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Transport on a nanoscale; quasi-elastic neutron scattering and molecular dynamic studies

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Lisa, in this house we obey the laws of thermodynamics!!

Homer J. Simpson
Acknowledgments

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Cast off and set sails, new adventures await!!
Summary

The objective of this thesis was to investigate how hydrogen is transported in the polymer electrolyte membrane fuel cell (PEMFC) electrodes. We wanted to investigate if the graphitic catalyst support material can contribute to the transport of hydrogen to the platinum (Pt) catalyst particles in the catalyst layer. Knowledge of the transport mechanism in the PEM fuel cell electrodes can help design better PEMFCs.

To perform such an investigation we need methods that can discriminate between hydrogen molecules adsorbed on the graphite surface and hydrogen molecules in the gas phase. One method that is able to do that is quasi-elastic neutron scattering (QENS), described in Chapter 3. At low temperatures QENS gives information on the movement of the hydrogen molecules adsorbed on graphitic materials. In our experiments we adsorbed hydrogen on XC-72, a graphitic material that is commonly used in PEMFC as catalyst support material. In Chapter 5 we report QENS data in the 40 to 70 K range for a hydrogen loading equal to a full monolayer at 2 K. The data show that the surface self diffusion coefficient on XC-72 is the same as on single wall nanotubes and oriented graphite. We found that the diffusivity is in the 1 to $4 \times 10^{-8}$ m$^2$/s range for the investigated temperatures. In this experiment the surface concentration was not measured during the QENS measurements. To examine the effect of the surface concentration on surface self diffusion we preformed a second QENS experiment. In Chapter 7 we report QENS data in the 40 to 90 K range for a hydrogen loading equal to half a monolayer at 2 K. In this experiment the surface concentration was measured during the QENS measurements. We found that the surface self diffusion increased in this experiment due to the lower hydrogen loading compared to the first QENS experiment. This can be seen from the change in the temperature dependence presented in Chapter 7.
To get additional data and better understanding of the system we did equilibrium molecular dynamics (EMD) simulations of hydrogen in contact with a graphite surface. The system is described in Chapter 6. From EMD simulations the motion and energies of all molecules are known and this makes it possible to obtain dynamic and thermodynamic properties of the simulated system. In Chapter 6 we report thermodynamic and kinetic properties of the simulated hydrogen-graphite system. We simulated isotherms from 70 to 370 K and used them to calculate the equilibrium constant of adsorption. We found that the density close to the graphite surface always was higher than in the gas phase. The isotherms were used to investigate the adsorption enthalpy and entropy as function of surface concentration. From the adsorption and desorption rates we proposed a new set of rate equations that give the same values for the equilibrium constant of adsorption as we get from the isotherms.

The simulated data was also used to find the surface self diffusion coefficient of hydrogen from 70 to 350 K at different surface concentrations, see Chapter 7. When using the temperature dependence of the surface self diffusion found from QENS, to calculate the diffusivity at 350 K, the values are 4 to 10 times lower than the values from EMD. From both the QENS and the EMD data we found that the diffusion activation energy was 3 times lower than the adsorption energy. The EMD values of $D^s$ was linear with $c_{H_2}^{s-1}$ for the high density regime, as predicted by kinetic theory. However it reaches a plateau in the low density regime. From the simulated data we also calculated the average time between adsorption and desorption events for the hydrogen molecules. This data followed an exponential trend that decreased with temperature. With the values of $D^s$ and the average time we calculated the mean displacement of the hydrogen molecules. This data enabled us to add to the main objective, to investigate the surface transport of hydrogen along the graphite surface to a catalyst particle in a PEMFC. By investigating an ideal system where we considered the catalyst as a hemisphere, described in Chapter 7, we found that the graphite support will transport at least 50% of the hydrogen reactant to the catalyst particle compared to direct adsorption from the gas phase.
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Chapter 1

Introduction

1.1 Energy demand and supply

The world's energy demand is growing and today the energy is primarily based on oil and coal. The scenario given by the International Energy Agency (IEA) of the world energy demand is an increase of 45% by 2030. Fossil fuels will account for two-thirds of this demand by their projections. To meet this demand the existing oil sources have to be replaced by new oil fields. Production of 64 million oil barrels per day needs to be installed by 2030. This is six times the current capacity of Saudi Arabia [1] which is the world's largest oil exporter. Because fossil fuel resources are not renewable, sometime in between 2010 and 2030 the production of these supplies are expected to peak. This scenario is neither sustainable from a supply point of view nor an environmental point of view, and efforts to prevent it must be taken. Development of sustainable energy sources and more energy efficient technology are crucial to prevent this scenario.

A step in the right direction is the effort to develop hydrogen as an energy carrier in the transport sector. The transport sector will use three-quarters of the projected increase in oil demand [1], and thus shifting from oil to hydrogen would make a significant impact. One way to produce hydrogen is by reforming of natural gas. One of the main exhaust to this process is CO₂. However, this CO₂ production is done at a large scale in factories and can be managed by capture and sequestration. This is not the final solution of the problem, but it will be a part of the transition from fossil fuels to hydrogen. More environment friendly ways of producing hydrogen is by electrolysis, photo-electrolysis,
high-temperature decomposition and photo-biological water splitting. These production methods are potentially 100% renewable, depending on their energy source, e.g. hydro, wind, solar, biomass or geothermal power.

To release the energy from the hydrogen gas, the hydrogen must react with oxygen. At the moment, the transport sector sees only two commercially available solutions to this problem. The first method is to use hydrogen in an internal combustion engine, instead of fossil fuels, and burn it with oxygen. This solution is embraced by Mazda and BMW. The Mazda RX-8 is a car which run on hydrogen and it is used by the Norwegian hydrogen project HyNor [2]. The second method is to use hydrogen in a proton electrolyte membrane fuel cell (PEMFC) to produce electricity for an electric motor. Several car companies have started to develop fuel cell vehicles and Honda is leasing a limited number of cars to private customers from summer 2008 [3]. The PEMFC is chosen by car manufacturer because of advantages such as low operating temperature, sustained operation at high current density, low weight, compactness, fast start up, and handling several starts and stops every day [4–7].

1.2 Polymer electrolyte membrane fuel cell

The PEMFC is a much anticipated device for delivering power to mobile and stationary applications. It has three primary components, the backing plates, electrodes and the proton conducting membrane. The electrodes and the membrane are often hot pressed together to form what is referred to as a membrane electrode assembly or MEA. These components contain several elements that are important for the operation of the PEMFC. Before we discuss these components in detail, let us first introduce the key idea of the fuel cells in general. Fuel cells, just like batteries, convert chemical energy to electric power and heat. But, in contrast to batteries, fuel cells can continuously be fed new fuels, like an internal combustion engine. One advantage of the PEMFC is that it has a greater theoretical efficiency than the internal combustion engine [8]. Thereby giving the PEMFC a promising future as an energy converter. Still, before its potential is realized there are many problems that needs to be solved.

To fulfil the theoretical efficiency of PEMFC technology several of the elements in the fuel cell need to be improved. There are problems with the lifetime of the membrane, catalyst support materials, and the catalysts themselves. The cost of production is high due to low production numbers and highly specialized materials. And, the efficiency in the PEMFC has not reached the values promised by the theoretical efficiency. Furthermore there are many auxiliary components needed to produce, deliver and feed fuel into the fuel
1.2 Polymer electrolyte membrane fuel cell

cells. All of these components have problems that are being tackled by many scientists around the world, and they have made progress every year [9].

Now let's take a closer look at the three primary components of the PEMFC.

![Diagram of PEMFC components]

Figure 1.1: In row 1 there is a drawing visualising the three main components of the PEMFC, a) is the backing plate, b) is the electrode and c) is the membrane. In row 2 the components are brought together. In row 3 there is a blowup of the membrane and electrode showing the catalyst layer, CL, and the porous transport layer, PTL.

In Figure 1.1, row 1, the main components are displayed. They are marked by a) - the backing plate with the flow field, b) - the electrode made by graphite paper or cloth and c) - the membrane made of a proton conducting polymer. These components are brought together in row 2) and are forming a simple PEMFC when pressed together. In row 3) there is a blowup of the electrodes pressed in contact with the membrane. The electrodes have two different parts,
the PTL and the CL. Close to the membrane there is a catalyst layer made of graphite catalyst support particles and a metal catalyst. This layer is called the catalyst layer (CL). On the outside of the catalyst layer there is a much thicker layer of graphite fibers, called the porous transport layer (PTL). This layer has large pores for transport of reactant gas to the CL.

In the left side CL in row 3) the hydrogen gas is split into protons, H\(^+\), and electrons, e\(^-\). The left side is thus the anode. The H\(^+\) is transported through the membrane to the right side CL while the e\(^-\) must flow through an external circuit. In the right side CL, O\(_2\) reacts with H\(^+\) and e\(^-\) and forms water, H\(_2\)O. The right side is thus the cathode. For this electrochemical reaction to occur the reactant gases in both anode and cathode must be transported through the two layers in the electrodes. First they must pass through the PTL before they reach the CL. In the CL the reactant gases then have to adsorb on the surface of the catalyst particles. This are two important steps in the overall reaction mechanism inside the fuel cell.

The transport of reactants by diffusion to the catalyst particles can give rise to a limiting step in the PEMFC. The diffusion limits the maximum current the PEMFC can deliver. At high currents the transport of reactants can be too slow and the PEMFC reaches a diffusion limited current. So by improving diffusion to the catalysts the maximum current can be increased. To improve diffusion we, need to know more about what mechanisms that are governing the diffusion inside the PTL and CL. The consensus today is that the transport mechanism through the PTL is diffusion in gas bulk. This is highly likely due to the large channels inside the PTL. Inside the CL the channels and pores are much smaller but still the consensus is that the mechanism is diffusion in gas bulk [10–13]. This means that there is gas diffusion all the way up to the catalyst particles where the reactant gases adsorb. We want to examine this view and look at surface diffusion along the catalyst support particles as a possible alternative route for transport of reactants to the catalysts.

### 1.3 Hydrogen interaction with carbon

There are several experimental methods to investigate the interaction between gases and solid surfaces. Gas adsorption/desorption techniques measure the amount of gas on the surface of the solid at constant temperature or under a linear temperature change, by measuring change in weight or gas volume. These techniques can give information on interaction energies, thermodynamic variables and kinetic factors. They are restricted to measure bulk or macroscopic averages as they see the system as a whole. Other methods for probing
the surface on a microscopic scale use some form of radiation or force field to see the adsorbate as well as the adsorbant [14]. The radiation can be photons, electrons, neutrons, ions or atoms. By knowing the incident energy of the radiation and measurement of the energy of the out coming radiation, information is obtained. What is typically measured is types of surface species, amount of surface species, bonding energies of surface species, structure of the surface and oxidation numbers. Experiments carried out on physical adsorption of light gases on carbon materials can only be done by some of these methods and in this work we limit the discussion to the adsorption/desorption and neutron scattering methods.

As previously mentioned, materials inside the PTL and CL are carbon based. Usually they are some sort of graphite, so it is of interest to know how hydrogen and oxygen interact with graphite/graphene. Much work has been done to study interaction between hydrogen molecules and carbon the last 10 years [15, 16]. The possibility of using graphite and other carbon materials for hydrogen storage spurred a high research activity on the hydrogen-carbon material interaction [17]. Both experimental techniques [18–22] and computational methods [23–27] have been used to examine the adsorption of hydrogen in these systems. The interaction energy between hydrogen and carbon materials, as graphite, is in the 1-10 kJ/mol range with an average of 4-5 kJ/mol [17, 28, 29]. There is only a small change in the interaction energy between the different allotropes of carbon and hydrogen, which is apparent as the amount of adsorbed hydrogen is a linear function of the surface area of the different carbon materials [30].

Other studies have been performed the last decades to look at the possibilities of using carbon nanotubes to separate gas mixtures. In these studies computational methods have been used to calculate both mixture and self diffusivities of light gases in pores and on surfaces [16, 31–34]. Diffusion measurements have also been conducted with the help of neutron scattering techniques. Early measurements of surface diffusion on graphite was done by Coulomb et al. in the late 70s. They measured the surface diffusion of methane on Papyex [35–37]. Later measurements of surface diffusion of hydrogen isotopes on graphite and carbon nanotubes were performed by Liu et al., Bienfait et al. and Narehood et al. [38–40]. Since neutron scattering is less available compared to adsorption, more adsorption data than dynamic data are reported.
1.4 Aim and outline of the thesis

The aim of this thesis is to look at the possibility that the graphitic support material in PEMFC assists in the transport of hydrogen from the PTL to the catalytic particles in the anode of the PEMFC. To find an answer to this question we have done quasi-elastic neutron scattering experiments of a hydrogen-graphite system at low temperatures from 2 - 90 K and molecular dynamics simulations.

Experiments were carried out at ILL in Grenoble, France, using the IN5 time-of-flight apparatus. This allowed us to see surface self diffusion of hydrogen on XC-72, a commercial fuel cell catalyst support material. The results gave us an overview of how the system behaves and gave us the initial knowledge we needed to decide further work. From the results we learned that the neutron scattering could not be used to investigate the hydrogen diffusion at temperatures above 90 Kelvin in our system.

To investigate the hydrogen diffusion at higher temperatures we had to use molecular dynamic simulations. From molecular dynamic simulations of the graphite-hydrogen system one can look at a larger temperature and pressure range and get additional information about the system. We get information about pressure, surface concentration, interaction energy, temperature, adsorption/desorption rates and surface self diffusion. Both of the two methods give useful information of the system, and they can verify each other.

The outline of the thesis is as follows:

Chapter 1-4 are short introductions to some of the relevant theory for this thesis.

In Chapter 5 the first paper is presented. This paper reports the findings of the first quasi-elastic neutron scattering experiment. We give the theory for how to analyse the measured data and obtaining the surface selfdiffusion coefficient.

In Chapter 6 the second paper is presented. This paper reports the results from the equilibrium molecular dynamics simulations of hydrogen adsorption on graphite. The surface is described by Gibbs excess properties and is regarded as an autonomous thermodynamic phase. We report the isosteric enthalpy and entropy as function of surface concentration together with the equilibrium constant. The adsorption and desorption rates are calculated and their variation with pressure and surface concentration is discussed.
In Chapter 7 we compare quasi-elastic neutron scattering (QENS) data with equilibrium molecular dynamics results. The surface self-diffusion of hydrogen is measured by QENS under controlled gas pressure and these values are in good agreement with molecular simulation values. From molecular dynamics simulation we find the residence time of hydrogen on graphite and the mean squared displacement. This is used to estimate the contribution of the catalyst support surface to the transport of reactant gas to the catalyst.
Chapter 2

Physical adsorption of hydrogen on graphite

In this work adsorption of hydrogen on graphite has been studied with quasi-elastic neutron scattering, described in Chapter 3, and molecular dynamic simulations, described in Chapter 4. The main aim was to evaluate surface transport of hydrogen on graphite, but since surface concentration and residence time are important parameters for transport properties, adsorption must also be evaluated. In the following chapter an introduction to adsorption processes will be presented.

2.1 Physical adsorption

When there is equilibrium between a gas (the adsorbate) and a solid surface (the adsorbent) the density of the gas molecules are always found to be greater close to the surface than in the free gas. The process which causes the increase in density is called adsorption. Adsorption can be separated in two different types, physical and chemical. In physical adsorption only weak intermolecular forces are involved, while in chemical adsorption there is a formation of a chemical bond between the adsorbate and the outer surface molecules. A common variable used to describe the physical adsorption is the so-called heat of adsorption. This value is a direct measure of the strength of the interaction between adsorbate and adsorbent. It has been used to measure the phase diagram of adsorbed hydrogen molecules on graphite. This was done by Freimuth et al. in 1985 [41] and their result is given in Figure 2.1. Physical adsorption from the gas phase is a spontaneous process and accompanied by a decrease in Gibbs
free energy ($\Delta G = \Delta H - T \Delta S$) of the system. Since the gas has maximum two translational degrees of freedom and the rotational degree of freedom must be less than in the gas phase, the entropy change ($\Delta S = S_{\text{ads}} - S_{\text{gas}}$) on adsorption is negative. Thus the adsorption is an exothermic process with $\Delta H < 0$.

Figure 2.1: The phase diagram of H$_2$ monolayers physisorbed on graphite. Remake of figure in [41]
2.2 Thermodynamics of adsorption

In this work adsorption of hydrogen on graphite in the temperature range 70 to 390 K has been studied. From Figure 2.1 it is seen that the adsorbed phase is in the fluid or 2D fluid gas phase. The system does never go into a solid state and the adsorbate is always mobile. The thermodynamic approach to equilibrium may be used to describe the equilibrium of adsorption processes. The adsorbed phase is then treated as a thermodynamic phase. There are two different perspectives in applying thermodynamic principles to the adsorption equilibrium [42–44]. The first approach is to treat the adsorbate and the adsorbent as a two component system in equilibrium with the unadsorbed gas. In this case the solid as well as the adsorbed gas molecules contribute to the properties of the thermodynamic properties of the adsorbed phase. This was developed by Hill [45]. The second way to describe the system is to assume that the properties of the adsorbent does not change with the adsorption of gas molecules or with variations in temperature. The adsorbent is thus treated as an inert solid. This assumption was formulated and applied by Gibbs [46]. In the continuing description of the adsorption equilibrium we will first give Gibbs description of a surface between two homogeneous phases, and then show how this general formalism give a description of the adsorbed phase in adsorption processes.

2.2.1 Two homogeneous phases separated by a surface in global equilibrium

In this paragraph a description of Gibbs excess values and dividing surface is presented. It follows the description given by Kjelstrup and Bedeaux [47]. The condition for equilibrium between two homogeneous phases is given by

\[ \mu^i = \mu^o \]  

(2.1)

The two homogeneous phases have their internal energies \( U^i \) and \( U^o \), entropies \( S^i \) and \( S^o \), and mole numbers \( N_j^i \) and \( N_j^o \) of components \( j \). For the total system, introducing the surface \( s \), these values are

\[ U = U^i + U^s + U^o \]
\[ S = S^i + S^s + S^o \]  

(2.2)
\[ N_j = N_j^i + N_j^s + N_j^o \]

The surface values of these variables are thus the total values minus the values of the two bulk phases. The surface has a thickness of molecules and is
negligible compared to the volume of the two bulk phases. The total volume is thus \( V = V^i + V^o \). The surface area, \( \Omega \), is the parameter used to describe the size of the surface, as the volume does for the bulk phases. The surface tension, \( \gamma \), describe the pressure in the surface in its two dimensions as \( p^i \) and \( p^o \) does in the two homogeneous phases. For the total heterogeneous system the differential internal energy is given by Gibbs equation

\[
dU = TdS - pdV + \gamma d\Omega + \sum_{j}^{n} \mu_j dN_j
\] (2.3)

From integration with constant \( T, p, \Omega, \) and \( N_j \) the energy of the system becomes

\[
U = TS - pV + \gamma \Omega + \sum_{j}^{n} \mu_j N_j
\] (2.4)

This is the energy of the two homogeneous phases plus the surface. To get a description of the surface alone we describe the same equation for the homogeneous phases

\[
dU^i = TdS^i - pdV^i + \sum_{j}^{n} \mu_j dN^i_j
\] (2.5)

This is the Gibbs equation for phase \( i \), and the same equation is valid for phase \( o \). By integration with constant temperature, pressure, and composition the total energy is

\[
U^i = TS^i - pV^i + \sum_{j}^{n} \mu_j N^i_j
\] (2.6)

For the surface the Gibbs equation becomes

\[
dU^s = TdS^s + \gamma d\Omega + \sum_{j}^{n} \mu_j dN^s_j
\] (2.7)

and by integration, this time with constant surface tension, \( \gamma \), temperature, and composition

\[
U^s = TS^s + \gamma \Omega + \sum_{j}^{n} \mu_j N^s_j
\] (2.8)

Now the thermodynamical relations for the surface are identical with the thermodynamical relations for the two homogeneous phases, see Equation 2.6 and Equation 2.8. The global equilibrium for all the three phases can now be
described. The chemical potentials and the temperature are constant in the system

\[
\mu_j^i = \mu_j^s = \mu_j^o, \quad T^i = T^s = T^o
\] (2.9)

If the surface is flat, the pressure normal to the surface is identical in all phases. However, this is not the case for curved surfaces. In the following a flat surface will be considered and the normal pressures are equal in all phases. The surface energy, surface entropy, and the surface mole number are now described by the total values minus the homogeneous phase values.

