Fundamental Study of Adsorption and Desorption Process in Porous Materials with Functional Groups

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Abstract

Adsorption is used in industries for gas separation and purification because of its less energy intensive than other traditional separation processes, such as distillation and gas absorption. However, its effective application depends on the theoretical understanding of the underlying phenomena of adsorption of molecules in porous solid adsorbents. With the advances in molecular simulation techniques, investigation into the microscopic mechanisms of adsorption phenomena can be realized and this will lead to a development of an unambiguous approach for the characterization of porous solids. This is the aim of this project to understand adsorption and desorption mechanisms in porous materials, especially porous carbons with functional groups because they are not fully studied in the literature.

One of the significant points of this thesis is the development of a novel molecular model for porous carbon. Graphitized thermal carbon black (GTCB) was used as model adsorbent modelled as a composite of basal plane of graphene layers with crevices (ultrafine micropores) and oxygen functional groups attached at the edges of the graphene layers. This model was used in adsorption of various gases, and was validated with high resolution experimental data and theoretically analysed with simulation results obtained with a grand canonical Monte Carlo simulation. Excellent agreement between the experimental data and the simulation results has led us to derive the structural properties of GTCB and the nature of the functional group. Furthermore, the experimental Henry constant and the isosteric heat at zero loading (in the region of very low loadings) are described correctly with the Monte Carlo integration of the Boltzmann factor of the pairwise interaction between an adsorbate molecule and the porous carbon. It was found that adsorbate dominantly adsorbs in the fine crevices at very low loadings because of the enhancement of the solid-fluid potential energy, followed by adsorption on the basal plane of graphene layers. This is the case for non-polar fluids, such as argon and nitrogen. On the other hand, polar fluids, such as ammonia and water, the dominance of the functional group in adsorption is manifested, especially water.

This novel model for carbon can be extended to describe practical porous carbons containing both micropores (for adsorptive capacity) and mesopores (for transport). Adsorption in mesopores is associated with capillary condensation and evaporation, and these are commonly used in the literature to derive the mesopore size distribution. For this determination to be realized, the fundamental understanding of condensation and evaporation must be understood, and this is the second objective of this thesis. We chose graphitic slit pores to model the mesopore, and investigated the effects of various parameters on the capillary condensation and evaporation. Grand
canonical Monte Carlo technique is used to obtain the isotherm and the isosteric heat, and we particularly investigate the mechanisms of adsorption and desorption and derived conditions under which hysteresis occurs. The microscopic understanding of hysteresis was particularly studied for pores of different topology: pores with both ends opened to the surrounding, pores with one end closed, ink-bottle pores composing of a cavity connected to the bulk surrounding by a neck smaller in size, wedge type pore. Analysing the adsorption isotherms of these pores led us to capture features of how molecules adsorb and are structured in pores which result from the interplay between a number of fundamental processes: (1) molecular layering, (2) clustering, (3) capillary condensation and evaporation and (4) molecular ordering. The results derived from this comprehensive study not only guide engineers and scientists to substantially improve characterisation methods using gas adsorption but also to better design adsorptive processes in separation and purification.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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**Contributions by others to the thesis**

Contributions by Prof Duong Do, Prof David Nicholson in designing the project, analyzing and interpreting the research data, providing the insight of the classical theories and revising the thesis.

**Statement of parts of the thesis submitted to qualify for the award of another degree**

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List of Abbreviations

CMC  Canonical Monte Carlo
dB    de Boer
DBdB  Derjaguin-Broekhoff-de Boer
FBP   Fluid-Basal Plane
FF    Fluid-Fluid
FS    Fluid-Solid
FFG   Fluid-Functional Group
GCMC  Grand Canonical Monte Carlo
GTCB  Graphitized Thermal Carbon Black
IUPAC International Union of Pure and Applied Chemistry
MTZ   Mass Transfer Zone
Chapter 1 Introduction

1.1 Background

Adsorption has emerged as an important process for various industrial applications, such as natural gas storage, pollution control, catalyst supports, especially gas separation and purification, because of its less energy intensiveness, highly flexible nature of cycling, and availability of diverse adsorbents. Moreover, adsorption has been considered as one of the standard methods for determining the surface area and porous size distribution of solid materials. Therefore a fundamental understanding of adsorption mechanism is demanding not only for the design and optimization of industrial adsorption process, but also for the purpose of characterization of the structure of porous solids.

The first mathematical model of adsorption process in molecular scale is developed by Langmuir in 1918, which describes the adsorption process of fluids on a homogeneous surface up to monolayer coverage. Later in 1938 Brunauer, Emmett and Teller derived the first equation for multilayer adsorption, which is now widely used for the determination of surface area. Both of these theories are derived from the simple assumptions: in Langmuir theory, the interaction between adsorbate molecules and the surfaces heterogeneity are ignored, and in BET theory the interactions of second and higher layers are equivalent to the liquid phase, therefore they usually deviates from the real experimental data. Followed by the pioneering work of Langmuir and Brunauer and co-worker, many modified equations have been proposed. Although these equations usually give better correlation with the experimental data, they are only applicable for a specified system and extra fitting parameters need to be determined before they apply.

With the fast development of computer science, many techniques have been introduced for the study of adsorption theory, such as the density functional theory, lattice gas theory and molecular simulations. These techniques can construct the adsorption system in the conditions that are hard to achieve by experiment study, and more importantly, they can probe into microscopic properties of the system. Among these techniques, molecular simulation is most widely applied. In principle, if the interaction potentials of the system are correctly described, all the thermodynamic properties of the adsorption system can be calculated. The two principle two principal approaches of molecular simulation are Molecular Dynamics and Monte Carlo simulations. Molecular Dynamics simulations solve the equations of motion of molecules and the fluid properties are calculated as a time average. Monte Carlo simulation uses important sampling with respect to the Boltzmann weight of configurations to calculate thermodynamic properties. These two techniques are
equivalent but Monte Carlo simulations are preferred for equilibrium adsorption studies due to their greater ability to sample the configurational space of an adsorption system. \(^5\)

The second aspect of the pioneering work of the adsorption study is the innovation the highly order mesoporous materials. In 1992, the Mobil scientists disclosed the synthesis of M41S family of silicate/aluminosilicate mesoporous adsorbents with the hexagonally arranged MCM-41, and subsequently the cubic MCM-48 and layered MCM-50 \(^6\), \(^7\). Later the synthesis changed in surfactants with notably materials such as the hexagonal SBA-15 and the cubic SBA-16 \(^8\). Since the discoveries of these order mesoporous materials, adsorption isotherms have been measured on many samples with different porous structure, pore size and temperature, which indeed facilitate the characterization of surface area, pore volume, pore size distribution, etc. \(^9\)

With the advances in molecular simulation techniques and the developments in the synthesis of order mesoporous materials, the comprehension of adsorption mechanism on porous materials can be promoted by reconciliation of simulation results with reliable experimental data and the development of molecular models to prediction the microscopic physics. A general classification of adsorption isotherms have been proposed by IUPAC \(^10\) and it has been evolved during the past decades \(^11\).

In practical industry, carbon materials are known to be the most widely used adsorbent. Although many works have been done for the study of adsorption behaviours on graphitized carbon black as well as activated carbon, there are still many unresolved issues. For example the presence of surface heterogeneity, such as ultrafine crevices and oxygen-containing functional groups, at the edge sites of highly graphitized carbon black has been rarely considered. The existence of hysteresis in uniform pore with one end closed has remained a controversial topic.

The fist aim of this work is to gain a fundamental understanding of the adsorption on graphitized carbon black with surface heterogeneity. This involves the development of new graphitized carbon black model and a systematic investigation of associating fluid adsorption on this model, as well as the characterization of the concentration of functional groups. Another aspect of this thesis is to investigate the mechanism of adsorption and desorption in pores with uniform and non-uniform structure, which is the foundation for characterization of porous materials.

1.2 Objectives

The aim of this thesis is to gain a fundamental understanding of the adsorption mechanism of adsorption of different gases in nonporous and porous carbon with functional groups. To achieve
Chapter 1 Introduction

this objective, a systematic and comprehensive study by molecular simulation is conducted; specifically the objectives of this thesis include:

1. To prove the existence of ultrafine pores and functional groups on \textit{GTCB} and to evaluate the relative strength of different fluids with these sites with regards to the initial adsorption
2. To investigate mechanism of associating fluid, such as ammonia, adsorption on \textit{GTCB} with the presence of ultrafine pore and functional groups.
3. To introduce a new and simple method of determining the concentration of surface oxygen groups on carbons using methanol and water as potential molecular probes.
4. To investigate the adsorption behaviours of argon in uniform open end pore and closed end pore to reveal the microscopic reason for hysteresis.
5. To study the adsorption behaviour in wedge pore for the determination of pore size distribution
6. To investigate the adsorption behaviour in inkbottle pore, to reveal the mechanism of cavitation and pore blocking

1.3 Development of This Thesis

This thesis composes of 9 chapters, with 6 chapters being based on the peer-reviewed publications accomplished throughout my PhD candidature. The 6 chapters can be divided in to two parts. Part one corresponds to Chapter 3 to 5, which focus on the adsorption on graphite surface with the presence of functional groups, while Part two consists of Chapter 6 to 8, which concerns the aspects of adsorption in porous materials. A brief description about each chapter is given below.

Chapter 1 Introduction

This chapter presents a background of adsorption process, the important of computer simulation for the characterization of solid adsorbent. Aim and scope of this thesis are also reviewed in this chapter as well as the outline of this thesis.

Chapter 2 Literature Review

In this chapter, a critical review of the literature related to this project is provided which leads to the specific topics in subsequent chapters. Since Monte Carlo simulation is employed for the study of adsorption, this chapter also presents the implement of different Monte Carlo ensembles, the potential models used in this study, as well as the measurements from Monte Carlo in this study.

Chapter 3 Ultrafine Crevices and Functional Groups on GTCB
Chapter 1 Introduction

In this chapter, a novel molecular model for GTCB is proposed, and it is examined with high resolution experimental data. A further step made in this chapter is to investigate the relative strength of potential interaction between associating and non-associating fluids with the different adsorption sites on the proposed model.

Chapter 4 Ammonia adsorption on GTCB

Chapter 4 presents the adsorption behaviours of ammonia adsorption on GTCB at two different temperatures, close to triple point and to the boiling point, which qualitatively agrees with the experimental data. Two different mechanisms are observed at the two temperatures and a detail discussion is provided in this chapter.

Chapter 5 Characterization of Functional group on GTCB

Chapter 5 proposes a novel method to determine the concentration of oxygen functional groups on GTCB using strong associating fluid such as water and methanol as a molecular probe. The simulation results give a more realistic amount than the conventional Boehm titration and a rigorous analysis is presented in this chapter.

Chapter 6 Open end closed end pore

A comprehensive study of adsorption in uniform open-ended and closed-end pores is presented in chapter 6. A number of parameters are considered in this study: pore size, pore length, shape of closed end, surface affinity, temperature and adsorbate and the underlying reason for hysteresis in these two pore models is explored.

Chapter 7 Adsorption in wedge pore

This chapter proposes the wedge pore as an alternative pore model for the determination of pore size. A microscopic analysis of the radius of the interface separating the gas-like phase and the adsorbate is presented and the surface tension is calculated by the $\text{DBdB}$ equations, which is more cohesive than the bulk phase due to the influence of the absorbent potential energy field.

Chapter 8 Adsorption in inkbottle pore

Chapter 8 presents a comprehensive study of adsorption behaviours in inkbottle pore. The adsorption and desorption processes can be elucidated by comparing the isotherm of simple pore, like open-ended pore, closed-end pore and closed pore. By investigating the effect of neck size, neck length and temperature, the evolution of isotherms in inkbottle is presented and the corresponding condensation and evaporation mechanisms.
Chapter 9 Conclusion and Perspectives

Chapter 9 explains contributions of the current Ph.D. thesis to the field by summarizing the most important findings of this study. Further investigations, as well as directions for the future studies are also recommended in this chapter.
Chapter 2 Literature Review

2.1. Structure of Carbon Adsorbents

The kernel of an adsorption process is the choice of adsorbent, because the behaviour of adsorbed molecules depends on the properties of both adsorbent solid and the adsorbate itself. Among the practical solids used in industries, carbon and its allotropes are one of the most versatile adsorbents, whose applications depend on their properties, such as pore size, topology and surface heterogeneity. In this section, we briefly review the carbon adsorbents that are relevant to this thesis and we especially emphasize on the structures of these carbon materials at the molecular level, which is the basis of building our molecular models for the subsequent study.

*Graphite Thermal Carbon Black*

Graphitized thermal carbon black (GTCB) has a homogeneous basal plane surface which is achieved by thermal decomposition of a carbonaceous precursor and graphitized to at least 2700°C. The homogeneous graphene layers are made up of carbon atoms in hexagonal packing. Figure 2.1 shows the Bravais lattice of the graphene. The unit cell is spanned by the two vectors, \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), and contains two carbon atoms. The basis vector \((\mathbf{a}_1, \mathbf{a}_2)\) have the same length \( |\mathbf{a}_1| = |\mathbf{a}_2| = a = \sqrt{3}b \), and form an angle, where \( b = 1.42 \text{Å} \) is the bond distance between two carbon atoms. The component of the vector, \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), with respect to the rectangular coordinates system are given by

\[
\mathbf{a}_1 = (\frac{\sqrt{3}a_0}{2}, \frac{a_0}{2}) \quad \mathbf{a}_2 = (\frac{\sqrt{3}a_0}{2}, -\frac{a_0}{2})
\]

*(2.1)*

Figure 2.1 Schematics of honeycomb lattice of graphene.
Chapter 2 Literature Review

**Carbon Nanotubes**

One of the well-defined polymorphic forms of carbon is carbon nanotubes (CNTs). The original discovered fullerene CNTs were referred as multi-wall nanotubes (MWNTs) by Iijima\textsuperscript{16}, but later the single-walled carbon nanotubes (SWNTs) were discovered as well. Due to the special cylindrical structure, CNTs exhibits unique properties of surface area, aspect ratio, mechanical strength, electrical and thermal conductivity, which is potentially useful in a wide variety of applications.

The structure of the SWNT can be imaged as rolling up a sheet of graphene into a seamless cylinder, as shown in Figure 2.2. The way the graphene sheet is wrapped is described by a pair of indices \((n, m)\), which his call the chiral vector, \(\overrightarrow{C}\).\textsuperscript{17} The two variable \(n\) and \(m\) are integers, which corresponds to the two unit vectors \(\overrightarrow{a}_1\), and \(\overrightarrow{a}_2\), respectively. In the case of \(m = 0\), the nanotubes are call ‘zigzag’. If \(n=m\), they are call ‘armchair’. Otherwise, they are ‘chiral’ nanotubes. The diameter, \(d_{CNT}\), and the chiral angle, \(\theta\), are given by

\[
d_{CNT} = \frac{\sqrt{3}a}{\pi} \left( n^2 + m^2 + nm \right)^{1/2} \quad \theta = \arctan \left( \frac{\sqrt{3}m}{m + 2n} \right)
\]

\[(2.2)\]

**Figure 2.2** Schematic of CNT construction from graphene sheet along the chiral vector.\textsuperscript{18}
Chapter 2 Literature Review

Activated Carbon

Activated carbons are made by thermal decomposition of carbonaceous precursors such as wood, coal, lignite, and coconut shell, followed by activation with a physical or chemical oxidizing agent. The application of activated carbon is versatile, because it provides not only a very high surface area and micropore volume which corresponds to high adsorption capacity, but also a network of mesopores and macropores that give a good transport pathway to molecules.

Depending on the carbonization temperature and activation process, activated carbon process different pore size distribution and surface chemistry which gives a complex structure. The molecular structure of activated carbon has been the subject of many investigation and numerous structure models have been proposed. In many theoretical studies, the uniform slit pore is used as a basis for modelling activated carbons in combination with density functional theory or MC simulation to establish a data base of isotherms for use as a kernel in pore size analysis. However, the structure of real activated carbons is generally more complex than is implied by this model.

In an extensive X-ray study of non-graftzing carbons, Franklin demonstrated that the strongly cross-linked, graphite-like crystallites are randomly oriented. On thermal treatment between 1700 °C and 3000 °C, the cross-linking becomes weaker and the crystallites realign, so that the inter-crystallite spaces approach parallel-sided slit pores. However, due to the pre-orientation of the crystallites, governed by the cross-linking and the spatial constraint of their relative positions, the pores do not have a uniform cross-sectional width, and even in this relatively well-ordered carbon, the pore width varies along the axial direction. On the basis of this evidence, there is a case to be made for modelling adsorption in activated carbon pores based on wedges of different lengths and angles.

![Figure 2.3 Schematic of activated carbon: (a) non-graftzing carbon; (b) graftzing carbon.](image-url)

Moreover, the real structure of activated carbon always involves a network of different size pore. Experimental isotherms of nitrogen adsorption on activated carbon always show a type H2 isotherm,
which have a gradual increase of adsorption branch and a steep desorption branch with evaporation at 0.4 of reduced pressure. This indicates that structure of activated carbon is in a form of aggregation of crystallites which form a network of necks and cavities.

2.2. Adsorption on Graphite Surface

Adsorption of gases on homogeneous graphene layers has been extensively studied because of the fundamental interest in developing adsorption theory and investigating the intrinsic interaction between different fluids and the basal plane of graphite. The first description of sub-monolayer adsorption process is proposed by Langmuir in 1918. Since Langmuir equation is derived from the simple assumptions which does not account for the interaction between adsorbate molecules and the surfaces heterogeneity, it usually deviates from the real experiment isotherm. Many empirical equations were proposed based on the Langmuir equations in order to fit the experimental isotherms, such as Freundlich equation, Sips equation, Toth equation and Unilan equation. Although these equations usually give better correlation with the experimental data due to the extra fitting parameters, they cannot shed the underlying mechanism of the adsorption process. With the introduction of molecular simulation, the mechanism of adsorption can be probed in microscopic detail by accounting the potential energy between the adsorbate molecules and adsorbent surface.

Graphitized thermal carbon black (GTCB) is a good experimental subject to represent graphene layers, because it is synthesized by thermal decomposition of a carbonaceous precursor and graphitized at very high temperatures (at least 2700°C) to produce highly homogeneous basal planes. However, experimental observations suggest that this material may nevertheless possess strong sites and that the interaction of adsorbate with the substrate is dominated by these sites at very low loadings. For example, Polley et al. measured the heat of adsorption of nitrogen at 77K on a series of Spheron 6 adsorbents having different degrees of graphitization, and found that the isosteric heat versus loading was very sensitive to the extent of graphitization, especially at very low loadings, suggesting the presence of strong sites. Other clear evidence of their presence was provided by Deitz, who measured very high resolution adsorption isotherms of carbon dioxide on GTCB Sterling (2700°C) at 273K. The isotherm shows a two-stage uptake at extremely low pressures; the first stage being attributed to the presence of strong sites and the second to adsorption on the basal planes. Similar experimental results have also been found for various gases on Pyrex.

Although the evidence for the presence of strong sites in GTCB is both clear and abundant; especially the numerous reports of isosteric heats at very low loadings, the question of the nature of these sites has not been fully resolved. One possibility is the effect of anisotropy of polarizability of
graphite on the attractive forces as proposed by Deitz and Meyer and Deitz; which alone is unlikely to be a major factor, another possibility is that there are ultra-fine crevices (defects) at the junction between two adjacent basal planes, where the adsorption potential field is enhanced by overlap of potentials from opposite pore walls. SEM and TEM images show that GTCB particles have polyhedral shapes with exterior surfaces composed of patches of two different energetic sites: (1) the homogeneous basal planes and (2) the prismatic edges at the junctions between the neighbouring basal planes, forming defects which may also be locations for functional groups. Although the importance of defects has been discussed in a number of simulation studies, their possible role in the quantification of high resolution of experimental isotherm and heat data has not been clarified.

The strong sites could also be due to chemical heterogeneities, particularly functional groups. Although it is commonly believed that functional groups are removed in highly graphitized thermal carbon black at very high graphitization temperatures, recent experimental evidence suggests that a small concentration of functional groups can still be found even after graphitization at extremely high temperature (~3000K). These groups are likely to be present at the unsaturated valencies at edge sites at the same locations as the ultra-fine crevices (defects) and they will carry partial charges which can undergo strong electrostatic interactions with molecules having high multipole moments, such as water and ammonia. The synergistic effect of crevices plus functional groups could enhance the initial interaction of associating adsorbates on a carbon surface.

Although the presence of these strong polar sites on GTCB is clear, the question is raised as to whether polar adsorbates are preferentially adsorbed on the basal planes or at the strong sites at the junctions. Experimental studies of non-associating fluids such as argon and nitrogen on graphite have been extensively reported, and it is well established that their adsorption is a molecular layering process due to the dominance of the fluid-basal plane interaction. On the other hand, the adsorption of strongly associating fluids such as water, is governed by the functional groups. For example, the isosteric heat of water is initially very high and decreases sharply with loading as a consequence of the formation and growth of water clusters on the functional groups.

Ammonia is an interesting associating fluid, because its adsorption behaviour is intermediate between non-associating fluids and strongly associating fluids like water. However, experimental data for ammonia on GTCB are very rare and the mechanism of ammonia adsorption has not been fully elucidated. Holmes and Beebe and Spencer et al. measured the adsorption isotherm at the triple point (195K) and found that the adsorbed amount is negligible at low relative pressures and that the onset of adsorption occurs at a relative pressure of 0.5 with a distinct hysteresis loop; so far
this has not been reproduced by any simulation study. The effect of temperature on the adsorption of ammonia is also interesting. Bomchil et al. $^{57-60}$, using neutron scattering and nuclear magnetic resonance, showed that the temperature plays an important role on the adsorptive properties of ammonia on graphitized carbon black: below the melting point of bulk ammonia nucleation takes place on the strong sites, rather than the basal plane; on the other hand, above the melting point the adsorbed ammonia strongly aggregates on the basal plane surfaces because of entropic effects.

With the development of computer science, molecular simulation has become an important tool to study the mechanism of adsorption on graphite surface. Many experimental observations have been successful reproduced by molecular simulation which can explore the underlying mechanisms by microscopic analysis. The experimental observations of heat spike of monolayer is reproduced by Fan and co-worker$^{31}$ using grand canonical Monte Carlo simulation, who proposed a mechanism in which the introduction of adsorbate molecules to the system at monolayer loading induce the rearrangement of molecules in the first layer that leads to the increase in FF and FF energies. Recently the observation of hysteresis on graphite surface is achieved by Prasetyo and co-worker$^{61}$ by both simulation and experimental study, and the hysteresis is elucidated by analysis of density distribution and compressibility.

2.3. Adsorption in Porous Material

Understanding the underlying physics of adsorption and desorption in porous materials has been a subject of great interest to both scientists and engineers for: (1) the purpose of characterization of the structure of porous solids and (2) the application of porous materials for gas separation or purification processes. $^9, 62$ One issue, which continues to be challenging, is the existence of hysteresis, because a strict application of thermodynamics demands that only one equilibrium state can exist for a given set of thermodynamic parameters. However, it is well established experimentally that (1) there exist distinct adsorption and desorption branches of an isotherm over a certain range of pressure, and (2) that the existence of hysteresis is associated with a demarcation between smaller (micropore) and larger (mesopore) pore widths relative to the adsorbate molecule size. $^{63}$ Unlike micropores in which adsorption isotherms are reversible because molecular filling and emptying processes occur by the same mechanism (in different directions), hysteresis associated with capillary condensation and evaporation is observed in mesoporous materials at temperatures below a critical hysteresis temperature ($T_{ch}$). $^{64}$
Experimental studies have shown that the presence of a hysteresis loop and its shape, size and position depend on the porous structure, pore size and temperature, and this dependence is extensively used in the characterization of porous structure and the calculation of pore size distribution. For this reason, attempts have been made to classify the various shapes of the hysteresis loop and this classification has evolved over the past decades as a consequence of: (1) advances in the synthesis of ordered mesoporous materials, (2) the use of high resolution apparatus for the measurement of physical adsorption and (3) the increasing power of computer simulation. Recently a new classification, shown in Figure 2.4a, has been proposed by IUPAC, which encompasses both the earlier (1985) IUPAC classification (based on experimental analysis) and the original, 1972, classification by de Boer, shown in Figure 2.4b.

