,
and such a configuration with the absence of a single tube, either by defect in packing or by design is examined in Chapter 6 as a gas storage container.

In Chapter 6, we investigate methane storage, and in particular the binding and suction energies of methane in (8,8) carbon and (10,10) silicon nanotube bundles. Employing the Lennard-Jones potential together with the continuous approximation, we determine the interaction energy, molecular force, and suction energy for a methane molecule in nanotube bundles. The results indicate that silicon nanostructures might be superior candidates for methane storage and at high temperatures, particularly in the range 200 - 400 K. Other molecular structures such as carbon nanocones have recently been gaining interest as molecular gas storage devices and in Chapter 5, we investigate hydrogen, methane and neon encapsulation and adsorption in open carbon nanocones. We exploit the 6 − 12 Lennard-Jones potential function and the continuous approximation to model the surface binding energies and the molecular forces between these gases and carbon nanocones of varying vertex angle and length.

The findings predict that for a hydrogen or methane molecule, or neon atom, interacting with a carbon nanocone, the binding energies of the respective systems are minimized when the gas is encapsulated inside the cone. However, we find that for the shorter carbon nanocones, there is a higher energy barrier preventing methane encapsulation in the nanocone. The modelling indicates that for the particular apex angle of 112.9°, the optimal minimum energy storage for the gases occurs in a nanocone of radius 7.1052 Å, and of length 4.7126 Å. The results agree with recent results suggesting that gas adsorption in carbon nanocones is more favourable at lower temperatures. Overall, it is shown that carbon nanocones might be good candidates for gas storage. However, the major advantage of the approach adopted here is the derivation of explicit analytical formulae from which numerical results for various physical scenarios may be readily obtained.
Appendix A

A.1 Evaluation of integral $J_n$ defined by (2.2.3)

In this appendix, a brief evaluation of the integral (2.2.3) is presented. We consider the integral (2.2.3) where $\rho$ is defined by (2.2.1). On substituting the value of $\rho$ into $J_n$ and evaluating the trivial $\theta$ integration, we derive

$$J_n = 2\pi \int_0^\infty \frac{1}{[b^2 + (z - Z)^2]^n} dz,$$

since the integrand is independent of $\theta$. On letting $z_* = z - Z$, we obtain

$$J_n = 2\pi \int_{-Z}^\infty \frac{1}{(b^2 + z_*^2)^n} dz_*,$$

and with the substitution $z_* = b\tan\psi$, we derive

$$J_n = 2\pi b^{1-2n} \int_{\psi_0}^{\pi/2} \sec^{2-2n} \psi d\psi = 2\pi b^{1-2n} \int_{\psi_0}^{\pi/2} \cos^{2n-2} \psi d\psi,$$

where $\psi_0 = \tan^{-1}(-Z/b)$. From [56] (f 2.512(2)), the above integral is given by

$$\int_{\psi_0}^{\pi/2} \cos^{2n-2} \psi d\psi = \left[ \frac{\sin \psi}{2n - 2} \left( \cos^{(2n-3)} \psi + \sum_{k=1}^{n-2} \left( \frac{(2n - 3)(2n - 5)...(2n - 2k - 1) \cos^{2n-2k-3} \psi}{2^k(n - 2)(n - 3)...(n - 1 - k)} \right) + \frac{(2n - 3)\psi}{2^{n-1}(n - 1)!} \right) \right]_{\psi_0}^{\pi/2}.$$
where \( \sin \psi_0 = -Z/(b^2 + Z^2)^{-1/2} \) and thus \( \cos \psi_0 = b/(b^2 + Z^2)^{-1/2} \). Upon substituting the values of \( n = 3 \) and \( 6 \), the above expression can be expanded and evaluated to yield

\[
J_3 = \frac{\pi}{b^5} \left[ \frac{3\pi}{8} + \frac{3}{4} \tan^{-1} \left( \frac{Z}{b} \right) + \frac{3Zb}{4(b^2 + Z^2)} + \frac{Zb^3}{2(b^2 + Z^2)^2} \right],
\]

and

\[
J_6 = \frac{\pi}{b^{11}} \left[ \frac{9\pi}{3840} + \frac{3}{640} \tan^{-1} \left( \frac{Z}{b} \right) + \frac{Zb^9}{5(b^2 + Z^2)^5} + \frac{9Zb^7}{40(b^2 + Z^2)^4} \right.
\]
\[
+ \frac{7Zb^5}{60(b^2 + Z^2)^3} + \frac{Zb^3}{16(b^2 + Z^2)^2} + \frac{3Zb}{80(b^2 + Z^2)} \right].
\]