![Diagram showing change of concentration of A going from phase i to phase o. Line a and line b indicates the boundaries of the interface. The dashed line p is the dividing surface.](image)

Figure 2.2: Change of concentration of A going from phase i to phase o. Line a and line b indicates the boundaries of the interface. The dashed line p is the dividing surface.

Gibbs introduced excess densities to describe the thermodynamic properties of an interface between two homogeneous phases. The interface is a thin layer between these two phases. Figure 2.2 shows an illustration of the interface between phase i and o. Through the interface the concentration of component A is changing. The position of boundary a is at the point where \( c_A(x) \) starts to differ from \( c_A^i \), and position b is where \( c_A(x) \) starts to differ from \( c_A^o \). These positions are not dictated by this relation. Gibbs defined the dividing surface
as a geometrical plane through the interfacial region. The position if this plane can be freely chosen, but it is normally between the vertical lines in Figure 2.2. The integration of \( c_A(x) \) over the thickness \( d=b-a \), as a function of \((y, z)\) give the excess surface concentration of component A along the surface

\[
\Gamma_A(y, z) = \int_a^p \left[ c_A(x, y, z) - c^i(a, y, z)\theta(p-x) \right] \, dx \\
- \int_p^b \left[ c_A(x, y, z) - c^o(b, y, z)\theta(x-p) \right] \, dx
\]  

(2.10)

Here \( \theta \) is the Heaviside function and it is by definition unity when the argument is positive. All excess properties of a surface can be defined by integrals as Equation 2.10 and the excess properties are the extensive variables of the surface.

![Diagram](image)

Figure 2.3: Change of concentration of A going from the gas phase to the solid surface at \( x=0 \). Lines \( a \) and \( b \) indicates the boundaries of the interface. The dashed lines \( P_1 \) and \( P_2 \) are two different dividing surfaces giving two different values for the excess surface concentration. They are both valid from Gibbs definition.

The definition of a surface between two homogeneous phases is also valid for adsorption systems. For adsorption of gases on solids it is convenient to put
the dividing surface at the beginning of the surface, at $p_1$ in Figure 2.3. Then the excess surface concentration is given by

$$\Gamma_A = \int_{p_1}^b c_A(x) - c_A^{\text{gas}}(b) \, dx$$

(2.11)

This is the value measured by isothermal adsorption experiments and it is increasing with pressure until it reach a maximum and then starts to decrease. The other alternative given in Figure 2.3 is to put the dividing surface at $p_2$. Then the excess surface concentration becomes

$$\Gamma_A = \int_{a}^{p_2} c_A(x) - c_A^{\text{solid}} \, dx$$

$$\Gamma_A = \int_{a}^{p_2} c_A(x) \, dx$$

(2.12)

in the second line $c_A^{\text{solid}}$ is removed since it is zero at the solid surface, there is no adsorbed gas inside the solid surface. This gives an excess surface concentration that is less convenient for adsorption experiments. This value will increase as the pressure increase. It is a convenient definition of the system when doing molecular dynamic simulations as the calculated excess surface concentration is given by the total number of molecules on the surface. This is the value that has been used in this work when evaluating thermodynamic and dynamic properties of the adsorbed phase. The rest of the extensive variables can not benefit from the same reduction as Equation 2.12 as they are not necessarily zero in the solid. Using the assumptions introduced by Gibbs, that the adsorbed is inert, the bulk properties of a clean solid can be used in equations similar to Equation 2.12. Then Gibbs equation can be described as

$$dU^s =TdS^s + \pi_a^s \, d\Omega^s + \mu^s \, dn_j^s$$

(2.13)

where $\pi$ is the so-called spreading pressure defined as $\pi = \gamma - \gamma^0$ [42–44].

The motivation for this description is to show that it is possible to define the adsorbed phase in different ways. In molecular dynamics it is possible to use any definition of the dividing surface since the positions of all molecules are known at all times. In this work the position of the dividing surface have been set at $p_2$ in Figure 2.3. This was achieved by using an energy criterion which is described in Chapter 6. Using the more practical energy criterion resulted in a small perturbation in the exact position of the dividing surface and negligible variations in the parameters for the adsorbed phase.
Chapter 3

Quasi-elastic neutron scattering

Low energy neutrons, or thermal neutrons, have energies of about 25 meV. The low energy neutrons have several properties that make them excellent probes for investigating molecular structure and motion. The neutrons interact with nuclei via the short-range nuclear force. Due to their energy, thermal neutrons have wavelengths that are larger than the size of a nucleus. Neutrons do not see the internal structure of the nucleus. This makes the neutron scattering isotropic and independent of the incident angle. The neutron scattering is characterized by a scattering length $b$, which has the same order of magnitude as the nucleus. The wavelengths of the neutrons are of the same order of magnitude as inter-atomic distances in solids. And the neutron energies match the energies typical for atomic or molecular vibrations. Since neutrons do not have long-range interactions, they can penetrate deep into the bulk phase of solids. Hydrogen is the strongest neutron scatterer and neutrons are thus well suited for doing experiments on hydrogen.

The scattering of neutrons or other radiation is usually divided in elastic or inelastic scattering. The difference between these two scattering events is the energy exchange between the neutron and the nucleus. For elastic scattering there is no energy exchange while for inelastic scattering there can be large energy exchange between the neutron and the nucleus. The term quasi-elastic neutron scattering (QENS) refers to small energy exchanges between the neutron and the nucleus, typically ±2 meV. This scattering gives a small broadening of the elastic line which is caused by particles diffusing or reorienting over a time-scale of ca $10^{-10}$ to $10^{-12}$ s.
3.1 Theory of quasi-elastic neutron scattering

Low energy neutrons are generated by a nuclear reaction or by spallation and they are thermalised by passing through a cooling or heating medium that change the wavelength of the neutron. This give a beam of neutrons with a energy distribution following a Maxwell law around an average speed $\overline{v}$

$$\overline{E} = \frac{1}{2} m\overline{v}^2 = \frac{3}{2} k_B T$$

(3.1)

where $k_B$ is the Boltzmann constant, $m$ is the mass of the neutron, $T$ is the temperature, and $\overline{E}$ is the average energy. By controlling the temperature of the medium the distribution of wavelengths can be controlled. From considering the neutrons as plane waves with the incident wave vector $k_i$

$$k_i = \frac{m}{\hbar} v_i$$

(3.2)

and wavelength $\lambda$

$$\lambda = \frac{2\pi}{|k_i|} = \frac{h}{mv_i}$$

(3.3)

we can express the kinetic energy by the wave vector

$$E_i = \frac{\hbar^2 k_i^2}{2m} = \frac{h^2}{2m\lambda_i^2}$$

(3.4)

where $\hbar$ is the reduced Planck constant. In scattering experiments two quantities are basically measured. The first is the energy transfer and the second is the scattering vector. The energy transfer is expressed as

$$\hbar \omega = E_f - E_i = \frac{\hbar^2}{2m} (k_f^2 - k_i^2)$$

(3.5)

where $\omega$ is the angular frequency, $E_i$ is the incident energy, $E_f$ is the final energy, $k_i$ is the incident wave vector, and $k_f$ is the wave vector after scattering and the scattering vector, $Q$, is

$$Q = k_f - k_i$$

(3.6)

By combining Equations 3.5, 3.6 the relation between $Q$ and wave vectors is

$$Q^2 = k_f^2 + k_i^2 - 2kk_0 \cos \phi$$

(3.7)

where $\phi$ is the scattering angle given by the incident direction and the scattered direction, see Figure 3.1. When an incident neutron comes close to a nucleus
3.1 Theory of quasi-elastic neutron scattering

Figure 3.1: 3 different scattering events at constant scattering angle $\phi$. We measure $E_1$ and $E_2$ and from Equations 3.5 and 3.7 we get $Q$.

in a sample there are two possibilities; absorption or scattering. These two outcomes are given by the cross sections $\sigma_a$ and $\sigma_s$ such that an incoming flux $I_0$ is divided in two parts

$$I_a = I_0 \sigma_a$$
$$I_s = I_0 \sigma_s$$

(3.8)

where $I_a$ is the part of the flux that is absorbed in the sample nuclei and $I_s$ is the part of the flux that is scattered by the sample nuclei. For the scattered cross section we can further divide the contribution into two parts, the coherent part and the incoherent part.

$$\sigma_s = \sigma_{coh} + \sigma_{inc}$$

(3.9)

As previously mentioned the scattering of neutrons by the nuclei is isotropic, and the scattering event can be characterized by a single parameter called the scattering length, $b_j$. The scattering length is different for each element and isotope and their spin states. The scattering length is a parameter in the potential describing the interaction between a neutron at position $r$ and a nucleus at position $R$. This potential is the Fermi pseudopotential and in a sample with many nuclei it is the sum over all the interactions.

$$V(r) = \frac{2\pi \hbar^2}{m} \sum_j b_j \delta(r - R_j)$$

(3.10)
The value of $b_j$ for each isotope and its spin state must be experimentally determined. Furthermore the average $\langle b_j \rangle$ over all the isotopes and spin states is the coherent scattering length. The incoherent scattering length is defined as the root mean square deviation of $b_j$.

$$b_j^{coh} = \langle b_j \rangle$$
$$b_j^{inc} = [(b_j^2 - \langle b_j \rangle^2)^{1/2}]$$

(3.11)

The values of $b_j^{coh}$ and $b_j^{inc}$ are tabulated for each isotope, e.g., as found in the book by Bée [48]. From these values the coherent and the incoherent scattering cross sections can be defined as

$$\sigma_{coh} = 4\pi b_j^{coh}$$
$$\sigma_{inc} = 4\pi b_j^{inc}$$

(3.12)

Coherent scattering, $\sigma_{coh}$, yields information about the correlation between motion of particles and interference effects. The coherent scattering can thus be a result of phonons or due to interference between neutrons scattered by atoms that has some short-range order. The incoherent scattering, $\sigma_{inc}$, is due to the non-correlated properties in the sample. Incoherent scattering is a result of neutrons scattered by different atoms and leaving the sample without interfering with each other. This means that the neutrons have information about single atom properties such as rotational and translational motions and vibration around an equilibrium point in space. These properties can be used to measure the self diffusion of an element.

To use this information we need a theory that explain how the diffusive motions of molecules can be found from measurements of energy transfers, scattering angles, and intensities. The theory given here is a short version of the discussion of scattering functions and pair correlations, for a more complete treatment see Bée [48] and Hempelmann [49].

First we introduce the general double differential which give the probability for a neutron leaving the sample in the solid angle element $d\Omega$, in the direction $\Omega$, with the incident energy $E_i$ and with an energy exchange between $\hbar \omega = E_f - E_0$.

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \left( \frac{m}{2\pi \hbar^2} \right)^2 \frac{k_f}{k_i} \sum_{n_i} p(n_i) \sum_{n_f} |\langle k_f n_f | V | k_i n_i \rangle|^2 \delta(E_{s,f} - E_{s,i} + \hbar \omega)$$

(3.13)
Here the subscripts $i$ and $f$ are used to separate the incident and final states. These refer both to the neutrons and the sample nuclei and represent the change in both. The energy in a sample nucleus before a scattering event is $E_{s,i}$, and $E_{s,f}$ is the energy in a sample nucleus after a scattering event. The interaction potential between a neutron and a nucleus in the sample is $V$. The ratio $k_f/k_i$ is related to the scattering cross section. The delta function at the end removes the final states where energy is not conserved. This equation relates the measurements from a neutron scattering experiment to a model of the physics of the sample. The right hand side gives the probability that the system, neutrons and nuclei, take the transition from the initial state to the final state. By inserting the Fermi pseudopotential from Equation 3.10 in Equation 3.13 it can be reduced into the following form.

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \frac{k_f}{k_i} \sum_{n_i} p(n_i) \sum_{n_f} \left| \left< n_f \mid \sum_j b_j \exp(iQR_j) \mid n_i \right> \right|^2 \delta(E_{s,f} - E_{s,i} + \hbar \omega)$$

(3.14)

This equation can be reduced by using quantum mechanical Heisenberg operators, see Hempelmann [49], to a form that gives the relation between the scattering function and the double differential cross section.

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \frac{k_f}{k_i} \bar{b}^2 S(Q, \omega)$$

(3.15)

In this equation the right hand side is the total scattering function. It can be divided into a coherent and an incoherent part as for the scattering cross section in Equation 3.9. The value of the coherent part is given by $\bar{b}^2$ and the value of the incoherent part is given by $b^2 - \bar{b}^2$. This gives the double differential cross section as

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \frac{N}{4\pi} \frac{k_f}{k_i} \left[ \sigma_{coh} S_{coh}(Q, \omega) + \sigma_{inc} S_{inc}(Q, \omega) \right]$$

(3.16)

These two scattering functions can thus be measured and they describe the measured intensity in $Q$ and $\omega$. As normal life happens in space $r$ and time $t$ it is nice to introduce another function which is called the pair-correlation function. For a full derivation of the pair-correlation the reader is directed to the book of Hempelmann [49], paragraph 3.3 and the citations therein.

The pair-correlation function gives the conditional probability that, given a particle was located at the position $r = 0$ at time $t = 0$, any particle is found
at position $r$ at time $t$.

$$G(r, t) = N^{-1} \sum_i \sum_j \langle \delta[r - R_i(t) + R_j(0)] \rangle$$  \hspace{1cm} (3.17)

If $j = i$, the pair-correlation function is called the self pair-correlation function. The double Fourier transform of the self and pair-correlation functions in $Q$ and $\omega$ gives incoherent and coherent scattering functions again. Thus the scattering function provides information about the motions in the sample as functions of energy and momentum. This is an approximation made in the classical limit, which means that if the particle is stationary for times shorter than $t \simeq 10^{-13}$ s this approximation is no longer valid.

### 3.2 Experimental aspects

In the previous paragraph a short introduction of neutron scattering was given. Equation 3.16 is the link between the measured values from a scattering experiment and the theory describing the scattering system. In this paragraph an introduction to the experimental aspect of neutron scattering will be given.

For QENS measurements there are several techniques available, but the time-of-flight (TOF) is the most common. In TOF experiments a detector bank simultaneously detects multiple points in $(Q, \omega)$ phase space. This is done by time resolved neutron detection within a large solid angle by several hundreds of detectors. In this work the time-of-flight multichopper spectrometer IN5, at ILL in Grenoble, France, has been used and this spectrometer will be discussed here. In Figure 3.2 there is a schematic layout of the spectrometer.

At IN5 the incoming white neutron beam from the neutron source is monochromated by 6 rotating disks, each with two openings. The disks are located in pairs, the first pair of disks chop the neutron beam in pulses of neutrons with a broad distribution in speed, the second pair refine the speed of the neutrons to remove overlap, and the last pair finally select the speed of the neutrons. The disks rotate with their openings phase shifted such that only neutrons which passes the openings will reach the sample. This process make it possible to calculate when a pulse of neutrons hit the sample and what energy these neutrons have. As a result a large part of the flux is lost but this allows for control of the resolution and of the incident wavelength. This type of TOF spectrometers are called direct geometry time-of-flight spectrometers. At the time a pulse is calculated to hit the sample, a clock starts and measure the time the scattered neutrons use to travel from the sample to the detectors. From the known flight path the energy of the scattered neutrons is then calculated.
This means that the time between the pulses must be larger than the flight time of the slowest neutrons, or the pulses will overlap.

![Diagram of a neutron scattering setup](image)

**Figure 3.2:** Figure showing the layout of IN5 at ILL, Grenoble. The disks are located in pairs and they decide the energy of the incident neutrons. The time the neutrons use to travel the distance from the sample to the detectors is used to calculated their energy.

Using TOF spectrometers the resolution of the apparatus can be found by doing controlled measurements. In theory the elastic line should be a peak at zero \( \omega \) but in practice this peak has a finite width in the measured intensity. This broadening of the elastic line is called the resolution function and describes the resolution of the spectrometer. In TOF this broadening comes from the uncertainty in the wavelengths of the incident monochromated neutrons, from the uncertainties in the different flight paths, and from errors in the sample and detector geometries. The actual broadening can be measured using a standard which only scatters elastically. Vanadium is commonly used as a standard but the geometry of the standard should match exactly the geometry of the sample. To avoid this problem it is often better to use the sample itself at low
temperatures where all motions are frozen and the scattering is purely elastic. The resolution function is needed to know how much of the broadening of the QENS is due to the sample and how much is due to the apparatus.

When the neutrons hit the sample they can pass through the sample, be absorbed, or be scattered. The scattered neutrons change their energies and momentum due to interaction with the sample. The distributions in energy and momentum transfers represent the physics of the sample. The energy transfer or $\omega$, of the neutrons is measured by the time they use from the sample to a detector. The energy transfer and the scattering angle give the momentum transfer, $Q$, of the neutrons. And the number of neutrons with a given energy and momentum transfer give the value of $S(Q, \omega)$ as the intensity. The measured $S(Q, \omega)$ gives an average value of the properties of all the elements in the sample. By planning the composition of the sample, it is possible to increase the relative intensity contribution from the element under investigation.

The scattering cross section for an isotope can be found in the literature, e.g. in the book of Bée [48]. As mentioned the values of the coherent and the incoherent cross sections change from isotope to isotope. This allows for experiments that investigate specific elements and their properties, given that it is possible to produce a sample with the right composition. In Table 3.1 the scattering cross sections of the materials relevant in this study are presented.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\sigma_{coh}$</th>
<th>$\sigma_{inc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.7599</td>
<td>79.91</td>
</tr>
<tr>
<td>Deuterium</td>
<td>5.597</td>
<td>2.04</td>
</tr>
<tr>
<td>Carbon</td>
<td>5.563</td>
<td>0.001</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>11.03</td>
<td>0.49</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.235</td>
<td>0</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.495</td>
<td>0.0085</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.0203</td>
<td>5.178</td>
</tr>
</tbody>
</table>

Hydrogen is the strongest incoherent scatterer and is often used to study dynamics of organic compounds. As seen from Table 3.1 it scatters incoherently almost 40 times more than deuterium. This means that in a system with two molecules containing hydrogen, it is possible to decrease the incoherent scattering from one of them. This is done by substituting hydrogen with deuterium in one of the molecules. This is an example of how the composition of a sample
can be changed to increase the relative intensity from the relevant compound. It is a common trick in neutron scattering.

In this study the sample is made from hydrogen and carbon atoms and there is no need to apply this trick. As seen from Table 3.1 carbon scatters only coherently and the coherent scattering of carbon is weaker than the incoherent scattering from hydrogen. The measured scattering is thus dominated by the incoherent properties of the hydrogen molecules. To further refine the measured scattering it is common to measure the background before starting the experiment. In our case it is possible to measure the pure graphite first and then introduce hydrogen later. By subtracting the measured scattering of the pure graphite from the measured scattering for the hydrogen-graphite mix, the resulting intensity is only from the incoherent hydrogen scattering.

