

# University of Wollongong - Research Online

## Thesis Collection

Title: Mathematical modelling of gas separation and storage using advanced materials

Author: Aaron William Thornton

Year: 2009

Repository DOI:

### Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

**Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.**

Research Online is the open access repository for the University of Wollongong. For further information contact the UOW Library: [research-pubs@uow.edu.au](mailto:research-pubs@uow.edu.au)

2009

## Mathematical modelling of gas separation and storage using advanced materials

Aaron William Thornton  
*University of Wollongong*

Follow this and additional works at: <https://ro.uow.edu.au/theses>

### University of Wollongong

#### Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

### Recommended Citation

Thornton, Aaron William, Mathematical modelling of gas separation and storage using advanced materials, Doctor of Philosophy thesis, School of Mathematics and Applied Statistics, University of Wollongong, 2009. <https://ro.uow.edu.au/theses/3102>

## **NOTE**

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

## **UNIVERSITY OF WOLLONGONG**

### **COPYRIGHT WARNING**

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

# Mathematical modelling of gas separation and storage using advanced materials

*A thesis submitted in fulfilment of the  
requirements for the award of the degree of*

Doctor of Philosophy

*from*

University of Wollongong

by

Aaron William Thornton, B Math (Hons)

Nanomechanics Group, School of Mathematics and Applied Statistics,  
University of Wollongong

2009



## **CERTIFICATION**

I, Aaron W. Thornton, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematics and Applied Statistics, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Aaron W. Thornton

28<sup>th</sup> August, 2009



# Acknowledgements

The completion of this thesis would not have been possible without the ceaseless support of my supervisors, family, friends, and colleagues. To my primary supervisor Jim Hill, I extend my gratitude and respect for his total commitment in supporting me during this endeavour. His energetic personality and mathematical mind has provided me with the inspiration and encouragement to complete this thesis. I would also like to thank my secondary supervisor Anita Hill, for her tireless support, encouragement and contagious passion to solve these problems. Her superhuman energy, numerous contacts and insightful logic have been crucial factors in making this work possible. Special thanks also go to Kate Nairn for her patience, guidance and contributions.

I am extremely grateful for my wife and her unswerving faith, love and hope which has carried me throughout this time. I would also like to thank my parents and parents-in-law for their ongoing love and support for which I am in their debt. I also thank my colleagues and friends Matt, Barry, Tamsyn, Ivy, Brandon, Allan, Justin and Joe for their assistance and support.

Finally, I would like to acknowledge the interaction that I had with the Freeman group, Wessling group, Sarti group and MTR where I met many helpful researchers who provided me with feedback, friendship and facilities.



# Abstract

Clean, sustainable and cost-efficient fuel alternatives are expected to replace conventional fossil fuel combustion systems as environmental and economic pressures rise. Alternative fuel candidates include synthetic gas, purified natural gas and hydrogen gas. The realization of an alternative fuel-based economy hinges on the efficient separation and storage of gases, for applications such as pollutant capture, synthetic fuel production, fuel purification and fuel storage. Membranes and adsorbents are materials characterized by an internal network of angstrom and nano-sized pores which are designed to separate and store gases, respectively. This thesis is concerned with the development of simple mathematical models to explain and predict gas transport and adsorption properties within advanced materials. Such models will guide the tailoring of porosity to optimize the desired properties. This thesis makes contributions to the following three areas:

- **Gas separation** Firstly, a new model that determines the transport properties of a gas within individual pores is presented. The model considers the interactions of the gas with the surface of the pore to characterize the various transport regimes within pores of different size, shape and composition. This is an entirely new approach to understanding and interpreting the various diffusion regimes known to occur within gas separation membranes. The new model can be used to determine the optimal pore characteristics that maximize the separation of gas mixtures. Secondly, a new empirical relationship between gas diffusion and the membrane free volume is introduced which is found to accurately describe known diffusion behaviour for a range of polymer membranes. This leads to a new method for determining the amount of free volume necessary to achieve a desired gas diffusion rate.

- **Gas storage** Based upon fundamental thermodynamic principles, a new model for gas storage within adsorbents is presented. The model incorporates the interactions between the gas and the internal surface area of the adsorbent, and proves to be an accurate and fast method for predicting storage performance within adsorbents of varying porosities. This novel approach can be used to determine the pore characteristics necessary to store the maximum amount of gas under the required operating conditions.
- **Physical aging** A new physical aging model based on the mechanism of vacancy diffusion is derived that accurately matches existing aging data. Using this model and the existing theory the mechanisms of physical aging are examined, particularly for thin polymer films. Specifically, the new approach provides new insights into the physical aging mechanisms responsible for polymer densification and can be used as a tool to predict the polymer's performance over time.