### A.2 Derivation of equation (2.2.8)

In this section we evaluate the double integrals appearing in (2.2.7). On evaluating the \( \theta \) integral first, by letting \( \varphi = \theta/2 \), the following general integral is obtained

\[
B_n = 2 \int_0^\pi \frac{d\varphi}{\left[ \tau_1^2 + (\tau_2^2 - \tau_1^2) \cos^2 \varphi \right]^n},
\]

where \( \tau_1^2 = (b + \epsilon \sin \phi)^2 + (z - \epsilon \cos \phi)^2 \), \( \tau_2^2 = (b - \epsilon \sin \phi)^2 + (z - \epsilon \cos \phi)^2 \), \( \tau_2^2 - \tau_1^2 = -4\epsilon \sin \phi \) and \( n \) takes on the values 3 and 6. Considering the symmetry of the integral and letting \( t = \cos^2 \varphi \), we have

\[
B_n = 4 \int_0^{\pi/2} \frac{d\varphi}{\left[ \tau_1^2 + (\tau_2^2 - \tau_1^2) \cos^2 \varphi \right]^n} = \frac{2}{\tau_1^{2n}} \int_0^1 \frac{t^{-1/2}(1-t)^{-1/2}dt}{\left[ 1 - (1 - (\tau_2/\tau_1)^2) t \right]^n}.
\]
From [56] (15, p. 995) the following relation is employed

$$
\int_0^1 t^{\beta-1}(1-t)^{\gamma-\beta-1}(1-tz)^{-\alpha} dt = B(\beta, \gamma - \beta)F(\alpha, \beta; \gamma; z),
$$

where $B(x, y)$ is the Beta function and $F(\alpha, \beta; \gamma; z)$ is the usual hypergeometric function so that the above integral is then given by

$$
B_n = \frac{2\pi}{\tau_1^{2n}} F\left(n, \frac{1}{2}; 1; 1 - \left(\frac{\tau_2}{\tau_1}\right)^2\right),
$$

where we have used the identity $B(1/2, 1/2) = \pi$. Following [104] (19, p. 64 and 69), the hypergeometric function given above is found to be degenerate, and using the Kummer relationship

$$
F(a, b; c; x) = (1 - x)^{c-a-b} F(c-a, c-b; c; x),
$$

the two degenerate functions are obtained

$$
F(3, 1/2; 1; x) = \left(\frac{\tau_1}{\tau_2}\right)^5 \left(1 - x + \frac{3x^2}{8}\right),
$$

and

$$
F(6, 1/2; 1; x) = \left(\frac{\tau_1}{\tau_2}\right)^{11} \left(1 - \frac{5x}{2} + \frac{15x^2}{4} - \frac{25x^3}{8} + \frac{175x^4}{128} - \frac{63x^5}{256}\right),
$$

for the values $n = 3$ and $n = 6$ respectively and where $x = 1 - (\tau_2/\tau_1)^2$. Upon expansion and substitution into equation (2.2.7), we find that

$$
E = 2\pi \eta b \left[ -A \left(\frac{K_{3.3}}{4} + \frac{3(K_{1.5} + K_{5.1})}{8}\right) \\
+ B \left(\frac{63(K_{1.11} + K_{11.1})}{256} + \frac{35(K_{3.9} + K_{9.3})}{256} + \frac{30(K_{5.7} + K_{7.5})}{256}\right) \right],
$$
where the integrals $K_{i,j}$ are defined by