The analysis method and the theory to calculate the surface self diffusion coefficient used in this work is given in Chapter 5.
Chapter 4

Molecular dynamic simulations

Computational techniques have been used to find the amount of hydrogen adsorbed as function of material and geometries. There are few results in the literature that describe the dynamics of this process. In this work we have used molecular dynamics to find thermodynamic and dynamic properties of hydrogen adsorbed on graphite. In the following chapter an introduction to molecular simulation theory and a brief review of the literature will be presented.

4.1 Molecular simulation

Molecular simulation is a powerful tool in materials science, physics, chemistry and biomolecular fields. Molecular simulation are becoming a more common technique as the computational power of computers are growing and the development of new simulation methods. Molecular simulation consists of three main steps, 1) constructing the model of the system, 2) setting the molecules in this system in motion and calculate their trajectories, and 3) the analysis of the calculated trajectories. The model of the system can be divided in two parts, one part describing the interactions between the molecules constituting the system, and one part describing the interaction between the system and its surroundings [50]. The intermolecular description is based on functions that give the shape and strength of the interaction energy between molecules. The interactions with the surroundings are described by boundary conditions given at specific positions. When these two descriptions are formulated, step 2) can be initiated. In step 2) the position of the molecules are calculated and the molecules are given energies. Then the trajectories of the molecules are
calculated and by averaging over the system and time properties may be calculated. There are two main approaches to perform the molecular simulations, they are known as Monte Carlo and molecular dynamics. These two methods differ in how the trajectories of the molecules are calculated. In molecular dynamic simulations the positions are calculated by numerically solving differential equations of motion. Then the positions are connected in time and the positions reveal dynamics of the individual molecules. In Monte Carlo simulations the positions of the molecules are generated stochastically and the molecular configuration depends only on the previous configuration. Other simulation methods compute the molecular positions from hybrid schemes that involve some stochastic feature, as in Monte Carlo, and some deterministic feature, as in molecular dynamics.

For determination of equilibrium properties such as the pressure in atomic fluids, both Monte Carlo and molecular dynamics require the same amount of computer time to reach similar levels of statistical precision. However, molecular dynamics are more effective in evaluating properties as the heat capacities, compressibility, and interfacial properties. Molecular dynamics also provide access to dynamic quantities such as transport coefficients and time correlation functions [50].

4.2 Molecular dynamics simulation

In molecular dynamics simulation a numerical solution of the classical equations of motion give the positions, velocities, and momentums as functions of time. For a simple system this may be written as

$$F_i = m_i a_i$$ (4.1)

where $F_i$ is the forces acting on the particle $i$, $m_i$ is the mass of particle $i$, and $a_i$ is the acceleration of particle $i$ ($a_i = dv_i/dt = d^2 r_i/dt^2$). To do this there must be a way of calculating the forces acting on the particles. This is done by using intermolecular pair potentials which describes the potential energy between particles $i$ and $j$. A common pair potential is the Lennard-Jones potential

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$ (4.2)

where $r_{ij}$ is the distance between particles $i$ and $j$, $\epsilon_{ij}$ is the well depth (or the minimum of the potential between the two particles), and $\sigma_{ij}$ is the collision diameter (the distance between the two particles where the interaction
potential is zero), see Figure 4.1. The Lennard-Jones potential describe both attractive and repulsive forces between the particles. The attractive part varies as \( r^{-6} \) and the repulsive part varies as \( r^{-12} \). The parameters \( \epsilon_{ij} \) and \( \sigma_{ij} \) are the cross-interaction parameters between particle \( i \) and \( j \). They are calculated from the self-interaction parameters by the Lorentz-Berthelot mixing rules

\[
\begin{align*}
\sigma_{ij} &= (\sigma_{ii} + \sigma_{jj}) / 2 \\
\epsilon_{ij} &= \sqrt{\epsilon_{ii} \epsilon_{jj}}
\end{align*}
\] (4.3)

To reduce the computing time the pair interaction can be neglected when it is close to zero. This is done by using a truncated Lennard-Jones potential, which is set equal to zero at some distance \( r_c \), the cut-off distance. This will introduces a discontinuity at the position \( r_{ij} = r_c \) when a pair of particles cross this boundary. As a result the total energy will not be conserved. To avoid this contribution and maintain a consistent description of the system, the potential can be subtracted a quantity equal to its value in \( r_{ij} = r_c \). As seen in Figure 4.1 this results in a shifted truncated Lennard-Jones potential. In the MD simulation also intra-molecular potentials are defined which describe

Figure 4.1: The Lennard-Jones potential describing the interaction potential between two atoms as a function of the distance \( r \). \( \epsilon \) is at the minimum of the potential and \( \sigma \) is the position where the potential is zero.
the stretching, the bending, and torsion in the bonds between each particle. When all the potentials are defined, the total potential acting on each particle can be calculated, and from this the total force, $F_i$, can be found from the gradient of the total potential

$$F_i = -\nabla U_i$$  \hspace{1cm} (4.4)

By integrating Newton’s equation of motion the interaction and energy exchange between the particles give the dynamics of the system

$$F_i = m_i \ddot{a}_i$$  \hspace{1cm} (4.5)

where $m_i$ is the mass of the particle $i$ and $a_i$ is the acceleration of the particle which is given by

$$a_i = \frac{dv_i}{dt} = \frac{d^2r_i}{dt^2}$$  \hspace{1cm} (4.6)

where $v_i$ is the velocity of particle $i$. These equations are numerically integrated in time steps and an often used algorithm to solve this problem is the velocity Verlet algorithm

$$r_i(t + \delta t) = r_i(t) + \delta t v_i(t) + \frac{1}{2} \delta t^2 a_i(t)$$

$$v_i(t + \delta t) = v_i(t) + \frac{1}{2} [a_i(t) + a_i(t + \delta t)]$$  \hspace{1cm} (4.7)

Here $\delta t$ is the time step in the integration. In MD the time step $\delta t$ should be small compared to any characteristic times involved in the atomic motions. There is a balance in the size of the time steps. If the time steps are too small, the calculated trajectories will only cover parts of the phase space in the system, and if the time steps are too large the integration can become unstable [51]. In molecular systems the time step is of the order $10^{-15}$ seconds.

### 4.3 Short review

Here we give some of the recent data found in literature to introduce the reader to the field of molecular simulation. Our data are presented in Chapter 5, 6, and 7. Molecular simulations have been used to investigate the adsorption and transport properties of H$_2$ on carbon nanotubes. There are many studies of carbon nanotubes as this group of carbon material has properties of interest for gas storage, separation, and electrode purposes. Skoulidas et al. performed MD of hydrogen and carbon nanotubes [34], and they report of H$_2$ transport inside carbon nanotubes. They found that the self diffusion through carbon
nanotubes at pressures from 0 to 900 bar was in the $10^{-5}$ m$^2$/s to $2 \times 10^{-9}$ m$^2$/s range. Chen et al. [52] also simulated hydrogen interaction with carbon nanotubes and found the self diffusion from $2.8 \times 10^{-8}$ m$^2$/s to $1 \times 10^{-7}$ m$^2$/s for hydrogen on carbon nanotubes at 300 Kelvin. Chen et al. [16] reported in 2004 self diffusion of H$_2$ in single-walled nanotubes in the order $1 \times 10^{-4}$ m$^2$/s to $1 \times 10^{-7}$ m$^2$/s for varying surface concentrations. The self diffusion is found to be a function of temperature and surface concentration in all these studies. To our knowledge there is no report on the hydrogen self diffusion on graphite from molecular simulations.

Studies of the adsorption of hydrogen molecules on graphite have been performed by several groups. Darkrim et al. [53] used Monte Carlo to investigate the effect of carbon nanotube diameters on the amount of hydrogen adsorbed. They found that the amount adsorbed decreased as the diameter increased. Wang et al. have also used Monte Carlo to compute the isosteric heat of adsorption for hydrogen in carbon slit pores [23]. From their simulations they found the isosteric heat of adsorption in the range of ca. -5 to -6 kJ/mol. Cheng et al. [52, 54] used MD simulations to investigate hydrogen adsorption on carbon nanotubes and found heat of adsorption in the range from -16.5 kJ/mol to -45.7 kJ/mol depending on where on the nanotube the adsorption takes place. Another study done by Kowalczyk et al. [55] using Monte Carlo simulations of idealized graphite slitlike pores showed small variations in enthalpy of adsorption from -7.28 kJ/mol to -7.85 kJ/mol. The values are varying depending on adsorbent material and simulation method.
Chapter 5

Quasi-elastic neutron scattering investigation of the hydrogen surface self diffusion on polymer electrolyte membrane fuel cell catalyst support.

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Abstract

Quasi-elastic neutron scattering (QENS) measurements have been performed to investigate the surface self diffusion of hydrogen molecules. A monolayer of molecular hydrogen was adsorbed on a carbon material commonly used in polymer electrolyte membrane fuel cells, called XC-72. QENS spectra were recorded at the time-of-flight spectrometer IN3 at Institut Laue-Langevin (ILL) in Grenoble at 40, 50, 60, and 70 K. By using the Chudley and Elliott model for jump diffusion, we found the diffusion coefficient at each temperature. The logarithm of the diffusion coefficient was plotted versus the inverse of the temperature to give the coefficient in the Arrhenius equation. From this, we can estimate the diffusion at higher temperatures as well. Our observed diffusion follows the same trend as that found for hydrogen molecules on the surface of single-walled carbon nanotubes and Grafite.

5.1 Introduction

Our motivation is to learn more about the gas transport through the backing electrode and catalyst layer in the polymer electrolyte membrane fuel cell (PEMFC). The PEMFC is in the most basic configuration made of two backing electrodes separated by a polymer electrolyte membrane (PEM). For a full description see the work of J. Larminie and A. Dicks [8] and P. Costamagna et al. [4]. The purpose of the polymer electrolyte membranes is to conduct H⁺ ions between the two electrodes. The electrodes are made of carbon paper or cloth that is electrical conducting, highly porous and let H₂ and O₂ gas diffuse to the catalytic layers located close to the PEM. In the catalytic layers the reaction sites are located on noble metal catalyst, often Pt or Pt alloy, which must be in contact with both the ionic and the electric conductor. This catalytic layer is a few microns thick and the noble metal catalysts are supported on electrical conducting carbon black particles, as XC-72 [56–58]. The noble metal particles have radiiuses of only a few nanometers, typically 2 - 10 nm as demonstrated by Stevens et al. [59]. Since the noble metal particles must be in contact with both the ionomer and the carbon the pore size surrounding them are small.

The purpose of this work is to examine the theoretical hypothesis made by Meland et al. [60] that access to the three-phase contact line in porous gas electrodes is via the interfaces between the homogenous phases that surround the contact line. It is therefore important to know whether surface diffusion takes place down the pore or crevice to access the Pt particle. This surface diffusion is in contradiction to the accepted view of reactant transport in the
5.1 Introduction

PEMFC today. But the recent work of Meland et al. gave an indication of H$_2$ adsorbing and diffusing along the carbon surface to the catalyst particles [60]. Their study is based on electrochemical impedance spectroscopy. They gave a theoretical estimate of the surface diffusion constant for H$_2$ on carbon black based on their findings. In recent years a lot of work has been done on the adsorption of H$_2$ in carbon materials. Main purpose of these investigations are the possibilities of using it as storage material in mobile applications [15, 19, 20, 22, 61–65]. Especially carbon nanomaterials have been tested after their introduction. As neutron scattering is an excellent probe to examine hydrogen properties, this technique have been extendedly used [39, 40, 66–69]. Only two studies give a diffusion coefficient for H$_2$ on carbon. Bienfait et al. and Narehood et al. [39, 40] have reported surface self diffusion constants for H$_2$ on oriented graphite and single wall nanotubes.

Carbon blacks have not been subject to the same dynamical studies with neutron scattering techniques, and to our knowledge there are no reports of surface self diffusion coefficients for carbon blacks. Mitchell et al. has given evidence for transport of hydrogen from platinum particles supported on carbon black to the carbon support [70]. They found that hydrogen atoms dissociated on the platinum and diffused over the carbon surface, which is the reverse process from what we want to study.

Electrodes of this type are central in the polymer electrolyte membrane fuel cell, so the overall aim of our effort is thus to contribute to an improved understanding of these complicated heterogeneous catalytic structures. The hypothesis stems from an analysis of the platinum electrode surface as a hydrogen gas anode [60], using non-equilibrium thermodynamics for the heterogeneous system [47]. With an experimental value of the surface diffusion constant on carbon black, it may be possible to test their prediction. If correct it may change the view of how to best explain the transport mechanism in the catalytic layer in a PEMFC.

Some experimental evidence for hydrogen surface diffusion along the carbon-gas interface up to the active sites on platinum was obtained using impedance spectroscopy [60, 71, 72]. In this work we have used quasi-elastic neutron scattering (QENS) experiments to find the surface diffusion of molecular hydrogen on a carbon black, XC-72. We have collected spectra for a large temperature range on the IN5, the time-of-flight (TOF) spectrometer at ILL. The results are presented as the calculated surface diffusion constant for low temperatures and an Arrhenius plot of these.
5.2 Experimental

5.2.1 Sample characterisation and preparation

![FESEM picture of the sample material XC-72](image)

Figure 5.1: FESEM picture of the sample material XC-72, working distance 8.4 mm, accelerating voltage 10.0 kV and magnification 100.000.

Our sample is a commercial carbon black, XC-72, from Cabot Corp. From BET measurements the surface area was found to be 204.3 m$^2$/g. From field emission scanning electron microscope (FESEM) the particle size of our sample material can be estimated to between 20 to 100 nm, see Figure 5.1. The sample (8.4 g) was heated to 900 K under vacuum for 15 hours to remove water. After this the sample was placed in a thin walled aluminium cylinder under inert gas and evacuated for 6 hours. The number of moles needed to form one commensurate monolayer of hydrogen was estimated from the BET surface area of the sample, and the molecular area of hydrogen found in literature, 15.6 Å$^2$ [73]. To measure the number of moles needed to form a monolayer, a second cylinder with know volume of 840 cm$^3$ was pressurised until the pressure reached 401.73 torr at room temperature. The pressure of n-hydrogen (0.75 o-H$_2$, 0.25 p-H$_2$) was measured with a Baratron pressure gauge at room temperature and hydrogen was introduced to the carbon in the aluminium cylinder at 2 K and the cell was then sealed.
5.2.2 Quasi-elastic neutron scattering experiments

The quasi-elastic neutron scattering (QENS) experiments were performed at the direct geometry time-of-flight spectrometer IN5, ILL, Grenoble, France. The incident wavelength was 5 Å (3.27 meV) with a resolution of 103 μeV. To estimate the resolution function a measurement of the sample with adsorbed hydrogen at 2 K was performed [49]. Measurements to estimate the diffusion were conducted at 2, 40, 50, 60 and 70 K with varying hydrogen coverage, due to shift of the equilibrium between adsorbent and gas phase. The time measured varied from 2 to 6 hours. As the hydrogen desorbs at higher temperatures, and for safety reasons, the aluminium cell has to be opened to prevent rupture of the cell due to increasing pressure. For all temperatures above 40 K the aluminium cell was kept open to the calibration volume. During the measurements the adsorbed hydrogen was in equilibrium with the desorbed hydrogen in the calibrated volume.

5.2.3 Data reduction and analysis

The collected data from the measurements were first normalised versus the monitor. This was done to remove changes in intensities between spectra due to changes in the incident neutron beam. To correct for variations in detector efficiencies a measurement of a vanadium sample was conducted. The spectra were then normalised to the vanadium measurements to correct the intensity at each momentum transfer $Q$ value. Further the measured spectra were divided into regions in $Q$ and $\omega$ (energy transfer) space to get constant $Q$ values. They were summed over $dQ = 0.1\,\text{Å}^{-1}$, to enhance the statistics. This was done using LAMP, the standard data evaluation program from ILL. After this treatment the plots of the scattering function $S(Q, \omega)$ were fitted with a Lorentzian function to estimate the half width at full maximum (HWHM) as a function of $Q$, $f(Q)$. The fit of the Lorentzian was done in QENS_fit, a fitting procedure within the LAMP program. In the QENS_fit program a measurement of hydrogen adsorbed on the carbon black at 2 K was used as the resolution function. The spectra from 40 to 70 K were used to estimate the diffusion coefficient. The fit to the broadening of $Q$ was done using the Cludley and Elliott model which describes the movement of a single molecule as it jumps between different sites in a lattice or between cages made of other molecules [49]. The smallest jump length $l_0$ is assumed identical for all sites whereas the jump directions are random. For this model it is assumed that the molecules remain for a time $\tau_0$ before moving further. Since the sample is a powder sample it had to be spatially averaged over the angle between the
normal to the scattering surface and the scattering vector $Q$

\[
f(Q) = \frac{h}{n\tau_0} \sum_{j=1}^{n} (1 - e^{-iQs_j}) = \frac{h}{\tau_0} \left( 1 - \frac{1}{2} \int_0^{\pi} e^{-iQl \cos \theta} \cos \theta \right)
\]

\[
= \frac{h}{\tau_0} \left( 1 - \sin \frac{Ql}{Ql_0} \right)
\]

(5.1)

Here $l$ is the jump length, $n$ is the number of atoms in the cell, $s_j$ are their positions, $\tau_0$ is their residence time before jumping from a site, $\theta$ is the angle between the normal of the scattering surface and the scattering vector $Q$ and $h$ is the Planck constant divided over $2\pi$. This model was modified including a distribution of the jump lengths, see Egelstaff [74]

\[
f(Q) = \frac{h}{\tau_0} \int \left( 1 - \frac{\sin \frac{Ql}{Ql_0}}{Ql_0} \right) a(l) dl = \frac{h}{\tau_0} \left( 1 - \frac{1}{1 + Q^2l_0^2} \right)
\]

(5.2)

This form is obtained with the assumption that the distribution of the jump lengths are on the form

\[a(l) = l \exp \left(-\frac{l}{l_0}\right)\]

(5.3)

It can be shown that $l_0^2$ is proportional to $(1/6)\lambda^2$ using the Einstein-Smoluchowski equation, see i.e. ref. [74]. This gives the diffusion coefficient as

\[D = \frac{l_0^2}{\tau_0}\]

(5.4)

To fit the model for $f(Q)$ to the experimental data, we used

\[\frac{1}{f(Q)} = \tau_0 + \frac{\tau_0}{l_0^2Q^2}\]

(5.5)

So by taking the experimental data and their HWHM as function of $Q^{-2}$ we fitted Equation 5.5 by linear regression. By plotting the diffusion coefficients found for each temperature versus $T^{-1}$, we obtained an Arrhenius plot. This was used to estimate the temperature dependence of the diffusion coefficient according to

\[D_T = D_0 \exp \left(-\frac{E}{k_BT}\right)
\]

(5.6)

Here $D_T$ is the diffusion coefficient as a function of temperature, $D_0$ is a prefactor, $k_B$ is the Boltzmann constant, $E$ is the activation energy and $T$ is the temperature.
Figure 5.2: HWHM$^{-1}$ meV$^{-1}$ as a function of $Q^{-2}$/Å$^2$ for experimental data at 40, 50 and 60 and 70 K. The straight lines are the linear regression giving the best fit of Equation 5.5 at each temperature.

