Non-Equilibrium Thermodynamics in Porous Media: Battery Degradation, and Sorption and Transport in Porous Materials

by

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PhB, The Australian National University (2008)

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Abstract

Porous media offer many interesting problems in physics and engineering due to the interaction of phase transitions, surface effects and transport. In this thesis I examine two such problems: the degradation of lithium-ion batteries, and sorption and transport of fluids in porous materials.

The dominant capacity fade mechanism in many lithium-ion batteries is the loss of cyclable lithium to a solid-electrolyte interphase layer on the surface of the negative electrode. I develop a single-particle model of this fade mechanism, based on diffusion of the reacting species through the growing layer and reaction at the surface of the active material. This analytical model is justified by comparison with a computational porous electrode model. Temperature is identified as the most important variable influencing the capacity fade rate, and the model is able to make predictions for accelerated aging tests as well as the effect of mismatched internal resistances in battery packs.

The quantity of a fluid taken up by a porous material as a function of the partial pressure of the fluid relative to saturation can be used to measure the pore size distribution of the material. However, hysteresis between the wetting and drying paths complicates the interpretation of experimental results. I present a unified model of hysteresis that accounts for both single-pore and network effects, enabling the calculation of not only the pore size distribution but also a parameter measuring the connectivity between large and small pores. I then use the ideas of the model to examine drying shrinkage in hardened cement paste, demonstrating that the hysteresis in this shrinkage is primarily due to water inserted between molecular layers in calcium-silicate-hydrate. Finally, I outline a model of transport of a sorbing fluid with hysteresis, and suggest possible extensions to allow quantitative comparison with experimental results.

Thesis Supervisor: Martin Z. Bazant
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Chapter 1

Introduction

This thesis examines the problems of lithium-ion battery degradation, and the sorption and transport of fluids in porous materials. Although these problems may seem rather far removed, they are in fact linked by several important features.

First, in both systems phase transformations are crucial in determining behavior, and these phase transitions are strongly influenced by surfaces and other features of the microstructure of the materials. For example, the potential at which a lithium iron phosphate particle will phase separate into lithium-rich and lithium-poor regions is dependent on its size [41], while the relationship between sorbate partial pressure and pore filling has long been used as a tool to measure the pore size distribution of porous materials [14].

Second, measurements are usually made at the system level. In batteries, measurements generally relate voltage, current and state of charge, while sorption experiments control the sorbate pressure and measure sorbed mass (or equivalent) as a function of time. Information about the microscopic behavior of system constituents is thus indirect, relying on models that relate microscopic and macroscopic properties.

Third, there is an interaction between transport and phase separation processes. In lithium-ion batteries, transport effects can suppress phase separation during fast discharge [7], or mitigate the degradation that results from the formation of unwanted products, as discussed in this thesis. In porous materials, hysteresis in the sorption process can complicate transport modeling, and knowledge of the location of con-
densed fluid may be crucial in accurately determining permeability.

Fourth, both problems are of enormous technological importance. Lithium-ion batteries are widespread in electronic devices, and their prevalence is only expected to increase with further demands such as electric vehicles. Concrete is one example of an extremely heavily used porous material, and its degradation is heavily influenced by sorption and transport processes.

Chapter 2 provides an overview of the modeling of lithium-ion batteries, especially of their degradation. Chapter 3 then presents my model of degradation and its application to accelerated aging testing as well as understanding the degradation of battery packs. Switching to porous solids, chapter 4 outlines accepted models of sorption and transport in these materials. Chapter 5 combines accepted hysteresis mechanisms with a new analytic model of pore blocking in a network, to obtain a method for determining pore size and connectivity from sorption isotherms. Chapter 6 uses such information in the specific case of water in hardened cement paste to explain drying shrinkage and its hysteresis. Chapter 7 presents a model of transport through porous media, presenting some results and discussing future extensions of the model. Finally, chapter 8 discusses the application of the models of this work to systems of technological importance, and how they may be extended and combined with other ideas to provide further insights.
Chapter 2

Degradation of lithium-ion batteries

2.1 Lithium-ion batteries

Lithium-ion batteries comprise two active materials into which lithium can be intercalated, divided by a separator that allows the transmission of lithium ions but not electrons [88, 151]. The materials are generally present in the form of a fine powder, to minimise the impact of the slow transport of lithium through the solid. A conductive powder such as carbon is mixed with the active materials to allow the transport of electrons between the active material and a current collector located in each electrode. When these current collectors are connected by an external circuit, lithium ions can move from one active material to the other, while the associated electrons travel around the circuit. The existence of a free energy difference between lithium atoms located in each active material means that the battery can provide a voltage and sustain a current, while lithium moves from the high to the low free energy material. Alternatively, applying an external voltage across the terminals can drive electrons in the opposite direction, causing the transport of lithium ions from the low to the high free energy material, recharging the battery.

Lithium-ion batteries are widespread in electronic appliances [164], and considerable research is focused on broadening their application, such as to electric vehicles [5] and power grid load leveling [50]. To be competitive in such applications, battery life of thousands of cycles and years to decades is required. The important degradation
The desired electrochemical reaction is the intercalation of lithium, but lithium can also react with components of the electrolyte to form a solid-electrolyte interphase. Therefore, mechanisms of lithium-ion batteries must be understood and mitigated.

### 2.2 Degradation mechanisms

#### 2.2.1 Solid-electrolyte interphase formation

One important degradation mechanism is the loss of lithium to a solid-electrolyte interphase layer (SEI). This layer forms when, instead of intercalating into the negative electrode material, lithium ions react with substances present in the electrolyte, as indicated schematically in figure 2-1. Such substances can include the electrolyte solvent itself, as typical electrolytes are not stable at the charging potential of the negative electrode. This reaction takes place on the surface of the active material, and forms an SEI here [164]. The SEI can include an enormous variety of compounds including lithium carbonate, lithium fluoride, lithium oxide, and many organic compounds [165, 172].

The initial formation of an SEI is beneficial to battery operation, as it protects against solvent decomposition at large negative voltage. However, there are also two ways in which SEI formation can degrade a battery: a loss of capacity as previously active lithium is trapped in the SEI [127], and an increase in impedance due to the
resistance of the SEI to the diffusion of lithium ions [186, 173]. Additionally, the compounds forming the SEI can react exothermically if the temperature becomes too high, potentially leading to hazardous thermal runaway [189].

Many researchers have studied the role of the SEI in battery degradation, and the factors that influence its formation. Ozawa found a gradual decline in capacity and increase in impedance due to SEI formation, and identified lithium, carbon, oxygen and fluorine as the main constituents of the SEI [120]. Peterson et al. observed slow degradation of batteries containing graphite electrodes under simulated driving conditions (95% capacity remaining after 2000 days), with capacity loss proportional to the number of intercalation and deintercalation events [131]. Zhang et al. studied degradation as a function of temperature, finding that the increase in impedance due to SEI formation was far more important at low temperature than at high temperature [188].

2.2.2 Other degradation mechanisms

SEI formation is not the only mechanism by which lithium-ion batteries can degrade. Degradation due to damage to the crystal structure of the active material has been found in cells using lithium manganese oxide [181] and lithium nickel cobalt oxide [162] as the positive electrode active material. Komaba et al. studied the dissolution of manganese from LiMn$_2$O$_4$, used as a positive electrode. They found that a small quantity of dissolved manganese was sufficient to severely decrease the capacity of the battery, as it formed a film on the surface of the negative electrode, preventing intercalation [82]. Amine et al. showed that this dissolution could be prevented by using an electrolyte that does not contain fluorine [2]. Shim, Striebel and Cairns observed capacity fade due to the dissolution of lithium polysulfides [154]. Mikhaylik and Akridge studied this mechanism further, showing that increasing salt concentration in the electrolyte lowers the rate of lithium dissolution [109]. Shim, Kostecki et al. observed the build-up of an organic layer on the positive electrode, with much higher resistance than the SEI generally found on the negative electrode [153]. Kostecki et al. examined a similar system and found that the surface resistance of active material
particles in the positive electrode increased over time [84].