Most of the early work on adsorption and desorption mechanisms focus on simple pore models, typically with cylindrical or slit pore geometry with both ends open to the gaseous surroundings. The classical explanation of pore-filling and emptying in a cylindrical pore was proposed by Cohan, in which both adsorption and desorption follow equilibrium paths, and the hysteresis depends solely on the difference in the curvature (cylindrical on adsorption and spherical on desorption) of the
meniscus separating the adsorbed phase and the gas-like region. However, the derivation of Cohan’s equations assumes the validity of macroscopic thermodynamics and does not account for the possibility of an undulating interface separating the adsorbed phase and the gas-like phase in the confined space. Furthermore, it takes no explicit account of the adsorbent potential energy field (despite its dependence on the existence of an annular adsorbate layer during adsorption). An additional deficiency of the Cohan model, not widely recognized in the literature, is its failure to describe the disappearance of hysteresis at high temperatures. In contrast, it has been confirmed, by both experimental and simulation studies, that the hysteresis loop is a function of temperature and shifts to higher pressure and shrinks in area as the temperature is increased, eventually disappearing at the critical hysteresis temperature (Tch). Moreover, according to the Cohan-Kelvin theory, adsorbate would not condense in open end slit-shaped pores until the saturation vapour pressure is reached, because the radius of curvature of the adsorbate phase is infinite at a planar interface, an argument which has now been proved to be incorrect. Everett and Haynes proposed a mesoscopic thermodynamic mechanism for capillary condensation in cylinders, in which the nucleation of adsorbate condensation originates at an unduloidal interface and leads to liquid bridge formation. Recently, Fan et al. proposed a new undulation theory based on molecular simulation to describe the microscopic origin of the critical hysteresis temperature and the critical hysteresis pore size. Undulation of the interface separating the condensed phase and the gas phase has also been addressed by Kornev et al.

Although the presence of hysteresis in open-ended pores is clear, the question of whether hysteresis exists in pores with only one end connected to the gas surroundings, and closed at the other end, is unresolved. The classical Cohan-Kelvin mechanism is frequently invoked as an argument against the existence of a hysteresis loop in closed-end pores, on the grounds that the curvature of the interface separating the adsorbed phase and the gas phase is the same for both adsorption and desorption. In contradiction to this prediction of the Cohan-Kelvin theory, experimental isotherms in aluminium and silicon adsorbents with closed end pores have shown hysteresis loops. However, microscopic analysis shows that these materials have corrugated pore walls (at least at the atomic level), and this, coupled with the possible deformation of the adsorbent induced by adsorption, could be the origin of the hysteresis, rather than pore geometry. Recently, the synthesis of a highly ordered porous anodized aluminium oxide (AAO) has been achieved by nanolithography, and a clear hysteresis loop was observed for a closed-end pore whose adsorption and desorption boundaries envelop the desorption branch of the corresponding open end pore of the same size, an experimental result which is supported by simulations. Theoretical studies of this question have not reached a conclusive consensus: DFT or lattice model calculations have tended to
support the classical thermodynamic theory that hysteresis is absent in closed-end pores. On the other hand, recent molecular simulations of closed-end pores show that hysteresis does exist. The disagreement between experimental measurements, classical theory and DFT, and simulation studies demands that further work is needed to resolve the issue of hysteresis in closed-end pores.

Among the IUPAC classification of hysteresis, type H2, which has a gradually increasing adsorption branch and a characteristically steep desorption branch (associated with the cavity), is commonly found for disordered solids. The desorption pressure is generally found to be independent of the cavity size and as such it can’t be used to determine pore size distribution. For example, the characteristic reduced pressure of cavitation for nitrogen at 77K, $P_{\text{cav}}/P_0$, is invariably found experimentally to occur at about 0.42, where $P_0$ is the saturation vapour pressure. Interconnected network structures in which large cavities are surrounded by smaller necks connected to the bulk gas (commonly described as ink-bottle pores) have been proposed as a possible explanation of this phenomenon. Desorption from filled ink-bottle pores has been shown to occur via two possible mechanisms: pore blocking or cavitation. The pore blocking mechanism is a process in which menisci formed at the mouth of the necks recede into the pore interior until the cavity is gradually emptied; cavitation occurs when the necks are so small that the condensed fluid in the cavity is stretched to the limit of its mechanical stability at which point the interior of the cavity empties while the necks remain (partially) filled. Recent simulation studies show that the desorption mechanism of a given gas can switch from pore blocking to cavitation when the necks are smaller than a critical size at a given temperature, or when temperature is increased for a given neck size, or when the adsorbate species altered.

Molecular simulation studies have helped to uncover the underlying mechanism of cavitation phenomenon: for example an investigation of adsorption and desorption in pores without connectivity, using molecular dynamics (MD) and Monte Carlo (MC) methods, led Sarkisov and Monson to question the validity of the network percolation theory. Ravikovitch and Neimark, using nonlocal Density Functional Theory (NLDFT), showed that the desorption mechanism changes from pore blocking to cavitation when the neck of an ink-bottle pore is smaller than a certain value. Using local compressibility as a measure of the cohesiveness of the adsorbate, Fan et al. proposed that the difference in the compressibility of the fluid in the neck and the cavity is a critical indicator to distinguish cavitation from pore blocking.
2.4 Monte Carlo Simulation

As reviewed above, the classical theories, like Langmuir approach, provides simple description for the behaviours of adsorbate molecules on a homogeneous adsorbent surface. However, these theories always involve empirical fitting parameters and assumptions that in invalid for real experiment. Unlike the empirical, Monte Carlo (MC) simulation is a very powerful method to investigate the equilibrium of adsorption systems, provided that the system is described correctly in the computer. As long as the microscopic reversibility is maintained during the course of a Monte Carlo simulation, equilibrium will be reached by generating a sequence of configurations of the Markov chain. The Metropolis procedure for generating a Markov chain can be summarized as follows. Details can be found in Frenkel and Smit. 4

1. Initialize the system with specified thermodynamic properties. For example, in canonical ensemble, the number of adsorbate molecule, system volume and temperature are specified.
2. Initialize the cumulative properties of the system as zero.
3. Select an event randomly with equal probability. The event could be displacement, insertion, deletion or volume change which depends on the ensemble.
4. Calculate the configuration of the system before the event take place, $U$.
5. Carry out the event and calculate the energy of the new configuration of the system, $U'$.
6. Evaluate whether the new configuration of the system should be accepted or rejected, with the corresponding probability of the event.
7. If the new configuration is rejected, the previous configuration is recounted. If accepted, then update the configuration of the adsorbate molecules and sum up the properties of the system. For $N$ step, the sum of the property $X$ is $\sum_{i=1}^{N} X_i$, where $X_i$ is the property at $i^{th}$ configuration.
8. The trials should be repeated over a sufficient number of configurations to ensure the Markov chain is long enough for fluids to reach the equilibrium. When the system reaches equilibrium, redo step 2 to 7 for the sampling stage to calculate the thermodynamic properties.
9. After the sampling stages, average the ensemble summation. The ensemble average for a thermodynamic property $X$, is

$$\langle X \rangle = \frac{\sum_{i=1}^{N} X_i}{N} \quad (2.3)$$
2.4.1 Canonical Ensemble (NVT)

The canonical ensemble describes an isolated system with constant number of adsorbate molecules \((N)\), the system volume \((V)\), and temperature \((T)\) and the thermodynamic properties derived from this ensemble usually are pressure and chemical potential.

The canonical ensemble is conducted by randomly displacing a particle to a new position in order to minimise the free energy of the system. The Boltzmann distribution law is applied to the probability of a molecular arrangement. The probability of accepting the displacement is given by:
\[ P_{\text{move}}^{\text{acc}} = \min\left(1, \exp\left\{ -\beta(U' - U) \right\} \right) \]  (2.4)

where \( \beta \) is the reciprocal temperature, \( \beta = 1/k_B T \), with \( k_B = 1.38066 \times 10^{-23} \) \( \text{J/K} \) is Boltzmann’s constant, \( U \) and \( U' \) are the potential energy before and after the displacement, respectively. If the trial displacement is accepted, the new configuration will be recorded; otherwise the old configuration is recounted.

2.4.2 Grand Canonical Ensemble (GCMC)

The grand canonical ensemble is first proposed by Norman and Filinov \(^9^5\) and later it is introduced for fluid system by Adams \(^9^6\). In this ensemble, the adsorbate chemical potential \( \mu \), the system volume \( V \) and temperature \( T \) are kept constant and the number of adsorbate molecules is allowed to fluctuate, in the sense that the system is like connecting to an infinite bulk reservoir with the same chemical potential and temperature. Therefore, GCMC is the most extensively used ensemble in adsorption studies, which mimics the same conditions that generally used in adsorption experiment.

Apart from the displacement of a particle, GCMC involves two additional steps: insertion and deletion of a particle. The insertion is carried out by selecting a random position within the simulation box and inserting a molecule with a random orientation.

The probability of accepting the insertion is given by:

\[ P_{\text{acc}}^{\text{acc}} = \min\left(1, \frac{V}{\Lambda^2(N+1)} \exp\left\{ -\beta\left[\mu - U' + U \right] \right\} \right) \]  (2.5)

where \( U \) and \( U' \) are the energies of the system before and after the insertion, respectively, \( N \) is number of particles in the simulation box, and \( \Lambda \) is the thermal de Broglie wavelength.

The deletion is conducted by randomly selecting a molecule from the existing \( N \) molecules in the system and its probability of acceptance is given by:

\[ P_{\text{acc}}^{\text{del}} = \min\left(1, \frac{\Lambda^3 N}{V} \exp\left\{ -\beta\left[\mu + U' - U \right] \right\} \right) \]  (2.6)

where \( U \) and \( U' \) are the energies of the system before and after deletion, respectively.

Similar as the displacement of particle, if the trial insertion or deletion was accepted, the new configuration of the system will be updated to Markov chain, otherwise the old configuration will be recounted.
In grand canonical ensemble, in order to maintain the microscopic reversibility, the system must have equal probability for insertion and deletion. For the GCMC simulation in this work, we use equal probability for displacement, insertion and deletion in each cycle, which consists of 1000 steps. In the equilibration stage, the maximum displacement length was initially set as one half of the largest dimension of the simulation box and was adjusted at the end of each cycle to give an acceptance ratio of 20%. If it is less than 20%, the maximum displacement length is reduced by a factor of 0.95; otherwise it is increased by a factor of 1.05. The final maximum displacement attained at the end of the equilibration stage was then kept constant and used in the sampling stage.

2.5 Interaction potential Models

2.5.1 Fluid-Fluid Potential

For interaction between two dispersive sites, the most commonly used potential model is the Lennard-Jones model, because it is relatively simple and the parameters are readily available for a wide range of fluids. Moreover, this model is consistent with the well-known Steele potential to describe the solid-fluid interaction, which will be shown later in this section. The interaction energy between two isolated fluid molecules which are the same type is calculated with the Lennard-Jones 12-6 potential equation shown as below.

\[
\varphi_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]
\]  

(2.7)

where \( r \) is the separation distance between two molecules, \( \varepsilon_{ij} \) is the well-depth of interaction energy and \( \sigma \) is the collision diameter at which \( \varphi_{ij} \) is zero.

For a molecule with many dispersive sites and fixed partial charges, the interaction energy between two molecules is given by the sum of the LJ and the Coulomb interactions:

\[
\varphi_{ij} = \sum_{i=1}^{C} \sum_{d=1}^{D} 4\varepsilon_{ij}^{cd} \left[ \left( \frac{\sigma_{ij}^{cd}}{r_{ij}^{cd}} \right)^{12} - \left( \frac{\sigma_{ij}^{cd}}{r_{ij}^{cd}} \right)^{6} \right] + \sum_{a=1}^{A} \sum_{b=1}^{B} \frac{q_a^i q_b^j}{4\pi\varepsilon_0 r_{ij}^{ab}}
\]  

(2.8)

where \( \varphi_{ij} \) is the interaction energy between fluid molecules \( i \) and \( j \), \( A \) and \( B \) are the number of partial charges on the molecules \( i \) and \( j \), respectively, \( C \) and \( D \) are the numbers of LJ sites on the molecules \( i \) and \( j \) respectively, \( \varepsilon_0 \) is the permittivity of a vacuum, \( r_{ij}^{ab} \) is the separation distance between the charge \( a \) on molecule \( i \) and the charge \( b \) on molecule \( j \) having charges \( q_a^i \) and \( q_b^j \), respectively, \( r_{ij}^{cd} \) is
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the separation between the LJ site \(c\) on molecule \(i\) and the LJ site \(d\) on molecule \(j\) with a combined LJ collision diameter of \(\sigma_{cd}^{ij}\) and a combined LJ well-depth of \(\varepsilon_{cd}^{ij}\) for the two sites. The combined collision diameter and well-depth are given by the Lorentz-Berthelot (LB) mixing rules:

\[
\sigma_{cd}^{ij} = 0.5(\sigma_i^c + \sigma_j^d) \quad \varepsilon_{cd}^{ij} = \sqrt{\varepsilon_i^c \varepsilon_j^d}
\]

In this thesis, we considered a range of adsorbates with increasingly strong electrostatic interactions from argon, nitrogen and carbon dioxide, which are non-associating fluids, though to ammonia and water, which are strong associating fluids.

Argon is modelled as a single dispersive site molecule, and the molecular parameter are given by Michels and Wijker\(^9\)\(^8\). Nitrogen is described by the TraPPE model, which is proposed by Proff and Siepmann\(^9\)\(^9\). In this model, one of the three charges is placed at the centre of the molecular axis joining the centres of nitrogen atoms and two symmetric negative charges are on two nitrogen atoms at a bond length of 0.11nm. Carbon dioxide is described by the TraPPE model proposed by Proff and Siepmann\(^9\)\(^9\), which has three LJ sites and three fixed partial charges. The ammonia model was proposed by Kristof et al.\(^1\)\(^0\)\(^0\) with one LJ site and four fixed partial charges. For water, the rigid non-polarizable polyatomic SPC/E model from Berendsen et al.\(^1\)\(^0\)\(^1\) is employed. This model has a single LJ site located at the centre of the oxygen atom and three fixed point charges representing the charge distribution of the molecule. Two positive charges are located at the centres of the hydrogen atoms, and a single negative charge is located at the centre of oxygen atom. The potential parameters and geometric parameters for argon, nitrogen, carbon dioxide, ammonia and water models are summarized in Table 2.1 and 2.2, respectively.
Table 2.1 Potential parameters of adsorbates used in this work.

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Interacting site</th>
<th>$\sigma$ (nm)</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Ar</td>
<td>0.3045</td>
<td>119.8</td>
<td>--</td>
</tr>
<tr>
<td>N$_2$</td>
<td>N</td>
<td>0.331</td>
<td>36</td>
<td>-0.482</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.331</td>
<td>36</td>
<td>-0.482</td>
</tr>
<tr>
<td></td>
<td>COM of N$_2$</td>
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<td>--</td>
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</tr>
<tr>
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<td>27</td>
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<td></td>
<td>O</td>
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<td>79</td>
<td>-0.35</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.305</td>
<td>79</td>
<td>-0.35</td>
</tr>
<tr>
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<td>170</td>
<td>-1.035</td>
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<tr>
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<td>--</td>
<td>0.345</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>--</td>
<td>--</td>
<td>0.345</td>
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<td>H</td>
<td>--</td>
<td>--</td>
<td>0.345</td>
</tr>
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<td>CH$_3$OH</td>
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<td>0.265</td>
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<td></td>
<td>O</td>
<td>0.302</td>
<td>93</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>--</td>
<td>--</td>
<td>0.435</td>
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<tr>
<td>H$_2$O</td>
<td>O</td>
<td>0.3166</td>
<td>78.23</td>
<td>-0.8476</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>--</td>
<td>--</td>
<td>0.4238</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>--</td>
<td>--</td>
<td>0.4238</td>
</tr>
</tbody>
</table>

Table 2.2 Geometric parameters of the adsorbate

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Bond</th>
<th>Length (nm)</th>
<th>Angle</th>
<th>Degree(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>N-N</td>
<td>0.11</td>
<td>--</td>
<td>--</td>
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<tr>
<td>CO$_2$</td>
<td>C-O</td>
<td>0.116</td>
<td>$\angle$ COC</td>
<td>180</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>N-H</td>
<td>0.10124</td>
<td>$\angle$ HNH</td>
<td>106.68</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>C-O</td>
<td>0.143</td>
<td>$\angle$ COH</td>
<td>108.5</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>0.0945</td>
<td>$\angle$ HOH</td>
<td>109.47</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>O-H</td>
<td>0.1</td>
<td>$\angle$ HOH</td>
<td>109.47</td>
</tr>
</tbody>
</table>
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2.5.2 Solid-Fluid Potential

There are two common approaches to model the surface of carbon adsorbents. One is the discrete carbon model, which takes account of the periodic arrangement of carbon atoms on a graphene layer or on a carbon nanotube, whose structures have been reviewed above in section 2.1. The other one is the unstructured model where the solid consist of structureless graphene layers with constant surface density of carbon atoms. It has been proved that both of the models yield identical simulation results, provided the temperature of the system is high enough so that the barrier between the hexagonal sites is less than \( kT \).

1. Infinite Unstructured Surface

The solid fluid interaction energy between a particle \( i \) and the homogeneous flat solid substrate of infinite extent is calculated by the following 10-4-3 Steele potential \(^{102,103}\):

\[
\phi_{i,s} = 2\pi \rho_s \varepsilon_{sf} \sigma_{sf}^2 \left\{ \frac{2}{5} \left( \frac{\sigma_{sf}}{z_i} \right)^{10} - \left( \frac{\sigma_{sf}}{z_i} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta + z_i)^3} \right\}
\]

where \( \rho_s \) is the surface carbon atom density of a graphene layer (38.2 nm\(^2\)) and \( \Delta \) is the spacing between the two adjacent graphite layers (0.335 nm). The solid-fluid molecular parameters, the collision diameter \( \sigma_{sf} \) and the interaction energy \( \varepsilon_{sf} \) are calculated from the LB mixing rule with \( \sigma_{ss} = 0.34 \text{nm} \) and \( \varepsilon_{ss}/k = 28 \text{K} \).

2. Finite Unstructured Surface

A finite sized surface of constant surface density can be described by a Bojan-Steele model, which is infinite in extent in the \( x \)-direction and finite in the \( y \)-direction. The solid-fluid interaction of this surface is given by \(^{104-107}\):

\[
\phi_{f,S} = 2\pi \rho_s \varepsilon_{sf} \sigma_{sf}^2 \left\{ \left[ \phi_{rep}(z, y^+) - \phi_{rep}(z, y^-) \right] - \left[ \phi_{att}(z, y^+) - \phi_{att}(z, y^-) \right] \right\}
\]

where \( z \) is the shortest distance between a particle and the surface, \( \rho_s \) is the density of the surface, \( \sigma_{sf} \) and \( \varepsilon_{sf} \) are the solid-fluid molecular parameters.
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Figure 2.6 Configuration of the finite stripe, which is finite in the y-direction and is infinite in the x-direction (perpendicular to the page).

Configuration of a finite strip is shown in Figure 2.6, which is finite in the y-direction and infinite in the x-direction. The variables \( y^+ \) and \( y^- \) are the y-coordinates of the right hand edge and the left hand edge, relative to the position of the fluid particle:

\[
y^+ = \frac{W}{2} - y; \quad y^- = -\frac{W}{2} - y
\]  

(2.12)

The repulsive and attractive functions on the RHS of eq. (2.1) are given by:

\[
\phi_{\text{rep}}(z, y) = \frac{y}{\sqrt{y^2 + z^2}} \left[ \frac{1}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} + \frac{1}{10} \frac{\sigma_{sf}^{10}}{z^8 \left(y^2 + z^2\right)^2} + \frac{3}{40} \frac{\sigma_{sf}^{10}}{z^6 \left(y^2 + z^2\right)^2} ight] \\
+ \frac{1}{16} \frac{\sigma_{sf}^{10}}{z^4 \left(y^2 + z^2\right)^3} + \frac{7}{128} \frac{\sigma_{sf}^{10}}{z^2 \left(y^2 + z^2\right)^4} 
\]  

(2.13)

\[
\phi_{\text{att}}(z, y) = \frac{y}{\sqrt{y^2 + z^2}} \left[ \frac{1}{2} \left( \frac{\sigma_{sf}}{z} \right)^4 + \frac{1}{4} \frac{\sigma_{sf}^4}{z^2 \left(y^2 + z^2\right)^2} \right]
\]  

(2.14)

The potential equation, (2.11) are valid for any particle around the strip. When a particle is positioned exactly on the same level as the strip (i.e. at \( z=0 \)), eqs. (2.13) and (2.14) were Taylor expanded to find the limits when \( z \) approaches zero:

\[
\lim_{z \to 0} \phi_{\text{rep}} = -\frac{y}{\sqrt{y^2}} \left[ \frac{1}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} - \frac{63}{1280} \left( \frac{\sigma_{sf}}{z} \right)^{10} + O(z^2) \right]
\]  

(2.15)
\[
\text{lim}_{z\to 0} \varphi_{\text{eff}} = \frac{y}{\sqrt{y^2}} \left[ \frac{1}{2} \left( \frac{\sigma_{sf}}{z} \right)^4 - 3 \frac{\sigma_{sf}}{16} \right] + O(z^3) \quad (2.16)
\]

Substituting eqs (2.15 and 2.16) into the solid-fluid potential (eq. 2.11), get the final solution for the potential at \(z = 0\):

\[
\varphi_{f,S} = \psi 2\pi \rho_s \sigma_{sf}^2 \varepsilon_{sf} = \left\{ \frac{63}{1280} \left( \frac{\sigma_{sf}}{y^+} \right)^{10} - \left( \frac{\sigma_{sf}}{y^+} \right)^{10} \right\} - \frac{3}{16} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^4 - \left( \frac{\sigma_{sf}}{y^+} \right)^4 \right] \}
\]

(2.17)

where \(\psi = 1\) for positive \(y^+\) and \(y^-\), and \(\psi = -1\) for negative \(y^+\) and \(y^-\). It can be seen there is no singularity in the solid-fluid potential energy, as one would physically expect. The potential energy in the region of small \(z\) can be calculated from a Taylor series expansion of the Bojan-Steele equation as:

\[
\varphi_{f,S} = \psi \frac{2\pi \rho_s \sigma_{sf}^2 \varepsilon_{sf}}{2} \left\{ \frac{63}{1280} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{10} - \left( \frac{\sigma_{sf}}{y^+} \right)^{10} \right] - \frac{3}{16} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^4 - \left( \frac{\sigma_{sf}}{y^+} \right)^4 \right] \right\}
\]

\[
- \left( \frac{z}{\sigma_{sf}} \right)^2 \left\{ \frac{231}{1024} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{12} - \left( \frac{\sigma_{sf}}{y^+} \right)^{12} \right] - \frac{5}{16} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^6 - \left( \frac{\sigma_{sf}}{y^+} \right)^6 \right] \right\}
\]

\[
+ \left( \frac{z}{\sigma_{sf}} \right)^4 \left\{ \frac{1287}{2048} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{14} - \left( \frac{\sigma_{sf}}{y^+} \right)^{14} \right] - \frac{105}{256} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^8 - \left( \frac{\sigma_{sf}}{y^+} \right)^8 \right] \right\}
\]

\[
- \left( \frac{z}{\sigma_{sf}} \right)^6 \left\{ \frac{45045}{32768} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{16} - \left( \frac{\sigma_{sf}}{y^+} \right)^{16} \right] - \frac{63}{128} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{10} - \left( \frac{\sigma_{sf}}{y^+} \right)^{10} \right] \right\}
\]

\[
+ \left( \frac{z}{\sigma_{sf}} \right)^8 \left\{ \frac{85085}{32768} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{18} - \left( \frac{\sigma_{sf}}{y^+} \right)^{18} \right] - \frac{1155}{2048} \left[ \left( \frac{\sigma_{sf}}{y^+} \right)^{12} - \left( \frac{\sigma_{sf}}{y^+} \right)^{12} \right] \right\}
\]

\[
+ O \left( \frac{z}{\sigma_{sf}} \right)^{10}
\]