$$K_{i,j} = \int_0^\infty \frac{dz}{\tau_i^r \tau_j^s}.$$ 

### A.3 Evaluation of $K_{i,j}$ integral defined by (2.2.8)

In this section, the integrals given by $K_{i,j}$ are evaluated. In full, the integral is given by

$$K_{i,j} = \int_0^\infty \frac{dz}{((b + \epsilon \sin \phi)^2 + (z - \epsilon \cos \phi)^2)^r((b - \epsilon \sin \phi)^2 + (z - \epsilon \cos \phi)^2)^s},$$

where $i = 2r$ and $j = 2s$. Making the substitution $(z - \epsilon \cos \phi) = (b + \epsilon \sin \phi) \tan \alpha$, we find

$$K_{2r, 2s} = \int_{\alpha_1}^{\pi/2} \frac{(b + \epsilon \sin \phi) \sec^2 \alpha d\alpha}{((b + \epsilon \sin \phi)^2 + (b + \epsilon \sin \phi)^2 \tan^2 \alpha)^r((b + \epsilon \sin \phi)^2 + (b + \epsilon \sin \phi)^2 \tan^2 \alpha)^s},$$

where $\alpha_1 = \tan^{-1}(-\epsilon \cos \phi/b + (\epsilon \sin \phi))$ and $p = (b - \epsilon \sin \phi)/(b + \epsilon \sin \phi)$. Upon making the further substitutions $w = \cos^2 \alpha$ and $w = w_1 u$,

$$K_{2r, 2s} = \frac{(b + \epsilon \sin \phi)^{1-2r-2s}}{2} \int_0^{c_1} \frac{c^{r-1+s} dc}{c^{1/2}(1-c)^{1/2}[1 - (1-p^2)c]^s},$$

$$= \frac{(b^2 + 2b\epsilon \sin \phi + \epsilon^2)^{1/2-r-s}}{2} \int_0^1 u^{r+s-3/2}(1 - c_1 u)^{-1/2}(1 - (1-p^2)c_1 u)^{-s} du,$$
where \( w_1 = (b + \epsilon \sin \phi)^2 / (b^2 + 2b\epsilon \sin \phi + \epsilon^2) \). On using the relation from [105] (16, p. 77), namely

\[
\int_0^1 u^{\alpha-1}(1-u)^{\gamma-\alpha-1}(1-ux)^{-\beta_1}(1-uy)^{-\beta_2} du = B(\alpha, \gamma - \alpha)F_1(\alpha; \beta_1, \beta_2; \gamma; x, y),
\]

so that \( K_{2r,2s} \) can be written as an Appell hypergeometric function of two variables of the first kind, thus

\[
K_{i,j} = \frac{(b^2 + 2b\epsilon \sin \phi + \epsilon^2)^{-I}}{i + j - 1}F_1(I; \frac{j}{2}, \frac{1}{2}; J; (1-p^2)w_1, w_1),
\]

where \( I = (i + j - 1)/2 \) and \( J = (i + j + 1)/2 \).

**A.4 Evaluation of offset angle \( \phi \) appearing in 2.2.8**

![Figure 1.4.1: (a) Representation of molecule on unit cube with carbon at the center of the cube; (b) Representation of offset angle on unit cube.](image)

In this appendix, we evaluate the offset angle appearing in equation 2.2.8. The schematic representation of the assumed arrangement of the atoms in the CH\(_4\) molecule and the offset angle \( \phi \) may be given by the unit cube shown in Fig. 1.4.1(a). The offset angle is obtained as shown in Fig. 1.4.1(b). Using the cosine rule, the angle \( \psi \) is obtained as \( \psi = \cos^{-1}(-1/3) \simeq 109.47^\circ \), or in radians \( \simeq 11\pi/18 \), so
that the offset angle is given by $\phi = \pi - \psi = 70.53^\circ$, or in radians ($\simeq 7\pi/18$).
Appendix B

B.1 Evaluation of equation (3.2.5):