Despite this variety of degradation mechanisms, SEI formation is generally considered to dominate capacity fade in lithium-ion batteries suitable for commercial use [173], and thus I focus on this mechanism in this thesis. The model presented here will not be applicable when other sources of fade dominate.

2.2.3 Degradation of silicon anodes

Most studies of lithium-ion battery degradation, including those cited in subsection 2.2.1, have focused on batteries with a graphite negative electrode, as graphite is found in almost all commercial lithium-ion batteries. A promising electrode material for future application is silicon. Silicon has a much higher capacity for lithium intercalation than graphite does [27], but it experiences large expansion on intercalation, and this large volume change can lead to degradation [115]. Cracking and pulverization can lead to the loss of electrical contact and hence capacity loss [3], though this can be minimized by using small silicon particles as the active material [21, 177, 81, 37, 45]. An SEI also forms on silicon: it is very similar to that on graphite but shows cracks due to the volume change of the underlying silicon [38].

2.3 Degradation modeling

The most common approach to the modeling of lithium-ion battery degradation has been based on fits of data to empirical models, not a theory of degradation mechanisms. For example, Rong and Pedram developed a single-cycle model of battery behavior that was built on physical processes, but described degradation empirically, using a very large number of parameters [146]. He et al. described capacity fade by a sum of exponentials, and used measured capacity over early cycles to predict the continuing capacity fade [76].

A model will be more useful, especially in the prediction of fade for a system different from that used to determine model parameters, if it is based on the real physical processes that lead to degradation. Various authors have modeled different
degradation processes, such as crack propagation, modeled using an equivalent circuit model [110], but we focus here on models of fade due to SEI formation.

Two approaches to modelling capacity fade due to SEI formation have been put forward. The first uses a porous electrode model, developed to model the single-cycle behavior of a cell or electrode, and adds a side reaction forming SEI. This enables spatial differences in SEI formation to be examined, but previous examples of such models developed by Ramadass et al. [139] and Sikha et al. [157] included the dependence of the SEI formation rate on local potential, but not on lithium ion concentration or the thickness of the existing SEI. Neglect of the latter in particular means that the predicted capacity fade is linear in time, which contradicts experimental observations of a decreasing fade rate [159]. The second approach has been to assume that the reaction forming SEI is indeed hindered by the existing layer as it grows, but to ignore any possible spatial variation in SEI formation through the electrode, and the reaction limitation of SEI formation when the existing layer is very thin [135].

In chapter 3, I present a porous electrode model that combines features of both approaches. The model accounts for gradients in lithium ion concentration as well as potential, and also the effect of the growing layer. This model shows that gradients in SEI formation are unimportant, so a single particle model may be used. The single particle model I present is a reaction-diffusion model, an important step forward from a previous diffusion model that assumed very fast reactions [135].
Chapter 3

Modeling of solid-electrolyte interphase formation

The content of this chapter is based heavily on the published articles “Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction” by the author and Bazant [132], and “Internal Resistance Matching for Parallel-Connected Lithium-Ion Cells and Impacts on Battery Pack Cycle Life” by Gogoana, the author et al. [67]. Material from these articles is copyright 2013, The Electrochemical Society and copyright 2014, Elsevier, respectively and reproduced with permission.

3.1 Advantages of a physical model

One way of assessing capacity fade is purely experimental: operate a battery in the expected use conditions, and measure its capacity over time. An important disadvantage of this method is that it is necessarily very time-consuming, especially for a good, long-lived battery. To overcome this difficulty, experiments are frequently performed at high temperature, where the rate of capacity fade is increased [168]. To interpret such experiments, and make predictions that are valid at use temperatures, it is necessary to have a model of degradation that is based on the physical processes that lead to capacity fade.
In this chapter, I present a theory of SEI growth and capacity fade. In section 3.2, I use a porous electrode model to quantify capacity fade due to SEI formation, focusing especially on any spatial variations through the electrode. Since spatial variations are insignificant, I present in section 3.3 a simple, single particle model. This model improves upon previous models that simply assert a $\sqrt{t}$ dependence of capacity fade due to the increasing thickness of the SEI layer [135, 160], as it takes into account the rate of the reaction forming SEI. In section 3.4, I examine the effect of temperature, treating the two situations of accelerated aging tests and mismatched cell resistances in battery packs. In section 3.5, I use the theory to predict battery lifetime statistics. In section 3.6, I discuss extensions to account for additional degradation mechanisms that accelerate capacity fade, such as area changes and SEI delamination resulting from volume expansion of the active particles.

### 3.2 A porous electrode model

This work models capacity fade by considering only the loss of lithium to the SEI on the negative electrode, assuming that other sources of capacity fade can be neglected. The SEI is produced by the reaction between lithium ions and various other species at the surface of the active material in one of the electrodes. If SEI formation were sustained throughout battery operation, it would render Li-ion batteries unusable due to the continual loss of lithium. The reason that Li-ion batteries can operate is that the SEI does not conduct electrons, and is almost impenetrable to electrolyte molecules [172]. Once an initial SEI layer has formed, the inability of electrolyte molecules to travel through the SEI to the active material surface, where they could react with lithium ions and electrons, suppresses further SEI growth [135]. Intercalation is suppressed far less, because lithium ions can easily pass through the SEI through the exchange of ions between the solvent, SEI compounds and the lithium intercalated in the active material [172]. Thus the battery is able to experience many charge-discharge cycles with little additional SEI build-up.

The model presented here is a one-dimensional porous electrode model [179, 48,
that accounts for concentration gradients in the primary direction of lithium propagation.

The porous electrode model is based on a diffusion-reaction equation,

\[
\frac{\partial c_i}{\partial t} = -\frac{\partial N_i}{\partial x} - \sum J(i),
\]

which expresses mass balance in a volume-averaged sense. Here \(c_i\) is the concentration of species \(i\) in the electrolyte, \(N_i\) is the flux of species \(i\) and \(\sum J(i)\) is the sum of all interfacial reactions consuming species \(i\). We let \(i\) range over positive and negative ions, assuming that the consumption of electrolyte molecules by reactions forming SEI is slow enough that it does not significantly affect electrolyte concentration. The fluxes \(N_i\) are calculated using the Nernst-Planck equation. The rate of the reaction \(\text{Li}^{+}_{\text{dissolved}} + e^- \rightarrow \text{Li}_{\text{intercalated}}\) is modeled using a symmetric Butler-Volmer equation:

\[
J = 2i_0 \sinh\left(\frac{-e\eta}{2k_BT}\right).
\]

Here \(\eta\) is the overpotential driving the reaction: the potential difference across the surface of the active material, where the reactions take place, minus the equilibrium potential difference, i.e.

\[
\eta = \phi_{\text{electrode}} - \phi_{\text{electrolyte}} - \Delta \phi_{\text{equilibrium}} + JR.
\]