(2.18)

where \(\psi = 1\) for positive \(y^+\) and \(y^-\), and \(\psi = -1\) for negative \(y^+\) and \(y^-\).
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3. Finite Cylindrical Surface

The solid fluid interaction energy between a particle and a finite cylinder is given by \(^{108,109}\):

\[
\varphi_{f,s} = 4\varepsilon_{sf} \rho_s R a \sum_{n=3,6} a_n \sigma_{sf}^{2n} \int_0^{2\pi} \int_{u^n}^{u^+} \frac{du}{u^2 + (R^2+r^2-2Rr\cos\theta)^n} d\theta
\]  

(2.19)

where \(\rho_s\) is the density of the surface, \(\sigma_{sf}\) and \(\varepsilon_{sf}\) are the solid-fluid molecular parameters, \(R\) and \(L\) are the radius and length of the cylinder, respectively, \(r\) is the shortest distance between a particle and axis of the cylinder. The variables \(u^+\) and \(u^-\) are the vectors of the \(y\)-position of the particle to the two edges of the cylinder, which is given by

\[
u^+ = \frac{L}{2} - y; \quad u^- = -\frac{L}{2} - y;
\]  

(2.20)

The second term in the denominator can be defined as \(G\), physically which is the distance between the particle and the carbon atom at angle \(\theta\), as shown in Figure 2.7:

\[
G = R^2 + r^2 - 2Rr\cos\theta
\]  

(2.21)

![Figure 2.7 Schematics of the finite cylinder model, which is finite in y- direction.](image)

To calculate the following integral:

\[
I_n = \int_{u^-}^{u^+} \frac{du}{u^2 + G^n}
\]  

(2.22)

We consider the following substitution:

\[
x = \frac{u}{\sqrt{G}} \quad du = \sqrt{G} dx
\]  

(2.23)
Thus, \[ x_1 = \frac{u^+}{\sqrt{G}} \quad x_2 = \frac{u^+}{\sqrt{G}} \] (2.24)

Then the eq. (2.22) becomes:

\[ I_n = \frac{1}{G^{n-0.5}} \int_{x_1}^{x_2} \frac{dx}{(1 + x^2)^n} \] (2.25)

where \[ \int \frac{1}{(1 + x^2)^n} dx = \frac{1}{2n-2} \frac{x}{(1 + x^2)^{n-1}} + \frac{2n-3}{2n-2} \int \frac{dx}{(1 + x^2)^{n-1}} + C \]

when \( n = 1 \), \[ \int \frac{1}{1 + x^2} dx = \tan^{-1} x + C \]

In the case of \( G \) approaches to zero, the eq. (2.25) become undefined. In that case, we take the Taylor series expansion of eq. (2.25) and we will have:

\[ I_3 = -\frac{1}{5} \left[ \frac{1}{(y^+)^5} - \frac{1}{(y^-)^5} \right] - \frac{3G}{7} \left[ \frac{1}{(y^+)^7} - \frac{1}{(y^-)^7} \right] \]

\[ -\frac{2G^2}{3} \left[ \frac{1}{(y^+)^9} - \frac{1}{(y^-)^9} \right] + \frac{10G^3}{11} \left[ \frac{1}{(y^+)^{11}} - \frac{1}{(y^-)^{11}} \right] + O(G^4) \] (2.26)

\[ I_6 = -\frac{1}{11} \left[ \frac{1}{(y^+)^{11}} - \frac{1}{(y^-)^{11}} \right] - \frac{6G}{13} \left[ \frac{1}{(y^+)^{13}} - \frac{1}{(y^-)^{13}} \right] \]

\[ -\frac{7G^2}{5} \left[ \frac{1}{(y^+)^{15}} - \frac{1}{(y^-)^{15}} \right] + \frac{56G^3}{17} \left[ \frac{1}{(y^+)^{17}} - \frac{1}{(y^-)^{17}} \right] + O(G^4) \] (2.27)

Since the calculation of finite cylinder potential involves multistep of integration which takes a long time in computation, especially when the number of molecule in the system is great. To solve this problem, two-dimensional interpolation method has been introduced to calculate the interaction between a molecule and the finite cylinder from the energy database. The energy data is chosen as equal size in both directions, i.e. \( \Delta r = \Delta y = 0.01 \sigma_f \). For a specified radius \( r \) and axial distance \( y \), the potential of the finite cylinder can be calculated by the bilinear interpolation given by

\[ f(r, y) = \left[ 1 - r \right] \left[ f(r^1, y^1) \right] \left[ 1 - y \right] + \left[ r \right] \left[ f(r^2, y^1) \right] \left[ 1 - y \right] \]

\[ + \left[ 1 - r \right] \left[ f(r^1, y^2) \right] \left[ y \right] + \left[ r \right] \left[ f(r^2, y^2) \right] \left[ y \right] \] (2.28)

where \( r^1 \) and \( r^2 \) are the neighbouring bins of \( r \), respective, and \( y^1 \) and \( y^2 \) are the neighbouring bins of \( y \). \( f(r^a, y^b) \) represents the potential energy of the bin \( r^a \) and \( y^b \).
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2.5.3 Fluid-Functional Group Potential

The importance of functional groups on adsorption of associating fluid, especially water has been well reported in a number of studies. In this thesis, the functional groups we considered are carboxyl, hydroxyl and carbonyl groups, which are the most common oxygen-containing groups. Figure 2.8 presents the side view of various surface oxygen groups which are attached to the graphite surface. The potential and geometric parameters of these groups are proposed by Jorge et al.\textsuperscript{110} and listed in Table 2.3 and Table 2.4, respectively.

The pairwise interaction potential energy between a adsorbate molecule and a functional groups is calculated by the sum of the 12-6 Lennard-Jones and Coulomb interactions, as given in eq. (2.8).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2.8}
\caption{Schematic representation of the oxygen-containing functional groups on graphite surface: (a) carboxyl group; (b) hydroxyl group, (c) carbonyl group.\textsuperscript{110}}
\end{figure}

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Interacting site</th>
<th>$\sigma$ (nm)</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$q$ (e)</th>
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</thead>
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<td>0.375</td>
<td>52.0</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>O(=C)</td>
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<td>105.7</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>O(-H)</td>
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<td>85.6</td>
<td>-0.58</td>
</tr>
<tr>
<td></td>
<td>H(-O)</td>
<td>--</td>
<td>--</td>
<td>0.45</td>
</tr>
</tbody>
</table>

C\textsuperscript{a} is the carbon located on the basal plane of graphene layer.
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Table 2.4 Geometric parameters of the adsorbate

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>Bond</th>
<th>Length (nm)</th>
<th>Angle</th>
<th>Degree(°)</th>
</tr>
</thead>
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<tr>
<td>Carbonyl</td>
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<td>--</td>
</tr>
<tr>
<td>Hydroxyl</td>
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<td>C°OH</td>
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<td></td>
<td>O-H</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carboxyl</td>
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<td>C°CO</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
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<td>OCO</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>0.1364</td>
<td>COH</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>0.097</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ca° is the carbon located on the basal plane of graphene layer.

2.6 Measurement from MC Simulation

2.6.1 Adsorption Isotherm

In experiment, the volumetric apparatus report the adsorption isotherm in terms of excess amount, which is the difference between dosing amount in the adsorption cell and the amount that would occupy an apparent volume at the density of the bulk phase.

\[
N_{ex} = N - N_b = N - \rho_b V_{app}
\]  

(2.29)

where \( N \) and \( N_{ex} \) are the absolute and excess amount of adsorbate in the adsorption cell, \( N_g \) is the number of particle occupying the apparent void volume \( V_{app} \) with the bulk gas density, \( \rho_b \).

In experimental procedures, helium is commonly used to obtain the apparent void volume. Experimentally, this is measured by dosing a known amount of helium into the system at temperature \( T_{He} \) where the He concentration is relatively low. The helium void volume, \( V_{He} \), is defined as the one that gives zero excess amount, \( N_{ex}^{He} \approx 0 \):

\[
V_{He} = \int_{\Omega} \exp\left[-\varphi_{He}(r)/k_B T_{He}\right] d\Omega
\]  

(2.30)

where \( \varphi_{He}(r) \) is the helium-solid potential energy at the any position of \( r \) in the system, and \( \Omega \) is the volume of the whole system.

Since some helium adsorbs at \( T_{He} \), \( V_{He} \) is always greater than the actual void volume of the system and that is a function of temperature. The problem of helium adsorption was encountered by
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Malbrunot and co-workers in 1992\textsuperscript{111}, and rectified by high temperature helium expansion in 1997.\textsuperscript{112}

An alternative determination of apparent volume in simulation is proposed by Do et al.\textsuperscript{113,114} with the concept of accessible volume. The accessible volume is defined as the volume accessible to the centre of the mass of a molecule at zero loading.\textsuperscript{115}

The accessible volume is calculated as follows: The centre of mass of a molecule is inserted at a randomly chosen position in the box and then the molecule is given $M$ different orientation (for multi-sites molecules). If all potential energies of these $M$ orientations are positive then that insertion is regarded as failure; otherwise, the insertion is a success. This process is repeated and the accessible volume is calculated as the fraction of success with the volume of the simulation box:

$$V_{acc} = V_\Omega f = V_\Omega \left( \frac{N_{success}}{N_{trial}} \right)$$

(2.31)

where $f$ is the fraction of success with number of success insertion, $N_{success}$, and number of trial insertion, $N_{trial}$, and $V_\Omega$ is the volume of the simulation box.

According to the above method, the surface excess density can be defined as

$$\Gamma = \frac{\langle N \rangle - V_{acc} \rho_G}{S}$$

(2.32)

where $\Gamma$ is the surface excess density, $\langle N \rangle$ is the ensemble average of the number of molecules in the system, $\rho_G$ is the density of gas phase calculated by the equation of state, $S$ is the surface area of the solid.

Similarly, the absolute pore density with respect to the accessible volume is given by:

$$\rho = \frac{\langle N \rangle}{V_{acc}}$$

(2.33)

where $\langle N \rangle$ is the ensemble average of the number of molecules in pore.

2.6.2 Isosteric Heat

Like adsorption isotherm, the measurement of experimental isosteric heat is always performed in the presence of bulk phase. By this means, the physical meaning of isosteric heat is the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the excess adsorbed
amount. In simulation, the fluctuation of thermodynamic properties during a simulation can be used to calculate a number of thermodynamic partial derivatives. The detail derivation can be found in many books about statistical mechanics. In the GCMC ensemble, the isosteric heat can be obtained by applying the thermodynamic fluctuations:

\[ q_{st} = k_B T \frac{f(U, N)}{f(N, N) - N_G} \]  

(2.34)

where \( N_G \) is the number of molecule of an ideal gas that would occupy the adsorption space. Most work on adsorption neglects the second term in the denominator, and the equation is commonly used in the following form:

\[ q_{st} = k_B T \frac{f(U, N)}{f(N, N)} \]  

(2.35)

where \( U \) is the configurational energy of the simulation box and \( N \) is the number of particle. The function \( f \) is defined as \( f(X, Y) = \langle X, Y \rangle - \langle X \rangle \langle Y \rangle \), where the notation \( \langle \rangle \) represents the ensemble average.

The above equation is only applicable with the assumption of ideal gas and smaller molar volume of the adsorbed phase compared to the gas phase. When the contribution of energy mostly comes from gas phase, the denominator in eq. (2.35) will increase and the second term is effectively zero, therefore this equation is invalid for supercritical fluids. A general equation account for the excess isosteric heat is proposed by Do et al. which is available at subcritical and supercritical condition. Here we briefly introduce this method.

First of all, the differential enthalpy of adsorption is defined as the enthalpy change of the system per unit change in the number of particles added to the excess adsorbed phase at a constant temperature and total number of particles.

\[ \Delta h_{ex} = \left( \frac{\partial H}{\partial N_{ex}} \right)_{T,N} \]  

(2.36)

where \( H \) is the total enthalpy of the whole system, and involves the enthalpies of the gaseous reference phase, \( H_g \); the solid adsorbent, \( H_s \); and the excess enthalpy, \( H_{ex} \), given as

\[ H = H_{ex} + H_g + H_s \]  

(2.37)
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Analogous to this, the internal energy, $U$, number of molecules, $N$, and volume of the system, $V$, can be defined by the following.

$$U = U_{ex} + U_g + U_s$$ \hspace{1cm} (2.38a)

$$N = N_{ex} + N_g + N_s$$ \hspace{1cm} (2.38b)

$$V = V_{ex} + V_g + V_s$$ \hspace{1cm} (2.38c)

where the subscripts $ex$, $g$ and $s$ represent the excessed adsorbed phase, gas phase and solid, respectively. Apparently, the number of molecules in solid phase is zero, $N_s = 0$. The excess volume is zero, $V_{ex} = 0$, by virtue of the definition of the system volume being the sum of accessible volume and the solid volume. Furthermore, since the total number of molecules in the system is constant, the number of molecules leaving the gas phase should equal to the number of molecules entering the adsorbed phase, i.e., $dN_g = -dN_{ex}$.

Substituting eq. (2.37) to eq. (2.36), we obtain

$$\Delta h_{ex} = \left( \frac{\partial H_{ex}}{\partial N_{ex}} \right)_T \left( \frac{\partial H_g}{\partial N_g} \right)_T$$ \hspace{1cm} (2.39)

Since $V_{ex} = 0$, the above equation can be rewritten as

$$\Delta h_{ex} = \left( \frac{\partial U_{ex}}{\partial N_{ex}} \right)_T - \left( \frac{\partial U_g + \partial p V_g}{\partial N_g} \right)_T$$ \hspace{1cm} (2.40)

As mentioned above $dN_g = -dN_{ex}$, the above equation can be

$$\Delta h_{ex} = \left( \frac{\partial U_{ex}}{\partial N_{ex}} \right)_T - \left( \frac{\partial p V_g}{\partial N_g} \right)_T$$ \hspace{1cm} (2.41)

Since isosteric heat is defined as the negative of the differential enthalpy of the excess phase, giving a positive value of the isosteric heat, that is

$$q_{st} = -\Delta h_{ex} = \left( \frac{\partial p V_g}{\partial N_g} \right)_T - \left( \frac{\partial U_{ex}}{\partial N_{ex}} \right)_T$$ \hspace{1cm} (2.42)
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For ideal gas, \((\partial pV_s / \partial N_g) = kT\), the above equation becomes \(q_{st} = kT - (\partial U / \partial N_{\text{st}})_T\), which is only applicable for low density adsorption of subcritical fluids.

To compute the excess isosteric heat, eq. (2.42) can be rewritten as

\[
\Delta h_{\text{ex}} = \left[ \frac{\partial U}{\partial (N - N_g)} \right]_T - \left( \frac{\partial pV_s}{\partial N_g} \right)_T
\]  

(2.43)

Introducing the chemical potential and applying the chain rule of differentiation, we will get

\[
\Delta h_{\text{ex}} = \frac{(\partial U / \partial \lambda)_{T}}{(\partial N / \partial \lambda)_{T}} - \frac{(\partial p / \partial \lambda)_{T}}{(\partial N_g / \partial \lambda)_{T}}
\]  

(2.44)

where \(\lambda = \mu kT\), with \(\mu\) being the chemical potential. According to Gibbs-Duhem equation, at constant temperature, \((\partial p / \partial \lambda)_{T} = \rho kT\), the above equation becomes

\[
\Delta h_{\text{ex}} = \frac{(\partial U / \partial \lambda)_{T}}{(\partial N / \partial \lambda)_{T}} - \frac{N_{\text{st}}kT}{(\partial N_g / \partial \lambda)_{T}}
\]  

(2.45)

In grand canonical ensemble, eq. (2.45) can be written in to the form of fluctuation formula

\[
\frac{1}{T}(\partial U / \partial N) = f(U, N) \quad \frac{1}{T}(\partial N / \partial N_g) = f(N, N_g) \quad \frac{1}{T}(\partial N_g / \partial \lambda) = f(N_g, N_g)
\]  

(2.46)

Therefore, the final formula for the isosteric heat is

\[
q_{st} = \frac{N_{\text{st}}k_BT}{f(N_g, N_g)} - \frac{f(U, N)}{f(N, N) - f(N_g, N_g)}
\]  

(2.47)

Unlike the eq. (2.35) which is only valid for subcritical fluids, Do et al.’s approach is very general and unambiguous in its application to both subcritical and supercritical conditions.\(^{116}\)

2.6.3 Henry Constant

The amount of pure component adsorbed on a solid adsorbent at very low loadings can be expressed by the following Henry’s law:

\[
C = K(P / R_gT)
\]  

(2.48)
where $C$ is the surface excess concentration, $P$ is the absolute pressure, $R_g$ is the gas constant, $T$ is the temperature of the system and $K$ is the Henry constant. The Henry constant $K$, is a measure of the interaction between a single molecule and the solid which includes all adsorption sites on the adsorbent and, the strongest sites will dominate the Henry constant.

In simulation, the intrinsic Henry constant can be defined as the ratio of the excess amount to the bulk gas density, which is given by $^{117-119}$:

$$K_{\text{intrinsic}} = \left( \frac{N_{\text{ex}}}{\rho_b} \right) = \int_{\Omega} \exp \left( -\frac{\varphi(r)}{k_B T} \right) \, dr - V_{\text{app}}$$  \hspace{1cm} (2.49)

where $N_{\text{ex}}$ is the surface excess concentration, $\rho_b$ is the bulk phase density, $\Omega$ is the volume of the whole system, $\varphi(r)$ is the fluid-solid potential energy at the any position of $r$ in the system and $V_{\text{app}}$ is the apparent volume.

The determination of apparent volume has been a subject for long. Figure 2.9 shows schematically the difference between the two terms in the integrand on the RHS of eq. (2.49). The first integral is the area under the curve of the Boltzmann factor and the second integral is the area under the horizontal dashed line. When the area of the region I is less than that of region II, which will happen at sufficiently high temperatures, the Henry constant becomes negative, which is not physically acceptable.

![Figure 2.9 Local density distribution versus distance from a solid surface](image)

Figure 2.9 Local density distribution versus distance from a solid surface
Do et al proposed the choice of accessible volume, which is the region II minus the inaccessible region III (shade region). In this definition, the Henry constant is valid for both subcritical and supercritical temperature.  \[ \text{(2.49)} \]

There eq. (2.49) can be written as:

\[
K_{\text{intrinsic}} = \left( \frac{N_{\text{ex}}}{\rho_b} \right) = \int_{\Omega} \exp \left[ -\frac{\varphi(r)}{k_BT} \right] dV - V_{\text{acc}}
\]

(2.50)

where \( V_{\text{acc}} \) is the accessible volume which is calculated by the method in section 2.6.1. The intrinsic Henry constant, \( K_{\text{intrinsic}} \) has units of volume (expressed in nm\(^3\)), and its physical meaning is the volume that would occupy by the adsorbate if the excess amount is allowed to expand to the bulk gas density.

The Henry constant can also be expressed in terms of surface area and volume. The surface Henry constant (\( K_A \)) and volumetric Henry constant (\( K_V \)) are given by:

\[
K_A = \frac{K_{\text{intrinsic}}}{A} = \frac{1}{A} \int_{\Omega} \exp \left[ -\frac{\varphi(r)}{k_BT} \right] dA - V_{\text{acc}}
\]

(2.51a)

\[
K_V = \frac{K_{\text{intrinsic}}}{V} = \frac{1}{V} \int_{\Omega} \exp \left[ -\frac{\varphi(r)}{k_BT} \right] dV - V_{\text{acc}}
\]

(2.51b)

The Henry constant with respect to surface area has units of length (expressed in nm), while the Henry constant with respect to volume is dimensionless.

*Henry constant with respective to a functional group*

The Henry constant between a molecule and functional group \( \alpha \), \( K_{\alpha} \) can be calculated by integrating the Boltzmann factor over the volume space around the functional group and over all possible orientations of the molecules:

\[
K_{\alpha} = \int_{\Omega} \int_{\Omega} \exp[-\beta\varphi(r, \omega)] dV d\omega - \int_{\Omega} \int_{\Omega} H[-\varphi(r, \omega)] dV d\omega
\]

(2.52)

where \( \varphi(r, \omega) \) is the potential energy between an adsorbate molecule at the position \( r \) and orientation \( \omega \) with a functional group grafted at the edge of the graphene layers. \( K_{\alpha} \) has the units of volume (nm\(^3\)).
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2.6.4 Microscopic Analysis

2D Density Distribution

The 2D-density distribution is defined as the local density of a two-dimensional bin:

$$\rho(z, y) = \frac{\langle \Delta N(z, y) \rangle}{L_z \Delta z \Delta y}$$  \hspace{1cm} (2.53)

where $\Delta N(z, y)$ is the number of particles in the bin bounded by $[z, z+\Delta z]$ and $[y, y+\Delta y]$. Bin size in both directions was $\Delta z = \Delta y = 0.1 \sigma_{ff}$. The result was smoothed by averaging the density over a sphere of $0.5 \sigma_{ff}$ radius.

Local Density Distribution

The local density distribution is defined in a similar way as in eq. (2), with density in the $z$- or $y$- direction from the pore wall given by:

$$\rho(z) = \frac{\langle \Delta N(z) \rangle}{L_z L_y \Delta z} \quad \text{or} \quad \rho(y) = \frac{\langle \Delta N(y) \rangle}{L_x L_y \Delta y}$$  \hspace{1cm} (2.54)

where $\Delta N(z)$ and $\Delta N(y)$ are the number of particles in the bin bounded by $[z, z+\Delta z]$ and $[y, y+\Delta y]$, respectively, and $L_x$, $L_y$, and $L_z$ are the dimensions of the pore.

Local Compressibility

Compressibility is defined as the negative of the relative volume change with respect to pressure at constant temperature. In GCMC, local compressibility can be expressed in terms of the corresponding particle number fluctuation $F_k$, as:

$$\kappa = 1 - \frac{1}{V} \frac{\partial V}{\partial p} = \frac{1}{kT \langle \rho_k \rangle} \frac{f(N_k, N_k)}{\langle N_k \rangle} = \frac{F_k}{kT \langle \rho_k \rangle}$$  \hspace{1cm} (2.55)

where $\rho_k$ is the density of bin $k$. $F_k$ is the local number fluctuation. When the gas phase is very dilute, the local number fluctuation approaches unity, i.e. $\lim_{N_k \to 0} f(N_k, N_k)/\langle N_k \rangle = 1$.