5.3 Results

Figure 5.2 shows the fitting of Equation 5.5 to the experimental data from 40, 50, 60 and 70 K for $Q$ values up to 1.0 Å$^{-1}$. This figure shows the variation of the inverse of the measured HWHM as a function of $Q^{-2}$. The values of the diffusion coefficients, $D$, the residence times, $\tau_0$, and jump lengths, $l_0$, are presented in Table 5.1. The HWHM increases with increasing $Q$. The self diffusion coefficients found for 40, 50, 60 and 70 K from Equation 5.5 and Equation 5.4 are plotted in an Arrhenius plot in Figure 5.3. From the slope of the Arrhenius plot in Figure 5.3 the $D_0$ and $E/k_B$ coefficients in Equation 5.6 was found to be, $D_0=1.9\times10^{-7} \pm 0.2\times10^{-7}$ m$^2$/s and $E/k_B = 112 \pm 5$ K (1030 \pm 50 J/mol). Comparing with liquid hydrogen which have the Arrhenius coefficients $D_0=8.58\times10^{-8} \pm 0.98\times10^{-8}$ m$^2$/s and $E/k_B = 44.8 \pm 1.6$ K (372.5 \pm 13.3 J/mol) [75]. Using Equation 5.6 to estimate the change in the self diffusion coefficient at higher temperatures, we found a self diffusion coefficient of $1.4\times10^{-7}$ m$^2$/s at 398 K, a typical fuel cell temperature. In Figure
5.4 the values of the natural logarithm of the surface diffusion coefficient, from this work together with the data from Bienfait et al. and Narehood et al. \cite{39,40} is plotted versus the inverse of the temperature are plotted.

![Graph showing ln(D) vs 1/T]  

Figure 5.3: The natural logarithm of the self diffusion coefficients found from our experimental data plotted as function of $T^{-1}/K^{-1}$. The full line is the linear regression between the four points.

5.4 Discussion

5.4.1 Hydrogen-carbon interaction

Our sample is a carbon black which consists of particles made of small graphene sheets that overlap. The size of the particles varies and they have micropores of varying size \cite{76}. Jawhari et al. found that the average length of the graphene sheets in XC-72 is 2 nm by using Raman spectroscopy \cite{77}. Stoeckli et al.
showed by adsorption and calorimetric techniques that the average micropore width in XC-72 is 0.9 nm [78]. In a study by Wu et al. XC-72 was found to form aggregates of 100 nm to 200 nm size built up by particles of 50 nm [79]. The particles in the aggregates of carbon blacks are kept together by van der Waals forces and they are not easily broken down [80, 81]. This complex system has both planar and curved surfaces and crevices of varying sizes. The different surfaces and crevices will give different adsorption potentials for hydrogen to interact with. So the measurements will give a surface diffusion that is an average of the diffusion taking place on the different graphite surfaces. Similar surfaces or crevices are found in the carbon materials used by Narehood et al. and Bienfait et al. [39, 40, 67]. Narehood et al. used single walled carbon nanotubes (SWNT) [40, 67]. The SWNT used by Narehood et al. were present
Table 5.1: Parameters obtained from the fit of Equation 5.5 to experimental data.

<table>
<thead>
<tr>
<th>T /K</th>
<th>$\tau_0 /10^{-12}$ s</th>
<th>error /$10^{-12}$ s</th>
<th>D /$10^{-8}$ m$^2$/s</th>
<th>error /$10^{-8}$ m$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.5</td>
<td>$\pm 0.21$</td>
<td>1.1</td>
<td>$\pm 0.13$</td>
</tr>
<tr>
<td>50</td>
<td>1.2</td>
<td>$\pm 0.13$</td>
<td>2.1</td>
<td>$\pm 0.25$</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>$\pm 0.13$</td>
<td>3.0</td>
<td>$\pm 0.51$</td>
</tr>
<tr>
<td>70</td>
<td>0.9</td>
<td>$\pm 0.11$</td>
<td>3.7</td>
<td>$\pm 0.65$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T /K</th>
<th>$l_0 /10^{-10}$ m</th>
<th>error /$10^{-10}$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.3</td>
<td>±0.11</td>
</tr>
<tr>
<td>50</td>
<td>1.6</td>
<td>±0.10</td>
</tr>
<tr>
<td>60</td>
<td>1.7</td>
<td>±0.19</td>
</tr>
<tr>
<td>70</td>
<td>1.8</td>
<td>±0.21</td>
</tr>
</tbody>
</table>

in large bundles of 50 - 200 tubes with a mean diameter ranging from 1.3 - 1.4 nm. These nanotubes were closed tubes so only the exterior was accessible for the H$_2$ molecules [67]. So the interaction between hydrogen and carbon would be in grooves between tubes or on the surfaces of tubes. The carbon material used by Bienfait et al. was exfoliated graphite called Papyex described in [37]. This is a material made of graphite with oriented crystals. The interaction between hydrogen and carbon would consist mostly of graphene surfaces. Our experiments were therefore compared to the results of Bienfait et al. and Narehood et al. [39, 40] in an Arrhenius plot, see Figure 5.4. It is evident that the self diffusion coefficient of hydrogen varies in the same manner in the three experiments. The carbon in all of the three experiments is in graphene layers. The graphene layers are combined in different ways, but the materials have similar surfaces and crevices that hydrogen can interact with. This can then explain why the hydrogen diffusion is similar in all cases. Our results are in agreement with these studies, since the Arrhenius plot of the surface self diffusion coefficient of the three different carbon materials have the same slope within the statistical error. Recent experimental and theoretical adsorption studies of hydrogen on carbon materials support our findings of similar adsorption energies in various carbon types [17, 68, 82–86]. These studies show that the adsorption energies for hydrogen on different graphene configurations are similar, from 464 - 1160 K (3.86 - 9.65 kJ/mol) which is a weak adsorption energy resulting in physisorption. Compared to the diffusion activation energy from our work these values are still 3 - 9 times larger.
5.4.2 The model used for the surface self diffusion coefficient

Data were fitted to Equations 5.4 to 5.6 with $l_0$ as a temperature dependent parameter. Bienfait et al. and Narehood et al. on the other hand used $l_0$ equal to the constant distance between the carbon atoms in the graphene layers. A discussion of our model is therefore appropriate. Our experiment is done well within the liquid state for hydrogen on carbon and with less than one commensurate monolayer [38, 87-89]. These experimental conditions give a first argument for a jump length that varies with temperature. Furthermore according to Arellano et al. [83], the energy differences between four different H$_2$ orientations, see Figure 5.5, on the graphene are small. A study done by Cabria et al. [86] supports these results for binding energy between hydrogen and graphene rolled up in nanotubes. So it is not clear that the molecules will have a strong affinity for only one specific site. This is a second argument against a constant jump length. It is unlikely that the molecules will only move one length of 2.46 Å, but rather move a varying number of jump lengths at different temperatures. The situation is illustrated in Figure 5.5. The shortest jump length will be between position A and B, which is 1.23 Å, while the longest is from position C / D to C / D, which is 4.25 Å. Furthermore the position A and B in the hexagonal structure has the lowest binding energies and will be less populated at higher temperatures. Positions C and D has the highest binding energies and will be most populated at high temperature. The value we obtain for the $l_0$ parameter is an average of all the different jumps done by hydrogen in the system. The observed variation can be explained with a change in the mobility at the four different positions above the graphene layer as the temperature change. At low temperatures the molecules have highest mobility at the positions with lowest binding energy, namely position A and
B and the jump length is closer to 1.23 Å. While at higher temperatures the hydrogen molecules have an increasing mobility also at the sites with strongest binding energy, positions C and D. These sites correspond to a jump length of 4.25 Å. The observed value of $l_0$ can then be interpreted as hydrogen having a varying probability of jumping between the different positions. This would then give an increasing value of the averaged jump length with temperature. The calculated surface self-diffusion coefficient is not only a function of temperature, but also a function of surface concentration of hydrogen molecules. When the system is heated some hydrogen escapes from the carbon and leaves the surface. This may lead to a higher mobility as the concentration decreases. From Figure 5.3 we can see that the diffusion coefficient follows the Arrhenius equation. If the diffusion of the system changes strongly with other properties independent of temperature we would see a deviation from this trend. This is not the case and we can assume that the temperature effect on the jump length is the dominating effect. Using Equation 5.6 to estimate the change in the self diffusion coefficient at higher temperatures, we found a self diffusion coefficient of $1.3 \times 10^{-7}$ m$^2$/s at 303 K, the same temperature at which Meland et al. found their surface diffusion coefficient. From their measurements they found a surface diffusion coefficient of $1.0 \times 10^{-7}$ m$^2$/s. So our result supports their findings of surface diffusion in the fuel cell catalyst layer. This interpolation of the surface diffusion, based on our measurements at 40 - 70 K, at 303 K is done under the assumption that the mechanism behind the surface diffusion does not change in this temperature interval.

5.5 Conclusion

From QENS measurements the surface self diffusion of normal hydrogen molecules on XC-72 has been studied in the temperature range 40 - 70 K. From the QENS experiments the surface diffusion coefficient for 40, 50, 60 and 70 K was calculated and from the Arrhenius equation the activation energy for movement of hydrogen was found to be $E/k_B = 112 \pm 5$ K (1030 ± 50 J/mol) and the minimum self diffusion coefficient was $D_0=1.9\times10^{-7} \pm 0.2\times10^{-7}$ m$^2$/s. It was found that the values for each temperature follow the same trend as found earlier for carbon nanotubes and oriented graphite as illustrated in Figure 5.4. Our findings are thus not in conflict with the prediction made by Meland, that gases have access to the catalytic surface via the two-phase contacts that surround the catalyst. A diffusion coefficient was found that seems specific of diffusion in an adsorbed layer with a weak interaction between gases and solid.
5.6 Acknowledgements

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Chapter 6

Molecular dynamic simulations of equilibrium adsorption of H$_2$ on graphite


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Abstract

We have determined equilibrium properties and rate constants for adsorption and desorption of hydrogen on graphite as a function of temperature, from 70 to 390 K, using equilibrium molecular dynamic simulations. The surface, defined according to Gibbs, possesses an activation energy of adsorption at low temperatures only. The isotherms follow a Langmuir expression, but this model fails to explain the physics involved, i.e. the kinetics of adsorption and desorption. The rate coefficients in combination with surface potential energy profiles indicate that the surface free space is not critical for adsorption, but well for desorption. At low temperatures, the surface contains two types of molecules; those positioned close to the graphite and those more loosely connected and more mobile. The varying isosteric enthalpy of adsorption confirms that the adsorption process is non-ideal. The results indicate that hydrogen may move easily along the graphite surface also e.g. at fuel cell conditions.

6.1 Introduction

Graphite is an important material in electrochemical contexts, because it is a good electrical conductor, is relatively stable under reducing and oxidizing conditions and has a low cost [90]. Graphite is therefore used as a catalyst support for the expensive platinum (Pt) catalyst [8]. This applies for instance to the polymer electrolyte membrane fuel cell (PEMFC). This fuel cell has a polymer electrolyte membrane which conducts H\(^+\) ions between two catalytic layers. These layers are supported by carbon paper or cloth that is electrically conducting and highly porous, or a porous transport layer (PTL). Hydrogen fuel and oxygen gas diffuse through the PTL to the catalytic layers (CL) located next to the PEM. The CL is a few microns thick and the noble metal catalysts are supported on graphitic particles that form agglomerates.

The fuel cell may experience mass transfer limitations in these layers. It is therefore of interest to know how the reacting gases are transported through graphite, porous transport layer and catalytic layer until they reach the active sites. This is important for the fuel cell efficiency and therefore for fuel cell design. The energy efficiency can be raised if we can reduce mass transfer limitations [90–94].

Hydrogen is transported in the gas phase in the porous transport layers. However, in the nanoporous catalytic layer, the mode of transport is less certain. Does hydrogen move to the catalytic site via the gas phase, or does it migrate to this site along the graphitic or other surfaces as adsorbed gas?
Hydrogen storage in carbon materials \[15, 17\] depends on variables as surface area and pore size \[24, 25, 55, 95, 96\] however in the description of the working conditions of the PEMFC the hydrogen-graphite interactions have so far been neglected. Some evidence is now emerging, indicating that these interactions may be important. Kjelstrup and Bedaux \[47\] postulated that gas access to the three-phase contact line occurred via the interfaces between the homogeneous phases that surround the contact line. Experiments by Meland et al.\[60, 71\] and Paulus et al. \[72\] support this view. These questions have motivated the present study. In order to understand transport of hydrogen along the graphite surface, equilibrium properties are essential, and this work reports such data.

Molecular dynamics (MD) simulations are well suited to give an understanding of the gas-graphite interface. In such simulations, the forces interacting between the particles are defined and the movement of all particles are known by solving Newton's equations. The macroscopic properties are obtained from molecular properties using statistical mechanics. In this study we want to know how the surface phase behaves over a large temperature and concentration ranges. As a first step, we shall compute equilibrium properties of hydrogen at the graphite surface, and characterise both the dynamics and thermodynamics of the equilibrium state. The advantage of molecular dynamic simulations is that such information can be directly connected to molecular behaviour and that there is no bias towards a particular macroscopic description.

The Langmuir model have since long been used to characterize adsorption, and this model shall be used also here. The model explains adsorption as an ideal process, where the probability for adsorption depends on the gas pressure and on the free space on the surface, while desorption depends on the surface coverage only. Molecular dynamics simulations shall be used to investigate the process and we shall see that that the Langmuir assumptions fail. Another interpretation, consistent with the Langmuir equilibrium constant, is proposed from the variation of the rate coefficients for adsorption and desorption. We shall also construct the potential profile seen by the hydrogen in front of the surface, calculate isosteric enthalpies and entropies of adsorption, and discuss the possibility of lateral migration of hydrogen.
6.2 Theory

6.2.1 Surface thermodynamics

The surface is an open thermodynamic system, positioned between two homogeneous phases, the gas phase and the graphite phase. According to the phase rule, there are 2 degrees of freedom in a system of two components and two phases. Once the temperature is given, the only variable is the pressure. The system is then monovariant. Any gas pressure defines a unique surface concentration. In general, the surface is therefore also characterized by no more than two variables, the concentration and the temperature.

Consider hydrogen adsorbed at a surface in equilibrium with the gas above it. The reaction is

\[ \text{H}_2(g) \rightleftharpoons \text{H}_2(s) \]  \hspace{1cm} (6.1)

The chemical potentials in the gas phase and the surface are equal at equilibrium, giving:

\[ \mu^g = \mu^s \]  \hspace{1cm} (6.2)

where \( \mu^i \) is the chemical potential of hydrogen in the phases \( s \) or \( g \). We can always assume ideal gas in the present case. The chemical potential of the gas is then:

\[ \mu^g = \mu^0 + RT \ln \frac{p}{p^0} \]  \hspace{1cm} (6.3)

Here \( \mu^0 \) is the standard chemical potential, where the standard state is defined at pressure \( p^0 = 1 \) bar while \( p \) is the actual gas pressure. The standard chemical potential is normally tabulated at 298 K [97]. For the surface, we have

\[ \mu^s = \mu^* + RT \ln a^s \]  \hspace{1cm} (6.4)

where \( \mu^* \) is the chemical potential for the Henry’s law standard state, and \( a^s \) is the surface activity, to be defined in Equation 6.7. Henry’s law on dimensionless form is

\[ \frac{c^s}{c^*} = K_H \frac{p}{p^0} \]  \hspace{1cm} (6.5)

where \( c^s \) and \( c^* \) are respectively the unit concentration (of the hypothetical standard state) and the actual concentration in moles per m\(^2\), and \( K_H \) is Henry’s law constant. The value of \( K_H \) can be determined at low surface coverage, by extrapolation to zero surface concentration. When Henry’s law applies, \( a^s = c^s/c^* \). We introduce this and Equation 6.5 into Equation 6.4 and
obtain an expression for the surface standard state in terms of well defined constants
\[ \mu^* = \mu^0 - RT \ln K_H \] (6.6)

The activity of any adsorbed state is:
\[ a^s = \gamma \frac{c^s}{e^s} \] (6.7)

The activity coefficient \( \gamma \) measures the deviation from Henry’s law. The equilibrium constant of reaction (6.1) is equal to the Henry’s law constant with this choice for standard state
\[ K_H = \frac{c^s p^0}{e^s p} \gamma \] (6.8)

### 6.2.2 Langmuir isotherm

The Langmuir isotherm is one of the most common adsorption models for gases at a surface covered with less than a monolayer. It was first derived for chemisorption of gases using kinetic considerations, but it can also be obtained from statistical mechanics. One then assumes that the adsorbing gas is ideal, that the number of adsorption site is fixed and energetically equivalent, and that adsorbed molecules do not interact. The last assumptions imply that the heat of adsorption depends on the interaction energy between the sorbate and the sorbent, and is independent of surface coverage. Ruthven [43] gave other thermodynamic justifications for the success of the Langmuir model for physisorbed systems.

The Langmuir isotherm links the fractional coverage \( \theta \) (the ratio between the actual surface concentration and the concentration at saturation), to the gas pressure:
\[ \theta = \frac{c^s}{e^{sat}} = \frac{K_L \frac{p}{p^0}}{1 + K_L \frac{p}{p^0}} \] (6.9)

Two parameters are needed, the concentration at saturation, \( e^{sat} \), and \( K_L \), the Langmuir equilibrium constant. Both are unique functions of the temperature and depend on the nature of the couple adsorbate/adsorbent. Equation 6.10 can be rearranged to express \( K_L \):
\[ K_L = \frac{\theta \frac{p^0}{p}}{(1 - \theta) \frac{p^0}{p}} \] (6.10)
By comparing Equation 6.10 with the equilibrium constant of Equation 6.8 we find that

\[ \gamma = \frac{1}{1 - \theta} \]  

(6.11)

and

\[ K_L = K_H \frac{c^*}{c_{sat}} = K'_H \]

\[ K'_H = \frac{c^* p^0}{c_{sat} p} \gamma \]

\[ K_H = K'_H \frac{c_{sat}}{c^*} \]  

(6.12)

The constants \( K_L, K_H, K'_H \) and the variable \( \gamma \) shall be calculated from the MD simulation. \( K_L \) and \( c_{sat} \) shall be obtained by fitting the simulation data to the Langmuir model. \( K_H \) and \( K'_H \) shall be calculated from data for the region where Henry's law applies, while \( \gamma \) shall be directly obtained from the simulation data as a correction factor to Henry's law, and compared with the data from Langmuir isotherm, Equation 6.11.

**Kinetics**

As mentioned above, Langmuir kinetics was first applied to chemisorbed (non-mobile) molecules. In this model the adsorption rate, \( J_a \), is proportional to the gas pressure, \( p \), and the free space on the surface is given by \((1 - \theta)\), while the desorption rate \( J_d \) is simply proportional to the surface coverage:

\[ J_a = k^L_a \frac{P}{p^*}(1 - \theta) \]

\[ J_d = k^L_d \theta. \]  

(6.13)

In these expressions, \( k^L_a \) and \( k^L_d \) are the rate constants for adsorption and desorption. At equilibrium, when the fluxes are balanced these two equations can be combined and reduce directly to the Langmuir isotherm Equation 6.10 where the ratio \( k^L_a / k^L_d \) is the Langmuir equilibrium constant \( K_L \). As we will see in the following (cf. Section 6.4.3 and Figure 6.7(b)), this kinetic model fails for our system. The desorption and adsorption unidirectional rates follow
rather these expressions:

\[ J_a = k_a \frac{P}{P^0} \]

\[ J_d = k_d \frac{c^s}{c^{sat}} \gamma \]  

(6.14)

At equilibrium, when \( J_a = J_d \), the combination of these two equations also gives the Langmuir isotherm with \( K_L = k_a/k_d \) and \( \gamma = 1/(1 - \theta) \).