The equilibrium potential for each electrode, relative to lithium, is drawn from figure 5 of Liu et al. [93]: these potentials are approximated by the functions

\[
\Delta \phi_{\text{equilibrium}}^{\text{graphite}} = (0.132c^{-0.425} - 0.0903) \text{ V}
\]
\[
\Delta \phi_{\text{equilibrium}}^{\text{LiFePO}_4} = (-0.0039c + 3.405 - 908.954(c - 0.470)^{11}) \text{ V},
\]

where \(c\) is the concentration of intercalated lithium, divided by the concentration of lithium in LiC\(_6\). The slight dependence of \(\Delta \phi_{\text{equilibrium}}\) on \(c_+\) is ignored. We assume that the concentration \(c\) is uniform throughout a given active material particle, that is,
we neglect transport and phase transformations [75] in the solid. \( R \), in the case of the graphite electrode, is the resistance of the SEI layer, proportional to SEI thickness. The positive electrode is assumed to have no interfacial resistance. The exchange current density \( i_0 \) depends on concentration: we assume that

\[
i_0 = k \sqrt{c_+}
\]

for the intercalation, where \( k \) is a constant: this is the simplest implementation of a symmetric Butler-Volmer equation. The concentration of lithium ions, \( c_+ \), varies through the electrode but is assumed to be constant through the depth of the SEI layer. Capacity fade is modeled through a competing current that leads to SEI formation, with rate

\[
J_{SEI} = 2i_{0SEI} \sinh \left( \frac{-e\eta_{SEI}}{2k_B T} \right):
\]

this models the reaction \( \text{Li}^{+}_{\text{dissolved}} + \text{E} + e^- \rightarrow \text{LiE} \) where \( \text{E} \) is some species from the electrolyte that can react with lithium, and \( \text{LiE} \) is the product, which forms the SEI layer. Overpotential is calculated in the same way as for the intercalation current,

\[
\eta_{SEI} = \phi_{\text{electrode}} - \phi_{\text{electrolyte}} - \Delta \phi_{SEI} + JR.
\]

Here \( \Delta \phi_{SEI} \) is the equilibrium potential for SEI formation, approximately 0.8 V [51, 33, 172]. In this case the reaction requires not only a lithium ion but also an electrolyte molecule, so

\[
i_{0SEI} = k_{SEI} \sqrt{c_+ c_s}.
\]

The electrolyte concentration \( c_s \) should be measured at the bottom of the SEI layer. Assuming that the concentration outside the SEI layer is constant, and also assuming linear diffusion, we can write

\[
c_s = (1 - Zc_{SEI}J_{SEI})c_0,
\]

where \( Z \) is a constant inversely proportional to the diffusivity of electrolyte in SEI,
Figure 3-1: The single particle model (solid line) and porous electrode model (dotted line) both closely fit experimental data (points). Data from Liu et al. [93] with a lithium iron phosphate opposite electrode.

c_{SEI} measures the amount of SEI present at a location in space, given by

\[ \frac{\partial c_{SEI}}{\partial t} = J_{SEI}, \]  

(3.9)

and \( c_0 \) is the concentration of the relevant electrolyte molecule outside the SEI; its value can be absorbed into \( k_{SEI} \).

Using these equations along with standard modeling of transport [48, 161, 47], SEI formation was modeled over many cycles. Figure 3-1 compares experimental [93] capacity fade with the predictions of the single particle and porous electrode models. Using the values of \( \rho, k, k_{SEI} \) and \( Z \) needed to fit these experimental data, capacity fade was simulated over a wide range of discharge rates. The results are plotted as a function of cycle number and of time in figure 3-2. It is clear that time, rather than cycling, is the dominant factor in SEI growth, under this model.
Figure 3-2: Simulated capacity fade depends on time, not on number of cycles.
Figure 3-3: The top graph shows simulated voltage-capacity curves for the 1st, 161st, 366th, 1054th, 1914th and 2628th cycles, assuming that the SEI has infinite lithium ion conductivity. The bottom graph shows the same curves for finite lithium ion conductivity. Voltage is decreased in the latter case, while the capacity fade is not substantially affected.

The best fit to the experimental results of Liu et al. [93] includes zero SEI resistivity. To ensure that this parameter choice, which simplifies computation substantially, does not interfere with the accuracy of the results, simulations were performed with a non-zero resistance. Results are shown in figure 3-3. The SEI resistance lowers the output voltage, but has little effect on capacity fade.

An important feature of the porous electrode model is that it can assess the degree of spatial variation in SEI formation. Results of the model demonstrate that in realistic battery operating conditions, SEI formation is very uniform. Only in ex-
treme charging conditions, where the lithium concentration gradient in the electrolyte is large enough to cause substantial underutilization of the battery, do significant non-uniformities in SEI formation occur. Figure 3-4 compares SEI formation in an electrode of width 50 µm, which is uniform even for fast charging, with that in a 250 µm electrode, where fast charging causes a moderate degree of non-uniformity. This non-uniformity is dependent on strong depletion of the electrolyte during charging. Thus although the variation of SEI through the electrode should be considered when a battery is operated in extreme conditions such as at ultra-high rate or with very thick electrodes, a single particle model ignoring this spatial non-uniformity will be valid in normal circumstances.

3.3 Single particle model

3.3.1 Model formulation

Our single particle model relies on the following assumptions.

Uniformity We assume that the amount of lithium in the SEI can be parameterized by a single variable \( s \), the thickness of the SEI. This thickness is assumed to be independent of location within the negative electrode, meaning that the electrode is homogeneous and is thin enough in the direction of lithium propagation that significant concentration gradients do not form.

Negligible solid deformation All intercalation compounds experience local expansion (and in some cases, also anisotropic contraction [40] due to lattice mismatch) on lithium insertion. If the lattice mismatch is not too large (< 5% strain), as in graphite [49, 15], then the solid expands reversibly with a concomitant, small increase in the internal surface area. The area available for SEI growth is thus fluctuating, but for practical battery electrodes it is reasonable to assume a constant surface area as we do in our initial model. The SEI layer also experiences small enough strain that it is likely to remain uniformly adhered to the surface.

For certain emerging electrode materials, it is well known that solid deformation
Figure 3-4: Computational results show that a thin electrode (top) displays no significant spatial variation in SEI formation, while a thicker electrode (bottom) does display some variation when charged at a high rate. The numbers of cycles were chosen to achieve equal average SEI density.
plays a major role in limiting the performance and cycle life by accelerating the rate of SEI formation. In particular, silicon is a very attractive high-energy-density anode material for Li-ion batteries, but lithium insertion causes isotropic volume expansion by a factor of four [27]. During expansion and contraction of the active particles, the area for SEI growth changes, and the SEI layer is placed under large cyclic stresses that can lead to delamination. We neglect these effects until section 3.6.

**Constant base reaction rate** We assume that, if electrolyte concentration were constant at the reaction surface, the rate of SEI formation would remain constant. At first glance, this assumption may seem shaky because it ignores any dependence of SEI formation rate on the state of charge of the electrode and even on the magnitude and direction of the intercalation current. However, the SEI formation rate should depend on these factors only through its dependence on potential, and open circuit potential is close to constant over a wide range of lithium concentration in graphite [183]. The local potential will not differ too much from the open circuit potential provided the battery is not cycled at an extremely high rate, so the potential at the graphite surface remains rather constant.

**First-order solvent decomposition kinetics** We make the further assumption that the SEI formation rate is proportional to the concentration of the reacting electrolyte species. The most important part of this assumption, particularly in the limit of long times, is the observation that the formation rate must go to zero with reactant concentration. Experimental data (see subsection 3.3.2 for a comparison of this model with experimental results [93, 159]) suggest that the large time limit is reached within a few days.