Radial Distribution

The radial distribution in the core region $K$ of the pore is defined as the probability of finding the centre of a molecule at a radial distance $r$ from the centre of any given molecule:
\[ g(r) = \frac{\langle \{\Delta N\}_{N_k} \rangle}{\frac{4}{3} \pi [(r + \Delta r)^3 - r^3]} \langle \rho_K \rangle } \] (4)

where \( \{\Delta N\}_{N_k} = \frac{1}{N_k} \sum_{j=1}^{N_k} \Delta N(r \to r + \Delta r) \), \( N_k \) is the number of particles in core region \( K \), \( \Delta N(r \to r + \Delta r) \) is the number of particles in the spherical bin bounded by \([r, r+\Delta r]\) and \( \rho_K \) is the mean density of in core region \( K \).
Chapter 3 Existence of Surface Heterogeneity on GT CB

3.1 Introduction

Adsorption of gases on homogeneous graphite has been extensively studied with both for the purpose of understanding the interaction between an adsorbate and the graphite surface. Graphitized thermal carbon black (GT CB) is commonly considered as an appropriate representative of graphene layers. However, experimental observations suggest that, despite the fact that GT CB presents as polyhedral particles with homogeneous basal planes on the exposed faces, it possesses high energy sites at the junction between the adjacent basal planes, where adsorption occurs predominantly at low loadings. These strong sites could be due to (i) the ultrafine pores at the junctions (crevices) where the adsorption potential field is enhanced by the overlapping of the potential fields from the opposite pore walls, and (ii) the residual polar functional groups which are retained at edge sites at the junctions even after the process of graphitization.

In this chapter, we put forward a molecular model for GT CB, composed of flat basal graphene layers with ultra-fine pores and hydroxyl groups at the junctions. The specific volume of the ultra-fine pores is very small in the sense that if the amount of adsorbate in these pores is spread over the surface it will only account for a small fraction (typically 0.2%) of the monolayer coverage density. Hydroxyl groups were chosen to represent functional groups because experimental evidence suggests that a small quantity of hydroxyl groups is detectable even after thermal treatment\(^{121,122}\). The two analysis tools that we used to investigate the potential of this new molecular model are: (1) The Henry constants for the basal plane of graphite and for the strong sites, obtained by Monte Carlo integration of the Boltzmann factor of the solid-fluid potential energy and (2) Monte Carlo simulations of this model to obtain the isotherm and isosteric heats, especially their behaviour at very low loadings, at which the role of ultra-fine pores and functional groups are important.

3.2 Simulation Model

The model for GT CB with ultra-fine crevices and attached phenol groups is illustrated in Figure 3.1. It is composed of two patches of adsorption sites: (1) the basal plane and (2) crevices with the functional groups. The two basal planes are homogeneous graphene layers, which are finite in the \(x\)-direction and infinite in the \(y\)-direction, and the solid-fluid potential energy was calculated from the Bojan-Steele equation as shown in eq. (2.11). The length of the basal plane in the \(x\)-direction is 40 nm, and that in the \(y\)-direction is 20 times the collision diameter of the adsorbate. The LJ parameters for a carbon atom in a graphene layer are \(\sigma_{ss}=0.34\) nm and \(\epsilon_{ss}/k_B=28\) K. The interlayer
distance between two graphene layers is 0.3354 nm and the surface density of carbon atom in a graphene layer is $\rho_s = 38.2 \text{ nm}^{-2}$.

Figure 3.1 (a) SEM image for GTCB (b) Schematic model of basal planes with a micropore crevice and functional groups. The dimensions of the crevice in the x- and z- directions are width (W) and height (H). (c) Top view of the arrangement of hydroxyl groups attached to edge sites.

Figure 3.2 The edge pore wall of an ultra-fine crevice: (a) Side view of the pore wall: The red dashed lines show the position of pore walls of the ultra-fine crevice. (b) Top view of the pore wall: The red dashed lines show the boundaries of the pore wall.

The ultra-fine pore was modelled as a slit at the junction between the two basal planes. The slit is formed from the gap between two graphene edges; the potential energy of adsorption in such a slit may be modified by anisotropy in the polarizability of graphite. The width and height of the ultra-fine pore were 0.65 nm and 0.7 nm, respectively. The potentials were calculated for a pore with walls consisting of carbon layers having alternating interlayer separations of 0.07 nm and 0.142 nm and a surface density of 18 nm$^{-2}$. Details of how these parameters are estimated as follows. The structure of the edge site of graphite surface is illustrated in Figure 3.2 and the interaction of a fluid particle with the walls of the ultra-fine pore is modelled by the Bojan-Steele potential. From Figure 3.2a, the interlayer distance $\Delta$ of carbon planes (1,2), (3,4) etc. can be calculated as

$$\Delta = \sin 30^\circ \times D_1 = 0.5 \times 0.142 \text{nm} = 0.071 \text{nm}$$

(3.1)
Chapter 3 Existence of Surface Heterogeneity on GTCB

Planes (2,3), (4,5) etc. are separated by 0.142 nm.

The surface plane of the pore wall is constructed as a parallelogram unit cell (Figure 3.2b) and each unit cell contains one carbon atom. Therefore, the surface density is

\[ \rho = \frac{1}{D_2 \times D_3} = \frac{1}{0.246 \text{nm} \times 0.3354 \text{nm}} = 12 \text{nm}^{-2} \]  

(3.2)

As discussed by Deitz, by Meyer and Deitz, and others, the attractive part of the dispersion interaction is modified by the anisotropy of the graphite polarizability. The polarizability of graphite parallel to the graphene planes is about 1.5 times the polarizability normal to the plane and, because the inverse 6th power attractive term in the LJ potential is directly proportional to polarizability, this increases the strength of the attractive interaction at the edges. Since there is no precise geometry for the edge site crevices, and some uncertainty about the effect of anisotropic polarizability on repulsive interactions, we have accounted for this factor by simply increasing the edge density by a factor of 1.5 to 18 nm⁻².

Figure 3.3 shows the solid-fluid potential profile for an argon atom with a deep well in the ultra-fine pore, compared to that for the potential on the flat basal plane of graphene layers.

![Figure 3.3 Solid-fluid potential profile for argon on a basal plane and in an ultra-fine crevice.](image)

The functional groups were modelled as 7 hydroxyl groups grafted onto sites on the top graphene sheet, with a separation between two adjacent groups of 0.492 nm. The same number of hydroxyl groups was also grafted onto the opposite wall.

3.3 Results and Discussion

3.3.1 Adsorption on two patches of adsorption sites

Before discussing the analysis of experimental data, we present some interesting features of the adsorption isotherm that may not have been widely recognised, for a model adsorbent with two
patches of different energy. Following Deitz, we use a dual Langmuir equation to describe adsorption in ultrafine pores and at sub-monolayer coverage on the graphene surface. The implicit assumption in using the dual Langmuir equation is that there is no interaction between adsorbate molecules, and therefore none between molecules on the two types of adsorption site. Although this is a reasonable first approximation, it should be kept in mind that the interaction between molecules on different patches can lead to interesting behaviour, such as the spill over phenomenon, recently proposed by our group, as a possible mechanism for physical adsorption in some systems and not previously recognized.

The dual Langmuir isotherm can be written in the following form:

\[ n = n_1 \frac{b_1 P}{1 + b_1 P} + n_2 \frac{b_2 P}{1 + b_2 P} \]  
(3.3)

with the following constraints:

\[ b_1 \gg b_2 \]  
(3.4a)

\[ n_1 \ll n_2 \]  
(3.4b)

\[ K_1 = n_1 b_1 \gg n_2 b_2 = K_2 \]  
(3.4c)

These inequalities imply that the first site has a stronger affinity for the adsorbate than the second site, but has a much smaller concentration, and that the Henry constant of the first site is greater than that of the second. The patch of high energy sites (the first term in eq. (3.3)) is identified with the ultrafine pores and that of low energy sites with the basal plane of graphene layers.

Figure 3.4 shows isotherms, calculated from eq. (3.3), as \( (n/n_2) \) plotted against pressure on a log-log scale, where the Henry law isotherm would have a slope of unity. The parameters used here, which satisfy eqs. (3.4), were:

\[ b_1 = 10^8, \ b_2 = 100, \ n_1/n_2 = 0.01 \text{ and } 0.1 \]  
(3.5)

The plot has two regions; the first corresponds to the onset of adsorption on the first patch of sites and the second to the onset of adsorption on the second patch. A GTCB adsorbent having ultrafine crevices is expected to show these two distinct regions because of the wide difference in adsorbate
affinity in the crevices and on the basal planes. The dashed line, which is the isotherm for the weaker patch when the strong sites are absent, shows a distinct Henry law region.

![Plot of the dual Langmuir isotherm on a log-log scale.](image)

**Figure 3.4** Plot of the dual Langmuir isotherm on a log-log scale. The upper (blue) solid line is for \( n_1/n_2 = 0.1 \) (strong site is 10% of the weaker), and the lower (red) solid line is for \( n_1/n_2 = 0.01 \) (strong site is 1% of the weaker). The broken line is the isotherm for the weaker patch alone if the strong sites are absent.

We first consider the case where the capacity of the ultrafine crevices is only 1% (bottom solid curve). The Henry law region of the strong sites occurs at relative pressures of less than \( 10^{-9} \), and these sites are saturated when the relative pressure is greater than \( 10^{-7} \). As pressure is further increased the isotherm asymptotically approaches the isotherm calculated for the weaker sites alone (dashed line) and a second Henry law region (with a slope of unity) can be identified. Interestingly when the capacity of the stronger patch is one tenth that of the weaker sites (top curve in Figure 3.4), we observe the Henry region of the strong sites, but the presence this strong patch masks the Henry law behaviour of the weaker sites. This is the reason why the isotherm of gas adsorption on a solid with patches of different energies, but comparable capacities, does not show any Henry law region, a model surface that can be used as a basis for deriving the Freundlich equation. This masking of the Henry law behaviour of progressively weaker sites has not been widely recognized in the literature.

3.3.2 Adsorption of argon on graphite with ultra-fine pores

We now turn to the comparison between the simulation results for adsorption of argon on a graphite surface with ultra-fine pores (crevices) and the experimental data on mineralogical graphite from Lopez - Gonzalez *et al.*\(^{128}\). We carried out *GCMC* simulations for several combinations of the pore dimensions (width and depth), and found that an ultrafine pore with width and depth of 0.65 nm and 0.67 nm, respectively and a length of 40 nm (which accounts for a pore capacity of around 2% of the monolayer concentration on the basal plane) gives good agreement between the *GCMC*
simulation results and the experimental data as shown in Figure 3.5. Allowing for possible large errors in the measurements at very low pressures and the possibility of a distribution of crevice size in the graphite, this can be regarded as an excellent agreement between simulation and experiment.

![Figure 3.5 Adsorption isotherms of argon at 90K on a graphite surface with ultra-fine pores. The width of the model pore is 0.65nm and its depth is 0.7nm. The open circles are taken from experimental data for graphitized carbon black (mineralogical graphite).](image)

A comparison of Figure 3.5 with Figure 3.4, shows that both the simulation results and the experimental data of Lopez - Gonzalez et al. show two distinct Henry law regions. The range of the reduced pressure in the first region is less than $10^{-6}$ and in the second region is between $10^{-4}$ and $10^{-3}$. The possible origin of the strong sites, as suggested in the introduction and highlighted by our model, is either ultra-fine pores or functional groups. However, argon has no electrostatic charges and therefore cannot interact with charges on a functional group; furthermore, since the concentration of the functional groups would be very low any enhancement of the dispersive interaction between argon and a functional group will be negligible, compared to its dispersive interaction with the carbon of the ultrafine pores. The remaining explanation for the presence of strong sites, observed in the experimental data of Lopez - Gonzalez et al., must therefore be due to ultrafine pores. This is supported by the SEM and TEM data for GTCB 41, 129, 130 which clearly show basal plane faces forming the surface of polyhedra, and leads to the conclusion that the ultrafine pores must be at the junctions between these basal planes. The second Henry law region, is due to adsorption on the basal planes of the graphene layers, as confirmed by the fact that the experimental Henry constant of this region agrees well with the theoretical value (calculated from eq. (2.52)) for argon adsorption on a perfect graphite surface.

Between the two Henry law regions, there is a plateau that spans a wide range of pressure (because of the very different affinities of the two sites) and the adsorption capacity associated with this plateau is the saturation capacity of the strong sites. Given the adsorption capacity at this plateau,
taken from Figure 3.5 of the data of Lopez - Gonzalez et al.\textsuperscript{128}, of 0.01 cc(STP)/g, and assuming the argon adsorbate in the ultrafine pores to be liquid-like at saturation (with a density of 1.4 g/cc) we estimated the pore volume of the ultrafine pores to be $1.3 \times 10^{-5}$ cc/g. This is very small compared to a typical pore volume for porous carbons, which is of the order of 0.3 cc/g. To get a better estimate of the relative contribution to the overall adsorption capacity, from the ultrafine pores we compared it with the monolayer density of argon on a graphite surface of $11 \mu\text{mol/m}^2$ and find that the ultrafine pores (strong sites) amount to no more than 2% of the monolayer capacity.

Further confirmation of the role played by these strong sites in argon adsorption is given in Figure 3.6a, where we show plots of the isosteric heat versus loading for argon adsorbed on our graphite model at 90K (filled symbols). Our first observation is that this heat curve is very different from the heat curve for argon adsorbed on a basal graphite surface (shown as a dashed line). The enhancement of the heat, compared to that on a graphite surface, is due to the ultrafine pores, and shows that even a small concentration of strong sites (ultrafine pores) has a significant impact on the heat curve. Similar heat curves have been reported in many earlier experimental papers\textsuperscript{22,131-133}. Figure 3.6a also shows the separate contributions from the solid-fluid interaction and the fluid-fluid parts of the energy. The isosteric heat at zero loading is much higher (17.7 kJ/mol) than that for adsorption on a basal graphite surface (9 kJ/mol)\textsuperscript{117}, and as loading increases the heat remains constant up to Point A on the isotherm in Figure 3.5, where the loading is 2% of the monolayer coverage. The constant heat up to Point A is due to the balance between the decrease in the solid-fluid interaction and the increase in the fluid-fluid interaction in the ultrafine pores. The separated heat curves also show that the enhancement of the heat, compared to the graphite surface, comes mainly from the deep potential well in the ultrafine pores (see Figure 3.3). As loading is further increased to Point B, the isosteric heat decreases steeply because the ultrafine pores have been filled with adsorbate and adsorption begins to build up on the basal planes. As the loading on the basal plane increases there is an increase in the heat up to Point D on the isotherm; this is due to the constant solid-fluid interaction in the sub-monolayer and the approximately linear increase in the fluid-fluid interaction, and is typical of adsorption of simple gases on graphitic surfaces. Beyond Point D, adsorption begins in the second layer and the heat decreases because of the reduction in the solid-fluid interaction for molecules further away from the surface.
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Figure 3.6 (a) Simulated isosteric heat of argon adsorption on graphite surface with ultra-fine crevices at 90K. (b) Isosteric heat for argon on mineral graphite at 90K from Lopez-Gonzalez et al.

Figure 3.6b shows the experimental isosteric heat for argon adsorption on mineral graphite at 90K from Lopez-Gonzalez et al., and we see that this heat curve has a pattern very similar to the simulated heat curve presented in Figure 3.6a. Therefore we can tentatively conclude from the analysis of the isotherm and the heat curve versus loading that the molecular model of basal plane with ultrafine pores at the junction of the basal planes is suitable to describe the experimental data and suggests that GTCB has ultrafine pores at the junctions of the basal planes of the polyhedra after the GTCB has been graphitized at 2700°C.

Figure 3.7 shows snapshots taken from the simulations at various points marked in Figure 3.5, and add further support to the foregoing discussion.
Chapter 3 Existence of Surface Heterogeneity on GTCB

Figure 3.7 Snapshots of argon molecules on a surface with an ultra-fine crevice: (a) Point A; (b) Point B; (c) Point C; Point D. The points are as labelled in Figure 3.5. The grey shaded region is the adsorbent solid. The snapshots in (a’), (b’), (c’) and (d’) are 3D version of (a), (b), (c) and (d), without the graphene layers plotted.

3.3.3 Adsorption of other adsorbates on GTCB

It is now clear that the ultrafine pores in GTCB are strong sites for argon adsorption, and our next goal is to enquire whether they have the same significance for other adsorbates? To address this question, we considered a range of adsorbates with increasingly strong electrostatic interactions from nitrogen and carbon dioxide through to ammonia and water which form associating fluid phases. The adsorption isotherms for these adsorbates with our model of composite basal plane and ultrafine pore are shown in Figure 3.8a on log-log scales which highlight the adsorption at low loadings, and in Figure 3.8b on linear scales to better compare different adsorbates at higher loadings. To quantify the strength of adsorption of the two different adsorption sites we present in Table 3.1 the Henry constants for three systems:

1. a plane surface of pure graphite,
2. a surface with an ultrafine pore and
3. a surface with an ultrafine pore grafted with functional groups.

Figure 3.8 Adsorption isotherms of different adsorbates on the model graphite surface with an ultrafine micropore: (a) logarithmic scale; (b) linear scale.
Chapter 3 Existence of Surface Heterogeneity on GTCB

Table 3.1 Comparison of the Henry constants on the surface of pure graphite, a graphite surface with an ultrafine pore and a graphite surface with an ultrafine pore grafted with hydroxyl groups

<table>
<thead>
<tr>
<th>Fluid</th>
<th>basal plane (nm)</th>
<th>surface with crevice (nm)</th>
<th>surface with crevice and hydroxyl groups (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar at 87K</td>
<td>$1.2 \times 10^4$</td>
<td>$2.3 \times 10^6$</td>
<td>$2.6 \times 10^9$</td>
</tr>
<tr>
<td>N$_2$ at 77K</td>
<td>$6.8 \times 10^4$</td>
<td>$3.3 \times 10^7$</td>
<td>$3.7 \times 10^7$</td>
</tr>
<tr>
<td>CO$_2$ at 210K</td>
<td>$9.5 \times 10^2$</td>
<td>$8.3 \times 10^3$</td>
<td>$1.2 \times 10^4$</td>
</tr>
<tr>
<td>NH$_3$ at 195K</td>
<td>48</td>
<td>103</td>
<td>$1.3 \times 10^5$</td>
</tr>
<tr>
<td>H$_2$O at 298K</td>
<td>1.6</td>
<td>1.65</td>
<td>285</td>
</tr>
</tbody>
</table>

For N$_2$ and CO$_2$, the adsorption proceeds in the same way as described earlier for argon, through a two-stage uptake of adsorbate at low pressures. We can tentatively conclude that for non-associating fluids, adsorption initially occurs in the ultrafine pores because the Henry constant for a graphite surface with ultrafine pores is much greater, by three orders of magnitude (column 3 of table 3.1), than that of a pure graphite surface (column 2).

For NH$_3$, by contrast, the dispersion interactions are quite weak and the Henry constant for the graphite surface with ultrafine pores is only twice that for the planar surface, but it is 3000 times greater when the crevices are grafted with functional groups. Therefore adsorption occurs initially around the functional groups, which act as nucleation sites for ammonia molecules to form clusters which then grow as pressure is increased until ammonia molecules spill-over onto the graphite basal planes because the interaction between ammonia molecules (primarily electrostatic interactions), and the interaction of ammonia with the graphite surface are of comparable magnitude $^{119}$. For the same reason, the second Henry law region, corresponding to the molecular layering on the basal plane, and seen with the electrostatically weaker adsorbates, is absent.

The adsorption experiments of Easton and Machin $^{134}$ for water on highly graphitized thermal carbon black show that adsorption does not occur at pressures lower than the saturation vapour pressure $^{134}$ because, like ammonia, the dispersion interaction between water and basal plane is very weak. This is confirmed by a number of simulation studies of water on basal graphite surfaces $^{110, 135, 136}$. In this study our simulations show that water does not adsorb at all on a graphite surface with an ultrafine pore, at pressures below the saturation pressure. Even with the enhancement of the potential in the ultrafine pores, the dispersion interactions are not strong enough to induce water adsorption at pressures lower than the saturation vapour pressure.
3.3.4 The importance of functional groups

In the introduction we argued that the most probable location for the functional groups is at the edges sites on the walls of ultrafine pores formed at the junctions of the adjacent basal planes, and it is expected that the synergistic effects of two strong sites acting on one molecule is greater than twice the interaction between one site and one molecule. To examine this argument, we added 14 hydroxyl groups at the exposed edge sites to give a ratio of 0.1% of O/C for the functional groups. The simulated adsorption isotherms for the different adsorbates considered in this work are shown in Figures 3.9a, b on log-log scales and linear scales, respectively.

The presence of hydroxyl groups makes an insignificant contribution to the adsorption of the adsorbates with weak or no electrostatic interactions (argon, nitrogen and carbon dioxide), in agreement with the Henry constants reported in Table 3.1, because the dispersive interaction with the functional groups is very small compared to that from the walls of the ultrafine pore.

In contrast the theoretical Henry constant of ammonia on a surface with an ultrafine pore grafted with functional groups is three orders of magnitude greater than when the functional group is absent. The enhancement is due to the electrostatic interaction between ammonia and functional groups. The onset of adsorption is observed at around $P/P_0=0.5$ which is in good agreement with experimental observation 137. Like ammonia, the Henry constant of water is around 200 times larger due to the presence of functional groups and the adsorption of water occurs at pressures close to the saturation vapour pressure. This indicates clearly that functional groups play an important role in the adsorption of water on GTCB.

![Figure 3.9](image_url) Adsorption isotherms for different adsorbates on a graphite surface with an ultrafine pore and hydroxyl groups: (a) logarithm scale. For comparison, the isotherms with no hydroxyl groups are shown as open symbols.
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3.4 Conclusion

In this Chapter we have presented a comprehensive simulation study, using grand canonical Monte Carlo simulation and Monte Carlo integration, of the adsorption of a range of adsorbates with increasing strength of electrostatic interaction on GTCB. The adsorbent was modelled as a composite of a basal graphite surface with an ultrafine pore grafted with functional groups at the edges of the graphene layers. For argon, we found two Henry law regions at extremely low relative pressures as observed experimentally by Deitz et al.\textsuperscript{35,128} and the isosteric heat curves were also in general agreement with these experiments. Similar results for nitrogen and carbon dioxide provide further evidence for the importance of ultra fine pores in the adsorption of weakly electrostatic adsorbates. However, for adsorbates with strong electrostatic multipoles but weak dispersive interactions, such as ammonia or water, the functional groups are shown to play a vital role in adsorption \textit{on} GTCB.
4.1 Introduction

In Chapter 3, we proposed a molecular model for GTCB which is composed of flat basal planes with ultrafine pores and hydroxyl groups at the junctions. Our simulation results successfully explained the experimental data of Lopez-Gonzalez \(^\text{128}\) confirming the existence of strong sites on GTCB. In the present work, we use this model to study ammonia adsorption at its triple point (195K) and boiling point (240K), and our simulation results are compared with the experimental data of Holmes and Beebe \(^\text{56}\). We place particular emphasis on microscopic and mesoscopic adsorbate configurations and their behaviour with temperature, in order to elucidate the mechanism of ammonia adsorption.

4.2 Simulation Model

The significance of the contribution from the ultra-pore, at the junction between two adjacent sets of graphene layers, to the adsorption of non-associating fluids and associating fluids on carbon material has been investigated in Chapter 3. In this study, we introduce a wedge shape ultra-pore with an angle \((\alpha = 30^\circ)\) at the junction between two basal planes. The width \((W)\) and height \((H)\) of the pore are 1.38nm and 1.94nm, respectively.

![Schematic model of basal planes with micropore crevice and functional groups at the junction. The grey area is the non-accessible region.](image)

The functional groups considered in this study are hydroxyl groups grafted at the end of the top 4 graphene layers (Figure 4.2). The distance separating two hydroxyl groups on the same graphene layer is 0.984nm which is four times the distance between two neighbouring carbon atoms at the edges (0.246nm). The parameters for the hydroxyl groups were based on those given by Mooney et al. for phenol \(^\text{138}\): the collision diameter and the reduced well depth for the oxygen atom are 0.307nm and 78.2K, the partial charges on the C, O and H atoms are 0.2e, -0.64e and 0.44e,
respectively, the OH and CO bond lengths are 0.096nm and 0.1364nm, and the angle of COH is 110.5 degree.