### 6.2.3 Gibbs surface

![Graph](image)

Figure 6.1: Here is a density plot for a system with 300 molecules at 90 Kelvin. The Gibbs surface is located between line a and line b. The excess density is the integral of Equation 6.17 from line a to line b.

The surface concentration needs specification in this context. We shall follow the definition of Gibbs and allocate the excess concentration in the surface region to the two-dimensional surface for the thermodynamic description. On a molecular scale; or the scale of simulations, also this surface has an extension, however. It is natural to locate one of the surface borders at the limit of the crystallographic surface. This border is located at position \( a \) in Figure 6.1, on an axis perpendicular to the surface. The axis is denoted as the \( z \)-axis. The surface now extends to position \( b \), where surface forces have negligible effect on the hydrogen molecules. At this position, the concentration of hydrogen becomes the equilibrium concentration in the gas, \( c^0 \). The surface is thus contained between the parallel planes at \( a \) and \( b \).
In Gibbs description, the exact position of the surface is allocated to a dividing surface. This can be located anywhere within the surface. Its exact position affects the values of the excess properties, but not the thermodynamic relations. In the following description we shall locate this plane of the dividing surface at position d in Figure 6.1 following a criterion discussed in Section 6.3.3. With the above surface positions, the excess concentration of hydrogen is defined by

\[ c^e = \int_a^d \left[ c_{H_2}^e(z) - c^e(a) \theta(d - z) \right] \, dz - \int_d^b \left[ c^e(z) - c^e(b) \theta(z - d) \right] \, dz \quad (6.15) \]

Here \( \theta \) is the Heaviside function and it is by definition unity when the argument is positive and \( z \) is the axis perpendicular to the graphite surface. Here \( c^e(a) \) is zero so

\[ c^e = \int_a^d \left[ c_{H_2}^e(z) \right] \, dz - \int_d^b \left[ c^e(z) - c^e(b) \right] \, dz \quad (6.16) \]

As a further approximation, we assume that \( c^e(z) - c^e(b) \) between d and b is close to zero. This gives us the final expression

\[ c^e = \int_a^d \left[ c_{H_2}^e(z) \right] \, dz \quad (6.17) \]

This choice gives a surface excess concentrations that in good approximation is equal to the real concentration at the surface. The description is thus the same as given by Ruthven [43]. The concentration is integrated out over the thickness, giving \( c^e \) in units of mol/m\(^2\). An example of a surface density variation is shown in Figure 6.1 for 90 K. We see a large peak close to the graphite, about 1.5 Å from a, and a slow decline in value towards the plane b. The position of line d is based on an energy criterion which is described in Section 6.3.3. We shall use this definition in a determination of \( K_H \) and other thermodynamic properties.

### 6.2.4 Activated processes

It is possible to make a finer description of the states within the surface, than that provided by Gibbs. The description dates back to Kramers [98] who described a chemical reaction as diffusing over its activation energy barrier, see de Groot and Mazur for more details [99]. We introduce an internal variable. In the present case, we can use the degree of adsorption as such a variable, and measure its variation from 0 (the gas state) to 1 (the state at position a). We may use the already defined \( z \)-axis for the purpose. The equilibrium condition in Equation 6.1 is extended to

\[ \mu^e = \mu(z) = \mu^g \quad (6.18) \]
where $\mu(z)$ is the chemical potential of hydrogen in the surface at degree of adsorption $z$. The chemical potentials are constant at equilibrium, but the potential energy of each term may vary. We introduce the relation $\mu = H - TS$ where $H$ and $S$ are respectively the partial molar enthalpy and entropy and compare all surface states along the $z$-axis to the state of the gas

$$\mu(z) = H(z) - TS(z) = H^g - TS^g$$  \hspace{1cm} (6.19)

With an ideal entropy, also inside the surface, we have:

$$H(z) - H^g = -RT \ln \frac{c(z)}{c^g}$$  \hspace{1cm} (6.20)

The right hand side of this expression gives the potential profile faced by a hydrogen molecule on the way to the surface from the gas. Such information is available here, through the molecular dynamics simulations. For a chemical reaction, this relation can be used to describe its activation energy barrier, in principle this should also apply to the adsorption reaction. We shall see that hydrogen adsorption does not possess a barrier in this sense, adsorption takes mostly place into a potential well.

### 6.2.5 Isosteric adsorption enthalpy and entropy

When we rather compare all of the total surface state to the gas state, we obtain:

$$H^s - TS^s = H^0 - TS^0 + RT \ln \frac{p}{p^0}$$  \hspace{1cm} (6.21)

Here $H^0$ and $S^0$ are the standard molar enthalpy and entropy of the gas, while $H^s$ and $S^s$ are the molar enthalpy and entropy of the adsorbate at a given surface concentration, $c^s$. We rearrange and obtain

$$\ln \left( \frac{p}{p^0} \right)_{c^s} = \frac{\Delta_{ads} H}{RT} - \frac{\Delta_{ads} S}{R}$$  \hspace{1cm} (6.22)

By plotting the natural logarithm of $p/p^0$ versus the inverse of temperature at constant surface concentration, we can find the enthalpy of adsorption, $\Delta_{ads} H = H^s - H^0$, as slope, and the entropy of adsorption, $\Delta_{ads} S = S^s - S^0$, as intercept. The quantities $\Delta_{ads} H$ and $\Delta_{ads} S$ are the so-called isosteric enthalpies and entropies of adsorption.
Figure 6.2: A snapshot of an equilibrium configuration of crystalline graphite at 90 K. The total number of H$_2$ molecules are 300. The carbon atoms are painted light grey and the hydrogen molecules are dark grey. Hydrogen molecules are adsorbed on the graphite surface, these molecules are in equilibrium with the gas phase.

6.3 Simulation details

6.3.1 The system

The molecular dynamics system was built of an infinite sheet of crystalline graphite in contact with dihydrogen molecules, H$_2$, see Figure 6.2. The graphite has a hexagonal crystallographic structure with space group $P6_3/mmc$ without any defects. The crystal is made from 9 sheets of graphene and contains 5184 carbon atoms. Following the crystallographic structure, the graphene sheets are oriented in our simulation box such that the surface of the sheets are perpendicular to the z direction. The size of the crystal is 44.208 Å and 34.0313 Å in x and y directions respectively and about 30 Å in the z direction [100]. Periodic boundary conditions are applied in x and y directions in the limits of the crystal and in the z direction at 95.254 Å from the center of the crystal. This symmetry gives in effect an infinite succession of two infinite graphite crystal surfaces separated by a gaseous zone of about 160 Å in the z direction, where the H$_2$ molecules are located. The model uses an atomic description of the graphite and hydrogen. The atoms interact through intermolecular and intramolecular potentials. To describe the stretching potential, we used a Morse potential and a harmonic potential for H$_2$ and the graphite, respectively. The expression of the Morse potential, $V_M$, is:
\[ V_M (r_{ij}) = D_e \left(1 - \exp\left(-a (r_{ij} - r_0)\right)\right)^2 \]  

(6.23)

where \( D_e \), \( r_0 \) and \( a \) are the input parameters of the potential and \( r_{ij} \) is the distance between atom \( i \) and \( j \). The expression of the carbon-carbon intramolecular stretching potential, \( V_S \) is:

\[ V_S (r_{ij}) = \frac{1}{2} k_S (r_{ij} - r_0)^2 \]  

(6.24)

where \( k_S \) is the force constant. A harmonic angle form was used to calculate the potential, \( V_B \), for bending:

\[ V_B (\theta_{ijk}) = \frac{1}{2} k_B (\theta_{ijk} - \theta_0)^2 \]  

(6.25)

in this equation the \( \theta_{ijk} \) is the angle between the three atoms \( i \), \( j \) and \( k \), \( k_B \) is the force constant and \( \theta_0 \) is the angle of minimum energy. Torsion is described by the following potential equation:

\[ V_T (\omega_{ijk}) = \frac{1}{2} k_T \left(1 - \cos\left(2 \omega\right)\right) \]  

(6.26)

where \( \omega \) is the torsion angle and \( k_T \) is the force constant. Non-bonded potentials \( V_{nb} \) are applied between hydrogen and carbon atoms, hydrogen atoms belonging to different molecules, between carbon atoms in different graphene sheets or separated by more than 3 bond lengths within the same graphene sheet. The non-bonded potential was given by a shifted and truncated 12-6 Lennard-Jones (LJ) type potential:

\[ V_{LJ} (r_{ij}) = 4\epsilon_{ii} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]  

(6.27)

\[ V_{nb} (r_{ij}) = \begin{cases} 
V_{LJ} (r_{ij}) - V_{LJ} (r_C) & r_{ij} \leq r_C \\
0 & r_{ij} > r_C 
\end{cases} \]  

(6.28)

where \( r_{ij} \) is a distance between atoms \( i \) and \( j \), \( \epsilon_{ij} \) and \( \sigma_{ij} \) are the LJ potential parameters and \( r_C \) is the cutoff radius. It is equal to 2.5 \( \sigma_{cc} \). The LJ interaction parameters between different types of atoms are calculated from the Lorentz-Berthelot mixing rules \([51]\):

\[ \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} \]  

(6.29)
\[
\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj})
\]  

(6.30)

The potential parameters for the Lennard-Jones are taken from the MM2 force field[101], while the parameters of the bonded potentials comes from the DREIDING force field[102] for graphite and Delft Molecular Mechanics (DMM) force field[103] for the hydrogen molecules. All the potential parameters are summarized in Table 6.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hydrogen</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon )</td>
<td>27.655 /K</td>
<td>25.89 /K</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>2.63984 /\AA</td>
<td>3.34380 /\AA</td>
</tr>
<tr>
<td>Stretching</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen, Morse</td>
<td>Graphite, Harmonic</td>
</tr>
<tr>
<td></td>
<td>( D_e = 458.0 ) /kJ/mol</td>
<td>( k_S = 4393.9 ) /kJ/mol</td>
</tr>
<tr>
<td></td>
<td>( a = 1.946 ) /\AA(^{-1})</td>
<td>( r_0 = 1.42 ) /\AA</td>
</tr>
<tr>
<td></td>
<td>( r_0 = 0.7414 ) /\AA</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bending</td>
<td>Torsion</td>
</tr>
<tr>
<td></td>
<td>( k_B = 418.2 ) /kJ/mol/( \text{rad}^2 )</td>
<td>( k_T = 26.15 ) /kJ/mol</td>
</tr>
<tr>
<td></td>
<td>( \theta = 120 ) /degrees</td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Simulation procedures

Five different systems were simulated to investigate the adsorption as a function of pressure variation. It was implemented by simulating with five different global densities. The five different numbers of hydrogen molecules were \( N_{H_2} = 50, 100, 150, 200, 300 \). For each \( N_{H_2} \) simulations were performed at seventeen different temperatures, ranging from 70 to 390 K at 20 K intervals. This gave a total of 85 simulations describing the equilibrium between surface concentration and gas pressure. The volume of the total system subtracted by the volume of the graphite crystal gives the volume available to the H\(_2\) molecules in the gas phase.

The dynamics were obtained by integrating Newton’s equations of motion using the velocity Verlet algorithm [51]. All simulations had time steps of 0.001
picoseconds. The initial configuration was constructed by randomly distributing the H₂ molecules in the gas phase. Molecules are located such that they do not overlap with each other or the graphite crystal. The system was stabilized during 400000 time steps by fixing the temperature at an imposed value using a simple rescaling of the velocities. When the system was in thermal equilibrium, the conditions of the simulations were changed to those of a micro canonical ensemble (constant energy).

A total of 1700000 time steps were performed under micro canonical conditions. During the simulation time, variables where computed every 10⁴ th time step and averaged over 1000 time steps and stored. In addition, the five different systems were simulated at 40 K to investigate the structure of the surface and to find the full monolayer.

![Graph showing interaction potential energy](image)

Figure 6.3: The interaction potential energy of hydrogen molecules at 70 K as a function of distance from the surface of the graphite. The full line marks the energy were we define whether the hydrogen molecules are adsorbed or not.

### 6.3.3 Calculated variables

#### The surface concentration

In Figure 6.3 the interaction potential energy between graphite and hydrogen at 70 Kelvin is plotted, as a function of distance from the crystallographic surface(zₘ). The interaction energy is calculated for each molecule as the sum
of all interaction contribution with the graphite sheet within the cutoff radius using Equation 6.28 and averaged between all the molecules as a function of the distance from the crystallographic graphite surface. The interaction energy is zero in the gas phase and decreases down to a minimum of -6 kJ/mol when the molecules are adsorbed. If the interaction potential energy is lower than -1.5 kJ/mol, below the line in Figure 6.3, the hydrogen molecule is defined as adsorbed. This gives an energy criterion for finding \( c^a \). It was established that this method of finding \( c^a \), was in good agreement with Equation 6.17, and therefore obeyed the approximation leading up to this equation.

Temperature calculation

The kinetic temperature, \( T \), was obtained by combining two definitions of the internal kinetic energy, \( K \), one coming directly from the equipartition of the energy and the second obtained from the kinetic contribution of the simulated particles;

\[
K = \frac{1}{2}(3N_{at} - 6)k_B T = \frac{1}{2} \sum_{i=1}^{N_{at}} m_i \left\langle |v_i - \bar{v}|^2 \right\rangle, \quad (6.31)
\]

At the left hand side of this equation \( N_{at} \) is the total number of atoms of the system, \( 3N_{at} - 6 \) is total number of degrees of freedom of the system, \( k_B \) is the Boltzmann constant and \( T \) the temperature. At the right hand side, \( v_i \) is the instantaneous velocity of the atom \( i \) and mass \( m_i \), and \( \bar{v} \) is the barycentric instantaneous velocity.

Pressure calculation

The gas pressure, \( P \), was obtained by using the ideal gas law:

\[
P V_{gas} = (N_{H_2} - N_{ads})k_B T, \quad (6.32)
\]

where \( N_{H_2} \) is the total number of hydrogen molecules in the system, \( N_{ads} \) is the total number of hydrogen molecules adsorbed and \( V_{gas} \) is the volume of the gas phase.
Figure 6.4: (a); The data points form the simulations plotted together with the Langmuir isotherm as dotted lines and Henry isotherm as full lines. The temperature decreases from 70 Kelvin at the top left to 390 Kelvin at the bottom right. (b); The inverse activity coefficient versus surface coverage. Values from Equation 6.11 are plotted as the full line and the values calculated using Equation 6.8 are plotted as +.
6.4 Results

6.4.1 Equilibrium constant, Langmuir parameters, isosteric enthalpy and entropy

The data points for the surface concentration as a function of pressure for temperatures between 70 and 390 K are plotted in Figure 6.4(a) together with the Langmuir and Henry isotherms. The absence of stepped isotherms and the value of adsorbed molecules smaller than the saturation number 0.0181 mmol/m$^2$ at 70 K, show that there is always less than a monolayer at the surface. By fitting the Langmuir Equation, Equation 6.9, to the data simulated at 70 to 170 K, we found the temperature dependence of $c_{sat}$ and the values of $K_L$. From fitting the Henry equation, Equation 6.5, and by using the extrapolated values of $c_{sat}$ to data simulated at 190 to 390 K we found $K'_H$. The parameters are given in Table 6.2. From these parameters we could find the activity coefficients as given by Equations 6.8 and 6.11. The results are plotted in Figure 6.4(b).

By plotting the natural logarithm of $c_{sat}$, $K_L$ and $K'_H$ versus the inverse of the temperature we obtained the temperature dependence of $c_{sat}$ and $K'_H$ as:

$$c_{sat} = c_0 \exp \left( \frac{-E_{sat}}{RT} \right) = 1.35 \times 10^{-2} \exp \left( \frac{180 \text{ J/mol}}{RT} \right)$$

$$K'_H = K_0 \exp \left( \frac{-E_{eq}}{RT} \right) = 1.72 \times 10^{-4} \exp \left( \frac{6000 \text{ J/mol}}{RT} \right), \quad (6.33)$$

In this expression the unit of $c_{sat}$ is mmol/m$^2$. From these relations follows also $K_H$.

In Figure 6.5 the natural logarithm of $L_{P}$ is plotted against the inverse of the temperature in Kelvin. The pressures in each linear plot are calculated from the Langmuir equation for different temperatures at constant surface concentrations using the parameters in Table 6.2. This gives isosteric plots as defined by Equation 6.22. From these plots the isosteric enthalpy of adsorption was found from the slope and entropy the isosteric entropy of adsorption was found as the intercept. The results for the isosteric enthalpy and entropy of adsorption are plotted in Figure 6.6(a) and Figure 6.6(b). The values in both plots are changing with surface concentration, and both decrease with increasing surface concentration towards a minimum around 0.015 mmol/m$^2$. For the isosteric enthalpy the value is almost constant until 0.01 mmol/m$^2$. Above 0.01 mmol/m$^2$ the value starts to decrease rapidly until the surface concentration approaches
Figure 6.5: Adsorption isosteres for 17 different adsorption concentrations in mmol/m². The slope of the linear fit gives the enthalpy of adsorption and the intercept gives the entropy of adsorption.

0.0145 mmol/m². At this value the isosteric enthalpy apparently reaches the lowest value, -7.7 kJ/mol. The isosteric entropy has a rapid decrease below 0.0025 mmol/m² and then decreases linearly with the surface concentration until 0.011 mmol/m². Then the value of the isosteric entropy drops to its lowest value, approximately -110 J/Kmol at 0.015 mmol/m².

6.4.2 Adsorption potential profile

Equation 6.20 describes the potential profile through the surface located between the graphite surface and the bulk gas phase. In Figure 6.7(a), -RT ln(c(z)/c^0) data are shown for the system containing 300 H₂ molecules in the 70 - 330 K range as a function of the distance from the crystallographic surface of the graphite. The plot shows the presence of a potential well and no activation barrier.

The position of the well is located around 1.5 Å from the graphite, and it moves slightly away from the graphite as the temperature increases. This value is much smaller than the Lennard-Jones interaction well between hydrogen and carbon, 3.36 Å. It is the result of all the attractive contributions of the
Figure 6.6: (a) Isosteric enthalpy of adsorption as a function of surface concentration. (b) Isosteric entropy of adsorption as a function of surface concentration.
Table 6.2: Equilibrium parameters found from the simulation data. \( K'_{H, isotherms} \) are the results found by using Equation 6.9 in the 70 -170 K range and Equation 6.12 in the 190 -390 K range. \( K'_{H, rates} \) are the results found by using Equations 6.14 and the fit in Figure 6.9.

<table>
<thead>
<tr>
<th>Temperature /Kelvin</th>
<th>( c^{sat} )/mmol/m²</th>
<th>( K'_{H, isotherms} )</th>
<th>( K'_{H, rates} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.0181</td>
<td>6.14</td>
<td>5.05</td>
</tr>
<tr>
<td>90</td>
<td>0.0179</td>
<td>0.485</td>
<td>0.530</td>
</tr>
<tr>
<td>110</td>
<td>0.0163</td>
<td>0.124</td>
<td>0.126</td>
</tr>
<tr>
<td>130</td>
<td>0.0161</td>
<td>4.68×10⁻²</td>
<td>4.67×10⁻²</td>
</tr>
<tr>
<td>150</td>
<td>0.0157</td>
<td>2.23×10⁻²</td>
<td>2.26×10⁻²</td>
</tr>
<tr>
<td>170</td>
<td>0.0154</td>
<td>1.34×10⁻²</td>
<td>1.29×10⁻²</td>
</tr>
<tr>
<td>190</td>
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<tr>
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</tr>
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</tr>
<tr>
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<tr>
<td>310</td>
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<td>1.70×10⁻³</td>
</tr>
<tr>
<td>350</td>
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<td>1.51×10⁻³</td>
</tr>
<tr>
<td>370</td>
<td>0.0143</td>
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<td>1.35×10⁻³</td>
</tr>
<tr>
<td>390</td>
<td>0.0143</td>
<td>1.08×10⁻³</td>
<td>1.22×10⁻³</td>
</tr>
</tbody>
</table>

interaction potential between hydrogen molecules and the graphite within the cutoff radius. The depth of the potential well obtains its largest value at the high temperatures, below -5 kJ/mol. This in good agreement with the results from Equation 6.33. Additional analyses at constant temperature, with different densities show clearly that the decrease of the well with temperature is the result of a density effect that favors repulsive interactions.