**Linear solvent diffusion in the SEI** The very slow transport of electrolyte molecules through the SEI is the rate-limiting part of the SEI formation process. We assume that this transport can be modeled as being driven by a concentration gradient between the outer and inner surfaces of the SEI, and that the concentration difference is directly proportional to the thickness of the SEI and the reaction rate consuming electrolyte at the inner surface.

Under these assumptions, the SEI thickness can be described by two equations.
The first,
\[
\frac{ds}{dt} = \frac{Jm}{\rho A},
\]  
relates the rate of increase of SEI thickness to the reaction rate \( J \), the mass \( m \) of SEI formed by a single reaction, the density of SEI \( \rho \) and the graphite surface area \( A \). We arbitrarily choose lithium fluoride [172] as a typical SEI component: its molar mass is 26 g mol\(^{-1}\) and density is 2.6 g cm\(^{-3}\). The reaction rate \( J \) can be described by

\[
J = kA(c - \Delta c),
\]

where

\[
\Delta c = \frac{Js}{AD}
\]

is the concentration difference between the outside and the inside of the SEI, needed to transport electrolyte molecules through with flux \( J/A \). In equation 3.11, \( k \) is a reaction rate constant, a fitting parameter in our model. \( D \) is the diffusivity through the SEI of the species that reacts with lithium to form SEI, while \( c \) is the concentration of this species in the bulk of the electrolyte. Since we do not know exactly which species is dominant in the continuing formation of SEI during cycling, we assume that \( c \) is 1 M, a typical concentration of anions. We have made several arbitrary assumptions in order to present \( D \) and \( k \) in useful units; their values should scale appropriately (e.g. with temperature) but will only be a vague guess at the correct values.

Equations 3.10 and 3.11 can be solved analytically to give the SEI thickness as a function of time:

\[
s = \frac{\sqrt{2cpmk^2Dt + D^2\rho^2} - D\rho}{\rho k}.
\]

In the limit of large \( t \), this becomes

\[
s = \sqrt{\frac{2cmDt}{\rho} - \frac{D}{k}},
\]

which reproduces the \( \sqrt{t} \) dependence of Ploehn et al. [135] and Smith et al. [160].
3.3.2 Comparison with experiment

To assess the ability of this simple model to explain SEI formation, we compare the prediction of equation 3.14 to experimental results, treating $k$ and $D$ as adjustable parameters. For example, we apply the model to the results of Liu et al. [93] Inferring the SEI thickness from the percentage capacity loss (assuming an average particle radius of approximately $5 \mu m$), we find that the approximation of equation 3.14 is valid even after the first charge-discharge cycle. Using this equation we find $D = 2 \times 10^{-17} \text{ cm}^2 \text{s}^{-1}$ at $15 ^\circ \text{C}$ and $D = 3 \times 10^{-16} \text{ cm}^2 \text{s}^{-1}$ at $60 ^\circ \text{C}$: see figure 3-1. In the latter case, capacity loss between 707 and 757 cycles is much larger than is expected under the model. This demonstrates that some other loss mechanism is important in this instance. The most likely mechanism is the delamination of graphite from the current collector: figure 10 of Liu et al. [93].

3.3.3 Multiple reacting species

The above analysis has considered only one species from the electrolyte reacting to form SEI. Experimental work [165] has shown that many reactions can take place to form SEI, involving a wide range of solvent species, anions or impurities. A more complete model would consider multiple reacting species, each with a characteristic $k$ and $D$. However, since experimental results very quickly reach the large time limit, we can model the process effectively simply by assuming that the $D$ implied by experiment is given by $D = \sum_i D_i$ where $i$ references the different species. The capacity fade will be dominated by the species with higher diffusivity through the SEI. This suggests that capacity fade can be reduced by constructing the cell in a way that avoids the presence of substances with high diffusivity in SEI, for instance small molecules.

The presence of multiple reacting species also provides a mechanism by which denser SEI may form at higher temperature. At higher temperature, all diffusivities are higher, and the dominance of the most easily diffusing species will be lower. If the less diffusive species form a denser SEI, as seems likely from experimental observation
of denser SEI towards the bottom of the layer [172], this will result in lower diffusivity for the remainder of the aging process and hence slower continued SEI formation.

### 3.4 Temperature effects

Since the single particle model, whose important parameter is the diffusivity of electrolyte molecules through the SEI, appears to completely explain the loss of capacity due to SEI formation, it is interesting to provide a theoretical model attempting to explain the temperature dependence of this diffusivity. The model of this work applied to the experimental data of Liu et al. [93] shows a clear temperature dependence of diffusivity. To quantify this dependence, we compared the single particle model with the experimental data of Smith et al. [159], which span many days at temperatures from 15 °C to 60 °C. The diffusivities calculated from these data were consistent with an Arrhenius dependence,

$$D = Ae^{-\frac{E}{k_B T}},$$

(3.15)

with activation energy $E = 0.52$ eV. Figure 3-5 shows the prediction of the single particle model, with diffusivities (and reaction rate constants) fit to the Arrhenius description.

#### 3.4.1 Accelerated aging

The observed temperature dependence enables the single particle model to be used to draw quantitative conclusions from accelerated aging experiments, where an increased temperature is used to hasten capacity fade. A simple application is to estimate battery life at room temperature from data taken at elevated temperatures. The most accurate way to do this is to measure the progress of capacity fade at different temperatures, and use the results to calculate $D(T)$. As a test of this procedure, data from only the first 105 days at 30-60 °C in the work of Smith et al. [159] were used to calculate $D(T)$ and $k(T)$, using equation 3.14. Results for these times and temperatures were fit to an Arrhenius equation. The resulting values of $D$ and $k$ at
Figure 3-5: The single particle model accurately describes capacity fade over a range of temperatures, with diffusivity fit using an Arrhenius dependence (shown in the inset). Data from Smith et al. [159] with a lithium opposite electrode.
Figure 3-6: The single particle model enables data from up to 105 days at 30-60 °C to be used to provide a reasonable prediction of capacity fade up to 400 days at 15 °C; assuming a simple $\sqrt{t}$ dependence of capacity fade is less predictive. Data from Smith et al. [159] with a lithium opposite electrode.

15 °C were used to predict capacity fade for 400 days: results are shown in figure 3-6. Though the agreement is not perfect, it is reasonable given that no data at the temperature or time of the predicted region were used in producing the prediction. In particular, simply assuming $s = \alpha \sqrt{t}$ [135, 160] (i.e. neglecting the second term in equation 3.14) and using an Arrhenius equation to find $\alpha(T)$ is not as predictive: the best prediction using this method is shown by the dotted line in figure 3-6.

In addition, we applied the model to the data of Broussely et al. [30], predicting capacity fade at 15 °C for 14.5 months using data at 30-60 °C for 6 months. In this case, the second term in equation 3.14 was statistically indistinguishable from zero, meaning that a simple $t^{1/2}$ capacity fade model would give the same result. It is possible that the second term cannot be distinguished in this case because capacity loss was not measured directly, as in Smith et al. [159], but inferred from measured
Figure 3-7: The single particle model, using accelerated aging data from 6 months at 30-60 °C, can be used to predict aging over 14.5 months at 15 °C. Data from Broussely et al. [30] with a lithium cobalt oxide opposite electrode.