During the simulation process, a functional group is selected randomly at the end of each cycle and it is rotated around the C-O sigma bond. The rotation angle is selected randomly between 0 and $2\pi$. The change in the total potential energy is equal to the difference between the potential energy of the selected hydroxyl group (say, $k$th functional group) and all $N$ molecules in the simulation box before and after the rotation:

$$
\Delta U = U^{(\text{new})} - U^{(\text{old})} = \sum_{i=1}^{N} \phi_{i,k}^{(\text{new})} - \sum_{i=1}^{N} \phi_{i,k}^{(\text{old})}
$$

(4.1)

where $\phi_{i,k}$, calculated from eq. (2.8), is the pairwise interaction energy between the selected hydroxyl group ($k$) and an ammonia molecule $i$.

![Figure 4.2 Schematic model showing the locations of the hydroxyl groups at the edge of a graphene layer.](image)

### 4.3 Experiment Method

A highly graphitized carbon black, Carbopack F (supplied by Supelco, USA) was used in this study. Nitrogen adsorption on Carbopack F was measured at 77 K using a high resolution volumetric adsorption apparatus (BELSORP-max, MicrotracBEL). Ammonia adsorption was also measured using the same apparatus at 194 and 227K. The samples were degassed at 473K for 5h under vacuum at pressure less than 0.1mPa to remove any physically adsorbed amount before each measurement. The isosteric heat of ammonia adsorption on Carbopack F was calculated by applying the Clausius-Clapeyron equation on the isotherms data at the two adsorption temperatures.
4.4 Results and discussion

4.4.1 Adsorption of ammonia at the triple point (195K)

The simulated isotherm for ammonia adsorption on our GTCB model at the triple point, 195K, is presented in Figure 4.3a, and the experimental data on carbon black (Sterling MT 3100) taken from Holmes and Beebe and our measurement results on Carbopack F are shown in Figure 4.3b.

![Graph of adsorption isotherms for ammonia on GTCB at 195K](image)

**Figure 4.3** Adsorption isotherms for ammonia on GTCB at 195K: (a) simulation results (b) experimental data of Sterling MT 3100 and Carbopack F. The filled circles represent the adsorption branch and unfilled circles are the desorption branch.

It is important to note that Sterling MT 3100 is a highly graphitized carbon black prepared by thermal treatment at 3100°C, followed by hydrogen treatments at 1000°C five times, and as result it possesses highly homogeneous graphitic surfaces with a BET area of 6.3 m²/g. Carbopack F is also a highly graphitized carbon black and its BET area is 4.9 m²/g, and it is expected that the Sterling MT 3100 of Holmes and Beebe is more homogeneous because of their additional hydrogen treatment.

As seen in Figure 4.3a and b, the simulation results are in good qualitative agreement with the experimental data and capture the essential features of the experimental isotherm: low loadings at P/P₀ less than 0.45, followed by a steep 2D condensation and a gradual increase in the adsorbed amount after the condensation. As shown in the inset in Figure 4.3a, the adsorbed amount from the simulation just before condensation is around 1 μmol/m², which is only 7% of the theoretical monolayer concentration of ammonia on a surface (14 μmol/m²). On the other hand, the experimental adsorbed amounts at low relative pressures are different on Sterling MT 3100 and Carbopack F. The adsorbed amount of Sterling MT 3100 is similar to the molecular simulation results, because the sample was pre-treated by hydrogen at a high temperature. The adsorbed
amount on Carbopack F is 3 times higher than that on Sterling MT 3100 over the low pressure region, indicating that the functional group concentration in Carbopack F is 3 times higher than that of Sterling MT 3100. The isotherm in Figure 4.3 is Type III in the Brunauer classification, typical of those generally observed for associating fluids such as water, ammonia and methanol. It shows a clearly defined inflexion point at the onset of adsorption which occurs at higher relative pressure for the more strongly associating fluids (0.2, 0.45 and 0.9 for methanol, ammonia and water, respectively). As the reduced pressure is increased to about 0.5 the adsorption uptake increases rapidly to 20μmol/m² due to the 2D condensation occurring on the graphite surface. We note especially that both the experimental data and the simulation results show that this adsorbed amount, just after the condensation, is more than 40 per cent of the monolayer density. This suggests that more than one layer has condensed above the surface. As will be seen later this is a bilayer adsorption where two layers can form at the condensation stage and is distinct from the 2D condensation of simple gases, such as argon, nitrogen and ethylene. This bilayer formation occurs for ammonia because of the hydrogen bonding due to the strong electrostatic interaction between hydrogen and nitrogen in ammonia. Another distinguishing feature is that both experimental and simulation isotherms exhibit hysteresis; this again can be attributed to the strong interaction between ammonia molecules. To our best knowledge, this is the first time that hysteresis has been observed for adsorption of ammonia on a graphite surface by computer simulation.

To shed further light into the origin of the hysteresis, we show in Figure 4.4 and 4.5 snapshots at the points marked in Figure 4.3a along the adsorption and desorption branches.
Figure 4.4 Snapshots of ammonia at 195K on the GTCB surface with ultra-pores and hydroxyl groups during adsorption, the labels correspond to the points marked in Figure 4.3a. The left panel (A-D) shows the top view and the right panel (A‘-D‘) shows the side view.

At very low loadings, ammonia molecules adsorb predominantly around the hydroxyl groups to form primary clusters, whose electrostatic interactions with functional groups are much stronger than the deep dispersive potential well formed by overlapping interactions from the walls of the ultrafine pores\(^5^4,\,1^3^9\). Once these primary clusters have formed, they act as nucleation sites for further ammonia adsorption and the formation of larger clusters. As the loading is increased, the clusters merge with neighbouring clusters to fill the ultrafine pores (Point A). When the reduced pressure has reached the condensation reduced pressure of 0.45, ammonia molecules begin to spill over onto the basal plane (Point B), as a result of the combination of the FF interaction with the clusters and the SF interaction with the basal plane. This spill-over mechanism was first proposed by Do et al.\(^1^1^9\), and this computer simulation is the first time it has been advanced as an explanation of ammonia adsorption on a graphite surface. The strong uptake of ammonia at this stage is a striking demonstration of the FF interaction between newly adsorbed ammonia molecules and the clusters around the functional groups and the fluid-basal plane (F-BP) interaction, which becomes more important at higher temperatures, as entropic effects increase (Section 4.4.2). A further rise in pressure leads to bilayer condensation on the graphite surface at Point C. When the bilayer formation is completed, the FF interaction dominates the other interactions and further layers condense as pressure is increased to point D.
Chapter 4 Adsorption of Ammonia on GTCB

Figure 4.5 Snapshots of ammonia at 195K on graphite surface with ultra-pore and hydroxyl groups during desorption; labels correspond to the points marked in Figure 4.3a. The left panel (E-G) shows the top view and the right panel (E’-G’) shows the side view.

When desorption starts from point E, where three layers have been formed on the surface, we observe that molecules are desorbing gradually from the third and second layers, along the desorption branch. As desorption of molecules from the first layer begins, the desorption branch traces a different path from the adsorption branch, giving a hysteresis loop, the molecular origin of which is the strong cohesion of molecules in the first layer. The cohesiveness apparently increases with the amount of adsorbate present prior to desorption.

To shed further light on the enhancement of the first layer cohesiveness, we present in Figure 4.6 the local density distributions of ammonia above the basal plane at various points along the adsorption branch. It is clear immediately that, after the condensation has occurred, two layers are formed on the surface, from a negligible loading at Point B to a bilayer loading at Point C, where 45% of the second layer is covered with adsorbate. As the pressure is further increased, the first and second layers are completely filled and, most importantly, the first peak of the local density distribution (the first layer) becomes sharper and more distinct, indicating an increase in cohesion between molecules in the first layer. This is the microscopic origin of the hysteresis observed for the first layer.
4.4.2 Adsorption of ammonia at the boiling point (240K)

To improve our understanding of bilayer condensation and spill-over, we studied ammonia adsorption at its boiling point (240K). The simulated and experimental isotherms are shown in Figures 4.7a and b, respectively and the snapshots for various points are shown in Figure 4.8.

Compared with the simulated isotherm at the triple point (195K), the isotherm at 240K exhibits the following features:

(i) The adsorbed amount before the 2D condensation is higher at 240K: 2μmol/m², compared to the 1μmol/m² at 195K. A similar increase before the condensation was also observed for Carbopack F, where the adsorbed amounts were 4μmol/m² and 6μmol/m² at 195K and 240K, respectively. This indicates that adsorption occurs in both the ultrafine pores and on the basal planes, and is enhanced by the augmented entropic effect at the higher temperature.

(ii) The condensation at both temperatures occurs at the same reduced pressure. The values for $P_0$ at 240K and 195K were taken from the extrapolated simulation results$^{100}$. 

(iii) The adsorbed amount immediately after the condensation is around 12μmol/m² at 240K for both simulated results and experimental data, compared to the monolayer coverage of 14μmol/m², indicating that less than one layer is formed initially, in contrast to the bilayer adsorption that occurs at 195K.

(iv) There is no hysteresis, which suggests that the increase in cohesiveness of the first layer only occurs at temperatures below the triple point.

Figure 4.6 Density distribution from the basal plane of ammonia at 195K as a function of pressure.
Chapter 4 Adsorption of Ammonia on GTCB

Figure 4.7 Adsorption isotherm for ammonia on GTCB model at 240K: (a) simulation results (b) experimental data of Carbopack F. The filled circles are adsorption points and unfilled circles desorption points.

Figure 4.8 shows snapshots of configurations at pressures just before (B2) and just after (C2) the condensation. Compared to the snapshots at 195K, the ammonia molecules are more delocalised due to their higher kinetic energy. Even at pressures just before the 2D condensation (B2) ammonia molecules adsorb on the basal plane in the form of clusters (highlighted as red circles), in conjunction with adsorption on the functional groups. This is an entropic effect, and because of this there is no spill-over phenomenon similar to that which occurred at the triple point, where the FF interaction and the F-FG interaction are balanced. The first layer is not completely filled with adsorbate after the 2D condensation (C2), due to the high mobility of ammonia at this temperature.

Figure 4.8 Snapshot of ammonia at 240K on the GTCB model adsorbent. The labels correspond to the points marked in Figure 4.7.

To further substantiate the above observations, we show in Figure 4.9 the local density distribution of ammonia above the basal plane. At Point B2, just prior to condensation, the first layer is clearly present, in contrast to adsorption at 195 K (Figure 4.6). Just after the condensation there is a sharp increase in the first layer concentration, and a small peak in the second layer, showing that...
adsorption does occur in the second layer even though only 70% of first layer is covered. As the pressure is further increased the first layer becomes denser and the second and higher layers are loaded with more molecules; multi-layering proceeds with greater overlap between peaks associated with higher layers; i.e. there is less structure in the adsorbate.

![Graph showing local density distribution of ammonia above the basal plane at 240 K.](image)

**Figure 4.9** Local density distribution of ammonia above the basal plane at 240 K.

To quantify the cohesiveness of the adsorbate further, we show the 2D compressibility at 195K and 240K in Figure 4.10. Before the 2D condensation at the triple point (195 K) the compressibility of the adsorbate on the basal plane is of the order of $10^{-5}$Pa$^{-1}$, and that in the small region close to the ultrafine pore is two orders of magnitude lower ($10^{-7}$Pa$^{-1}$). This indicates that the onset of condensation on the basal plane occurs by the spill-over mechanism. However, prior to condensation at 240 K (Point B2), the compressibility of the adsorbate on the basal plane is significantly lower ($10^{-7}$Pa$^{-1}$) because the ammonia molecules start to adsorb on the graphite surface in the form of clusters. After the condensation, bilayer formation occurs at 195 K and the corresponding compressibility is decreased to $10^{-10}$Pa$^{-1}$, due to the strong FF interaction (hydrogen bonding). On the other hand, the compressibility of adsorbate just after the condensation at 240 K ($10^{-9}$Pa$^{-1}$) is an order of magnitude greater, due to the increase in thermal fluctuation.
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Figure 4.10 2D compressibility of ammonia on the basal plane. The labels correspond to the points marked in Figure 4.3a and 4.7.

4.4.3 Isosteric heat of adsorption for ammonia on GTCB

Figure 4.11 Isosteric heat of ammonia adsorbed on graphite: (a) simulation results at 240K; (b) experimental data of Sterling MT 3100 and Carbopack F. The dashed line is the heat of condensation for ammonia obtained from GEMC simulations.

Figure 4.11a shows the simulated isosteric heat at 240K versus loading, and the experimental data for Sterling MT 31003 and Carbopack F are shown in Figure 4.11b. To gain further insight, the simulated isosteric heat is decomposed into contributions from FF, F-BP and F-FG interactions. The simulated isosteric heat at zero loading is 32 kJ/mol, in excellent agreement with the experimental heat of Sterling MT 3100 of 30 kJ/mol, and both values are higher than the heat of condensation (shown as a dashed line). This enhancement is due to the strong interaction between the partial charges on the ammonia molecules and the functional groups at the edge of the basal plane. As the loading is increased, the isosteric heat decreases rapidly to a minimum of 16.6 kJ/mol due to the growth of ammonia clusters for which the F-FG contribution diminishes sharply and the increase in the FF contribution cannot compensate. The experimental minimum, in the heat curve for Carbopack F, is at 12 kJ/mol. This behaviour is also observed for the adsorption of methanol...
and water on Carbopack F, and can be regarded as a fingerprint for an associating fluid. However, there is no minimum in the experimental data for Sterling MT 3100 which show a monotonic decrease with loading, possibly because the discrete measurements were not fine enough to detect the minimum. Beyond the minimum, there is a further increase in the heat, mainly due to the FF interaction and the heat eventually reaches the heat of condensation (24kJ/mol).

4.5 Conclusion

We have presented a comprehensive simulation and experimental study of ammonia adsorption on GTCB close to the triple point (195K) and the boiling point (240K). The Monte Carlo simulations were made in the grand canonical ensemble using a new molecular model for GTCB. The model is a composite of two sets of graphene layers joined at an ultrafine pore, which is grafted with functional groups at its edges. We observed good qualitative agreement between simulation and experimental data: At the triple point, we found that the ammonia molecules first adsorb on the functional groups in the ultrafine pore but that insignificant adsorption occurred on the basal plane, due to the dominance of F-FG interaction over F-BP interaction. Once the ultrafine pore has been filled, ammonia molecules spill-over onto the basal plane and instantly two layers are formed on the basal plane because of the strong FF interaction (hydrogen bonding). At this temperature, hysteresis was observed experimentally. For the first time in the literature, this hysteresis has been reproduced by simulation and is attributed to restructuring of the adsorbate in the first layer. At the boiling point, the adsorption process is different; adsorption occurs on the basal plane as well as around functional groups before the 2D condensation and only one layer is formed after the condensation because of the disordering due to the thermal fluctuations. The simulated isosteric heat has been decomposed into contributions from various interactions; we found that the heat is very high at zero loading due to the strong F-FG interaction; then decreases steeply, when the functional groups are saturated, and eventually reaches the heat of condensation because of the increasingly dominant FF interaction.
Chapter 5 Characterization of Functional Groups on GTCB

5.1 Introduction

Boehm titration is valuable widely used technique to detect and quantify the functional group concentration on carbon surfaces. It is the most frequent use stems from its relative simplicity and the fact that it is inexpensive compared to spectroscopy analysis. However, the method is time consuming and may modify the surface chemistry of the adsorbent. More importantly, it is subject to large errors when the functional groups are at low concentrations. There is therefore a need for a new method that circumvents these problems.

In this chapter, we proposed an alternative method that meets this need based on the adsorption of strong associating fluid such as water on activated carbon. At low enough pressures the interaction between water and the adsorbent surface is dominated by the functional groups, and the strength of this interaction is described by the experimental Henry constant ($K$). The theoretical Henry constant ($K_\alpha$) for a specific group, can be determined from a volume integration of the Boltzmann factor over the rotational coordinates and the accessible space around the group. Knowing the experimental Henry constant $K$ and the intrinsic single-site constant $K_\alpha$, the functional group concentration ($C_\alpha$) is simply calculated as $C_\alpha = K/K_\alpha$. This new method is easy to implement and has been found to give good agreement with concentrations measured on an active carbon by Boehm titration.

5.2 Experimental

5.2.1 Materials

Two carbons with widely different concentrations of functional groups and porous structure were chosen: (1) A5 (supplied by Ad’all Co. in Japan) which is a porous activated carbon with high concentrations of functional groups and (2) a highly graphitized thermal carbon black, Carbopack F (supplied by Supelco, USA), which is highly homogeneous and non-porous, and has very low concentrations of functional groups. The BET surface area, which is obtained from the nitrogen isotherm at 77K, for A5 and Carbopack F are 510m$^2$/g and 4.9m$^2$/g, respectively.

5.2.2 Measurement

Water and methanol adsorption were measured at temperatures in the range between 263K and 298K using a constant volume adsorption apparatus (BELSORP-max, BEL Japan); for each point on the isotherm, we used an equilibrium time of 300s with 0.3% error in pressure measurement to define an (quasi) equilibrium. The samples were degassed at 473K for 5h under vacuum at pressures less than 0.1mPa to remove any physically adsorbed components before each measurement.
The concentrations of surface functional groups for each carbon were measured by Boehm titration and are listed in Table 5.1. Only carboxylic and phenolic groups were detected in A5 and Carbopack F. For A5 carbon, approximately 0.1g of solid was added to excess (100cm$^3$) standard base solution (0.01N NaOH, 0.001N Na$_2$CO$_3$, and 0.001N NaHCO$_3$), and the acidic oxides on the surface were determined by back-titration with HCl after allowing the mixture to stand for 48 hours at 298K. For Carbopack F, larger quantity (1g of solid) was used because of the low concentrations of functional groups.

Table 5.1 Concentrations of functional groups on A-5 and Carbopack F from Boehm titration

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Carboxylic (mmol/g)</th>
<th>Lactonic (mmol/g)</th>
<th>Phenolic (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>0.103</td>
<td>0.000</td>
<td>0.184</td>
</tr>
<tr>
<td>Carbopack F</td>
<td>0.019</td>
<td>0.000</td>
<td>0.054</td>
</tr>
</tbody>
</table>

5.3 Simulation

5.3.1 Henry’s law

Henry’s law expresses the amount adsorbed on the surface of a solid at very low loadings as a linear function of the bulk gas concentration, given in eq. (2.48):

5.3.2 Experimental Henry constant

Figure 5.1 Adsorption isotherms of methanol on A5 at different adsorption temperatures, 263, 283 and 298K, plotted against the relative pressure.
Chapter 5 Characterization of Functional Groups on GTCB

For water and methanol adsorption on carbons, the oxygen containing functional groups are much stronger sites than the basal plane of the graphene layers. At low concentration the adsorbate will be localised in the region of these groups and the weaker interaction with the basal carbon atoms can be neglected. Therefore, to an excellent approximation, the Henry constant $K$ is a measure of the interaction between the adsorbate molecule and all the functional groups. The adsorption isotherms of methanol on A5 are shown in Figure 5.1 and those for methanol and water on Carbopack F are shown in Figure 5.2. The insets in these figures depict isotherms plotted on

<table>
<thead>
<tr>
<th>$K$ for Methanol on A-5</th>
<th>263K</th>
<th>273K</th>
<th>283K</th>
<th>298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>K for Methanol on Carbopack F</td>
<td>$1.20\times10^{-5}$</td>
<td>$7.85\times10^{-6}$</td>
<td>$5.97\times10^{-6}$</td>
<td>$2.09\times10^{-6}$</td>
</tr>
<tr>
<td>$K_a$ for Methanol (Dihedral angle:180°)</td>
<td>1318.61</td>
<td>833.75</td>
<td>631.86</td>
<td>214.48</td>
</tr>
<tr>
<td>$K_a$ for Methanol (Dihedral angle:90°)</td>
<td>10595.00</td>
<td>2962.57</td>
<td>1999.39</td>
<td>887.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$K$ for Water on Carbopack F</th>
<th>263K</th>
<th>273K</th>
<th>283K</th>
<th>298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>K for Water (Dihedral angle:180°)</td>
<td>$3.55\times10^{-5}$</td>
<td>$2.54\times10^{-5}$</td>
<td>$1.99\times10^{-5}$</td>
<td>$1.30\times10^{-5}$</td>
</tr>
<tr>
<td>$K_a$ for Water (Dihedral angle:180°)</td>
<td>2741.70</td>
<td>1412.55</td>
<td>1006.99</td>
<td>458.12</td>
</tr>
<tr>
<td>$K_a$ for Water (Dihedral angle:90°)</td>
<td>16354.94</td>
<td>7781.09</td>
<td>4126.57</td>
<td>1721.60</td>
</tr>
</tbody>
</table>

For water and methanol adsorption on carbons, the oxygen containing functional groups are much stronger sites than the basal plane of the graphene layers. At low concentration the adsorbate will be localised in the region of these groups and the weaker interaction with the basal carbon atoms can be neglected. Therefore, to an excellent approximation, the Henry constant $K$ is a measure of the interaction between the adsorbate molecule and all the functional groups. The adsorption isotherms of methanol on A5 are shown in Figure 5.1 and those for methanol and water on Carbopack F are shown in Figure 5.2. The insets in these figures depict isotherms plotted on
logarithmic scales to confirm that data at low pressures obey Henry’s law. The experimental Henry constants $K (m^3/g)$, determined from these plots, are listed in Table 5.2 and Table 5.3.

### 5.3.3 Theoretical Henry constant

The Henry constant between a molecule and one functional group, $K_\alpha$, can be calculated by integrating the Boltzmann factor over the volume space around the functional group and over all possible orientations of the molecule, which is given in eq. (2.52).

The theoretical values of $K_\alpha$ for water and methanol with various functional groups are presented in Figure 5.3a and b, respectively.

It should be noted that the initial adsorption occurs at those sites whose affinities are highest. As was found earlier for water, the carboxyl group has the highest affinity in the range of temperatures investigated in this work (263-298K); its Henry constant is two orders of magnitude higher than those for the carbonyl and hydroxyl groups. Therefore, unless the carboxyl group is absent from the surface or its concentration is at least two orders of magnitude lower than the other groups the initial adsorption is dominated by the carboxyl group. It is interesting, but not surprising, that the affinities of water and methanol towards the oxygenated groups attached at the edge of graphite are comparable as both models have two positive partial charges ($q^+$) and a single negative charge ($q^-$) of comparable magnitude as shown graphically in Figure 5.4.
Chapter 5 Characterization of Functional Groups on GTCB

5.3.4 Concentration of surface oxygen-containing groups

Knowing the experimental Henry constant ($K$) which measures the interaction of an adsorbate molecule with all adsorption sites on the surface and the theoretical Henry constant ($K_\alpha$) which measures the interaction by one functional group with the adsorbate molecule, the functional group concentration $C_\alpha$ (mol/g) can be calculated from the following equation:

$$K = C_\alpha K_\alpha N_A$$  \hspace{1cm} (5.1)

where $N_A$ is the Avogadro number.

In a previous study by Morimoto and Miura\textsuperscript{121,142}, no carboxyl groups were detected on a graphite sample of 99.5% purity with 0.5% ashes, and BET surface area of 8.63 m$^2$/g after heat treatment at temperatures above 1000°C; although there was a measurable amount of phenolic group. By contrast, our results from Boehm titration on Carbopack F show a detectable concentration of carboxyl group, possibly because the highly ordered structure of Carbopack F stabilizes these groups.

5.4 Result and Discussion

The experimental $K$ (m$^3$/g) and theoretical $K_\alpha$ (m$^3$) for carboxyl group at ambient temperatures obtained from eq. (2.48) and eq. (2.52), respectively, are listed in Table 5.2 and Table 5.3 for methanol and water, respectively. The concentrations $C_\alpha$ (mol/g) for A5 and Carbopack F are determined using eq. (5.1) and are given in Tables 5.4, 5.5 and 5.6.