We have the integral

\[ H_n = b \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \frac{1}{(b - \lambda)^2 + 4b\lambda \sin^2(\theta/2) + [z - Z(2i)]^2} dz \, d\theta, \]

where \( n = 3 \) or 6. On letting \( \tau^2 = (b - \lambda)^2 + 4b\lambda \sin^2(\theta/2) \), and then we make the substitution \( z = \tau \tan \psi \), we obtain the integral

\[ H_n = b \int_{-\pi/2}^{\pi/2} \cos^{2n-2} \psi \, d\psi \int_{-\pi}^{\pi} \frac{1}{\tau^{2n-1}} d\theta, \]

\[ H_n = bB(n - 1/2, 1/2) \int_{-\pi}^{\pi} \frac{1}{\tau^{2n-1}} d\theta, \]

where \( B(x, y) \) is the beta function. Now upon making the further substitution \( t = \sin^2(\theta/2) \), we obtain

\[ H_n = \frac{2b}{(b - \lambda)^{2n-1}} B(n - 1/2, 1/2) \int_0^1 t^{-1/2} (1 - t)^{-1/2} (1 - \omega t)^{1/2-n} dt, \]

where \( \omega = -4b\lambda/(b - \lambda)^2 \). The above integral is now in the Euler form and may be given by

\[ H_n = \frac{2b\pi}{(b - \lambda)^{2n-1}} B(n - 1/2, 1/2) F(n - 1/2, 1/2; 1, \omega). \]
Using the quadratic transformation [104] (31, p. 119) given by
\[
F(a, b; 2b; z) = [1/2 + 1/2(1-z)^{1/2}]^{-2a} F \left[ a, a - b + 1/2; b + 1/2; \left( \frac{1 - (1 - z)^{1/2}}{1 + (1 - z)^{1/2}} \right)^2 \right],
\]
we obtain
\[
H_n = \frac{2b\pi}{(b - \lambda)^{2n-1}} B(n - 1/2, 1/2) \left( \frac{b - \lambda}{b} \right)^{2n-1} F(n - 1/2, n - 1/2; 1; \lambda^2/b^2),
\]

where \( F(a, b; c; z) \) is the usual hypergeometric function. On expansion and writing the hypergeometric function as a series expansion, we obtain
\[
H^1_k = \frac{2\pi}{b^{2n-2}} B(n - 1/2, 1/2) F(n - 1/2, n - 1/2; 1; \lambda^2/b^2),
\]

where \( F(a, b; c; z) \) is the usual hypergeometric function. On replacing the Pochhammer function with gamma functions, we obtain
\[
H_n = \frac{2\pi}{b^{2n-2}} \frac{\Gamma(1/2) \Gamma(n + m - 1/2)}{\Gamma(n) \Gamma(n - 1/2)} \sum_{m=0}^{\infty} \left( \frac{(n - 1/2)_{m}\lambda^m}{m!b^m} \right)^2.
\]

Using the duplication formula, we may show that
\[
\Gamma(n - 1/2) = \frac{\pi^{1/2} \Gamma(2n - 1)}{2^{2n-2} \Gamma(n)},
\]
which can be substituted back to obtain
\[
H_n = \frac{2\pi^2}{(2b)^{2n-2} \Gamma(2n - 1)} \sum_{m=0}^{\infty} \left( \frac{\Gamma(2n + 2m - 1)\lambda^m}{\Gamma(n + m)m!(4b)^m} \right)^2,
\]

where \( n = 3 \) or 6. On substituting the values of \( n \) and replacing the gamma functions
with the factorial operator, and then substituting into (3.2.2), we obtain (3.2.5).
B.2 Evaluation of equation (3.2.6)