A more sophisticated application of the single particle model would be to predict the total capacity fade of a battery subject to varying temperature. This information could be used to construct a protocol to optimize lifetime given a particular set of unavoidable temperature constraints. For example, is it possible to increase battery life by cycling it a small number of times at particularly high or low temperature, in order to produce an initial SEI with low electrolyte diffusivity? Answering this question will require experimental work to check whether the measured electrolyte diffusivity depends on the temperature history of the battery as well as the current temperature.
3.4.2 Resistance mismatch in battery packs

The discussion above considers temperature differences that are purely external, but high rate use of a battery can lead to significant heating due to the battery’s internal resistance. Since this can alter the temperature of the battery, it must be taken into account in order to accurately predict capacity fade. One instance where this is important is the case of battery packs comprising two cells charged and discharged in parallel. Experiments on this system were performed by my collaborator, Radu Gogoana. I then analysed the experimental results with respect to my capacity fade model.

When two cells with different internal resistance are charged in parallel, the current experienced by each cell is not constant. Early in the charging process, the less resistive cell experiences a higher current. This may cause it to approach a fully charged state sooner than the more resistive cell, resulting in an increase in current to the more resistive cell towards the end of charging. A large difference in internal resistance thus results in high maximum charging current to both cells in the cell group, which is shown in figure 3-8. The less resistive cell 2 has higher current early in discharge and charge; the later increase in current to cell 1 is more apparent on discharge than on charge.

It is important to note that the shape of the current distribution curve in figure 3-8 is linked to shape of the voltage vs capacity curve of LiFePO₄ cells, which is relatively flat between approximately 10% and 90% state of charge. For other Li-ion cell chemistries that have more sloped voltage vs capacity curves (e.g. LiMn₂O₄, LiCoO₂), we expect a “balancing-out” effect to occur throughout the charge and discharge cycles. Because capacity and voltage are more closely related for those chemistries, we expect that both cells in a parallel-connected configuration will reach end-of-discharge more evenly without a large difference in current between the two cells toward the end of the cycle.

Gogoana’s experimental results showed that cells with higher mismatch in internal resistance fade more quickly. This implies that a higher maximum current increases
the capacity fade rate, even when average current is fixed. This could arise because resistive heating causes an increase in temperature, which exponentially increases the rate of capacity fade [6]. The impact of temperature on the cycle life of lithium-ion cells has been studied by several groups [6, 173, 26, 118]. Although the temperature of all cells increased during cycling, there was no significant correlation between the external temperature of an individual cell and either current or the rate of capacity fade. Thus, if the dependence of capacity fading on current is due to a temperature increase, this temperature increase must be highly localized inside the cell. Alternatively, the accelerating effect of very high current on capacity fade may be separate from any temperature effect.

To apply the model of this work to explaining the effect of mismatched internal resistances, it is necessary to hypothesize a particular dependence of $D$ on C rate. If $D$ has an Arrhenius dependence on temperature,

$$D \propto \exp \left(\frac{-E}{k_B T}\right),$$  \hspace{1cm} (3.16)
the cell temperature is elevated above room temperature by an amount proportional to the C rate, and this elevation is much smaller than room temperature, then equation 3.16 can be expressed as

\[ D = D_0 \exp(\alpha I), \]  

(3.17)

where \( I \) is the C rate and \( \alpha \) is a constant. Combining this with an assumption that any dependence of \( k \) on C rate was unimportant, we used equation 3.10 to model capacity fade. A least squares fit to Gogoana’s experimental data was used to calculate values of the parameters \( D_0 \), \( \alpha \) and \( k \). The value of \( D \) as a function of C rate is shown in Figure 3-9. The model was sufficient to describe capacity fade until 75% capacity for most of the cells studied by Gogoana. One cell showed anomalously slow capacity fade and was excluded from the analysis, as including it caused the calculated fade rate of other cells to differ from the obvious cluster.

Figure 3-10 compares experimental capacity fade with the model prediction for the two cells with smallest and largest error.

Using this model of capacity fade, lifetime to 75% of total capacity can be predicted for a pair of cells with arbitrary difference in internal resistance. This prediction relies
Figure 3-10: Experimental and model capacity fade for two cells.

on the assignment of a maximum charging current to each cell at each cycle. For the cell with lower resistance, this can be calculated assuming that the ratio of resistances does not change with degradation.

The maximum charging current to the cell with higher resistance will come at the end of charging, when the other cell nears a fully-charged state. It was observed that the maximum charging current measured experimentally for the more resistive cell in a pair was linearly related to the “excess capacity” $Q_x$, defined by

$$Q_x = Q_1 - \frac{Q_2 R_2}{R_1}$$  \hspace{1cm} (3.18)

where $Q_1$ and $R_1$ are the capacity and resistance of the more resistive cell and $Q_2$ and $R_2$ the capacity and resistance of the less resistive cell. The excess capacity is thus the charging capacity remaining in the more resistive cell when the less resistive cell has finished charging, assuming that the charging rates remain constant. The observed linear relationship, shown in Figure 3-11, was used as an input into the model-based prediction.

This increase in maximum charging current from 9.5A to 12A (4.3C to 5.5C) can be a significant factor in the capacity fading of the cell. Observed data by Wang et al.
Figure 3-11: Maximum charging current to the more resistive cell as a function of the excess capacity of this cell (defined by equation 3.18). More capacity remaining in one cell at the end of a charge cycle leads to higher maximum charge current to that cell.
on the same LiFePO$_4$ cells that Gogoana tested showed an exponential increase in capacity fade with C-rate. The curve-fitted model that they obtained from their experimental data is shown in Figure 3-12. Although they only tested the impact of higher discharge currents (their charge current in testing was a constant 2C), it is possible that a similar relationship exists on charging C-rate, and that the jump from 4.3C to 5.5C on charging was responsible for this difference in capacity fade.

The model of this work includes a degradation rate that is independent of current. In fact, since the model identifies time rather than charge throughput as the determinant of capacity fade, cells exposed to higher C rates are expected to have a longer cycle life. The model does display a strong dependence of degradation rate on temperature, and it is likely that the importance of fast charging is that it increases temperature, through resistive heating within the cell. In the experiments of Gogoana, there was no apparent relationship between the measured temperature at the outside of the cell and fade rate, so if heating is indeed the cause of increased capacity fade, it must be somewhat localized within the spiral-wound electrode. This localized temperature rise can be estimated by comparing the change in the rate of
capacity fade due to a C-rate increase, with that due to an increase in ambient air temperature. According to the SEI formation model, a 10 °C increase in temperature increases the capacity fade rate by approximately 40%, due to a doubling of the diffusivity of electrolyte molecules through the SEI. The same increases were found in Gogoana’s experiments when maximum charging current was increased by 0.7C. In other words, a 10 °C increase in background temperature or a 0.7C increase in maximum charging rate apply approximately equal stress to the battery in terms of capacity fade rate.

Figure 3-13 shows the predicted lifetime as a function of relative resistance difference, calculated by combining equations 3.10, 3.17 and 3.18 with the empirical relationship shown in figure 3-11. The top curve accounts only for gradual capacity fade due to SEI formation. In addition, many cells experienced a sudden capacity loss of up to 100 mAh towards the beginning of the cycling process. These capacity losses could result from isolation of active material from the conductive matrix, due to SEI growth or physical separation. The bottom curve represents a worst-case scenario, where both cells experience a 100 mAh capacity loss at the beginning of cycling, followed by gradual SEI formation. The model explains the observed decrease of lifetime with an increase in internal resistance mismatch, and that the observed scatter is due to random sudden capacity losses. These random losses can drastically reduce cycle life, and so are important to monitor (and ideally prevent), even though on average most capacity fade is due to gradual SEI formation.