Finally, the new mathematical models that are presented here provide considerable insight into complex physical processes, and will serve to accelerate the development of alternative energy technologies by providing simple guidelines for material design.

# Contents

<b>I</b>	<b>Introduction</b>	<b>1</b>
<b>1</b>	<b>Overview</b>	<b>2</b>
1.1	Aim of thesis .....	2
1.1.1	Gas separation .....	3
1.1.2	Gas storage .....	5
1.1.3	Physical aging in polymers .....	7
1.2	Thesis structure .....	8
<b>II</b>	<b>Gas separation</b>	<b>11</b>
<b>2</b>	<b>Introduction to gas separation</b>	<b>12</b>
2.1	Previous work .....	12
2.1.1	Fundamental theory .....	12
2.1.2	Transport (diffusion) mechanisms .....	14
2.1.2.1	Activation diffusion .....	15
2.1.2.2	Surface diffusion .....	15
2.1.2.3	Knudsen diffusion .....	17
2.1.3	Membranes: Porous structures .....	17
2.1.4	Transition State Theory (TST) .....	19
2.1.5	Transport models for ordered pore networks .....	21
2.1.5.1	Parallel transport model .....	21
2.1.5.2	Resistance in series transport model .....	21
2.1.6	Modelling approaches .....	22
2.1.6.1	Gas-pore interactions .....	22
2.1.6.2	Free volume theory within polymers .....	26
2.2	Thesis work overview .....	31

2.2.1	Nano-scale: Individual pore transport .....	31
2.2.2	Macro-scale: Bulk free volume transport .....	32
3	Gas transport regime within pores .....	41
3.1	Introduction .....	41
3.2	Mathematical formulation of gas-pore interactions .....	41
3.3	Transport mechanisms .....	49
3.3.1	Size-sieving activation diffusion .....	50
3.3.2	Surface diffusion .....	51
3.3.3	Suction diffusion .....	52
3.3.4	Knudsen diffusion .....	53
3.4	Enhanced separation by tailoring pore size .....	53
3.5	Determining diffusion regime from experimental flux .....	57
3.6	Comparison with experimental results .....	58
3.7	Predictions of the model .....	59
3.8	Conclusion .....	64
4	Free volume and gas transport .....	69
4.1	Introduction .....	69
4.2	Free volume, permeability, diffusivity and solubility .....	70
4.2.1	Transport properties vs fractional free volume ...	70
4.2.1.1	New classes of polymers .....	77
4.2.2	Permeability vs gas-specific free volume .....	79
4.2.3	Diffusivity vs simulated accessible volume .....	80
4.3	Physical interpretation of new relation .....	81
4.4	Parameter values related to gas diameter .....	82
4.5	Conclusion .....	83
III	Gas storage .....	89
5	Introduction to gas storage .....	90
5.1	Previous work .....	90
5.1.1	Storage methods .....	90

5.1.2	Physisorption .....	92
5.1.3	Modelling approaches .....	97
5.1.3.1	Geometry-based calculations .....	97
5.1.3.2	Molecular simulations .....	99
5.1.3.3	Ab-initio calculations .....	101
5.2	Thesis work overview .....	102
<b>6</b>	<b>Gas adsorption model</b>	<b>110</b>
6.1	Introduction .....	110
6.2	Gas adsorption model .....	110
6.3	Comparison with experimental results .....	116
6.4	Predictions of the model .....	121
6.5	Conclusion .....	127
<b>7</b>	<b>Impregnated metal-organic frameworks</b>	<b>131</b>
7.1	Introduction .....	131
7.2	Method .....	132
7.3	Comparison with experimental and simulation data .....	138
7.4	Model prediction of impregnated MOF structures .....	140
7.5	Conclusion .....	148
<b>8</b>	<b>Nanotubes</b>	<b>153</b>
8.1	Introduction .....	153
8.1.1	Hydrogen storage requirements .....	153
8.1.2	Storage methods .....	153
8.1.3	Nanotubes: Properties and synthesis .....	154
8.2	Method .....	155
8.3	Model prediction of nanotubes .....	161
8.4	Conclusion .....	165