For 70 K there is also a potential well around 4 Å from the crystallographic surface. This second well is a result of the H₂-H₂ interactions. It corresponds barely to the position of the well of the Lennard-Jones interaction between hydrogen atoms. This potential well vanishes when the temperature increases.
Figure 6.7: (a) Enthalpy profile given by Equation 6.20 facing the H₂ molecules in front of the graphite as a function of distance from the crystallographic surface and temperature. (b) Desorption rate at 110 K as a function of surface coverage. The trend is not a linear function of the coverage, contrary to the Langmuir model.
6.4.3 Rate equations and adsorption dynamics

In the previous sections we have shown that the adsorption isotherm can be well modelled with a Langmuir isotherm. As we saw in Section 6.2.2 this isotherm can be obtained at equilibrium from a balance between an expression for adsorption and desorption rates. Molecular dynamics simulations can give direct access to these rates and give the possibility to test the validity of the Langmuir kinetics models in the case of this very simple system and help to propose an alternative expression that agrees with the Langmuir isotherm.

Kinetic equations for adsorption of hydrogen on graphite

The desorption rate at a temperature of 110 K is plotted as a function of the surface coverage in Figure 6.7(b). At low coverage it increases linearly according to the Langmuir model. At the contrary at higher density it increases more rapidly than the linearity, the shape of the curve is similar at different temperatures. As a consequence, the constants, \( k_a^L \) and \( k_d^L \), presented in Figure 6.8(a) for different temperatures as a function of the surface coverage, are not constant for each temperature. However it is worth noting that the ratio between the adsorption and desorption rate constants are constant with surface coverage, and the equilibrium constant \( K_L \) is then constant with the surface coverage as expected.

The value of the rate constants \( k_a \) and \( k_b \), cf. Equation 6.14, are plotted as a function of the surface coverage in Figure 6.8(b), they are within statistical uncertainty independent of surface coverage at constant temperature. This result shows that the Equations (6.14) are valid for this system within the investigated temperature and pressure ranges.

Equilibrium constant from kinetics

As can be seen in Figure 6.8(b), the values of \( k_a \) and \( k_d \) increases as a function of the temperature following an exponential law:

\[
k = k_0 \exp \left( \frac{-E}{RT} \right)
\]

The natural logarithm of the rate constants versus the inverse of the temper-
Figure 6.8: (a); Langmuir rate constants as calculated from Equation 6.13 as function of the surface coverage for 70-110 K. They are not constant with surface concentration as expected from the Langmuir kinetic model. (b); Rate constants as calculated from Equation 6.14 as function of the surface coverage for 70, 90 and 110 K. They are constant with surface concentration.
Figure 6.9: Logarithm of the rate constants as function of the inverse of temperature.

Temperature gives the apparent activation energies \( E \) as the slope and the preexponential parameters as the intercept \( k_0 \). To get better statistics we used the average value from each temperature as an estimate as seen in Figure 6.9. The results are:

\[
\begin{align*}
    k_a &= 3.5 \times 10^3 \exp \left( \frac{-1500 \text{ J/mol}}{RT} \right) \\
    k_d &= 1.8 \times 10^7 \exp \left( \frac{4400 \text{ J/mol}}{RT} \right)
\end{align*}
\] (6.34)

The units of the activation energy and of the constant are respectively J/mol and mol/s m\(^2\).

From the ratio \( k_a/k_d \) the equilibrium constant \( K'_H \) was calculated. The values of \( K'_H \) are presented in Table 6.2. By plotting the natural logarithm of \( K'_H \) versus the inverse of the temperature we found the temperature dependence as:

\[
    K'_H = 1.9 \times 10^{-4} \exp \left( \frac{5900 \text{ J/mol}}{RT} \right)
\]

which is in agreement with the equilibrium constant found from the isotherms, cf. Equation 6.33.
Figure 6.10: Change in the potential well for adsorption with surface coverage. Here at 70 K.

6.5 Discussion

6.5.1 Thermodynamic properties of the model

As seen from Figure 6.4(a), the Langmuir isotherm fits the data from 70 to 170 K very well, whereafter the isotherms follow Henry’s law for temperatures from 190 to 390 K. From Equation 6.33 and Equation 6.35 we furthermore see that the thermodynamic and the kinetic description of the system agrees. This means that the model is thermodynamically consistent. Similar trends were also observed by Benard et al., Hirsch et al., Panella et al. and Zhou et al.[20, 28, 65, 96]. We can compare the amount of maximum adsorbed H₂ in mol/m² at 70 - 77 K. Our results give $1.85 \times 10^{-5}$ mol/m², while the values of the experimental papers are in the range of $5.62 \times 10^{-5}$ to $8.93 \times 10^{-6}$ mol/m². So our results are within the range of experimental values.

The isosteric enthalpy values in Figure 6.6(a), -6.0 to -7.7 kJ/mol, agree with physical adsorption [14] and with the total potential interaction energy shown in Figure 6.10. The values were calculated from $\ln(p/p₀)$ in 6.5, where $p/p₀$ was obtained from the parameters in Table 6.2 and Equation 6.9 (not directly from the simulations). The values are thus sensitive to the model and to the fit of the model to the isotherms. At low surface concentration, hydrogen on the surface
has an interaction potential equal to that of the graphite-hydrogen interaction. As the surface gets filled with hydrogen molecules, the hydrogen-hydrogen interaction becomes more attractive and the total potential interaction energy decreases. The change in enthalpy of adsorption is then decreasing. The value decreases with growing surface coverage until the monolayer on the surface is close to completion, and reaches a relatively constant minimum. A higher increase in the pressure would result in a second layer and an increase in the enthalpy of adsorption, since the interaction of the second layer is much weaker than that of the first layer [27]. The stabilizing effect by hydrogen-hydrogen molecule interaction is apparent in Figure 6.7(a) and will be discussed in Section 6.5.3.

The isosteric entropy is plotted in Figure 6.6(b). As the loading increases there is a large change in the value of the isosteric entropy due to condensation effects. The value of the activity coefficient from Equation 6.8 is on the whole somewhat smaller than the value found by Equation 6.11 as seen in Figure 6.4(b). This is usually a sign of attractive forces being stronger than expected in a system, in agreement with the attractive interactions between adsorbed molecules described above.

6.5.2 Apparent adsorption activation energy

Equation 6.20 gave a description of the energy profile for adsorption. The function was plotted for 70, 150, 230 and 330 K in Figure 6.7(a). Clearly, there is no real barrier for adsorption in this system. The apparent activation energy barrier is therefore negative. The observed potential well stabilizes the molecules as they approach the surface. Such a potential well is common for systems that exhibit physical adsorption [14], but also for other weakly exothermic chemical reactions [104]. The value of this potential well in Figure 6.7(a) has an unknown reference. However, the change with temperature is quantitative and show us how much the apparent activation energy change with temperature. The closeness of the well to the graphite, indicates that both atoms in the hydrogen molecule are touching the graphite. At 70 K there is a second potential well around 3.8 - 4.1 Å which tells us that the hydrogen molecules are relatively stabilized at this distance from the surface at high surface concentrations, possibly also with their axis aligned with the surface.

This particular hydrogen-hydrogen interaction will allow the hydrogen molecule to move in and out of the influence of the graphite without needing to escape completely into the gas phase. This possibility disappears at higher temperatures, as the interaction energy between hydrogen molecules no longer are
strong enough to stabilize the molecules. While still in the surface, the hydrogen molecules obtain more gas like properties as the temperature increase. The hydrogen molecules become then more mobile (higher kinetic energy) [27].

6.5.3 A surface with mobile gas molecules

The rate equations from the Langmuir model Equation 6.13 and our alternative Equations 6.14 give the same expression for the equilibrium constant but they give a very different pictures of the kinetics. We have found that the rate of adsorption depends only on the temperature and the gas pressure, as described by Equation 6.14. This fits well with the other finding, that a large part of the surface has gas-like properties. Langmuir kinetics was never obtained, not even by locating position b in Figure 6.1 closer to the graphite. At the contrary, we always found that the rate equations obeyed the alternative equations. We explain this unexpected behavior by the absence of an activation energy barrier in combination with a laterally rather mobile layer within the surface. The second layer of molecules are not trapped on specific adsorption sites, but are rather mobile within the surface. They can move along the surface, away from the graphite, and still be considered as being adsorbed. This means also that adsorption can happen, independent on the availability of free sites. Therefore, the rate becomes only a function of the pressure. It is also worth noting that as the temperature increases, the rate of adsorption/desorption increases exponentially, while the amount of adsorbed molecules decreases. This may in practice mean that adsorption or desorption can be rate limiting, if this step is one of several consecutive steps in a reaction, like for instance, carbon based hydrogen storage or hydrogen reaction on a catalyst.

A physical explanation of the desorption rate is not so easy. The molecules desorbe with a rate that is proportional to the surface coverage, and inversely proportional to the free space. In the regime where Henry’s law applies, the last term is not significant. Close to saturation, the pressure is high, but a relatively large increase in the pressure has a small influence on the number of adsorbed molecules. The term $k_d \theta$ term is relatively constant, so the remaining factor must count for the increase in the unidirectional rate. This factor is the activity coefficient $\gamma$, a non-ideal factor that magnifies the ideal rate.

We have studied adsorbed states under equilibrium conditions. Under non-equilibrium conditions when net adsorption takes place, the chemical potential of hydrogen in the gas phase is larger than the chemical potential of hydrogen on the surface. The net rate can also be formulated as a function of this driving force, $-\Delta G/RT = -(\mu^s - \mu^g)/RT$. Using mesoscopic non-equilibrium
thermodynamics [99], we can give a thermodynamic basis for the rate of the adsorption by the following equation:

\[ J_a = \frac{L}{R} \left( \exp \left( \frac{-\Delta G}{RT} \right) - 1 \right) \]  

(6.35)

where \( L \) is the conductivity along the internal coordinate axis, \( z \). This rate equation contains the activity in the chemical potential of the product. The expression we obtained for the desorption or adsorption rate is meaningful in this context.

### 6.5.4 Catalysis in PEM fuel cells and hydrogen adsorption in graphitic materials

It is interesting to put the results in the perspective of the PEMFC. Under operating conditions the PEMFC has temperatures in the range of 350 - 370 K, so the hydrogen molecules are denser at the surface of the graphite. This is beneficial for transport of hydrogen to the catalytic particles in the PEMFC. We can support the postulate made by Kjelstrup and Bedeaux [47], that the graphite support in the PEMFC is a route for transport of reactant gas to the catalytic particles, in accordance with the findings of Meland et al. [60, 71] and Paulus et al. [72].

Lateral surface transport may also be important for hydrogen storage in graphitic materials. As we mentioned before, kinetics of adsorption and desorption already at equilibrium can estimate how fast hydrogen can be inserted or extracted from these materials [105]. The transport along the surface and the residence time of hydrogen at the surface will be discussed in detail in a forthcoming paper on the same system.

### 6.6 Conclusion

In this paper we have done equilibrium molecular dynamics simulations of hydrogen adsorption on graphite. We found that the hydrogen density is larger at the graphite surface than in the gas phase at all temperatures. The observed adsorption and desorption rates are not described by Langmuir kinetics in this system. We propose a new set of rate equations which give the same expression for the Langmuir constant, and they give the same values for the Langmuir and Henry constants as those found from the adsorption isotherms. This system has mobile molecules in the adsorbed phase and there is no energy barrier for adsorption and this can explain that the adsorption rate is a function of the
pressure. The rate of desorption is dependent on the surface coverage and this can be explained with the non-ideality of the adsorbed molecules.

6.7 Acknowledgements

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Chapter 7

Surface self diffusion and mean displacement of hydrogen on graphite and a PEM fuel cell catalyst support.


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Abstract

Quasi-elastic neutron scattering (QENS) measurements together with equilibrium molecular dynamic (EMD) simulations have been performed to investigate the surface interaction between hydrogen molecules and a carbon material commonly used in polymer electrolyte membrane fuel cells (PEMFC), called XC-72. Half a monolayer of molecular hydrogen was adsorbed on to the carbon material at 2 Kelvin. QENS spectra were recorded at the time of flight spectrometer IN5 at 40, 45, 50, 60, 70, 80 and 90 Kelvin. Simultaneously the pressure was measured as a function of time to monitor the equilibrium surface coverage at each temperature. By using the Chudley and Elliott model for jump diffusion we found the diffusion coefficient at each temperature. At 350 K, a typical fuel cell temperature, the temperature function was extrapolated to a self diffusion coefficient of $2.3 \times 10^{-7}$ $\text{m}^2/\text{s}$. We simulated graphite in contact with hydrogen molecules using EMD simulation. We simulated the system at different temperatures from 70 to 350 K in 20 K intervals and for five numbers of $\text{H}_2$ molecules $N_{\text{H}_2} = 50, 100, 150, 200$ and 300. The graphite was made of 9 sheets of graphene in a sandwich. The surface self diffusion was found from the mean square displacement, and the values from EMD simulations are the same order of magnitude as the experimental values, but systematically higher, probably due to the ideal surface. From EMD simulation, we also calculated the average time between adsorption and desorption events on the surface. This was used to find the mean displacement of the hydrogen molecules between adsorption and desorption. This result showed that $\text{H}_2$ molecules can move 80 Å, at ambient temperatures and pressures, along the surface. Using this data, we conclude that catalyst support material in PEMFC contributes to the transport of reactant.

**Keywords:** QENS, Adsorption, Graphite, Hydrogen, Surface Diffusion, PEM fuel cell, Molecular Dynamics, Catalyst support, Reactant transport
7.1 Introduction

One of the limiting factors for a realisation of the polymer electrolyte membrane fuel cell as an energy converter may be the catalyst utilization in the cell. The impressive catalyst loading that now has been reached in many recent works [106, 107], may still not be sufficient for an introduction of fuel cells in the transport sector. The amount of catalyst in the world is limited, so the material available must be efficiently used. Work that can help reduce the loading, and reduce mass transfer limitations in the cell is therefore important. The present work can be seen in this context.

The cell consists of two catalytic layers, a few microns thick, separated by a proton conducting water-filled polymer electrolyte membrane. A detailed description is given by Larminie et al. and Costamagna et al. [4, 8]. The reactive sites in the catalytic layers are located on Pt or Pt alloy particles, with diameters of typically 2 - 10 nm [59]. The particles must be in contact with the membrane as well as an electronic conductor, for instance carbon black (XC-72) [56-58, 108]. The catalytic layers are further supported by a layer made of carbon paper or cloth. This layer, as well as the catalytic layer, are both porous. They allow reactant gases H2 and O2 to diffuse to the catalytic sites. The question to be examined in this article is the mechanism of hydrogen’s transport. Which path does hydrogen take on its way to the catalytic site, and what is the corresponding transport parameter?

There is contact between the gas, the catalyst, and the ionic conductor at the three phase contact line between the phases. These lines provide a rather limited number of sites. Direct access of hydrogen gas to the three-phase contact line via the gas phase is also impossible: Gas molecules can not go directly to a contact line from the gas phase as this would lead to an infinite velocity of the gas close to the contact line [47]. A supply of gas to the active sites must then come via the carbon surface or membrane surface in contact with Pt. Accordingly, Meland et al. [60] proposed that the path to the catalytic site is via the relevant surfaces. Some evidence to support this hypothesis was obtained by impedance spectroscopy [60, 71, 72]. A surface diffusion coefficient for hydrogen on carbon was estimated to 1x10^{-7} m^2/s.

These investigations indicate that surface diffusion can be essential for supply of reactants to the catalytic sites. It is then important to have precise knowledge of its value and variation. This is the aim of the present work, to obtain such knowledge. Some initial studies of hydrogen diffusion on carbon have already been done using quasi-elastic neutron scattering experiments, by us [109]
and others [40, 73]. Adsorption of H₂ on carbon materials has been studied by many authors [15, 19, 20, 22, 61–63, 65, 110]. But these investigations have been directed towards use of carbon materials as hydrogen storage materials, and not as catalyst support in PEMFCs.

We give here further evidence supporting the idea that significant hydrogen transport can take place along carbon or graphitic surfaces. Quasi-elastic neutron scattering (QENS) experiments are well suited to find surface diffusion of molecular hydrogen on carbon materials [40, 66–69, 73] and we shall use this technique again to study carbon black, XC-72, reporting new data and improvements on the method [109]. The new experiments give a more accurate determination than reported before [109], another surface concentration at 2K, and values for additional temperatures. The variation in the surface self diffusion coefficient $D_s$ with surface concentration and temperature shall be presented for temperatures between 40 and 90 K.

The experimental technique is supplemented with equilibrium molecular dynamics simulations of hydrogen on graphite between 70 and 350 K, in order to reveal underlying molecular mechanisms. We shall see that there is a significant hydrogen transport to the Pt catalyst particles via the graphite support. This supports the proposition that hydrogen transport to the anode in a PEMFC may take place via the carbon surface.

In order to distinguish surface diffusion from diffusion in the homogeneous phase from each other, we shall use the symbol $D_s$ for diffusion parallel to the surface, $D_{s\perp}$ for diffusion into the surface, while $D$ shall be used for the gas phase only.

### 7.2 Experimental

#### 7.2.1 Sample characterisation and preparation

The sample used in this experiment is a commercial carbon black, XC-72, from Cabot Corp. From BET measurements the surface area of XC-72 ($A_{XC-72}$), was found to be 204.3 m²/g. From field emission scanning electron microscope the particle size of the XC-72 sample material can be estimated between 20 to 100 nm, see Figure 7.1. The thermal gravimetric analysis gave only low weight losses during heating, as shown in Figure 7.2. This indicates low levels of -OH-CH groups who could potentially create noise in the recorded neutron spectra. The sample ($m_{XC-72} = 8.1$ g) was placed in a thin walled aluminium cylinder and evacuated for 6 hours in order to remove water. The number of moles
needed to form half a monolayer of hydrogen \( n_{H_2}^{\text{total}} = 0.0086 \text{ mmol} \), was estimated from the BET surface area of the sample \( A_{XC-72} \), and the molecular area of hydrogen found in literature \( A_{H_2} \) equal to 15.6 Å² [73]. To measure the number of moles needed to form half a monolayer, a second cylinder with known volume of 1856 cm³ was pressurised until the pressure reached 85.63 torr at room temperature. The pressure of n-hydrogen (0.75 o-H₂, 0.25 p-H₂) was measured with a Baratron pressure gauge at room temperature and hydrogen was introduced to the graphite in the aluminium cylinder at 2 K and the cell was then sealed. The hydrogen was left at 2 K to equilibrate to para-hydrogen before the measurements were started. The surface coverage and surface concentration can be calculated from the pressure in the closed system measured at room temperature. From ideal gas law, the volume of the system and the pressure, we can calculate the amount of hydrogen in the gas phase. From knowledge of the total amount of H₂ in the system \( n_{H_2}^{\text{total}} \), the BET area of the sample \( A_{XC-72} \), the mass of the sample \( m_{XC-72} \), Avagadro's number \( N_A \), and the area of an adsorbed hydrogen molecule \( A_{H_2} \), we can find the
number of surface molecules, surface coverage, and surface concentration as

$$n_{H_2}^{s} = n_{H_2}^{total} - n_{H_2}^{g} = n_{H_2}^{total} - \frac{P V}{R T}$$

$$\theta = \frac{A_{H_2} N_A n_{H_2}^{s}}{A_{XC-72} m_{XC-72}}$$

$$c_{H_2}^{s} = \frac{n_{H_2}^{s}}{A_{XC-72} m_{XC-72}}$$

(7.1)

This gives an improvement in the experimental setup compared to our earlier work [109]. We can now correlate the surface concentration and the surface self diffusion.