The modeling described in this subsection could be applied to any situation where cells are charged at a C rate high enough to increase temperature. In order to obtain a prediction of lifetime, it is vital to know the actual C rate to which a cell is exposed. For instance, if more than two cells are connected in parallel, the extra current imposed when one cell reaches capacity will be shared between the others, and a detailed measurement or model of this sharing is necessary to allow a quantitative prediction of pack lifetime.
3.5 Lifetime prediction and statistics

Another application of the single particle model is to understanding the statistics of battery lifetime. If the typical diffusivity of electrolyte through the SEI is \( D_m \) and the battery is defined to fail when the SEI thickness reaches \( s_0 \), the average battery life will be \( \tau_m = (\rho s_0^2)(2cmD_m) \) (we have neglected the second term in equation 3.14).

Since a battery is made up of many, presumably identical, active particles \( i \) and the total SEI formation is proportional to \( \sum_i \sqrt{D_i t} \), we expect the measured \( \sqrt{D} \) to have a normal distribution, assuming the distribution of the true diffusivity \( D_i \) meets the conditions of the central limit theorem. Thus the inverse of the lifetimes of a collection of batteries should be normally distributed; SEI formation as modeled here will not cause anomalously short battery lifetime.

This prediction can be compared with other predicted battery lifetime distributions, such as the Weibull distribution from the theory of extreme order statistics [52, 122]. A Weibull distribution is expected when failure occurs in a “weakest link” situation, where failure of a single element causes failure of the entire cell. Math-
Figure 3-14: Lifetimes (calculated from data in Park et al. [122]) are consistent with a normal distribution (solid line), but not with a Weibull distribution, which would appear as a straight line on this Weibull plot. However, it is not possible to establish the presence or absence of a Weibull tail at low lifetime (dashed line).

Mathematically, it is the limiting distribution for the smallest outcome of a large set of independent identically distributed random variables which are bounded below, with a power law tail [66]. Additionally, a Weibull tail at short lifetime occurs in quasibrittle fracture when the system can be modeled as a bundle of fibers arranged both in series and in parallel [89].

In order to examine the experimental lifetime distribution, we converted the data in table 2 of Park et al. [122] to lifetime data by defining the lifetime to be the number of cycles taken to reach a relative capacity of 85.6

3.6 Extensions for rapid capacity fade

Until now, we have focused on gradual capacity fade due to the formation of a stable SEI film, well adhered to an electrode internal surface of nearly constant area. This
is the situation in practical Li-ion cells, but various emerging technologies, which offer certain benefits, such as high energy density, suffer from much faster capacity fade related to accelerated SEI formation. The canonical and most intensely studied example is silicon, which is a very attractive anode material for Li-ion batteries due to its theoretical high energy density of 4200 mAh g$^{-1}$ [45], but, as a result of its enormous volume expansion upon lithiation ($> 300$

3.6.1 Fresh surface

The single particle model assumes that the SEI is made up of a single layer growing smoothly from the surface of the active material. In a material that experiences a large volume change on lithiation, such as silicon [27], this assumption is no longer valid. Instead, the expansion during lithiation produces fresh surface area, on which SEI can form without hindrance from an already-existing layer. As the material shrinks during delithiation, the SEI formed on the newly exposed surface will be forced into the existing layer or possibly detached from the active material. In either case, it is likely that a substantial fraction of the new area formed on the next cycle is once again freshly exposed. This leads to capacity fade at a much faster rate than would be expected from the model in which the SEI layer remains uniform and area changes are ignored.

The effect of the fresh surface area can be modeled simply by applying the result of the single particle model, equation 3.13 or 3.14, to a single charge-discharge cycle, and finding the total capacity fade by adding that of each cycle. The total SEI thickness is

$$s = \frac{t}{\tau} \left( \sqrt{\frac{2cmD\tau}{\rho}} - \frac{D}{k} \right),$$

(3.19)

where $\tau$ is the time spent during one cycle at a voltage where SEI forms: we assume that this is the total charge and discharge time. This simple model predicts that capacity fade is linear in time, which is precisely what is seen for full cells using silicon electrodes [10, 45, 123, 96, 80]. Furthermore, since $t/\tau$ is the number of cycles, the rate of increase of $s$ per cycle should be linear in $\sqrt{\tau}$. Figure 3-15 shows experimental
data from figure 4c of Ji et al. [80], which exhibit capacity fade of 4 mAh g$^{-1}$ cycle$^{-1}$ at C/15 and 2 mAh g$^{-1}$ cycle$^{-1}$ at C/4, consistent with this prediction. Assuming a characteristic particle size of 1 Åm, this implies $D = 4 \times 10^{-15}$ cm$^2$ s$^{-1}$. This is two orders of magnitude higher than that found in the case of graphite, for which we offer two possible explanations. The first is that, even in the case of graphite, the new SEI formed each cycle may form primarily on the newly exposed area, though in this case the shape change is small enough that the SEI formed in the previous cycle is not fully lost. In this case, the smaller formation area means that the actual SEI thickness is higher than that calculated assuming the SEI forms evenly over the entire active surface, since capacity loss, which is measured, is proportional to SEI volume. This would mean that the true value of $D$ is higher than that calculated under the assumptions of the simple model. The second possibility is that the expansion of silicon is large enough to disturb the structure of the SEI, even within a single cycle. Such a disturbance might increase SEI porosity and is likely to increase $D$.

It is vital that full cell, not half cell, aging data are used to assess the impact of SEI growth on capacity fade. SEI growth leads to capacity fade due to the consumption of lithium that would otherwise be available for cycling. If an electrode is cycled against a lithium foil electrode containing excess lithium, this loss will not be observed, potentially leading to an overestimate of battery life. Indeed, experimental results demonstrate a substantially shorter lifetime for a full cell than a half cell using a silicon electrode: figure 4 of Baranchugov et al. [10] shows this particularly clearly. Considering only half cell data could lead to a falsely optimistic assessment of the lifespan of a silicon anode.

### 3.6.2 Unstable SEI

Another situation in which SEI formation could progress faster than suggested by the single particle model is when SEI is lost from the layer, by delamination or dissolution in a form from which Li remains unavailable. Significant SEI removal is known to occur in silicon anodes, as confirmed by direct observation [38]. Assuming that this loss is not so great as to reduce the layer thickness to zero or almost zero, it can be
Figure 3-15: A full cell with a silicon anode shows linear capacity fade at two charge-discharge rates. The main graph plots capacity against cycle number. The inset plots capacity against cycle number weighted by the square root of the charge-discharge time, as the model of this work predicts that capacity fade is proportional to this quantity. The experimental data, from Ji et al. [80], match the theory very well, after accounting for the constant offset due to the change in charge-discharge rate, which is well understood though not explicitly modeled in this work.
modeled by including a loss term in the differential equation for SEI formation:

\[ \frac{ds}{dt} = \frac{Jm}{\rho A} - f(s), \]  

(3.20)

where \( f \) is a general function characterizing the dependence of the SEI loss rate on SEI thickness. The rate of capacity loss remains

\[ \frac{dQ}{dt} = -J, \]  

(3.21)

and the dependence of \( J \) on \( s \) is unchanged. This alters the long time behavior of capacity. Assuming that \( f \) is an increasing function of \( s \) (strictly all that is necessary is that the right hand side of equation 3.20 is ultimately negative; in particular, a constant \( f \) is sufficient), \( s \) will eventually reach some maximum \( s_m \). Once this maximum SEI thickness is reached, the rate of capacity loss will be \( J(s_m) \). The overall result is a capacity fade rate that is linear due to reaction limitation for a short time, before moving through a \( t^{1/2} \) transition region to a second linear region with a lower rate. This behavior, which could be expected for a system where the charge-discharge process places a greater burden on the SEI layer than that in graphite but less than that in silicon, is represented in figure 3-16. In such a situation, capacity fade could be reduced not only by decreasing \( J(s) \), but also by decreasing \( f \).