Following the work of [55], it can be shown that by replacing the fractions over common denominators, expanding and reducing to fractions of powers of \((\rho^2 - a^2)\), the interaction energy between a carbon atom and the hydrogen-sphere given by

\[
G(\rho) = \frac{\pi a \eta_2}{\rho} \left[ \frac{-A}{2} \left( \frac{1}{(\rho - a)^4} - \frac{1}{(\rho + a)^4} \right) + \frac{B}{5} \left( \frac{1}{(\rho - a)^{10}} - \frac{1}{(\rho + a)^{10}} \right) \right],
\]

can be re-written as

\[
G(\rho) = 4\pi a^2 \eta_2 \left[ -A \left( \frac{1}{(\rho^2 - a^2)^3} + \frac{2a^2}{(\rho^2 - a^2)^4} \right) + \frac{B}{5} \left( \frac{5}{(\rho^2 - a^2)^6} + \frac{80a^2}{(\rho^2 - a^2)^7} + \frac{336a^4}{(\rho^2 - a^2)^8} + \frac{512a^6}{(\rho^2 - a^2)^9} + \frac{256a^8}{(\rho^2 - a^2)^{10}} \right) \right],
\]

where \(a\) is the radius of the hydrogen-sphere and \(\rho\) is the distance between the center of the hydrogen-sphere and a typical surface element on the nanotube and is given by

\[
\rho^2 = (b - \lambda)^2 + 4b\lambda \sin^2(\theta/2) + [z - Z(2i)]^2.
\]

Following precisely the same steps as in B.1, we may evaluate the general integral derived from performing a surface integral on the interaction energy between the carbon atom and the hydrogen-sphere over a nanotube given by

\[
J_n = b \int_{-\pi}^{\pi} \int_{-\infty}^{\infty} \frac{1}{[(b - \lambda)^2 - a^2 + 4b\lambda \sin^2(\theta/2) + [z - Z(2i)]^2]^n} d\theta dz,
\]

where in this case \(n \in \{3, 4, 6, 7, 8, 9, 10\}\). As in B.1 on evaluating the above integral, we obtain

\[
J_n = \frac{2b\pi B(n - 1/2, 1/2)}{[(b - \lambda)^2 - a^2]^{n-1/2}} F \left( n - \frac{1}{2}; \frac{1}{2}; -\frac{4\lambda b}{(b - \lambda)^2 - a^2} \right).
\]
It may be shown that

$$B(n - 1/2, 1/2) = \frac{\pi (2n - 3)!!}{(2n - 2)!!},$$

where !! denotes the double factorial operator such that

$$(2n - 1)!! = (2n)!/(2^n n!).$$

Upon simplifying, collecting terms, substituting the values of $n$, and then substituting into equation (3.2.4), we obtain (3.2.6).
Appendix C

C.1 Evaluation of $I_{cg}$ given by (4.2.2)

On making the substitution $p = (y^2 + \delta^2)^{1/2} \tan \psi$ in (4.2.2), we obtain

$$I_{cg} = B(n - 1/2, 1/2) \int_{-\infty}^{\infty} (q^2 + \delta^2)^{1/2-n} dq,$$

and a further substitution $q = \delta \tan \phi$, gives

$$I_{cg} = \delta^{2-2n} B(n - 1/2, 1/2) B(n - 1, 1/2), = \frac{\pi}{(n - 1)\delta^{2n-2}}.$$

C.2 Evaluation of $I_{hg}$ given by (4.2.4)

Since there is no dependence on $\theta$ in the integrand (4.2.4), we can perform this integration trivially to obtain

$$I_{hg} = \frac{2\pi^2 a^2}{n - 1} \int_0^{\pi} \frac{\sin \phi}{(\delta + a \cos \phi)^{2n-2}} d\phi,$$

and on making the substitution $t = \delta + a \cos \theta$, we obtain

$$I_{hg} = \frac{2\pi^2 a}{n - 1} \int_{\delta-a}^{\delta+a} \frac{dt}{t^{2n-2}} = \frac{2\pi^2 a}{(n - 1)(2n - 3)} \left[ \frac{1}{t^{2n-3}} \right]_{\delta+a}^{\delta-a},$$
which gives

\[ I_{hg} = \frac{2\pi^2 a}{(n - 1)(2n - 3)} \left[ \frac{1}{(\delta - a)^{2n-3}} - \frac{1}{(\delta + a)^{2n-3}} \right]. \]