<b>IV</b>	<b>Physical aging of polymer membranes</b>	<b>171</b>
<b>9</b>	<b>Introduction to physical aging</b>	<b>172</b>
9.1	Previous work .....	172
9.1.1	Kovacs model .....	174
9.1.2	Struik model .....	174
9.1.3	Constitutive kinetic equation .....	176
9.1.4	Kovacs, Aklonis, Hutchinson and Ramos model	177
9.1.5	Dorkenoo and Pfromm model .....	179
9.1.6	Zhou, Chung, Wang and Goh model .....	181
9.1.7	Curro, Lagasse and Simha (CLS) model .....	182
9.1.8	McCaig, Paul and Barlow (MPB) model .....	184
9.2	Thesis work overview .....	186
<b>10</b>	<b>Vacancy diffusion model</b>	<b>192</b>
10.1	Introduction .....	192
10.2	New empirically-derived vacancy diffusion model .....	193
10.3	Comparison with results in the literature .....	195
10.3.1	Comparison with MPB .....	195
10.3.2	Comparison with CLS .....	196
10.3.3	Comparison with constitutive kinetic equation	198
10.4	Model applied to thin film aging .....	199
10.5	Model predictions of transport in aging polymer .....	201
10.6	Conclusion .....	205
<b>V</b>	<b>Conclusion</b>	<b>209</b>
<b>11</b>	<b>Concluding remarks and future directions</b>	<b>210</b>
11.1	Summary .....	210
11.1.1	Gas separation .....	210
11.1.2	Gas storage .....	211
11.1.3	Physical aging in polymers .....	212
11.2	Final comments .....	212

11.3 Future directions .....	212
------------------------------	-----

## Appendix

### List of author's publications

# List of Figures

1.1: Schematic of membrane-based gas separation .....	4
1.2: Schematic of gas storage within adsorbents .....	6
1.3: Schematic of physical aging in polymers .....	7
2.1: Gas separation membrane with constant concentration gradient .....	13
2.2: Dominant transport mechanism within pore size ranges .....	14
2.3: Porous structure within various types of membranes .....	18
2.4: Computer simulations for free volume clusters within glass and rubber .....	19
2.5: Transition state theory representations .....	20
2.6: Schematic models for parallel transport and resistance in series transport .....	22
2.7: Potential energy $\varepsilon_{\text{=}}(z)$ between two parallel planes and two parallel slabs .....	24
2.8: Potential energy minimum $\varepsilon^*$ within cylindrical and slit-shaped pores .....	24
2.9: Separation regimes determined within pores of different sizes .....	25
2.10: Schematic model of the total flux components through membranes .....	26
2.11: O <sub>2</sub> permeability for glassy PS, PC, PA, PE and LCP .....	28
2.12: Carbon dioxide permeability versus inverse <i>FFV</i> and modified <i>FFV</i> .....	30
3.1: Geometry of molecule entering a cylindrical and slit-shaped pore channel .....	45
3.2: Force profile about the entrance of a cylindrical pore .....	46
3.3: Molecule entering smaller pore from larger pore .....	48
3.4: Suction energy ( <i>W</i> ) of a single oxygen molecule at the entrance of a tube .....	50
3.5: Suction energies for light gases at the entrance of a carbon tube .....	54
3.6: Model prediction of permeability <i>P</i> as a function of pore size .....	60
3.7: Model prediction of permeability <i>P</i> as a function of temperature .....	62
3.8: Model prediction of CO <sub>2</sub> /CH <sub>4</sub> selectivity vs CO <sub>2</sub> permeability for pore size .....	63
3.9: Model prediction of CO <sub>2</sub> /CH <sub>4</sub> selectivity vs CO <sub>2</sub> permeability for temperature ...	64



4.1: Permeability of light gases vs inverse fractional free volume $FFV$ .....	73
4.2: Diffusivity of light gases vs inverse fractional free volume $FFV$ .....	75
4.3: Solubility of light gases vs inverse fractional free volume $FFV$ .....	76
4.4: Permeability of oxygen vs inverse modified fractional free volume $FFV_{O_2}$ .....	77
4.5: Schematic of different diffusion processes within polymers .....	79
4.6: Diffusivity of oxygen vs inverse accessible volume fraction $AVF$ .....	81
4.7: The dependence of $\beta$ values found from fits to permeability and diffusivity .....	83
5.1: Gas storage methods .....	91
5.2: Storage methods for hydrogen .....	92
5.3: Lennard-Jones potential energy between atom and infinite flat surface .....	93
5.4: Surface area of graphite elements .....	96
5.5: Density profiles for gas molecules upon the surface of a MOF .....	97
5.6: Stacking arrangements of spheres upon a graphite surface .....	98
5.7: Stacking arrangements of spheres within tubes of different diameters .....	98
5.8: Molecular simulations of hydrogen adsorption .....	100
5.9: Ab-initio calculations for the binding energy of hydrogen to fullerenes .....	102
5.10: Ab-initio calculations for the binding energy of hydrogen to nanotubes .....	102
6.1: Potential energy for adsorption, total volume and free volume within cavities ...	114
6.2: Schematic of the new adsorption model, TIMTAM .....	115
6.3: TIMTAM fit to simulation results for hydrogen uptake with pore size .....	117
6.4: TIMTAM fit to simulation results for hydrogen uptake with pressure .....	119
6.5: TIMTAM fit to experimental methane uptake within activated carbon .....	119
6.6: TIMTAM fit of hydrogen uptake to exp. and sim. results for IRMOF-1 .....	120
6.7: TIMTAM results for $H_2$ uptake in carbon slits, tubes and spheres with pressure	122
6.8: TIMTAM results for gravimetric $H_2$ uptake in carbon slits, tubes and spheres ...	124
6.9: TIMTAM results for volumetric $H_2$ uptake in carbon slits, tubes and spheres ....	126
7.1: Schematic representation for $Mg-C_{60}$ @ MOF .....	132
7.2: Comparison of $H_2$ uptake in sphere with centered $C_{60}$ , offset $C_{60}$ and empty .....	135
7.3: Potential energy for adsorption within $Mg-C_{60}$ @ MOF .....	137
7.4: TIMTAM fit to experimental results for $H_2$ uptake in IRMOF-1 .....	138
7.5: TIMTAM fit to experimental results for $H_2$ uptake in IRMOF-1, -8, -10 & -16	139
7.6: Profile of potential energy for adsorption within MOFs .....	142