Although for most choices of \( f(s) \) it is not possible to find an analytic formula for \( Q(t) \), we can make progress in the simple case \( f(s) = s/t_0 \), in the limit \( k \to \infty \) (which experiments [93] suggest is reasonable: see above). Under these conditions,

\[ Q(t) = Q_0 - A \sqrt{\frac{pcDt_0}{m}} \left( \frac{t}{t_0} + \ln(1 + \sqrt{1 - e^{-2t/t_0}}) \right), \]  

(3.22)

where \( Q_0 \) is the initial capacity. We see that the long-term linear fade has the same prefactor as the \( t^{1/2} \) fade of the stable case, except for the dimensionally-required \( 1/(2t_0^{1/2}) \). This long-term behavior is not influenced by the assumption \( k \to \infty \).
Figure 3-16: When SEI dissolution or delamination occurs, capacity fade occurs in three regimes. Initially the SEI thickness $s$ is small, the SEI formation rate $J$ is very large, limited only by the reaction rate, and the SEI loss rate $f$ is small, so $s$ increases rapidly while capacity decreases rapidly. For intermediate times, SEI formation is limited by diffusion through the existing SEI, but $J$ is still greater than $f$, leading to an approximate $t^{1/2}$ rate of capacity fade. Eventually the SEI formation and loss rates will be equal, leading to constant $s$ and a steady rate of capacity loss.
Chapter 4

Overview of models of sorption in porous materials

4.1 Modeling of sorption in a single pore

4.1.1 Surface adsorption

The quantity of a fluid taken up by a porous material, as a function of the partial pressure of this fluid, is frequently used to analyse the pore structure of the porous material. In order to carry out this analysis, models of the relationship between pore properties, partial pressure and sorption are required.

If the sorption process begins at sorbate pressure zero, the conceptually simplest approach though not necessarily the technique used in experiment, the first mechanism of sorption is adsorption of the sorbate molecules to the solid material. Two simple models of this adsorption process have been developed, based on different assumptions.

Langmuir assumed that molecules from the vapor could adsorb onto the solid surface in a single layer, with heat of adsorption $E_{st}$. Assuming that adsorption occurs at independent sites, and that the adsorbed layer and vapor are in equilibrium, the coverage of the solid is then

$$t = \frac{ch}{1 + ch}$$

(4.1)
where \( c = e^{(E_{sl} - E_l)/k_BT} \), \( E_l \) being the heat of liquefaction of the sorbate, and \( h \) is the partial pressure of the sorbate, relative to the saturation pressure [87]. This equation is known as the Langmuir equation.

Brunauer et al. assumed that many layers could adsorb on the surface. They also assumed adsorption at independent sites and heat of adsorption \( E_{sl} \) for the first molecule at a site, but assumed that other molecules could adsorb in a tower above the first, with heat of adsorption equal to the heat of liquefaction. The average thickness of the adsorbed layer, in molecules, is then [32]

\[
t = \frac{c h}{((c - 1)h + 1)(1 - h)}. \tag{4.2}
\]

This equation is known as the BET equation.

The Langmuir and BET equations predict the same behavior at low pressure, but very different behavior as the pressure approaches the saturation pressure: \( t \) approaches a constant below 1 and infinity respectively. The BET equation is widely used in the calculation of surface areas of porous materials, though an area calculated in this way is not necessarily equal to the actual surface area of the porous material [63]. Figure 4-1 shows the predicted adsorbed layer thicknesses for the two models with \( c = 4 \), along with sample configurations of adsorbed molecules at 25\%, 50\% and 75\% relative pressure.

4.1.2 Pore filling

Even below its saturation pressure, a condensed phase of a sorbate can exist in a porous material. The Kelvin equation describes the radius of curvature of an interface between liquid and vapor at a particular partial pressure, in equilibrium [176]:

\[
\ln h = -\frac{2\gamma v}{r k_BT}, \tag{4.3}
\]

where \( \gamma \) is the surface tension between liquid and vapor and \( v \) is the average molecular volume in the liquid state. The Kelvin equation allows the calculation of the partial
Figure 4-1: Adsorbed layer thickness in monolayers according to the BET and Langmuir equations, along with example configurations of adsorbed molecules at 25%, 50% and 75% relative pressure.
pressure at which the filled and empty (apart from adsorbed layers) state will be in equilibrium for a particular regularly-shaped pore, provided the contact angle $\theta$ between liquid, vapor and adsorbed fluid is known or can be assumed. For instance, a cylindrical pore of radius $r$ has this equilibrium transition at

$$\ln h = -\frac{2\gamma v \cos \theta}{(r - t(h)a)k_B T}.$$  

(4.4)

Equivalent equations can be found for other geometries.

Experimentally, hysteresis is often found between sorbed quantities on increasing and decreasing partial pressure. One source of this hysteresis is when the filling and emptying processes follow different paths. For example, in the case of a cylindrical pore, the equilibrium interface between liquid and vapor is a hemisphere, and emptying occurs by the propagation of such an interface along the axis of the cylinder. If the pore has open ends, however, such an interface will not exist at low partial pressure, and the pore must fill radially from the wall to the axis. Neglecting the effect of the changing adsorbed layer thickness, the mean curvature of this cylindrical interface is half that of the hemispherical interface, so the pore fills at a relative pressure higher than that at which it will empty. Figure 4-2 illustrates a cycle of relative pressure. This difference between filling and emptying paths has been noted as an important source of sorption hysteresi [42, 29, 85].

4.2 Modeling of sorption hysteresis in porous materials

The existence of a network of pores can greatly increase hysteresis, and various models of sorption in a porous network have been proposed, applicable to different materials. The fundamental principle on which these models are based is that, since emptying occurs by propagation of an interface between the vapor phase and the condensed fluid, a pore cannot empty unless it is exposed to such an interface: that is, it is adjacent to an empty pore or the boundary of the system. The emptying of pores
can thus be described by a percolation model on some suitably designed lattice.

Mason [103] proposed a model of pores connected by windows, each with a characteristic radius drawn from a distribution [104]. Parlar and Yortsos [125] extended this model to more completely describe the case of scanning isotherms. Seaton [152] applied the model to the calculation of the average coordination number of pores in various materials, while Tanev and Vlaev [163] considered the relationship between assumptions about the pore shape and the corresponding hysteresis loop.

The models presented in these publications focus primarily on the percolation threshold. They make certain assumptions about the pore network, and assume that no emptying of a significant number of pores occurs until the vapor region is able to percolate through this network. This assumption seems to work well for materials where the pore size distribution is not too wide, such as porous glass [104]. An interesting and neglected case is that of a material with a broad PSD, such that an extensive number of macropores is empty when the partial pressure is immediately below the saturation pressure. This could be because these pores do not fill, or because they are able to empty without hindrance due to a connection to a continuous network of large pores.
Liu et al. modeled such a system, treating the pores as bonds of a simple cubic lattice, which in the undisturbed state has connectivity $Z = 10$. They controlled the actual average connectivity by randomly deleting bonds from the lattice. They also used a finite lattice to model the effect of finite-sized microparticles, between which condensation does not occur. The wetting process was assumed to occur at equilibrium, and the empty fraction during drying was calculated computationally [95]. Liu and Seaton then extended this work to allow for the case that some pores are never filled, and hence provide additional locations at which the vapor phase may be nucleated [94]. A missing element from these models was single-pore hysteresis. Kruk and Jaroniec studied sorption hysteresis in systems with single-pore hysteresis, but in simpler systems comprising large pores with small necks, rather than a network of similar pores [86]. Network modeling of sorption with single-pore hysteresis was carried out by Rojas et al. [145]. Cordero et al. extended this modeling to account for the nucleation and suppression of filling by adjacent pores [44].