5.4.1 Effect of dihedral angle

In the Monte Carlo integration of eq. (2.52), the theoretical Henry constant $K_\alpha$ was initially obtained by positioning the atoms in the carboxyl group with the hydrogen atom in the same plane as the other atoms, giving a C-C-O-H dihedral angle of 180°. With this arrangement, our result shows that
the calculated carboxyl concentrations for A5 using methanol as the molecular probe overestimated those measured with Boehm titration (see Table 5.4), indicating underestimation of the $K_a$ value. Clearly it is important to account for the variation in the orientation of the C-C-O-H group, and the one that gives the highest $K_a$ is the optimum dihedral angle that maximises the interaction between molecular probe and the carboxyl group. In our previous work, the optimum C-C-O-H dihedral angle was determined by rotating the O-H bond about the C-O bond. There it was found that the optimum C-C-O-H dihedral angle for water was 100°, which gives a $K_a$ value five times greater than that for a dihedral angle of 180°. For methanol, the optimum C-C-O-H dihedral angle was found to be 90° (See Figure 5.5). This gives a significantly higher value of $K_a$ which translates to lower concentrations of carboxyl groups for A5 as seen in Table 4.

![Figure 5.5 Theoretical Henry constant for methanol-carboxyl interaction, as a function of the C-C-O-H dihedral angle at 263K](image)

<table>
<thead>
<tr>
<th>C-C-O-H dihedral angle (degree)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>140</th>
<th>160</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a$ ($10^{13} \text{ m}^3/\text{functional group}$)</td>
<td>$10^1$</td>
<td>$10^2$</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.4 Estimated concentrations of carboxyl groups (mmol/g) of A-5** at various temperatures

<table>
<thead>
<tr>
<th></th>
<th>263K</th>
<th>283K</th>
<th>298K</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol on A-5 (180°)</td>
<td>190.19</td>
<td>104.35</td>
<td>94.75</td>
<td>129.76</td>
</tr>
<tr>
<td>Methanol on A-5 (90°)</td>
<td>23.67</td>
<td>32.98</td>
<td>22.89</td>
<td>26.51</td>
</tr>
</tbody>
</table>

*The concentration determined by Boehm is 0.103mmol/g.

**5.4.2 Comparison with experiment**

In our proposed method, the graphite was modelled as perfect graphene layers whereas the partial charges on the carboxyl group were taken from the potential optimized for a simulation (OPLS) of liquid acetic acid. Hence, it is very likely that there are discrepancies between the simulation results and the Boehm titration results as the calculated interaction energy may not correspond to that in the actual physical system because the partial charges on the carboxylic group are modified...
by the sea of electrons in the graphene layers. To account for this as well as other structural and energetic factors we introduced a factor $F$ in the calculation of the interaction energy between one adsorbate molecule and one functional group:

$$\Phi_{i,j} = F \phi_{i,j}$$  \hspace{1cm} (5.2)\]

where $\phi_{i,j}$ is the interaction energy between a fluid molecule $i$ and a carboxyl group $j$. In our previous work using water as the molecular probe, this factor was found to be $F=1.15$ (i.e. a 15% increase of interaction energy) and using this factor we find the carboxyl group concentration for A5 of about 0.11mmol/g, which is in good agreement with the Boehm titration result of 0.103mmol/g. Using methanol as the molecular probe, a factor $F=1.25$ was found to give a good agreement between the calculated concentration (0.1mmol/g) and Boehm titration results (0.103mmol/g) as tabulated in Table 5.5. We attribute the discrepancy between the F factors for methanol and water to the differences in configuration of oxygenated functional groups on the carbon surfaces. This is under investigation and will be reported in a future correspondence.

Table 5.5 Estimated concentrations of carboxyl groups (mmol/g) of A-5 with C-C-O-H dihedral angle of 90° and $F=1.15$, $F=1.2$ and $F=1.25$

<table>
<thead>
<tr>
<th></th>
<th>263K</th>
<th>283K</th>
<th>298K</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol on A-5 ($F=1.15$)</td>
<td>1.07</td>
<td>1.47</td>
<td>1.23</td>
<td>1.26</td>
</tr>
<tr>
<td>Methanol on A-5 ($F=1.2$)</td>
<td>0.33</td>
<td>0.45</td>
<td>0.44</td>
<td>0.41</td>
</tr>
<tr>
<td>Methanol on A-5 ($F=1.25$)</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*The concentration determined by Boehm is 0.103mmol/g.

To further demonstrate the applicability of the new method, we determined the carboxyl group concentrations of non-porous Carbopack F using water and methanol as molecular probes. A factor $F=1.2$ was employed in the Monte Carlo integration to estimate $K_a$ for the aforementioned reasons. This factor was chosen as the average of the factors $F=1.15$ and $F=1.25$, resulting from our analysis of carboxyl groups on A5 using water and methanol and bearing in mind that A5 has a high enough $C_a$ to be able to obtain viable results using the Boehm titration technique.

We see in Table 5.6 that measurements using either water or methanol give $C_a$ values of the same order of magnitude, but lower than those predicted by Boehm titration by about three orders of magnitude. This raises the question “which method gives credible results?”
Table 5.6 Estimated concentrations of carboxyl groups (mmol/g) of Carbopack F* with optimized C-C-O-H dihedral angle of 90° (for methanol) and 1000 (for water) and F=1.2

<table>
<thead>
<tr>
<th></th>
<th>263K</th>
<th>273K</th>
<th>283K</th>
<th>298K</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol on Carbopack F (F=1.2)</td>
<td>0.000029</td>
<td>0.000045</td>
<td>0.000067</td>
<td>0.000081</td>
<td>0.000055</td>
</tr>
<tr>
<td>Water on Carbopack F (F=1.2)</td>
<td>0.000021</td>
<td>0.000036</td>
<td>0.000078</td>
<td>0.000148</td>
<td>0.000071</td>
</tr>
</tbody>
</table>

*The concentration determined by Boehm is 0.019mmol/g.

5.4.3 BET surface area of Carbopack F

Here we show that the total concentration of functional groups (carboxylic and phenolic) determined by the Boehm titration on Carbopack F (0.073mmol/g) is incorrect: If this concentration is spread uniformly on a surface then, assuming a molecular projection area of 0.15nm², the functional groups would occupy an area of 6.6m²/g, which is larger than the BET surface area of 4.9m²/g! Since highly graphitized thermal carbon black consists predominantly of graphene basal planes, argon nitrogen adsorption on this material will give a monolayer coverage corresponding exactly to the BET surface area. We can conclude that the Boehm titration is seriously in error and is not reliable for carbons with low concentrations of functional groups.

5.4.4 Spacing of carboxylic groups on Carbopack F

To add further support to the above assertion, we calculated the spacing between adjacent functional groups on Carbopack F. The electron micrographs of Carbopack F, show that the particles have a polyhedron shape, typical of a highly graphitized thermal carbon black. To a first approximation, we can treat the particles as cubic then, given a BET surface area of 4.9m²/g and assuming a carbon density of 2000kg/m³, the linear dimension of the cubes is 600nm. Taking the concentration of the carboxylic functional groups to be that determined by the Boehm titration (0.019mmol/g) gives a figure of 220 molecules along every 0.3nm of edge; which is impossible! If, on the other hand, we use the value of $C_\alpha$ determined by methanol adsorption we find 0.6 molecules for every 0.3nm along the edge of the cubic crystal. This is a reasonable value, and it clearly shows the superiority of our method over the Boehm titration method for determining low surface oxygenated functional groups.

5.4.5 Comparative plot to estimate the concentration of oxygen functional groups

The concentration of oxygen functional group can also be estimated by comparative plot. In this section we present further evidence to support our method for determining the functional group concentrations ($C_\alpha$), in the form of the comparative plot shown in Error! Reference source not found. Figure 5.6, where the amount of water adsorbed in porous A5 is plotted against the amount
adsorbed in the non-porous Carbopack F. The comparative plot serves to show that $C_\alpha$ for porous A5 is greater than that for Carbopack F.

![Comparative plot of water adsorption on A5 and Carbopack F](image)

**Figure 5.6** Comparative plot of water adsorption on A5 and Carbopack F.

We can identify various stages of adsorption shown as dashed lines:

1. The first stage, AB, corresponds to water growth around each cluster and this mechanism is similar for both porous A5 and non-porous Carbopack F.
2. The second stage, BC, occurs when clusters at the edges of the same walls of A5 merge to cover the walls. The upward slope of the graph here reflects the higher concentration of functional groups in A5.
3. In the third stage CD there is a secondary merging, linking clusters across the pore walls.
4. In the fourth stage, DE, the micropores of A5 are filled, followed by the complete filling.

The schematic of these adsorption stages is illustrated in Appendices C. In figure 5.6, D corresponds to the point at which the clusters reach a critical size, $d_c$, and water starts to penetrate into the micropore. We may assume that $d_c$ is approximately equal to the width of 1.25nm of the micropores in A5 (see Figure 5.7). Knowing the size of the cluster occupying one functional group, we are able to estimate the amount of water in one cluster. Knowing the total amount of water adsorbed on Carbopack F at point D ($\text{mmol/g}$), we can estimate $C_\alpha$ ($\text{mmol/g}$) from the following equation:

$$\left(\frac{\pi d_c^3}{6} \times \rho_m\right) \times N_A \times C_\alpha = a_0$$

(5.3)
where $\rho_m$ is molar density of water (mol/m$^3$) at 298 K. The calculated $C_\alpha$ (0.000193 mmol/g) is approximately 100 times lower than Boehm titration result and is comparable to our previously determined $C_\alpha$ (See Table 5.6).

Figure 5.7 Critical cluster diameter $d_c$

5.5 Conclusion

This chapter explores the use of methanol as a promising molecular probe to determine the concentrations of functional groups ($C_\alpha$) by carrying out adsorption at ambient temperatures in the Henry's law region. To illustrate the potential of our method we applied it to a sample of activated carbon, A5, whose $C_\alpha$ is high enough for the Boehm technique to be accurately employed, and to a graphitized thermal carbon black, Carbopack F, where $C_\alpha$ is too low to obtain valid results by this method. For the A5 activated carbon, we found that $C_\alpha$, determined by methanol adsorption is comparable to that determined using water as the molecular probe, reported in our previous work, and these values are in good agreement with those measured by the Boehm titration method. When our method was applied to determine the concentration of functional groups in Carbopack F with methanol as the molecular probe, we found that $C_\alpha$ is very low as expected for a highly graphitized sample. On the other hand, however, the Boehm titration gave a high value of 0.07 mmol/g, which corresponds to an area of 6.6 m$^2$/g covered by the functional groups. This is clearly not realistic because: (1) the BET surface area of Carbopack F is only 4.9 m$^2$/g, (2) this sample is highly homogeneous and (3) its surface area consists mainly of basal planes of graphene which are unlikely to have attached functional groups. This example shows the superiority of our proposed method to determine functional group concentration for samples with a low concentration of functional groups. Further work on investigations with methanol will be applied to more samples of carbons, and reported in a future correspondence.
Chapter 6 Adsorption in Uniform Pores

6.1 Introduction

Adsorption in open-ended pore has been well studied in the characterization of porous structure and the calculation of pore size distribution. Hysteresis in open-ended mesopore is observed at temperatures below a critical hysteresis temperature \( T_{ch} \) and its shape, size and position depend on the porous structure, pore size and temperature. Although the presence of hysteresis in open-ended pores is clear, the question of whether hysteresis exists in closed end pore is unresolved.

In order to improve our understanding of adsorption and desorption hysteresis in both open end and closed end pores, we have made extensive studies of isotherms in pores that are open at both ends or closed at one end. The basic pore models are shown in Figure 6.1, and have been used to explore a wide range of parameters including: pore size, pore length, surface affinity and temperature.

6.2 Simulation models

![Figure 6.1 Schematics of the pore model.](image)

6.3 Results and discussion

6.3.1 Open end pore

The adsorption isotherms for argon at 87K in an open-ended pore of width 3nm and length 20nm obtained by the canonical (C) and grand canonical (GC) ensembles are shown in Figure 6.2. Depending on the initial configurations, the GC-isotherm traces either a sequence of stable states, which are the global minima in the Gibbs free energy profile with respect to density, or a sequence of metastable states, along local free energy minima separated from the global ones by high-energy barriers. On the other hand, the C-isotherm describes an isolated system with a finite number of
molecules, which are distributed between the adsorbed phase and the gas-like phase, so as to achieve a minimum in the Helmholtz free energy.

![Diagram of Adsorption in Uniform Pores](image)

**Figure 6.2** Canonical isotherm and Grand Canonical isotherm for argon adsorption at 87K in an open ended graphitic slit pore of 3nm width and 20nm length.

In the grand canonical ensemble, there are a number of processes occurring in an open-ended slit pore:

1. Up to the lower closure point A, of the loop, molecular layers of adsorbate form on the two opposite pore walls. At this point, the state of the adsorbed layers changes from a stable to a metastable configuration. We denote the thickness of the adsorbed layer at this point as the threshold thickness, which is the same as the thickness of adsorbed layers when the liquid bridge, the adsorbed layer and the gas-like phase coexist, at point D, in the C-isotherm (see below). As pressure increases from Point A, the metastable adsorbed layers increase in thickness, and the system can be broadly divided into three distinct regions: (1) the dense adsorbed phase, (2) an undulation region and (3) a gas-like region, as shown schematically in Figure 6.3. The undulation region is, hereafter, referred to as the mass transfer zone (MTZ) and is the region where molecules move in and out most frequently between the adsorbed layer and the gas-like phase, creating a travelling wave-like interface.
The formation of a liquid embryo occurs at point B when the two undulating interfaces (in a metastable state) from the two opposite walls approach each other to within a distance approximately equal to two collision diameters of the adsorbate molecule. This is the pairwise separation distance at which the potential energy is minimum, so that when the two opposite MTZs are 180 degrees out of phase a molecule in the gas-like core can “instantly” bridge these MTZs by way of fluid-fluid interactions, to form an embryo of liquid bridge. Once this bi-convex liquid embryo is formed, its cylindrical menisci have very small radii of curvature, which are unsustainable at the pressure of Point B, and condensation occurs immediately, fed by the infinite supply of adsorbate molecules from the bulk surroundings. The condensate then extends to the pore mouths forming cylindrical menisci with curvatures that satisfy the Kelvin/Cohan equation.

The density of point G is higher than that at point E of the C-isotherm where the menisci of the liquid bridge just reach the two ends of the pore maintaining a constant shape, indicating that the condensed phase formed just after condensation at point G is partially densified. A further increase in pressure from G to the saturation vapor pressure further densifies the condensate.

In the canonical ensemble where there is a fixed number of molecules in the system, the C-isotherm is identical to the GC-isotherm up to point B. In the GC simulation condensation then occurs since the adsorbate is exposed to an infinite supply of adsorptive from the gaseous surroundings. In the canonical simulation, molecules are incrementally added to the system, and the adsorbed layers increase in thickness until they reach a maximum thickness at the gas spinodal point C. At this point, a minute addition of molecules to the system changes its state from two metastable adsorbed layers to one in which a liquid bridge coexists with the adsorbed layers. The liquid bridge was found to have a thickness of about 10 times the collision diameter in the axial direction, and the molecules required to build this bridge come mostly from the adsorbed layers and partly from the gas-like phase. This has the consequences that: (1) the adsorbed layer is thinner at coexistence than...
the adsorbed layer at the spinodal point C, and (2) there is a decrease in pressure such that the Kelvin/Cohan equation is satisfied. The meniscus then advances to the pore mouth as more molecules are added, and equilibrium is always maintained between the adsorbed phase and the condensed phase.

In desorption from a filled open-ended pore, the following processes operate:

1. As desorption proceeds from the saturation pressure, a hemi-cylindrical meniscus develops from the pore mouth until it is fully developed at point G. This path is reversible because desorption proceeds by removal of molecules from the two interfaces with very large radii of curvature.
2. Once the interface has developed to point G, it recedes into the pore interior maintaining the same radius of curvature. There are two distinct regions along the axial direction of the pore: (1) the condensate in the middle of the pore and (2) the coexistence region of the adsorbed phase and the gas-like phase. We note that the thickness of the adsorbed layers in the coexistence region is the same as the threshold thickness in the canonical ensemble.
3. As the pressure decreases to point E, the two menisci approach each other until the axial thickness of the liquid condensate is about 10 collision diameters. This is the critical axial thickness, which is the same as the thickness of liquid embryo at point D in the canonical ensemble. At the critical axial thickness, the capillary condensate instantly evaporates, via a first order transition, and the thickness of the remaining adsorbed layers on the pore walls is equal the threshold thickness.

The interplay between these processes allows us to define the critical hysteresis temperature and the critical hysteresis pore size. To shed light on the physics of these, we first return again to consideration of the mass transfer zone.

6.3.1.1 The mass transfer zone

For a given pore size, and at temperatures less than the critical hysteresis temperature, $T_{ch}$; or for a given temperature and a pore size, greater than the critical hysteresis pore size, $H_{ch}$, adsorption on a surface follows a molecular layering mechanism with the formation of an adsorbed layer which grows with pressure ($T_{ch}$ and $H_{ch}$ are defined below in Section 6.3.1.2). An unambiguous definition of the adsorbed phase was presented in our recent publication as the region where the particle number fluctuation, $f(N, N)/\langle N \rangle$, is less than unity. The adsorbed phase is separated from the bulk gas phase by the mass transfer zone (MTZ) where the particle number fluctuation is greater than unity. The thickness of the MTZ is a function of temperature, and increases with temperature.
The demarcation of the MTZ between the adsorbed phase and the gas-like region can be determined by a newly developed method based on the concept of Fraction of Success (FoS). This is implemented in a simulation by: (1) freezing a configuration; (2) making trial insertions of molecules into bins and (3) recording the number of successful insertions where the potential energy of the inserted molecule is non-positive. For dense adsorbed phases, the FoS is very small, but is much higher in the gas-like region and is close to the unity in an ideal gas. Therefore, the plot of FoS versus distance from the pore surface increases from approximately zero to nearly unity across the mass transfer zone, and can be used to determine the boundaries of the mass transfer zone (MTZ). The MTZ determined in this way can also be used to construct the interface separating the adsorbed phase and the gas phase, in a similar way to a Gibbs interface constructed between two phases of semi-infinite extent in contact to each other. We should emphasize that the gas-like region in a pore is not at the same density as the bulk gas surroundings because it is compressed, by virtue of the interactions with molecules in the MTZ region, whose average density is greater than the density of the bulk gas surroundings.

6.3.1.2 Critical hysteresis temperature & critical hysteresis pore size

For a given pore size, the critical hysteresis temperature, \( T_{ch} \), is defined as the temperature at which the thickness of the mass transfer zone is equal to half of the pore width minus the thickness of a monolayer. The critical hysteresis temperature falls between the triple point and the bulk critical temperature.

For a given temperature, the critical hysteresis pore size, \( H_{ch} \), is defined in the same way, i.e. \( H_{ch}/2 \) is equal to the thickness of the mass transfer zone plus the thickness of a monolayer. Figure 6.4 shows the schematics of the critical hysteresis temperature and the critical hysteresis pore size.

![Schematic diagram of critical hysteresis temperature and critical hysteresis pore size.](image)

6.3.1.3 Pore filling at temperatures greater than the critical hysteresis temperature
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When the temperature is greater than the critical hysteresis temperature, for a given pore size, the adsorption isotherm is reversible because the MTZ spans across the pore. Therefore, there is no defined interface separating the adsorbed phase and the gas phase, and the process is akin to pore-filling, a concept originally introduced to account for the adsorption mechanism in micropores. Here we argue that this mechanism is not just restricted to micropores, but can also occur in mesopores, when the temperature is above the critical hysteresis temperature. The density distribution across the pore is much more gradual than at temperatures lower than $T_{ch}$ since there is no clear formation of layers and the density throughout the pore is greater than the bulk gas density because the MTZ spans across the whole pore.

6.3.2 Closed end pore

Figure 6.5 shows the effect of number of cycles on the adsorption isotherms of argon at 87K in a slit-shaped closed end graphitic pore of 3nm width and in a cylindrical closed-end pore of 3nm radius. The simulated isotherms from a run of 200,000 cycles with conventional GCMC show clear hysteresis loops, although their areas are much smaller than those at for the corresponding open-end pores. The hysteresis was attributed to the restructuring of the adsorbate as the meniscus reaches the pore mouth. However, when the number of cycles was increased to 2 million ($2 \times 10^9$ configurations) in using conventional GCMC, we find that the isotherms are reversible (red curves).

The general mechanisms of adsorption and desorption can be described as follows: During adsorption, molecular layering occurs on the two opposite pore walls as well as at the closed end. By virtue of the stronger solid-fluid potential at the corners of the closed end (because of potential field overlap from adjacent surfaces), a liquid bridge embryo is formed. As the pressure is increased, the radius of curvature of the meniscus developed at the closed end changes from...
relatively flat to cylindrical, and the meniscus advances to the pore mouth (condensation). It is to be noted that the thickness of the adsorbed layer (before condensation) is the same as the threshold thickness in the open-ended pore of the same pore width. After this condensation, the adsorbate continues to restructure and to densify at higher pressures, in the same way as in the open-ended pore. On desorption from a filled closed end a meniscus develops at the pore mouth and recedes towards the closed end, reversing the process of adsorption giving a reversible isotherm. Any structuring of the adsorbate that occurred as a result of densification during adsorption is destroyed as desorption proceeds. Although the new evidence presented in this work shows that the kinetics of this de-structuring are extremely slow on the time scale of a simulation.

The evidence for our exceptionally lengthy simulations show that adsorption-desorption isotherms for a closed-end pore are reversible when temperatures are greater than the triple point. When the temperature is much lower than the triple point, the isotherms may exhibit hysteresis because regions of the adsorbate become solid-like. This assertion is consistent with a number of experimental observations of hysteresis in the adsorption of noble gases (for example krypton, xenon) and simple gases such as methane, on a graphite surface at temperatures below 2D critical temperature. Hysteresis in closed end pores may also occur at temperatures above the triple point for strongly associating fluids, such as acetone, chloroform and NO when the adsorbent field is relatively weak and the surface is not wetted.

For temperatures above the critical hysteresis temperature, the adsorption-desorption isotherms for the open-ended pore and the corresponding closed-end pore of equal pore size are identical because the influence of a closed end is thwarted by the strong undulation from the two opposing surfaces. Adsorption and desorption occur by filling and emptying mechanisms.

**6.3.3 Parameters for hysteresis in open and closed end pores**

In this section we present the results of our extended parameter study of argon adsorption in graphitic slit pores open at both ends or closed at one end.

**6.3.3.1 Effects of pore size**

At a given temperature, the thickness of a wetting adsorbate increases with pressure. This increase comes mainly from the dense adsorbed phase, while the thickness of the MTZ remains essentially constant. For large open-ended pores whose widths are greater than twice of the MTZ thickness, the adsorption proceeds initially by a molecular layering mechanism, followed by condensation according to the undulation theory explained in Section 6.3.1. When the pore width is reduced to the critical hysteresis pore size, $H_{ch}$, where the MTZ thickness is about half the pore width, the
adsorption-desorption isotherm becomes reversible, irrespective of whether or not one end of the pore is closed.

The adsorption isotherms of argon at its boiling point (87K) as a function of pore size are presented as plots of the pore density versus the logarithm of pressure in Figure 6.6. Isotherms with a linear pressure scale are shown in Figure A1 in the appendices. Hysteresis is observed for the open-ended pores with widths greater than the critical hysteresis pore size, which in this system is 2nm. This corresponds to the widely cited demarcation between micropore and mesopore for adsorptives (more specifically for nitrogen at its boiling point) with a molecular size similar to argon. In a closed-end pore, the isotherms were found to be reversible for all pore sizes studied, because the closed end acts as a nucleation site for the liquid condensate to form.