7.7: Fractional free volume for adsorption of hydrogen and methane .....	143
7.8: Heat of adsorption within IRMOF-8 for hydrogen and methane .....	144
7.9: Modeling of total hydrogen uptake within IRMOF-8 and IRMOF-10 .....	146
7.10: Modeling of total methane uptake within IRMOF-8 and IRMOF-10 .....	147
7.11: Predicted methane uptake performance for impregnated MOFs .....	148
8.1: Potential energy for adsorption within carbon nanotubes .....	156
8.2: Contour potential energy for adsorption within carbon nanotubes .....	157
8.3: Fractional volume for adsorption within a carbon nanotube .....	158
8.4: Predictions of H <sub>2</sub> uptake isotherms in a carbon nanotube .....	161
8.5: Predictions of H <sub>2</sub> uptake in nanotubes with diameters 10, 15, and 20 Å .....	163
8.6: Predictions of H <sub>2</sub> uptake in nanotubes with mass 10, 20, and 30 g/mol .....	163
8.7: Predictions of H <sub>2</sub> uptake in nanotubes in DoE operating conditions .....	164
9.1: Diagrams of the physical aging process after a quench .....	173
9.2: The Struik model fitted to various aging data .....	175
9.3: Relationships between the parameters of Struik model and properties .....	176
9.4: Schematic example of each relaxation unit's contribution over time .....	178
9.5: KAHR model predictions of the relaxation process after quench .....	178
9.6: Schematic of the thickness-dependent glass transition temperature .....	180
9.7: The KAHR model fit to experimental N <sub>2</sub> permeability results .....	181
9.8: The ZWCG model fit to experimental O <sub>2</sub> permeability results .....	182
9.9: Schematic of the fractional free volume relaxation towards equilibrium .....	183
9.10: The CLS vacancy diffusion model and the KAHR model results .....	184
9.11: MPB dual vacancy diffusion and lattice contraction model .....	185
9.12: MPB dual mechanism model fitted to experimental O <sub>2</sub> permeability .....	186
10.1: Experimental oxygen permeability data for BPA-BnzDCA .....	195
10.2: Free volume predicted by the KAHR, CLS and the new EVD model .....	197
10.3: Experimental oxygen permeability of PSF films as a function of time .....	200
10.4: Fractional free volume profile predictions within a polymer sample at times $t$ ..	204
10.5: Gas uptake profile predictions within a polymer sample at times $t$ .....	204
10.6: Gas release profile predictions within a polymer sample at times $t$ .....	205
11.1: Membranes with identical pore size distributions but different arrangements ...	213

# List of Tables

Table 3.1: Lennard-Jones constants, molecular mass and average velocity .....	49
Table 3.2: Model results for $d_{min}$ , $d_{opt}$ , $W_{max}$ , $v_{max}$ and $d_K$ .....	55
Table 4.1: Gas permeability, diffusivity and solubility for high free volume polymers	71
Table 4.2: Best fit parameter values found from fits to experimental permeability .....	73
Table 4.3: Best fit parameter values found from fits to experimental diffusivity .....	75
Table 4.4: Comparison of CO <sub>2</sub> solubility, diffusivity and permeability enhancement	78
Table 6.1: Parameter values used to reproduce the data .....	120
Table 7.1: Lennard-Jones parameter values for framework atoms .....	134
Table 7.2: Cavity atomic surface density .....	134
Table 7.3: Fullerene properties .....	134
Table 7.4: Adsorbent molecular mass per cavity and adsorbate molecular mass .....	135
Table 7.5: Parameter values for $\alpha$ and $r_1$ found from fits to data .....	140
Table 8.1: Parameter values used in this chapter .....	158