![Graph](image)

Figure 7.2: Thermogravimetric analysis of XC-72 from 297 to 945 K. There is a total loss of 1.2 weight % after heating the sample for one hour at 945 K.

### 7.2.2 Quasi-elastic neutron scattering experiments

The quasi-elastic neutron scattering (QENS) experiments were performed at the direct geometry time-of-flight spectrometer IN5, ILL, Grenoble, France. The incident wavelength was set to 5 Å (3.27 meV) which give a resolution of 103 μeV. To estimate the resolution function a measurement of a cylindrical vanadium sample at 40 K was performed [49]. The background was measured with the sample container filled with XC-72 at 40, 45, 50, 60, 70, 80, and 90 K. Measurements to estimate the diffusion were conducted at 40, 45, 50, 60, 70, 80, and 90 K. The time measured varied from 4 to 6 hours. As the hydrogen
desorbs as the temperature increase, the aluminium cell had to be opened to prevent rupture of the cell. For safety reasons it was opened at 40 K and after this the adsorbed hydrogen was in equilibrium with the desorbed hydrogen in the sample and the calibrated volume during QENS measurements. To verify that the system was in equilibrium and stable during the measurements, the pressure was constantly measured, giving constant information on the surface concentration and surface coverage from Equation 7.1.

Data collected from the QENS measurements were first normalised versus the monitor. This was done to remove changes in intensities between spectra due to variations in the incident neutron beam. To correct for variations in detector efficiencies a measurement of a cylindrical vanadium sample at 40 K was conducted. Then the spectra were normalised to the vanadium measurements to correct the intensity at each Q value. Further the measured spectra were divided into regions in Q, ω space to get constant Q values by rebinning over dQ = 0.05 Å⁻¹, to enhance the statistics. This was done using LAMP, a program from ILL based on the IDL language. The background measurements of pure XC-72 was treated the same way and subtracted from the measurements of XC-72 with hydrogen. After this treatment the S(ω) plots were fitted with a Lorentzian function to estimate quasi-elastic broadening as a function of Q, f(Q). The fit of the Lorentzian was done in QENS_fit, a fitting procedure within the LAMP program. In the QENS_fit program a measurement of the vanadium sample at 40 K was used as the resolution function. The fit to the broadening as a function of Q was done using the Chadley and Elliott model that describes the movement of a single molecule as it jumps between different sites in a lattice or between cages made of other molecules [49]. The smallest jump length l₀ is assumed to be identical for all sites whereas the jump directions are random. It is assumed that the molecules remain at the surface a time τ₀, the residence time, before moving again. Since the sample is a powder sample the broadening function has to be spatially averaged over the angle between the normal to the scattering surface and the scattering vector Q

\[
f(Q) = \frac{\hbar}{n\tau_0} \sum_{j=1}^{n} (1 - e^{-iQs_j}) = \frac{\hbar}{\tau_0} \left( 1 - \frac{1}{2} \int_0^{\pi} e^{-iQl\cos \theta} d\cos \theta \right)
\]

\[
= \frac{\hbar}{\tau_0} \left( 1 - \frac{\sin(Ql)}{Ql} \right)
\tag{7.2}
\]

Assuming that there is a distribution of the jump lengths of the form

\[
a(l) = l \exp \left( -\frac{l}{l_0} \right)
\tag{7.3}
\]
we obtain as broadening function [74]

\[
f(Q) = \frac{\hbar}{\tau_0} \int \left(1 - \frac{\sin(Ql)}{Ql}\right) a(l) dl = \frac{\hbar}{\tau_0} \left(1 - \frac{1}{1 + Q^2 l_0^2}\right)
\]  

(7.4)

It can be shown that \( l_0^2 \) is proportional to \((1/6) l^2\) using the Einstein-Smoluchowski equation, see i.e. ref. [74]. This gives the surface diffusion coefficient

\[
D_s = \frac{l_0^2}{\tau_0}
\]

(7.5)

The subscript indicates that diffusion takes place along the surface, and the superscript \( s \) that the value is specific to the surface.

The model in Equation 7.4 was used to fit \( f(Q) \) to experimental data on the following form

\[
\frac{\hbar}{f(Q)} = \tau_0 + \frac{\tau_0}{l_0^2 Q^2} = \tau_0 + \frac{1}{D_s Q^2}
\]

(7.6)

Here the value of the broadening of \( S(Q, \omega) \), \( f(Q) \), is converted into seconds, and \( Q^{-2} \) into meters squared. So by plotting the experimental data and their half width at half maximum (HWHM) \( /s \) as function of \( Q^{-2} /m^2 \), we fitted Equation 7.6 by linear regression, and found \( D_s \) from the slope of the curve.

By plotting the logarithm of the diffusion coefficients found for each temperature versus \( T^{-1} /K^{-1} \), we obtained an Arrhenius plot. This was used to estimate the temperature dependence of the diffusion coefficient according to

\[
D_s(T) = D_0 \exp \left(\frac{-E}{k_B T}\right)
\]

(7.7)

We will compare the results from QENS with results from EMD.

### 7.3 Equilibrium molecular dynamics simulations

#### 7.3.1 The system

The EMD system was built of an infinite sheet of crystalline graphite in contact with hydrogen molecules, \( \text{H}_2 \). The graphite has a hexagonal crystallographic structure with space group \( P6_3/mmc \) without any defects. The crystal is made from 9 sheets of graphene and contains 5184 carbon atoms. Following the crystallographic structure, the graphene sheets are oriented in our simulation box such that the surface of the sheets are perpendicular to the \( z \) direction. The
size of the crystal is 44.208 Å and 34.0313 Å in \( x \) and \( y \) directions respectively and about 30 Å in the \( z \) direction [100]. Periodic boundary conditions are applied in \( x \) and \( y \) directions in the limits of the crystal and in the \( z \) direction at 95.254 Å from the centre of the crystal. This symmetry gives in effect an infinite succession of two infinite graphite crystal surfaces separated by a gaseous zone of about 160 Å in the \( z \) direction, where the \( \text{H}_2 \) molecules are located. The model uses an atomic description of the graphite and hydrogen. The atoms interact through intermolecular and intramolecular potentials. The intramolecular potentials are given in [103], Table 1 and Equations 2-4. The intermolecular potential is the Lennard-Jones potential [50]. The potential parameters for the Lennard-Jones are taken from the MM2 force field [101], while the parameters of the intramolecular potentials comes from the DREIDING force field [102] for graphite and Delft Molecular Mechanics (DMM) force field [103] for the hydrogen molecules.

**Simulation procedures**

Five different systems were simulated to investigate the surface diffusion coefficient as a function of surface concentration. It was implemented by simulating with five different global densities. The five different numbers of hydrogen molecules were \( N_{\text{H}_2} = 50, 100, 150, 200, 300 \). For each \( N_{\text{H}_2} \) simulations were preformed at seventeen different temperatures, ranging from 70 to 350 K at 20 K intervals. Additional simulations with \( N_{\text{H}_2} = 10 \) was performed at 70, 90, 110, 150, 170, 190, and 230 K to investigate the surface dynamics at low density at low temperature. This gave a total of 82 simulations describing the dynamics on the graphite surface as function of surface concentration and temperature. The volume of the total system subtracted by the volume of the graphite crystal gives the volume available to the \( \text{H}_2 \) molecules in the gas phase.

The dynamics were obtained by integrating Newton’s equations of motion using the velocity Verlet algorithm [51]. All simulations had time steps of 0.001 picoseconds. The initial configuration was constructed by randomly distributing the \( \text{H}_2 \) molecules in the gas phase. Molecules are located such that they do not overlap with each other or the graphite crystal. The system was stabilized during 400000 time steps by fixing the temperature at an imposed value using a simple rescaling of the velocities. When the system was in thermal equilibrium, the conditions of the simulations were changed to those of a micro canonical ensemble (constant energy). A total of 1700000 time steps were performed
under micro canonical conditions. During the simulation time, variables where computed every $10^{th}$ time step and averaged over 1000 time steps and stored.

**Surface self diffusion coefficient and mean displacement**

Here we present how we have analysed the EMD data to find the transport properties. From the EMD simulations all the movements of the particles are calculated and stored. This data gives us access to the diffusivities of the $\text{H}_2$ molecules. This diffusivity is known as the self diffusion or the tracer diffusion. It can be derived from the perspective of random walk [50, 111]. In this paper we have investigated the transport along the graphite surface. On a flat graphite surface it can be assumed that the surface is homogeneous and that the diffusion is characterized as uncorrelated. Then it is possible to define an expression for the surface self diffusion coefficient, $D^s_n$, from random walk. For random walk in two dimensions the mean square displacement is given by

$$\langle r^2(t) \rangle = a_x^2 n_x(t) + a_y^2 n_y(t) \quad (7.8)$$

Where $\langle r^2(t) \rangle$ is the mean square displacement, $a_i$ is the length moved by the particle in either $x$ or $y$ direction, $n_x(t)$ and $n_y(t)$ is the number of jumps done during the time $t$. If the system is homogeneous then it can be assumed that $a = a_x = a_y$ and that $n(t) = n_x(t) + n_y(t)$ and Equation 7.8 can be written as

$$\langle r^2(t) \rangle = a^2 n(t) \quad (7.9)$$

The self diffusion coefficient is characterized as

$$\langle r^2(t) \rangle = \lim_{t \to \infty} 2d D^s_n t \quad (7.10)$$

which it is possible to rearrange to get

$$D^s_n = \lim_{t \to \infty} \left[ \frac{\langle r^2(t) \rangle}{2dt} \right] \quad (7.11)$$

In the case of surface self diffusion coefficient the dimensionality $d$ is equal to 2 and it is independent of the nature of the jumps. For a group of $N$ distinguishable particles Equation 7.11 gives the surface self diffusion coefficient on the form

$$D^s_n = \lim_{t \to \infty} \left[ \frac{1}{2dNt} \sum_{i=1}^{N} \langle | \vec{r}_i(t) - \vec{r}_i(0) |^2 \rangle \right] \quad (7.12)$$
Where $\vec{r}_i(0)$ and $\vec{r}_i(t)$ are the position of molecule $i$ at an initial time and after a time delay of $t$. This equation can be used in molecular simulations to extract the surface self diffusion coefficient from the movements of each individual particle. Plots of $\langle r^2(t) \rangle$ as function of $t$ is shown in Figure 7.3 below. The slope of these plots give the $D_{ii}^s$ from the molecular dynamics simulation data. In the EMD simulations the time between adsorption and desorption events for each molecule was calculated, and this data was used to get the average time, $\langle t \rangle$, the molecules spent on the graphite surface at each simulated temperature and surface concentration. From the values of $D_{ii}^s$ and the average time on the surface the mean displacement, $r_{\text{mean}}$, is given by

$$r_{\text{mean}} = \sqrt{4D_{ii}^s \langle t \rangle} \quad (7.13)$$

The $r_{\text{mean}}$ is then the mean displacement the molecules have moved from the point they adsorb to the point they desorb. This value will be used later to estimate the contribution of the graphite catalyst support on the transport of reactant to a catalyst particle.

Figure 7.3: Examples of slopes of the mean squared displacement of hydrogen molecules as a function of the time for 170 and 350 K with $N_{H_2} = 300$. 
7.4 Results and discussion

7.4.1 Quasi-elastic neutron scattering experiments

Figure 7.4(a) shows the fit of Equation 7.6 to the experimental data at 40 and 90 K, for \( Q \) values from 0.45 to 1.35 Å\(^{-1}\). The values of the surface self diffusion coefficients, \( D^n_s \), the residence times, \( \tau_0 \), and the jump lengths, \( l_0 \), from Equation 7.6 are presented in Table 7.1 with the corresponding inaccuracies. The \( D^n_s \) values for 40, 45, 50, 60, 70, 80 and 90 K from Equations 7.6 and 7.5 are plotted in an Arrhenius plot shown in Figure 7.4(b). From the slope of this plot, we determined the coefficients \( D^n_s = (3.5 \pm 0.9) \times 10^{-7} \) m\(^2\)/s and \( E/k_B = 140 \pm 10 \) K (1160 \pm 80 J/mol) in Equation 7.7. Comparing with liquid hydrogen which has the Arrhenius coefficients \( D_0 = (8.6 \pm 1.0) \times 10^{-8} \) m\(^2\)/s and \( E/k_B = 45 \pm 2 \) K (373 \pm 13 J/mol) [75]. Using Equation 7.7, we estimated the self diffusion coefficient at higher temperatures. At 350 K, a typical fuel cell temperature, we found a self diffusion coefficient of \( 2.3 \times 10^{-7} \) m\(^2\)/s.

Table 7.1: Parameters found from the QENS experiment.

<table>
<thead>
<tr>
<th>Data form QENS with 0.5 monolayer of H(_2) at 2K</th>
<th>( c^n_{H_2} ) /mmol/m(^2)</th>
<th>Temp. / K</th>
<th>( \tau )/s ( 10^{-12} )</th>
<th>( l_0 )/m ( 10^{-10} )</th>
<th>( D^n_s )/m(^2)/s ( 10^{-8} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0051</td>
<td>40</td>
<td>1.21 \pm 0.07</td>
<td>1.20 \pm 0.05</td>
<td>1.18 \pm 0.07</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>45</td>
<td>1.22 \pm 0.06</td>
<td>1.37 \pm 0.05</td>
<td>1.53 \pm 0.09</td>
<td></td>
</tr>
<tr>
<td>0.0046</td>
<td>50</td>
<td>1.23 \pm 0.05</td>
<td>1.50 \pm 0.06</td>
<td>1.8 \pm 0.1</td>
<td></td>
</tr>
<tr>
<td>0.0029</td>
<td>60</td>
<td>1.26 \pm 0.05</td>
<td>2.15 \pm 0.01</td>
<td>3.7 \pm 0.5</td>
<td></td>
</tr>
<tr>
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<td>70</td>
<td>1.35 \pm 0.04</td>
<td>2.52 \pm 0.01</td>
<td>4.7 \pm 0.5</td>
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</tr>
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<td>0.0016</td>
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<td>2.79 \pm 0.02</td>
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<th>Temp. / K</th>
<th>( \tau )/s ( 10^{-12} )</th>
<th>( l_0 )/m ( 10^{-10} )</th>
<th>( D^n_s )/m(^2)/s ( 10^{-8} )</th>
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<tr>
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<td>1.8 \pm 0.2</td>
<td>3.7 \pm 0.7</td>
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Table 7.1 gives the results of the QENS experiments. Also the previous QENS results are presented for comparison. The two sets of results are also compared in Figure 7.4(b). We see that the new results can be given with accuracy better than 5% below 70 K. At 80 and 90 K, the accuracy becomes less. A clear increase can now be seen in the diffusion coefficient with temperature, and
Figure 7.4: (a); Fit of Equation 7.6 to the experimental data from the QENS measurements done at 40 and 90 K. The dashed line is the data from 40 K and the full line is the data from 90 K (b); Natural logarithm of the self diffusion coefficients found from our QENS experiment and EMD simulation data are plotted together with results from Narehood et al. and Bienfait et al. as a function of $T^{-1}/K^{-1}$. The dashed line is the linear regression giving the Arrhenius coefficients $D_{s0}$ and $E/k_B$ from our QENS data.
this can be ascribed to an increased jump length, since the residence time is constant within the accuracy given. The results for the diffusion coefficients agree in a qualitative way with the previous results. The accuracy in these experiments were then smaller, however. They pointed to a reduction in residence time with temperature, but this is probably not real, as these data did not have temperature-dependent background corrections.

The new experiments are done with half a monolayer of hydrogen at 2 K, while the previous were done with a full monolayer at 2 K. This may explain why the first measured diffusion coefficients on the average are somewhat larger (a factor of 1.1-1.4) than the new results; the surface concentration must be larger in the last case, but it was then not determined.

Cabria et al [86] found four different sites on a graphene layer with different binding energies. In a powder sample like here, the number of sites can be larger.

The temperature dependence of the two sets of data as found from Equation 7.7 are also slightly different. We find

\[
D^*_{0.5ML} = (3.5 \pm 0.9) \times 10^{-7} \exp\left(\frac{-1.2 \pm 0.1 \text{kJ/mol}}{RT}\right) \text{m}^2/\text{s}
\]

\[
D^*_{1ML} = (1.9 \pm 0.2) \times 10^{-7} \exp\left(\frac{-1.0 \pm 0.1 \text{kJ/mol}}{RT}\right) \text{m}^2/\text{s}
\]

(7.14)

By extrapolation to 350 K, we find \(D^*_{0.5ML} = 2.3 \times 10^{-7} \text{ m}^2/\text{s}\) and \(D^*_{1ML} = 1.4 \times 10^{-7} \text{ m}^2/\text{s}\). The effects of temperature and concentration are separable with the molecular dynamics simulation technique (see below).

### 7.4.2 Surface concentration, and enthalpy and entropy of adsorption.

The surface concentration, \(c^*_{H_2}\), was calculated for each temperature investigated by QENS from the pressure measurements, using Equation 7.1. The measured pressure and the corresponding surface coverage, \(\theta\), from Equation 7.1 were first used to find the Langmuir constant, \(K_L\), from

\[
K_L = \frac{\theta}{(1 - \theta)} \frac{p^0}{p}
\]

(7.15)

The logarithm of \(K_L\) is shown in Figure 7.5 as a function of the inverse of the temperature. A linear trend is found. This is remarkable since we only
Figure 7.5: The natural logarithm of the Langmuir constant from pressure measurements and EMD simulation [112] plotted versus the inverse of temperature. The simulation data is plotted as plus signs and the experimental data is plotted as squares.

have one experimental point for each temperature. This shows that the adsorption isotherm from the pressure measurement fits well with a Langmuir isotherm. The same was observed earlier with molecular dynamics simulations of hydrogen on graphite [112]. These results are also shown in the same figure for comparison. The two lines give direct access to the enthalpy (the slope) \( \Delta H \) and entropy (the intersection) \( \Delta S \) of adsorption at zero loading.

\[
\Delta H_{exp} = -3.3 \text{ kJ/mol} \quad \Delta S_{exp} = -34 \text{ J/Kmol} \\
\Delta H_{MD} = -6.0 \text{ kJ/mol} \quad \Delta S_{MD} = -72 \text{ J/Kmol} \quad (7.16)
\]

The results are of the same order of magnitude. The simulation of the pure graphite-hydrogen system give values that are twice the values of the experimental ones, but both sets of data are in good agreement with previous studies, both experimental and theoretical [17, 68, 82--86, 113].

### 7.4.3 Equilibrium molecular dynamics simulations

The surface self diffusion of hydrogen molecules on graphite, \( D_s^s \), was also obtained from equilibrium molecular dynamics simulations. The value of \( D_s^s \) was obtained by linear fit to the slope of the mean squared displacement from Equation 7.12, as shown in Figure 7.3. \( D_s^s \) for temperatures from 70 to 350 K
Figure 7.6: (a): $D_i^s$ for all temperatures simulated with EMD plotted as function of $c_{H_2}^s$. The $D_i^s$ values are following the same trend for all temperatures. The solid line in both plots are guides to the eye. (b): The change in $D_i^s$ as function of $c_{H_2}^s$ as found by QENS.
with 20 K intervals and at 82 different surface concentrations were found in this manner and plotted as function of $c_{H_2}^s$ in Figure 7.6(a). This plot shows that all data follows a similar trend regardless of temperature. In Figure 7.6(b) we plotted the experimental results reported above. We observed that $D_n^s$ have the same $c_{H_2}^s$ dependence as the data from QENS.