Figure 6.6 Adsorption isotherm for argon at 87K in open-ended and closed-end pores as a function of pore size. The closed symbols are the adsorption branches, and the open symbols are desorption branches. The isotherm for the pores with widths of 0.85, 1.0, 1.5, 2.0, and 3.0 nm are shifted up by 100, 80, 60, 40, 20 kmol/m³, respectively.

The condensation pressure for both types of pore shifts to a higher value as the pore width is increased. For pores whose widths are less than the value of $H_{ch}$ for the open-ended pore, the condensation pressure is identical in open and closed end pores. However, for pores whose widths are greater than $H_{ch}$, the onset of condensation occurs at higher relative pressure in the open-ended pore than in the closed-end pore, because more adsorbed layers are needed before the two undulating interfaces approach each other to within the critical distance needed for the liquid embryo to form. In fact the condensation pressure for the closed-end pores is always less than the
saturation pressure, \( P_0 \), because the closed end of the pore acts as a nucleation site for the formation of a liquid bridge. On the other hand, the condensation pressure for very large open-ended pores exceeds the saturation vapour pressure, because the separation distance between the two undulating adsorbate interfaces is too large for the formation of a liquid embryo at pressures below the saturation pressure.

There is a hysteresis loop associated with restructuring of the condensate in both the open and closed end pores of 1.5\text{nm} width over a pressure range above the condensation pressure \(^{149}\). To elucidate the mechanism of the restructuring we present, in Figure 6.7, the local density distributions and snapshots just before and just after Points A and B in Figure 6.6, where restructuring takes place. At Point A, the condensate has four layers with two contact layers on the pore walls and two inner layers (Figure 6.7a). The fluid-fluid (FF) energy per molecule at Point A is -4.43kJ/mol; the FF energies of the contact layers and the inner layers are -3.91kJ/mol and -
5.30 kJ/mol, respectively. The FF energy of the inner layer is stronger because each molecule has a greater number of near neighbours. As the pressure is increased to Point B (after the restructuring), both the contact layers and the inner layers evolve from a liquid-like to a solid-like state, and the inner layer bifurcates into two distinct layers (Figure 6.7b); at the same time the contact layers rearrange from a disordered packing to a hexagonal packing (Figure 6.7c). The FF energy at Point B is -5.45 kJ/mol, lower than the value of -4.43 kJ/mol at Point A. The FF energies of the contact layers and the inner layers are -4.5 kJ/mol and -6.49 kJ/mol, respectively, compared to -3.91 kJ/mol and -5.3 kJ/mol at Point A. This indicates that restructuring occurs in both contact and inner layers, but is greater in the inner layers. Therefore on desorption a lower pressure is required to melt the solid condensate, resulting in a so-called restructuring hysteresis loop, as distinct from a condensation/evaporation hysteresis loop. We identify this as first order freezing or melting of the contact layer and was previously noted in a simulation study by Abraham $^{150}$. It is interesting to note that for a graphitic pore with strong surface affinity, the restructuring loop is observed only for pore sizes around 1.5 nm. However, for pores with weaker surface affinity, a restructuring loop associated with the freezing and melting of the contact layers, is observed for a wider range of pore sizes, as shown in section 6.3.3.3.

6.3.3.2 Effects of pore length

![Figure 6.8 Adsorption isotherms for argon at 87K in open-ended pores and closed-end pores as a function of pore length. The closed symbols are the adsorption branches, and the open symbols are desorption branches. The isotherm for pores of length 10, 20 nm are shifted up by 60, 30 kmol/m$^3$, respectively.](image)
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Figure 6.8 shows the effects of pore length for argon adsorption at 87K in pores of 3nm width. With the exception of the very short pore, adsorption and desorption are not affected by the pore length for either open-ended pores or closed-end pores. For the open-ended pores, the undulations in the mass transfer zone are independent of the pore length. Once the liquid embryo has formed at the middle of the pore in the axial direction, the liquid bridge expands immediately to the pore mouth and the radius of curvature of the meniscus at the pore mouth satisfies the Kelvin/Cohan equation. This sequence of events is independent of the pore length. For the closed-end pores, nucleation occurs first at the closed end where the solid-fluid potential is strongest. After the meniscus has developed at the closed end, the capillary condensate advances immediately to the pore mouth, irrespective of the pore length. We note that condensation in the closed end pore is immediate, because the radius of curvature of the meniscus just before condensation cannot sustain any further increase in pressure until it reaches the pore mouth. Once the meniscus has advanced to the pore mouth, the overall solid-fluid energy is reduced and therefore a progressively higher chemical potential is required to fill the pore mouth.

6.3.3.3. Effects of the surface affinity

Motivated by the experimental observations of hysteresis in adsorption of argon at 85K in anodized aluminium oxide (AAO) pores with one end closed, we carried out simulations in pores having weaker adsorbent potential energies than graphite in which the very strong adsorbent potential can be attributed to the exceptionally high density of the C-atoms. Here we weakened the adsorbent potential by tuning the well depth ($\varepsilon_{ss}/k_B$) of a solid atom in a graphene layer from the standard value of 28K, to 1K. The isotherms in Figure 6.9, were calculated with this adsorbent for a pore of 2nm width and 20nm length. The extremely low energy of 1K was chosen to highlight the effects of a very weak adsorbent.
Figure 6.9 Isotherm for argon adsorption at 87K in closed end pores of 2nm width and 20nm length as a function of surface affinity ($\epsilon_{ss}/k_B$=28 K to $\epsilon_{ss}/k_B$=1K).

A number of key features may be noted:

1. The condensation pressure shifts to a higher pressure as the affinity of the pore wall is decreased because of the lower solid-fluid (SF) interactions\textsuperscript{151}. The condensation pressure in the 1K pore occurs at a pressure greater than the saturated vapor pressure, because of the system has now become non-wetting (the FF energy is much lower than the SF energy).

2. Compared with the graphite pore ($\epsilon_{ss}/k_B$=28K) in which molecular layering occurs on the pore wall and the adsorbed amount just before the condensation is relatively high, the corresponding amount adsorbed in the closed-end pore with ($\epsilon_{ss}/k_B$)=5K or less is very low; much lower than the monolayer coverage concentration. This is an indication that molecular layering is no longer the operative mechanism, but rather that condensation is induced by clustering of the adsorbate molecules, and subsequent merging of neighboring clusters, facilitated by the thermal fluctuation.

3. Hysteresis is observed in closed-end pores with weak surfaces and the area of the loop increases when the adsorbent becomes weaker (see for example the closed end pore with ($\epsilon/k_B$)=1K in Figure 6.9). This suggests that the mechanisms of adsorption and desorption do not follow those discussed above for more strongly adsorbing pores. A detailed mechanism will be presented below.

4. The isotherms for closed-end pores with ($\epsilon_{ss}/k_B$)=10 K and ($\epsilon_{ss}/k_B$)=5K exhibit a restructuring loop at pressures higher than the condensation pressure, which is associated with a two dimensional freezing of the contact layers as discussed in section 3.3. Compared with the graphite pore, in which restructuring of the condensate only occurs in pores with sizes around 1.5nm, the restructuring loop occurs for a range of pore sizes in weakly adsorbing
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...pores, where the adsorbed molecules just after condensation are still loosely packed because of the very low SF potential energy. At the restructuring pressure, the adsorbate re-arranges to form a closer and more ordered packing, and thus a lower pressure is required to melt the adsorbate, resulting in a restructuring hysteresis loop.

Figure 6.10 Canonical and Grand Canonical isotherms for argon adsorption at 87K in a closed end pore of width 2nm and length 20nm with $\frac{\epsilon_{ed}}{k_B}=1K$. The Canonical isotherms are obtained from $kMC$ and from Metropolis $MC$ using 100,000 cycles for both the equilibrium and sampling stages.

Figure 6.10 compares the C-isotherm with the GC-isotherm. The C-isotherm was obtained by carrying out a canonical Monte Carlo simulation (with a Metropolis algorithm) and separately, by running a canonical kinetic Monte Carlo simulation. Both simulations gave identical results and both exhibit a vdW loop. Before the gas-like spinodal point, the C-isotherm nearly overlaps the GC-isotherm, but after this spinodal point, the C-isotherm exhibits a vertical increase in the pore density at the coexistence pressure, which is exactly the same as the evaporation pressure of the GC-isotherm.

The adsorption and desorption mechanisms in closed-end pores with very weak surfaces can be elucidated from the facts that:

1. the pore density just before condensation is very low, only a few percent of the monolayer coverage concentration;

2. the evaporation branch of the GC-isotherm agrees with the vertical branch of the C-isotherm.

We can deduce that the adsorption begins with the formation of clusters at the junctions of the closed end, where the solid-fluid (SF) potential is a maximum. These clusters then grow as pressure is increased, and because of thermal fluctuations there is a mass transfer zone around the clusters similar to the $MTZ$ of the adsorbed phase in pores with a strong adsorption potential. On desorption
from the filled pore, the interface separating the condensate and the gas-like phase at the pore mouth, recedes into the pore interior.

### 6.3.3.4 Effects of temperature

Figure 6.11 shows the isotherms for open-ended and closed-end slit pores at temperatures ranging from below the triple point to supercritical. The temperature evolution of isotherms for cylindrical pores is presented in Figure A2 in Appendices.

For a given pore size, hysteresis is observed in open-ended pores, when the temperature is less than the critical hysteresis temperature, $T_{ch}$, because the curvatures of the interface separating the adsorbed phase and the gas-like phase in adsorption and desorption are different. A higher pressure is required to build up adsorbed layers thick enough for the formation of a liquid embryo at the undulating interface, while on desorption the menisci recede from the pore mouth towards the pore interior with a threshold thickness of the adsorbed phase. When the temperature is close to $T_{ch}$, the area of the hysteresis loop shrinks and the loop shifts to a higher reduced pressure because the interface separating the gas-like region and dense adsorbed phase becomes diffuse and there is competition between the movement of menisci and thermal fluctuations. For temperatures greater than $T_{ch}$, an isotherm for an open-ended pore is reversible, because the thickness of the MTZ is greater than half of the pore size, and adsorption and desorption proceed by pore-filling and emptying, as mentioned earlier.

Compared with the open-ended pores, the isotherms for argon in graphitic closed-end pores are reversible at all temperatures above the triple point. When the temperature is much lower than the triple point the adsorbate solidifies and uniform closed-end pores then exhibit hysteresis, as shown in Figure 6.12.

![Figure 6.11](image-url)
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(b)

(b')

(c)

(c')

(d)

(d')

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Figure 6.11 Adsorption isotherms for argon in slit pores as a function of temperature and pore size: (a), (b), (c), (d) and (e) are open-ended pores with widths of 1nm, 1.5nm, 2nm, 3nm and 4nm, respectively; (a'), (b'), (c'), (d') and (e') are closed-end pores with the same widths.

Figure 6.12 Adsorption isotherms for argon in a closed end pore of width 2nm and length 10nm at 30K.

3.3.6. Effects of adsorbate

To further test of our assertion that hysteresis is absent for simple molecules in closed-end graphitic pores, except for cases where the temperature is much lower than the triple point of the adsorbate, we carried out simulations of nitrogen and krypton adsorption in a graphitic slit pore with a closed ends with widths of 3nm and 20nm length at 77K. The results are shown in Figure 6.13. Compared with nitrogen, whose isotherm is reversible at 77K (the normal boiling point of nitrogen), the isotherm of krypton exhibits a clear hysteresis loop at this temperature. This is because 77K is well below the triple point where krypton becomes solid-like \(^{148}\), and therefore a lower pressure is required for desorption from a filled pore.
Figure 6.13 Isotherms for nitrogen and krypton at 77K in a closed-end pore of 3nm width and 20nm length.

6.4 Conclusions

By investigating a range of parameters including pore size, pore length, temperature and adsorbate, we have been able to elucidate the origin of hysteresis in open-ended and closed-end pores. Our conclusions can be summarized as follows:

In an open-ended pore, for a given pore size, hysteresis occurs when the temperature is below the critical hysteresis temperature, due to the different curvatures of the interface separating the adsorbed layer and the gas-like phase during adsorption and desorption. The critical pore size ($H_{ch}$) and critical temperature ($T_{ch}$) for hysteresis in open-ended pore is associated with the size of the mass transfer zone. When the pore size is less than $H_{ch}$ or the temperature is higher than $T_{ch}$, adsorption proceeds by pore-filling and the isotherm is reversible.

In closed-end pores, the adsorption isotherm is reversible for simple gases and strongly adsorbing graphite adsorbents because the curvature of the meniscus is the same for adsorption and desorption. However, hysteresis occurs on very weak adsorbents where adsorption and desorption proceed by different mechanisms: clustering of the adsorbate molecules on adsorption and a receding of meniscus on desorption. When temperature is well below the triple temperature, hysteresis is observed in a closed end pore, because the adsorbate becomes solid-like.
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7.1 Introduction

In pore size analysis, kernels based on parallel-sided pores are used to invert the adsorption branch of the isotherm. The mechanism for condensation in a parallel-sided slit pore has recently been elucidated in detail; simulation studies show that adsorbed layers on opposite surfaces each with an undulating interface between the dense adsorbate phase and the contingent rarefied phase eventually contact to form bridges bounded by cylindrical surfaces at which stage condensation is nucleated. A simple thermodynamic argument for condensation at a cylindrical surface, originally proposed by Cohan, leads to the equation:

\[
RT \ln \left( \frac{P_{\text{cond}}}{P_0} \right) = -\frac{\sigma v_M}{R^*} \tag{7.1}
\]

where \(P_{\text{cond}}\) is the condensation pressure, \(\sigma\) is the liquid-vapour surface tension, \(v_M\) is the liquid molar volume, \(R_g\) is the gas constant and \(T\) is the absolute temperature and \(R^*\) is the meniscus radius corrected for interfacial thickness \(t\).

However, the derivation of the Cohan equation assumes the validity of macroscopic bulk thermodynamics and takes no account of the adsorbent potential energy field on the interface, which becomes increasingly important as the pore width is reduced. Subsequently, Derjaguin (for pores with planar surfaces) and Broekhoff and de Boer (for cylindrical pores) added an extra term to equation (7.1), to account for the increased cohesiveness of the adsorbate under the influence of this field, but retained the product of the surface tension and the liquid molar volume expressed as properties of the homogeneous bulk fluid.

Previous studies of adsorption in wedge-shaped mesopores have shown that wedge angle and pore length can have significant effects on the shape of the hysteresis loop and the structure of the adsorbate. In this work, we report computer simulations of adsorption in finite wedge-shaped mesopores, and show that this model, though simple, is sufficiently flexible, to describe adsorption and desorption of gases in activated carbon. The model parameters are the wedge angle, the length and the pore size at the narrow end. The simulated isotherms are analysed for the radius of curvature of the interface between the adsorbed phase and gas phase, obtained from the microscopic 2D-density distribution in the neighbourhood of the interface, as a function of the equilibrium pressure. This dependence is then used in the Derjaguin-Broekhoff-de Boer (DBdB) equation to derive the interfacial energy parameter (the product of the surface tension and the liquid molar volume in equation (7.1)) and to confirm that this parameter is affected by the adsorbent potential energy field, and cannot be correctly calculated using parameters for the bulk liquid.
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7.2 Simulation model

![Figure 7.1 schematic diagram of a wedge pore](image)

Figure 7.1 schematic diagram of a wedge pore

Figure 2.3 shows a model for carbon materials, proposed in Franklin’s seminal paper\(^{20}\). Because the carbon planes are not perfectly aligned, the pore spaces resemble wedges with different angles, and the topological arrangement of these pores depends on the precursors and the method of preparation. The wedge model employed in this chapter is shown in Figure 7.1 and is characterised by the structural parameters: pore size at the narrow end, \(W_1\), the angle of the wedge, \(\alpha\), and the length along the axial direction, \(L\). Since the length can be estimated from Raman spectroscopy\(^{164}\), the adsorption-desorption isotherm will depend on \(W_1\) and \(\alpha\). This implies that the characterization of the pore volume distribution can be expressed in terms of these two parameters. The model reduces to the parallel-sided pore basis for characterization when \(\alpha=0\).

7.3 Results and discussion

7.3.1. Adsorption in an open-ended pore with a small angle

To illustrate the effects of non-uniformity along the cross section of a slit pore, we compare, in Figure 7.2, isotherms for a parallel-sided pore and a wedge pore of similar dimensions. The wedge pore had a length 15nm a width of 3nm at the narrow end and an angle \(\alpha=2.5^\circ\) (giving a width of 4.3nm at the wider end). The top panel shows a family of isotherms for uniform slit pores with widths between 3nm and 4.3nm. The pore width of 3.7nm is the average between the widths of the narrow and wide ends of the wedge pore.
Figure 7.2 Comparison of adsorption isotherms for argon at 87K in a wedge pore and in parallel-sided slit pores. All the pores are 15nm in axial length. The saturated vapour pressure is calculated from a correlation.

From Figure 7.2, we make the following observations:

1. The hysteresis loops for uniform pores are Type H1 according to the IUPAC classification \(^\text{165}\), whereas that for the wedge pore is Type C in the de Boer (dB) classification \(^\text{67,162}\), for any wedge angle \(^\text{161,162}\).

2. In uniform pores, as the pore size is increased, the condensation and evaporation pressures shift to a higher pressure, and the extent of this increase is greater for condensation than for evaporation, giving a larger hysteresis loop. The adsorption and desorption mechanisms have been discussed elsewhere\(^\text{146}\).

3. In the wedge pore, the adsorbed capacity associated with condensation is approximately the same as in the uniform slit pore of width 3.7nm that has the same volume; however, the capacity associated with evaporation is much smaller. See Section 7.3.3 for further discussion.

4. The position of the hysteresis loop for the wedge pore is also altered, as well as its shape. In the wedge pore, condensation and evaporation occur at pressures close to those for the uniform pore of width 3.4nm, which is narrower than the uniform pore of width 3.7nm that
has the same volume as the wedge. This implies that the uniform slit model underestimates the pore size.

To shed further light on the mechanisms underlying the above observations we show, in Figures 7.3a and 7.3b, the evolution of the interface separating the gas phase and the adsorbed phase for adsorption and desorption in the wedge pore.

**Figure 7.3** Evolution of the vapour-liquid interface: (a) adsorption, (b) desorption. The points are marked on the isotherms in Figure 7.2.

On adsorption into an empty wedge pore, the adsorbed layers build up on the pore walls and the interfaces move towards each other as the pressure is increased \(^{17}\). At point B, a liquid bridge embryo forms near the narrow end (see Figure A3 in the Appendices). Condensation then occurs instantly and adsorbate fills the pore up to Point C, where the radius of curvature, \(R^*\), of the equilibrium interface separating the adsorbate and gas phases, is approximately governed by the Cohan equation eq. (7.1). The equation is only approximate, because the solid-fluid potential is not included. This point is revisited in section 7.3.4 below.

The amount adsorbed at condensation is shown as the shaded region in Figure 7.3a. As pressure is increased further, the curvature of the meniscus decreases and eventually disappears at the saturation pressure (point D). It is clear that because of the formation of a liquid embryo at the narrow end, condensation occurs at a lower pressure than in the uniform slit pore (3.7nm) of the same pore volume, and is the reason for the underestimation of pore size, by the parallel-sided slit pore model.

As desorption proceeds from a filled pore, two menisci initially form at the pore mouths (Figure 7.3b). As the pressure is decreased from Point E to G, the menisci recede into the pore interior, and their radii of curvature correlate approximately with the pressure, according to the Cohan equation eq. (7.1). The meniscus retreats further from the wider end than from the narrow end. When the pressure reaches point G, the two radii of curvature of the bi-concave liquid bridge have reached a minimum and liquid evaporates from the core. The amount of adsorbate lost at this evaporation is shown as a shaded region in Figure 7.3b, and is clearly much smaller than the amount at
condensation (the shaded region in Figure 7.3a). This extended withdrawal of the two menisci, and evaporation of the bi-concave liquid bridge, are the microscopic reasons why a Type C hysteresis is observed for wedge-shaped pores. It is worth emphasising that the evaporation is governed by the narrow end of the wedge, which implies that the pore size estimated by the Cohan equation and a parallel-sided pore is not reliable.

7.3.2. Effect of pore length

![Figure 7.4 Isotherms for argon at 87K in wedge pore of 15nm, 20nm, and 30nm length with both ends open. The width at the narrow end is 3nm and the angle is 2.5°: (a) absolute pore density, (b) number of particles.](image)

Figure 7.4 shows the isotherms for wedge pores of lengths: 15nm, 20nm and 30nm, all with the same width at the narrow end, W₁, and the same angle α. A first observation is that the condensation and evaporation pressures remain the same for all pore lengths, because they are determined by the angle and the width of the small end, as explained in the previous section. Furthermore, the adsorbed pore density associated with condensation is almost the same for the pores of 15nm and 20nm length, but is much smaller for the 30nm pore. This means that the amount associated with condensation only partially occupies the 30nm pore. The reason for this partial filling of the long pore (30nm length) is that the radius of curvature of the interface separating the adsorbed phase and the gas phase at the wider end of the pore, immediately after the condensation, is correlated with the condensation pressure according to equation (7.1). Although the density of the adsorbate after condensation is smaller for longer pores, the number of molecules required to fill both pores is the same, as demonstrated in Figure 7.4b, which confirms the
correlation between the radius of curvature at the interface and the condensation pressure. This is also applies to evaporation, suggesting that condensation and evaporation depend only on the angle and the width of the narrow end.

![Figure 7.5](image)

**Figure 7.5** Evolution of vapour-liquid interface for desorption as a function of pore length. Points at the same pressure are plotted in the same colour.

To add further support for the above explanation we show, in Figure 7.5, the contours of the interface separating the adsorbate and the gas phase, as a function of pressure and pore-length. For a given wedge angle there are two distinct stages during the evolution of this interface. In the first stage of desorption from a completely filled pore, two menisci form at the pore mouth and their radii of curvature decrease with decreasing pressure from infinity for the initially flat interface. We refer to this as the developing meniscus stage. The developing menisci at the two ends rapidly recede into the pore interior as pressure is further decreased. At this pressure, the positions of the receding menisci, and their radii of curvature, are very nearly the same for pores of different length, and are governed approximately by the Cohan equation. Evaporation occurs at the pressure where the liquid bridges have the same thickness along the axial direction, supporting our earlier assertion that desorption in wedge pores depends only on the angle and the size of the narrow end.
7.3.3. Effect of angle

Figure 7.6 shows the effects of wedge angle on the isotherm. Here the mean pore width and axial length are kept constant at 3.7nm and 15nm respectively and the wedge angles are varied between 1° to 4°. For a wedge angle of 1° the hysteresis loop is a mixture of Type C (de Boer classification) and Type H1 (IUPAC classification). When the angle is increased to 4°, the adsorption and desorption branches shift to lower pressures and the hysteresis loop is smaller in size. This is because the narrow end of the 4° pore is smaller, resulting in an earlier condensation, but on desorption, the condensed fluid is more cohesive near the narrower end because the potential energy is more negative due to overlap from opposite adsorbent walls. This has the implication that the equation (7.1) becomes less reliable in wedge pores having large angles.

![Figure 7.6 Isotherms for argon at 87K in wedge pores with angles of 1, 2.5 and 4 degree; axial lengths of 15nm, and mean pore widths of 3.7nm.](image)

7.3.4. The effect of the adsorbent field on desorption

The Cohan equation (equation (7.1)) has been described above as being approximate because any contribution from the external potential energy field due to the adsorbent has been ignored. To illustrate the role of this field we plot \( R_g T \ln(P/P_{\text{cond}}) \) versus the inverse of the radius of curvature at the point just after condensation in Figure 7.7. The dashed line is calculated from equation (7.1) with the slope \( (\sigma v_M) \) calculated using the bulk liquid values for surface tension, \( \sigma = 14.7\text{mN/m} \) and molar volume, \( v_M = 28.8\text{L/kmol} \). The results from our wedge pore simulations have a higher slope, which means that the condensed fluid at the interface is more cohesive than in the isolated
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bulk liquid. To evaluate the influence of the solid-fluid potential on the interfacial parameter, we used a Derjaguin-Broekhoff-de Boer (DBdB) modification of eq (7.1) to separate the solid-fluid potential from the capillary potential. The modified equation has the form:

\[
RT \ln \left( \frac{P}{P_0} \right) = -\frac{\sigma^{1/2}}{R^*} + F_{sf} \tag{7.2}
\]

where \(F_{sf}\) is the contribution from the solid-fluid potential exerted on the interface of the adsorbed phase. \(R^*\) was calculated as \(R_A - D_F\), where \(R_A\) is the radius of the adsorbate-gas interface and \(D_F\) is the thickness of fluctuation region which approximately half the collision diameter \(^{71}\).

From linear regression of the simulation results, the interfacial tension and solid-fluid potential are:

\[
\sigma = 15.0 mN/m \text{ and } F_{sf} = -28.5 J/mol \tag{7.3}
\]

Compared with the bulk fluid, the surface tension in the wedge pore is slightly larger due to the solid-fluid interaction. This calculation shows that the SF interaction affects not only the condensation pressure in an additive manner, as in eq. (7.2), but also the interfacial energy parameter of the capillary force; i.e. the interface is more cohesive compared to that in the bulk vapour-liquid equilibrium.

Figure 7.7 DBdB equation for the cylindrical meniscus in a wedge pore during desorption.
7.3.5. Effect of temperature

Figure 7.8 shows the adsorption-desorption isotherms for a wedge pore at 77K, and reveals novel features distinct from the isotherms at 87K. The hysteresis loop is still essentially Type C (dB classification), but the desorption branch now has a step-like character in contrast to the smooth curve at 87K.

![Graph showing isotherms for argon in a wedge pore with an angle of 2.5° at 77K. The width of the narrow end is 3nm and the axial length is 15nm.](image)

The underlying mechanism for desorption at 77K can be analysed by studying the local compressibility distribution along the pore axis at the saturation pressure, and snapshots taken during the progress of desorption (Figure 7.9). The compressibility shows peaks and troughs, corresponding to ordered and disordered domains along the pore. These structures are associated with the commensurate and incommensurate packing seen in the snapshots at various pressures along the desorption branch. This structure variation is absent at 87K (Figure A4 in Appendices).
The snapshot at Point A shows that the pore can be divided into four domains, each of which contains a different number of adsorbate layers. In the junction between two adjacent domains, the packing of the adsorbate is incommensurate and therefore the compressibility is higher. As the pressure is decreased from Point A to B, the menisci from each end of the pore recede into the pore and there is a gradual decrease in the isotherm. When the meniscus approaches the junction between the domains IV and III, where the adsorbate is less cohesive, there is a sharp evaporation...
from Point B to C due to the instant evaporation of molecules from this junction. This process is repeated as the menisci receded through other domains until point F is reached where the two domains (I and II) evaporate together. This is because the two domains at the small end are more cohesive because of the stabilization brought about by the solid-fluid interaction.

7.4 Conclusions

We have presented a detailed simulation study of the adsorption and desorption of argon in a wedge-shaped pore. We argue that this geometry more closely represents the spaces inside real porous materials and should therefore be considered as an alternative model for the determination of pore size distribution in activated carbons, since the customary parallel-sided slit pore model could underestimate pore size. The effects on the hysteresis loop, of pore length, pore width at narrower end and the wedge angle have been studied, and it was found that latter two affect the shape and position of the hysteresis loop but that this is independent of the pore length, except when the pore is very short. Mesoscopic analysis of the interface separating the gas phase and the adsorbate, shows that desorption from a wedge can be described by the DBdB equation. We find that the effective surface tension at this interface is slightly greater than the bulk value, suggesting that the interface is only slightly more cohesive, than the vapour-liquid interface in a bulk phase, due to the influence of the adsorbent potential energy field. At 77K, the desorption branch of the isotherm has incipient steps due to the alternation of commensurate and incommensurate molecular packing along the direction of the pore axis.
Chapter 8 Adsorption in Inkbottle Pore

8.1 Introduction

In this chapter, we comprehensively examined the condensation evaporation mechanism in slit-shaped ink-bottle pores by Grand Canonical Monte Carlo (GCMC) simulation, for the purpose of describing the type H2 hysteresis which is commonly found for disordered solids. We focused our attention on the microscopic reason of evaporation mechanism, and obtained the functional dependence of the evaporation pressure on the neck dimension and temperature.

8.2 Simulation model

![Schematic diagram of three slit-shaped pores](image)

**Figure 8.1** Schematic diagram of three slit-shaped pores: (a) ink-bottle pore, (b) closed pore, (c) open end pore.

The three solid models we studied are illustrated in Figure 8.1, and the interaction of a fluid particle with pore walls is modelled by the Bojan-Steele potential.

8.3 Results and discussion

8.3.1 Adsorption in an ink-bottle pore with narrow neck

Evaporation from the cavity by cavitation is identified by a steep decrease in the adsorbed density at the so-called cavitation pressure, and is observed for an ink-bottle pore having a neck size smaller than a critical value. To better understand the contributions from the cavity and from the neck sections of an ink-bottle pore, we compared the simulation results for the three pore models shown in Figure 8.1. Model (a) is an ink-bottle model with cavity dimensions $W_1 = L_1 = 7\text{nm}$ and the neck dimensions $W_2 = 1.63\text{nm}$ and $L_2 = 10\text{nm}$. The other two models are: (b) a closed pore and (c) an open end pore, with dimensions the same as the cavity and neck in (a).

Adsorption isotherms for argon at 87K in the ink-bottle pore are shown in the top panel of Figure 8.2. There are two distinct hysteresis loops, corresponding to the pore filling and emptying of the neck and the cavity. The adsorption and desorption processes can be elucidated by comparing this isotherm with the isotherms of the closed pore and the open end pore shown in the bottom two panels of Figure 8.2.
During the first stage of adsorption in the ink-bottle pore, molecular layering occurs on the pore walls of both the cavity and the neck. Condensation first occurs in the neck at a reduced pressure of 0.1 (marked as A in Figure 8.2) which is the same as the corresponding open end pore (A’) because before condensation occurs the neck behaves like an open ended pore. Once the neck has been filled, the cavity behaves as a closed pore and therefore the adsorption in the ink-bottle pore should then be the same as that in a closed pore. Further increase in pressure results in more layers building up on the walls of the cavity until the gas-like core is small enough such that the attraction of adsorbates in the opposite surfaces induces the condensation to occur in the cavity at point C. On desorption from the filled ink-bottle pore the evaporation of the condensed fluid in the cavity is delayed, compared to a uniform pore (either open at both ends or closed at one end) having the
same size as the cavity. As pressure is reduced, the fluid in the cavity is stretched until the limit of mechanical stability of the condensed fluid has been reached and bubbles then form spontaneously via cavitation, resulting in a very steep drop along the desorption branch of the isotherm at a reduced pressure of 0.27 (point D). This cavitation pressure is identical to that in the closed pore (point D’). Once cavitation has occurred in the cavity, the neck behaves as an open ended pore with both ends of the neck exposed to the gas phase. Evaporation from the neck will then occur at a lower pressure (B), corresponding to the evaporation from the open end pore (B’). We can conclude that it is sufficient to use a closed pore model to study cavitation microscopically.

Figure 8.3 Radial distributions of liquid phase for Ar at 87K at the centre of the 7nm closed pore. The first peaks are shown on an enlarged scale and the full distribution function is shown in the inset. The dashed lines are at the distances 0.370nm and 0.374nm discussed in the text. The lines are labelled as in Figure 8.2.

The mean distance between neighbouring molecules is a measure of the extent of stretching in the condensed fluid, and it can be estimated from the position of the first maximum in the radial distribution function (RDF). Figure 8.3 shows the RDF for the argon adsorbate inside a 1nm cubic region at the centre of the 7nm square closed pore. At pressures above the cavitation pressure, the RDF maximum is at a separation of 0.37nm, and just before the cavitation this distance is increased to 0.374nm which just exceeds the mean distance between molecules in liquid argon at 77K \(^{167}\); the adsorbate fluid is therefore under tension and cavitation occurs.

8.3.2 Effect of cavity size

Although cavity formation is primarily dependent on the tensile strength of the bulk fluid, it is also modified by the presence of the adsorbent field which is intensified as the cavity size is reduced due to potential overlap \(^{88}\), and therefore the evaporation pressure is reduced below the intrinsic value of 0.27, in order to stretch the fluid to the critical separation distance of 0.374nm. To illustrate this we
show, in Figure 8.4, isotherms for the closed pore with square cross section of various dimensions (model (b) in Figure 8.1).

Figure 8.4 Adsorption isotherm for argon at 87K in closed pores with square cross section (W=L) and different cavity sizes.

The smallest pore (3nm), has a hysteresis loop that is significantly smaller that than in the larger pores with both condensation and evaporation pressures shifting to lower values.

In the pores with larger cavities (9nm and 11nm), the size of the hysteresis loop increases with pore size, mainly because a shift in the condensation pressure to higher values is necessary to build up the adsorbed layers to a thickness where the gas-like core is small enough for condensation to occur while the reduced pressure at evaporation, which is due to the tension of argon at 87K, remains at 0.27.
8.3.3 Effect of neck width

Our earlier studies of ink bottle pores have shown that a desorption passes from cavitation to pore blocking as the neck width increases \(^{109}\). This behaviour is confirmed in Figure 8.5 for a wide range of neck widths.

![Graph showing adsorption isotherms for argon at 87K in ink-bottle pores with different neck widths. The cavity size is 9x9nm (W₁=L₁=9nm) and the neck length L₂=10nm.](image)

**Figure 8.5** Adsorption isotherms for argon at 87K, in ink-bottle pores with different neck widths. The cavity size is 9x9nm (W₁=L₁=9nm) and the neck length L₂=10nm.

For pores with neck widths less than the critical size, which is 2.30nm for argon adsorption at 87K, isotherms show double hysteresis loops or a fused hysteresis loop. For pores having neck widths greater than the critical size, desorption proceeds by pore blocking, in which a meniscus formed at the mouth of the neck recedes into the pore interior until the cavity is emptied by a sharp evaporation of the residual concave lens at a single reduced pressure. This process results in a characteristic knee in the desorption branch of the isotherm with evaporation from the cavity occurring at a pressure higher than the intrinsic cavitation pressure. This phenomenon is better described by the term *cavitation-like pore blocking* \(^{168}\) because of the sequential processes of meniscus withdrawal from the neck and the sharp evaporation from the cavity and the neck. In this mechanism, the onset of evaporation is associated with the tension of the condensed fluid in the cavity and the extent of filling in the neck. As the pressure is decreased, the amount of adsorbate
Chapter 8 Adsorption in Inkbotte Pore

filling the neck is reduced when the meniscus recedes and at the same time the condensed fluid in the cavity is stretched. When the meniscus is close to the junction between the neck and the cavity, the condensed fluid in the cavity will evaporate at a pressure higher than the cavitation pressure. It should be emphasized that the process of cavitation-like pore blocking does not involve bubble formation in the interior, as distinct from cavitation where bubble formation is an essential part of the mechanism.

For those ink-bottle pores having small necks the adsorption branch shows two steps with the first condensation step being shifted to higher pressures as the neck size is increased, because a higher pressure is required for condensation to occur in the larger necks. When the neck is wide enough, adsorption proceeds by the advance of a meniscus, formed at the closed end, towards the neck, which induces filling of the neck at a lower pressure than in an open ended pore of the same width. This can be described as advanced condensation in the neck. Interestingly, the neck size for advanced condensation is larger than the critical neck size for cavitation.

8.3.4 Effect of neck length

Neck length also has a significant effect on the evaporation pressure since the forces holding the adsorbate are weaker for shorter necks. The effects of the neck length were studied by keeping the neck width of 2.3nm, which is the critical neck width at 87K, and the simulated isotherms are shown in Figure 8.6. When the neck length is reduced, there is a competition between two processes for the desorption of adsorbate from the cavity: (1) evaporation occurs followed by bubble formation in the cavity when the limit of the tensile strength of the condensed fluid is reached; (2) desorption starts from the junction between the cavity and the neck (when the neck has been emptied) and this process is similar to that in a closed end pore. Both processes are associated with a steep evaporation, but it should be noted that when emptying of the cavity is dominated by the second process, the corresponding evaporation pressure is higher than the cavitation pressure.
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Figure 8.6 Adsorption isotherms for argon at 87K in an ink-bottle pore with a neck width of 2.3nm and different neck lengths.

Figure 8.7 shows snapshots of the adsorbate just before and just after evaporation in the cavity. In the pore with an extra-long neck (10nm), the desorption mechanism is cavitation, occurring at a reduced pressure of 0.27 as discussed earlier. In this case desorption from the cavity is hindered by the constriction of the neck and the metastable fluid in the cavity is stretched because of the reduction in pressure. When the pressure is further decreased, the condensed fluid is stretched to its limit of mechanical stability, at which point the fluid in the centre of the cavity empties instantly leaving a gas-like bubble, while the neck remains (partially) filled. When the neck is shorter (5nm), a phenomenon termed advanced evaporation is observed in the neck, which occurs at the cavitation pressure, i.e. the condensed fluid in the cavity and the neck evaporate at the same time. This occurs because, when the condensed fluid in the cavity evaporates at the cavitation pressure, $P_{\text{cav}}$, the neck changes its status from that of a closed end pore to that of an open end pore and since the evaporation pressure of the neck having open ends is lower than the cavitation pressure, the fluid in the neck also evaporates as soon as cavitation occurs in the cavity. For pores having even shorter necks (less than 2nm), desorption is controlled by cavitation-like pore blocking in the cavity because the weaker adsorbent field at the neck does not hinder the removal of adsorbate, and the cavity therefore behaves like a closed end pore, in which the sole mechanism for desorption is pore
blocking. Thus evaporation from a cavity depends on the adjoining neck length, and the evaporation pressure is shifted to higher values as the neck length is reduced.

![Figure 8.7 Snapshots of argon at 87K in ink-bottle pores with of 2.3nm wide necks just before, and just after evaporation. The neck lengths for (a, a'), (b, b') and (c, c') are 10nm, 5nm and 2nm, respectively.]

To gain further insight into how molecules behave microscopically, the radial distribution functions shown in Figure 8.8, for ink-bottle pores with various neck lengths, were collected inside a 1nm cube at the centre of the cavity, at pressures just before evaporation. When the neck lengths are longer than 2nm, the maxima in the first peaks are located at 0.374nm, indicating that the fluid is under full tension and that evaporation will occur via a cavitation mechanism. On the other hand, when the neck length is <2nm the maximum is at 0.37nm, which implies that bubble formation does not occur in the pore interior and emptying of the pore is controlled by a cavitation-like pore blocking process.
Figure 8.8 Radial distributions from a cubic core region at the cavity centre for Argon at 87K in ink bottle pores with different neck lengths. The vertical dashed line is drawn at the position of the equilibrium separation (0.374nm).

8.3.5 Effects of temperature

We then investigated the effect of temperature on evaporation in a closed pore, where cavitation is the only mechanism of evaporation, and in an ink-bottle pore with relatively wide neck, where evaporation is via cavitation-like pore blocking. When the evaporation pressure ($P/P_0$) is plotted against reduced temperature (Figure 8.9), a number of interesting points may be noted:

1. The reduced pressure of evaporation from both pores shifts to a higher value as temperature increases.
2. Desorption from the ink-bottle pore is controlled by cavitation-like pore blocking at low temperatures but the mechanism switches to cavitation at some transition temperature.
3. The transition temperature is dependent on pore dimensions.
Figure 8.9 Temperature dependence of the evaporation pressure of argon from ink-bottle pores and a closed pore. The ink-bottle cavity has dimensions 9x9nm and a neck length of 3nm. The saturation vapour pressure for argon at different temperature was calculated.

8.3.6 Summary of condensation and evaporation mechanisms

In Figure 8.10, we summarize the evolution of isotherms obtained for an ink-bottle pore and the corresponding condensation and evaporation mechanisms.

For condensation, there are two possible mechanisms:

1. Condensation in the neck, followed by condensation in the cavity. This results in a double loop or fused loop hysteresis (see the adsorption branches of the top four isotherms in Figure 8.10. This typically occurs with narrow necks and at high temperatures.

2. A meniscus is formed at the closed end of the cavity, and advances to the junction of the cavity with the neck when advanced condensation in neck occurs. This typically occurs for larger necks and low temperatures.

For evaporation, we identify four mechanisms, depending on the neck dimensions:

1. When the neck is smaller than a critical size and sufficiently long, the desorption branch occurs in two-steps. The first step is associated with the cavitation of the condensed fluid in the cavity, and the second step (at a lower pressure) with the evaporation from the neck, which behaves as an open end pore prior to evaporation. This is shown in the desorption branch of the top two isotherms.
(2) When the neck is reduced in length or increased in width, evaporation in the neck is induced by cavitation in the cavity, resulting in a single step evaporation. We refer to this as advanced evaporation in the neck. This is shown in the third isotherm.

(3) When the neck is larger than the critical size, the evaporation mechanism is cavitation-like pore blocking which can be distinguished by a knee shape in the desorption branch and higher evaporation pressure than the cavitation pressure. This is shown in the fourth and fifth isotherms.

(4) In pore blocking, desorption is controlled by recession of the meniscus from the pore mouth to the closed end. This is only observed when the neck width is equal to the cavity size as illustrated in the last isotherm.

Figure 8.10 Evolution of condensation and evaporation mechanism in ink-bottle pores. All the isotherms shown can be obtained by increasing the neck width or reducing the neck length.
8.4 Conclusions

We have carried out a detailed GCMC simulation study of argon adsorption in ink-bottle pores and in closed pores to explore the effects of neck dimension and temperature on the evaporation of argon. From our microscopic analysis, we found that: (1) the average distance between molecules in the condensed fluid expands to a critical value ($0.374\,\text{nm}$) just before cavitation at $87\,\text{K}$, (2) besides the usual mechanisms of evaporation, cavitation and pore blocking, desorption in an ink-bottle pore can be governed by another mechanism (viz. cavitation-like pore blocking) which depends on the neck dimension and temperature, and (3) the reduced pressure at cavitation has a linear dependence on reduced temperature which is always lower than cavitation-like pore blocking when temperature is less than a threshold value.
Chapter 9 Conclusions and Recommendations

This thesis has presented a fundamental study on the adsorption behaviours of both non-associating and associating fluids on carbon adsorbent including both graphitized carbon surface and porous carbon. Monte Carlo simulation was carried out to investigate the mechanism by measuring the adsorption, isosteric heat curve, Henry constant and other microscopic analysis.

9.1 Conclusions

The first aim of this thesis is to develop a novel molecular model for graphitized thermal carbon black which is a composite of basal plane of graphene layers with crevices (ultrafine micropores) and oxygen functional groups attached at the edges of the graphene layers. This model was validated with high resolution experimental data and theoretically analysed with simulation results obtained with a grand canonical Monte Carlo simulation. Moreover, the experimental Henry constant and the isosteric heat at zero loading (in the region of very low loadings) are described correctly with the Monte Carlo integration of the Boltzmann factor of the pairwise interaction between an adsorbate molecule and the porous carbon. It is found that non-associating fluids and associating fluids are governed by different sites in the initial stage of adsorption: for nitrogen and carbon dioxide, similar to argon, dominantly adsorb in the fine crevices at very low loadings; on the other hand, polar fluids, such as ammonia and water, the dominance of the functional group in adsorption is manifested, especially water.

This model was then used in the study of ammonia adsorption on GTCB at different temperature: close to triple point and to the boiling point and a good qualitative agreement was observed between our simulation results and the high resolution experimental data. For the first time the hysteresis of ammonia at triple point was reproduced by simulation, which is due to the restructuring of adsorbate. Furthermore, We found that the preferential adsorption site of ammonia depends on the temperature: at triple point, ammonia molecules first adsorb on the functional groups (FG) on the ultrafine pore but insignificantly on the basal plane (BP), due to the dominance of F-FG interaction over the F-BP interaction; on the other hand, at boiling point, ammonia adsorption occurs on the functional groups as well as the basal plane due to the entropic effect at higher temperature.

Apart from describing the behaviours of adsorbate on graphitized carbon surface, we proposed a novel method to determine the concentration of surface oxygen-containing groups on carbon adsorbents. Our proposed method using strong associating fluid such as water and methanol as a molecular probe give more realistic concentrations than the experimental measurement by Boehm titration, especially in the case that the concentration of functional group is very low in the sample.
Another objective of this thesis is the investigation of adsorption behaviours in pores. This is first achieved by a systematic GCMC simulation of argon adsorption in uniform open-ended and closed-end pore by investigating a number of parameters: pore size, pore length, surface affinity, temperature, and adsorbate. Analysing the adsorption isotherms of these pores led us to capture features of how molecules adsorb and are structured in pores which result from the interplay between a number of fundamental processes: (1) molecular layering, (2) clustering, (3) capillary condensation and evaporation and (4) molecular ordering. We paid specially emphasis on the adsorption in closed end pore by generating extremely long Markov chain and we found that hysteresis in closed end pore is observed in two cases: (1) very weak adsorbents where adsorption and desorption proceed by different mechanisms: clustering of the adsorbate molecules on adsorption and a receding of meniscus on desorption; (2) well below the triple temperature in which the adsorbate becomes solid-like.

Following the study of uniform pore, we extended our study to wedge-shape pore and the effect of pore length, angle and temperature on the hysteresis loop is systematically studied. Mesoscopic analysis of the interface separating the gas phase and the adsorbate, has shown that desorption from a wedge can be described by the DBdB equation. We found that the effective surface tension at this interface is slightly greater than the bulk value, suggesting that the interface is only slightly more cohesive, than the vapour-liquid interface in a bulk phase, due to the influence of the adsorbent potential energy field. This suggests that wedge pore is a more appropriate model than the uniform pore for the determination of pore size distribution in activated carbons.

In the last section of this thesis, the hysteresis in inkbottle is investigated and we summarized the evolution of isotherms obtained for an ink-bottle pore and the corresponding condensation and evaporation mechanisms.

9.2 Recommendations

9.2.1 Henry constant for associating fluids on functional groups

As shown in Chapter 5, a factor $F$ is introduced in the potential energy calculation between an associating fluid molecule with one functional group for the integration of Henry constant. This is because in reality associating fluid preferentially forms a composite of dimer or trimer even at extremely low pressure, the composite has much stronger interaction with functional group than a single molecule. Therefore it is necessary to develop a new technique to calculate the Henry constant of a composite of dimer or trimer on the functional group.
Chapter 9 Conclusions and Recommendations

9.2.2 Water adsorption in micropore and mesopore
The molecular model of GTCB proposed in Chapter 3 and 4 can be further extended to study water adsorption in activated carbon which consists of micropores and mesopores with functional groups grafted at the edge of the pore mouth. Depending on the strong hydrogen bonding between water and functional groups, water will initially form clusters around the functional groups as illustrated in Chapter 5. It is logically expected that as pressure is further increased, these clusters grow at the pore mouths and merge together, and eventually enter the graphitic pores via a penetration process of a non-wetting fluid. It is recommended to pursue this with microporous carbons and then onto mesoporous carbons where the effects of temperature on adsorption isotherm were observed, in opposite to what would be expected by thermodynamic.
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Figure A1. Adsorption isotherm for argon at 87K in open-ended pores and closed-end pores with different pore sizes; plotted with a linear pressure scale.
Figure A2. Adsorption isotherms for Argon in cylindrical graphitic pores for different pore sizes and temperatures: (a), (c) and (e) are open-ended pores; (b), (d) and (f) are closed-end pores.
Figure A3. Snapshot of formation of liquid embryo in a wedge pore.

Figure A4. Compressibility at 87K as a function of distance along the pore axis.