Figure 7.7(a) gives $D_n^s$ at 70, 90, 110, 150, 170, 190, 230, and 350 K as a function of $c_{H_2}^{s-1}$. This plot is made to investigate the prediction of kinetic theory for surface diffusion. According to this theory, the diffusion coefficient varies with $c_{H_2}^{s-1}$ below approximately 1000 m$^2$/mmol [111, 114]. Our data starts to deviate from a linear relation above 1000 m$^2$/mmol. At this concentration the molecules on the surface are not colliding with each other anymore, and the $D_n^s$ approaches a (temperature dependent) maximum value. At temperatures from 190 K and up, and with a global number of $N_{H_2} = 10$, the density on the graphite surface is very low, and the uncertainty both in $D_n^s$ values and in the surface concentration are large and explain the discrepancy of the data. At high surface densities, the diffusion coefficient increases only slightly with temperature at a given density. From kinetic theory it is also predicted that for a given concentration $D_n^s$ increases linearly with the square root of the temperature. This was not observed in our data. In Figure 7.7(b) we plotted the logarithm of $D_n^s$ as a function of the inverse of temperature. The trend is linear as it is observed experimentally for constant number of molecules in the system. QENS results are also plotted in the same figure and are in good agreement. However the activation energies calculated from these curves are higher by about a factor 2 compared to the experimental results. The extrapolation of experimental data to 350 K gives values for the $D_n^s$ that are 4 to 10 times lower than the EMD values.

We know that the EMD simulations give an ideal picture of reality. Grooves, steps, and pores in a material causes barriers for free translation for adsorbed molecules [115, 116] and are absent in the simulated system. This can explain the discrepancy in the activated energy and then in the data at high temperature. Our finding is supported by that of Jobic et al. [117]. They did also find larger diffusivities in EMD simulations compared to QENS experiments for alkanes in zeolites.

### 7.4.4 Reactant transport via supporting surface

We have seen above that the activation energies for surface diffusion of hydrogen is about three times lower than the enthalpy of adsorption, both for EMD and QENS. This is in agreement with previous results from the literature both
Figure 7.7: (a) \( D^s \) plotted versus the inverse of the surface concentration, \( c_{H_2}^{-1} \), a zoom of the high density part is also shown and reveals a temperature effect. (b) Logarithm of \( D^s \) versus \( T^{-1} \) for the EMD data, and QENS data for the 0.5 monolayer loading.
from theory and experiments [17, 39, 40, 42, 68, 82–86, 113]. In these reports the adsorption energies are 3 to 9 times larger than the diffusion activation energy. This indicates that hydrogen molecules can be mobile at the graphite surface without escaping into the gas phase. At room temperature this effect is assumed to be negligible. The simulation data offer a means to further investigate this assumption, from low temperatures to room temperature.

The average time, \( \langle t \rangle \), between adsorption and desorption events was determined in the simulations. In Figure 7.8(a) the \( \langle t \rangle \) values for each global density \( N_{H_2} \) are given as the natural logarithm versus \( T^{-1} \). The average time follows an exponential trend as given by Clark [44], and the \( \langle t \rangle \) decrease with temperature which is in agreement with the isotherms we observed in our earlier EMD study [112].

From these values and the values of \( D_\parallel^s \) described above, we determined the mean displacement as \( r_{\text{mean}} = \sqrt{4D_\parallel^s\langle t \rangle} \). In Figure 7.8(b) \( r_{\text{mean}} \) is plotted as a function of the surface concentration. The plot shows that \( r_{\text{mean}} \) is decreasing with both increasing temperature and surface concentration. From an experimental point of view it is preferable to give these data as a function of gas pressure, see Figure 7.9(a). In this figure \( r_{\text{mean}} \) is decreasing with increasing pressure for a given temperature. At low pressure \( r_{\text{mean}} \) is decreasing with increasing temperature, while at high pressure the inverse happens. This means that there exists an intermediate zone where the trends cross. This result is not in contradiction with the trend in Figure 7.8(b). This is a consequence of the shape of the isotherms in this figure.

Extrapolation and interpolation of \( r_{\text{mean}} \) as a function of pressure was used to estimate the mean displacement at 1 bar, which is a usual operating pressure of PEMFCs. The results are given in Figure 7.9(b) for temperatures between 70 and 350 K at 1 bar. This curve show a maximum at 110 K of about 140 Å. This maximum can be understood from the temperature dependence in \( D_\parallel^s \) and the average time. Below this temperature, the effect of \( D_\parallel^s \) is dominating and the \( r_{\text{mean}} \) is increasing with temperature. Above 110 K it is the average time that is dominating, and \( r_{\text{mean}} \) is decreasing with increasing temperature. The increase above 290 K is not significant. It is worthwhile to notice that even at 350 K the \( r_{\text{mean}} \) is comparable to the lower temperature values of about 80 Å. Thus, the assumption that surface diffusion is negligible is doubtful, and we will in the following investigate this effect in PEMFC electrodes.

The effect of the catalyst support surface can now be investigated, by calculating the flux of reactants to a catalyst particle. In a PEMFC this translates
Figure 7.8: (a) Logarithm of the average time between adsorption and desorption events versus $T^{-1}$ for all investigated temperatures. (b) $r_{\text{mean}}$ as a function of $c_{\text{H}_2}^s$ for seven temperatures.
to the flux directed along the carbon surface to a platinum particle. To do this we assume that the average catalyst particle in a PEMFC has a radius \( R \) of 1 nm [118] and is shaped as a hemisphere. Further we assume that the flux of adsorbing gas molecules perpendicular to the carbon surface is uniform.

The area of the catalyst support material around the catalyst, with an influx of reactants, is equal to the area of a circle with radius equal to \( r_{\text{mean}} + R \), minus the area of the catalyst particle. It is given by

\[
A_{\text{support}} = \pi (r_{\text{mean}} + R)^2 - \pi R^2 = \pi (r_{\text{mean}}^2 + 2r_{\text{mean}}R)
\]  

This area is hereinafter referred to as the active support area. For a given temperature, the active support area is constant and it is equal to the area of the large circle minus the area of the inner circle in Figure 7.10. To estimate how many of the molecules that adsorb on the active support area and travel to the catalyst particle, we have to define the probability of an adsorbed molecule hitting the catalyst particle. This probability is a function of the distance from the catalyst particle where the molecules adsorb. In Figure 7.10 two examples of two different adsorptions, at positions \( r_1 \) and \( r_2 \), are shown. Assuming that the adsorbed molecules are just as likely to move in all directions after adsorbing at \( r_i \), and desorb first when they are outside a circle with radius \( r_{\text{mean}} \), the probability \( p_i \) can be given by the angle \( \alpha_i \), distance from the catalyst particle \( r_i \), and the position \( t_i \) on line \( l \). The probability of adsorbed molecules reaching the catalyst particle in an arbitrary position is then:

\[
p(r_i, t_i) = \frac{2\alpha_i}{2\pi} = \frac{2\arctan(t_i/r_i)}{2\pi} = \frac{\arctan(t_i/r_i)}{\pi}
\]  

where \( r_i \) is an arbitrary position within the active support area of the catalyst support and \( t_i \) is the position on the line \( l \) where line \( k \) intersects, see Figure 7.10. Since the position \( t_i \) changes with the position \( r_i \) we can give a function describing \( t_i \) with \( R \) and \( r_i \). This function is given by the functions of a circle and a line segment \( k \). We know that these two functions are equal where they meet at the intersection \( i \), and that the derivatives also are equal there. We then find the function for the position \( t_i \) as:

\[
t_i(r_i, R) = \frac{R}{\sqrt{1 - \frac{R^2}{r_i^2}}}
\]  

When we introduce this in Equation 7.18 we get

\[
p_i(r_i) = \arctan \left( \frac{R}{\sqrt{1 - \frac{R^2}{r_i^2}}} \right) / \pi
\]  

(7.20)
Figure 7.9: (a) $r_{\text{mean}}$ as function of pressure at constant temperature, the dashed line show an extrapolation of the data at 170 K, the full line show an extrapolation of the data at 350 K, the vertical line in the zoom show the position of 1 bar (101325 Pa) (b); Mean displacement of the adsorbed hydrogen molecules at 1 bar for 70 to 350 K.
To find the fraction of molecules adsorbed on the active support area that reach the catalyst particle, we integrate for the whole surface and normalise by the active support area:

\[
P = \frac{1}{A_{\text{support}}} \int_{r_i}^{r_i} \int_{0}^{2\pi} p(r_i, \phi) r_{\text{mean}} d\phi dr
\]

\[
P = \frac{1}{\pi(r_{\text{mean}}^2 + 2r_{\text{mean}}R)} \times \left[ \left( \arctan \left( \frac{R}{\sqrt{1 - R^2/r_i^2}} r_{\text{mean}} \right) \right) r_{\text{mean}}^2 + R \left( \sqrt{1 - R^2/r_i^2} r_{\text{mean}} \right) \right]_{r_i}^{r_i} \tag{7.21}
\]

Here \( P \) is the fraction of molecules adsorbed on the active support surface and reaching the catalyst particle. Since the adsorption flux is uniform this allows us to calculate the ratio between the flux from the gas phase directly to the platinum, \( J_{\text{gas}} \), and the flux from the active support area, \( J_{\text{support}} \), to the catalyst particle. The ratio between the fluxes is proportional to the active support area and the catalyst particle area and is given as:

\[
\frac{J_{\text{support}}}{J_{\text{gas}}} = \frac{A_{\text{support}} P}{A_{\text{catalyst}}} = \frac{\pi(r_{\text{mean}}^2 + 2r_{\text{mean}}R)P}{2\pi R^2} = \frac{(r_{\text{mean}}^2 + 2r_{\text{mean}}R)P}{2R^2} \tag{7.22}
\]

The results of Equation 7.21 and Equation 7.22 are given in Figures 7.11(a) and 7.11(b) with \( R \) equal 1 nm and a mean displacement up to 8 nm. In Figure
Figure 7.11: (a); The fraction $P$ from Equation 7.21 and $A_{support}$ as functions of the mean displacement plus $R$. (b); Ratio between the reactant flux from the active surface area and from the gas phase to the catalytic particle.
7.11(b) the ratio between $J_{\text{support}}$ and $J_{\text{gas}}$ is plotted. From Figure 7.11(b) and the values from Figure 7.9(b) we can find the contribution from the graphite support at 1 bar at different temperatures.

The results from the EMD simulation were used to estimate the amount of reactant that can be transported to a catalyst particle in a PEMFC. Figure 7.11(b) gives the ratio of the reactant transported via the active support area, $J_{\text{support}}$, and the reactant adsorbed from the gas phase, $J_{\text{gas}}$, plotted as a function of the mean displacement. We saw in the previous section that $D_{\text{n}}^s$ from EMD is 4-10 times larger than $D_{\text{n}}^s$ from QENS measurements at 350 K. We use $D_{\text{n}}^s = 1.4 \times 10^{-7}$ m$^2$/s as estimated from the QENS experiment at the highest hydrogen loading as the most realistic value, and calculate a ratio $J_{\text{support}}/J_{\text{gas}}$ close to 1. The transport of reactants to the catalyst via the active surface area according to this is 50% of the total amount.

In the actual PEMFC, the platinum metal catalyst is in contact with the graphite support and the polymer membrane. Only a small fraction of the catalyst may have an interface common with the gas phase. Hydrogen molecules in the gas phase might well have direct access to only a few of the active sites on the platinum catalyst. To reach the active sites, hydrogen must adsorb on platinum, graphite, or polymer membrane and then move to the site by diffusion. Hydrogen molecules on graphite surfaces must pass some three phase contact line before they arrive at the active sites. Gas molecules cannot go directly to a three phase contact line from the gas phase as this would lead to an infinite velocity of the gas close to the three phase contact line [47]. If the surface area of platinum in contact with the gas phase is only a fraction of the active surface area of the graphite, the ratio $J_{\text{support}}/J_{\text{gas}}$ can be much larger than estimated here. The catalytic reaction is also depending on protons reaching the polymer membrane. Only then will the hydrogen be transported away from the catalyst, allowing for further reaction. The diffusivity of hydrogen on platinum is in the order of $10^{-9} \text{ m}^2$/s [119], 3 orders of magnitude smaller than on graphite. The interface between catalyst and the polymer membrane should therefore be as close to the graphite surface as possible in order to increase the reaction rate.

7.5 Conclusion

From QENS and EMD surface self diffusion coefficients for hydrogen adsorbed on graphite have been found. The two methods give values in good agreement for low temperatures but at high temperatures EMD give $D_{\text{n}}^s$ values that are 4 to 10 times larger. Both the QENS data and the EMD data show that the
$D_{ii}^s$ is dependent on the surface concentration. At high surface concentrations
$D_{ii}^s$ follows a linear trend according to kinetic theory. At low surface densities
the $D_{ii}^s$ reach a maximum value at each temperature. From the simulations the
average time between adsorption and desorption events were calculated. They
followed an exponential trend, increasing with temperature. From the average
time and surface diffusion from EMD and QENS the mean displacement was
calculated. At 1 bar the mean displacement had a maximum value at 110 K
of about 140 Å. For ambient temperature and pressure the value was of about
80 Å. These results have been used to estimate the transport of reactants via
the catalyst support material in the PEMFC to a catalyst particle. From these
estimates the catalyst support is responsible for transporting 50% of the reac-
tants at a minimum. This suggests that the catalyst support is contributing
considerably to the reactant transport in the PEMFC.

7.6 Acknowledgements

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is much appreciated.
Concluding remarks

In this work we have investigated the dynamics and thermodynamics of hydrogen adsorption and transport on graphite. The main purpose was to investigate how graphite catalyst support material contributes to the reactant transport in PEM fuel cells. Quasi-elastic neutron scattering (QENS) and equilibrium molecular dynamics (EMD) simulations were used to obtain information on the hydrogen transport along graphite surfaces.

Two different QENS experiments were performed to measure the surface self diffusion coefficient $D_{ii}^s$ of hydrogen on XC-72, a catalyst support material used in PEM fuel cells. In the two experiments hydrogen loadings equal to one monolayer and half a monolayer at 2 K was used to investigate the effect of surface concentration on $D_{ii}^s$. By analysing the QENS data with the Chudley and Elliot jump diffusion model the $D_{ii}^s$ was found in the 40 to 90 K range. From the Arrhenius plots in Chapter 5 and 7 the temperature dependence was found and the preexponent increased with decreasing surface concentration. At 350 K the temperature dependence gave $D_{ii}^s$ in the range $1.4$ and $2.3 \times 10^{-7}$ m$^2$/s depending on the initial hydrogen loading. The trends in the Arrhenius plots are in agreement with previous QENS studies of hydrogen adsorbed on single wall nanotubes and oriented graphite.

We performed EMD simulations of a closed system made of hydrogen in contact with a graphite sheet. The simulations were performed at 70 to 370 K in 20 K intervals with 50, 100, 150, 200 and 300 hydrogen molecules present. This data gave the adsorption isotherms, adsorption enthalpy and entropy as function of surface concentration, adsorption and desorption unidirectional fluxes as function of temperature and surface concentration. From the EMD results at 70 K the amount of hydrogen adsorbed on the graphite surface was within experimental values obtained on graphite. The simulated isotherms agreed with the Langmuir isotherm from 70 to 170 K and with the Henry isotherm
from 190 to 370 K. The adsorption enthalpy and entropy varied with surface concentration which indicates that there is interaction between the adsorbed hydrogen molecules. From the isotherms and rate kinetics we calculated the adsorption enthalpy to -6 kJ/mol. From the unidirectional fluxes we found that Langmuir kinetics did not describe the system and we have proposed an alternative kinetic model that agrees with the Langmuir isotherm. The kinetic model gave equilibrium constants of adsorption that agrees with the equilibrium constant of adsorption found from the isotherms.

The data from the EMD simulations were used to calculate the $D_n^s$ of hydrogen on graphite from 70 to 350 K in 20 K intervals with 50, 100, 150, 200 and 300 hydrogen molecules present. In addition, simulations with 10 hydrogen molecules in the system was performed at 70, 90, 110, 150, 170, 190, and 230 K to investigate the surface dynamics at low density at low temperature. In Chapter 7, Figure 7.7(a), the $D_n^s$ at 70, 90, 110, 150, 170, 190, 230, and 350 K are plotted versus $c_{H_2}^{-1}$. This plot shows that the $D_n^s$ depends on the surface concentration at high concentrations but that this dependence decrease as the surface concentration decrease. Comparing the calculated $D_n^s$ values at 350 K from QENS with the value from EMD, the EMD values are 4 to 10 times larger.

Using the data from the EMD simulation we gave an estimate of the contribution of the catalyst support on the transport of hydrogen to a catalyst particle. We investigated an ideal system where the Pt catalyst was considered as a hemisphere and in direct contact with the gas phase. The EMD data at 350 K shows that 8 times as much hydrogen is transported to the catalyst particle via the catalyst support as compared to adsorption directly from the gas phase. When we consider the QENS data the contribution is reduced to equal amounts from the catalyst support and from the gas phase. This means that the transport of reactants to the catalyst via the catalyst support is still 50% of the total amount. Furthermore, in the PEM fuel cell the platinum metal catalyst is in contact with the graphite support and the polymer membrane, and only a small fraction of the catalyst has an interface with the gas phase. Hence the hydrogen molecules in the gas phase only have direct access to a small part of the active sites on the platinum catalyst. To reach most of the active sites the hydrogen must first adsorb on the platinum, graphite, or polymer membrane and then move to the rest of the platinum surface by diffusion. Before they arrive at the active sites the hydrogen molecules must pass some three phase contact lines. Gas molecules cannot go directly to a contact line from the gas phase as this would lead to an infinite velocity of the gas close to
the contact line [47]. Since the surface area of the platinum in contact with the
gas phase is only a fraction of the active surface area of the graphite, the ratio
between hydrogen transported via the catalyst surface and hydrogen adsorbing
directly from the gas phase, can be larger still than estimated in this work.
Furthermore, the electrochemical reaction depends on hydrogen reaching the
polymer membrane. Only then will hydrogen be transported away from the
catalyst, allowing for further reaction. As the diffusivity of hydrogen on plat-
inum is in the order of $10^{-9} \text{ m}^2/\text{s}$ [119], 3 orders of magnitude smaller than on
graphite, the interface between catalyst and the polymer membrane should be
as close to the graphite support as possible to increase the reaction rate.

Today it is possible to perform even better studies of hydrogen dynamics at
IN5, ILL, due to recent improvements of the instrument. Also with a setup
that allows for variation in the hydrogen loading at constant temperature it
would be possible to investigate further the surface concentration dependence
of $D_\theta^*$. One argument to study the anode was that with QENS we had a good
experimental method to support the EMD results. To further increase the
understanding of the transport of reactants in the PEM fuel cell, EMD simula-
tions of oxygen should be preformed. The cathode is the rate limiting part in
the PEM fuel cell so increasing the reaction rate there is of importance. Better
knowledge of the transport mechanism in the cathode could help designing
better PEM fuel cells. Reasoning from Chapter 7, Figure 7.9(a), we may have
more surprises in store.
Bibliography