These examples of network modeling of pore filling and emptying were carried out computationally on lattices produced using pores with sizes drawn randomly from a distribution. This technique can be effective, but a simpler method, more easily applicable to calculating parameters based on a particular experimental data set, would be to find analytic expressions for the relevant quantities. I present such an analytic model in this work.

### 4.3 Modeling of transport in porous materials

Models of transport in porous media are based on Darcy’s law, which can be written

$$q = \frac{\kappa}{\mu} (-\nabla p + \rho g). \quad (4.5)$$

$q$ is flux density, $\kappa$ is the intrinsic permeability of the porous medium, proportional to the square of a characteristic pore size, $\mu$ is fluid viscosity, $p$ is pressure in the fluid, $\rho$ is fluid density and $g$ is acceleration due to gravity. Gravity is dominant
in saturated flow but negligible in unsaturated flow because the scale of capillary pressure is around 100 MPa, so the gravity term is dropped hereafter. Darcy’s law can be derived by coarse-graining Stokes flow through the medium [180].

Two important sources of hysteresis have been included in various models of fluid flow in porous media. The first is that the permeability can depend not only on the current saturation, but also on the local saturation history. A reason for this is that permeability depends on which pores are occupied by the flowing fluid. If it takes some time for fluid in large and small pores to reach equilibrium locally, there will be a corresponding time-dependence of permeability. Barenblatt et al. model this effect through the use of an effective saturation that relaxes to the true saturation [11].

The second source of hysteresis is in the relationship between saturation and pressure. Various authors have used empirical relationships to represent the dependence of saturation on pressure history as well as the current pressure [170, 83, 124, 97]. A particularly important example of such a model, accounting for the microscopic source of the hysteresis, is due to Mualem. This work represents the fraction of pores that have emptied during drying as the product of the fraction that could have emptied based on an equilibrium consideration of the local pore structure, and the fraction of such pores that are not blocked by water in the broader pore system [112]. However, the model assumes a particular relationship between the equilibrium state of pores on wetting and drying: namely, that the fraction of pores empty on drying is the square of the fraction empty on wetting, assuming no blocking. A more general assumption would be that the equilibrium state is the same, and that any difference in filling must be due to some kind of blocking effect. In other words, blocking by local effects such as pore necks is considered in the same way as blocking by larger-scale effects of the pore network. It is this assumption that I use in my modeling of transport with hysteresis.
Chapter 5

A model of sorption in multiscale porous materials

The content of this chapter is based heavily on the article in preparation “Theory of Sorption Hysteresis in Multiscale Porous Media” by the author, Jennings and Bazant [133].

5.1 Single pore hysteresis model

5.1.1 Model

The starting point for modeling of sorption hysteresis in a pore network must be a model of sorption in isolated pores. I assume that the initial sorption mode is adsorption on the pore walls, and that the thickness of the adsorbed layer can be described by the BET equation, equation 4.2. I further assume that the Kelvin equation, equation 4.3 can be used to relate the radius of mean curvature of an interface between condensed fluid and vapor to the relative pressure of the sorbate. The use of the Kelvin equation relies on the assumption that a continuum treatment of water is valid down to small length scales, as suggested by the explanation of freezing point suppression by an analogous continuum equation [155]. I ignore any dependence of the surface tension on curvature, as this dependence is small and there is not even
consensus regarding its sign \cite{91,22}.

Using the above equations describing sorption in mesopores, is is possible to analyse experimentally observed sorption isotherms to obtain the PSD of a porous material. Here I assume cylindrical pores since, in some cases below, assuming slit pores predicts a greater than observed hysteresis loop even when neglecting network effects. If the distribution of pore radii $r$, by pore volume, is $v(r)$, the sorbed volume at relative pressure $h$ during drying is

$$m_d(h) = \int_{0}^{r_K(h)+at(h)} v(r) \, dr + \int_{r_K(h)+at(h)}^{\infty} \frac{r^2 - [r - at(h)]^2}{r^2} v(r) \, dr, \quad (5.1)$$

where

$$r_K(h) = \frac{2\gamma a^3}{kT \ln h} \quad (5.2)$$

is the radius, measured to the inner surface of the adsorbed layers, of a pore where the full and empty states are in equilibrium. The two terms on the right are the contribution of full pores and of the adsorbed layers on the walls of otherwise empty pores, respectively. The sorbed volume during wetting has the same form, but half the Kelvin radius instead of the Kelvin radius itself must be used in calculating the radius that divides full and empty pores, due to the cylindrical shape of the meniscus. This gives

$$m_w(h) = \int_{0}^{r_K(h)/2+at(h)} v(r) \, dr + \int_{r_K(h)/2+at(h)}^{\infty} \frac{r^2 - [r - at(h)]^2}{r^2} v(r) \, dr. \quad (5.3)$$

In principle, equation 5.1 allows the calculation of $v(r)$ directly from experimental data. However, the discreteness of experimental data and the difficulty in distinguishing adsorbed and condensed water can lead to spurious bumps in the PSD thus obtained. I therefore make the simple assumption of a log-normal distribution of pore widths, which is sufficient for good agreement with experimental data.
5.1.2  Application to simple porous materials

I apply the model to experimental sorption isotherms for dichlorofluoromethane in plugs of carbon black [34]. Experimental and modeled isotherms are shown in Fig. 5-1, and the PSDs in Fig. 5-2. The parameters of the model are the total volume in which fluid is sorbed, the mean and variance of the PSD, the offset of the experimentally measured “dry” mass from the truly dry mass, and the BET constant $c$, which mostly influences the low pressure sorption.

5.2  Network effects

This simple model, accounting for hysteresis due to differences in the shape of the liquid-vapor interface in a single pore on wetting and drying, accurately describes sorption in this particular porous material, which has a narrow distribution of small pores. In a system with a wide range of pore sizes, network effects can act to broaden hysteresis. The additional hysteresis is due to some pores remaining full below the relative pressure at which the empty state is thermodynamically favored, because they lack the connection with the vapor phase that is necessary to nucleate the liquid to vapor transition. This is frequently known as “pore blocking” [163] [141], though this term has the potential to mislead by suggesting a dynamic effect, whereas in fact a metastable state is achieved. Figure 5-3 illustrates a large pore kept full at low partial pressure during drying due to a small pore providing the only path to the atmosphere.

Various models of this hysteresis have been developed, and were discussed in section 4.2. I present here a unified model combining several important features. It allows for single-pore as well as network hysteresis, includes the effect of large pores that provide nucleation points for the liquid-vapor interface, and is analytic rather than computational. These all make the model, which is based on a simple, mean-field treatment of percolation, ideal for studying complex, hierarchical pore structures.
Figure 5-1: Experimental (points) and modeled (lines) sorption isotherms on wetting (blue) and drying (red) for dichlorofluoromethane in carbon black formed into plugs with porosity of (a) 0.50, (b) 0.58, (c) 0.66 and (d) 0.74 [34].
Figure 5-2: Pore size distributions of carbon black formed into plugs, obtained by applying the model of this work to the experimental data of Carman and Raal [34], as shown in Fig. 5-1.
Figure 5-3: Illustration of a system comprising a large pore whose only path to the atmosphere passes through a small pore, exposed to a cycle of relative pressure. The large pore remains full until the small pore empties and provides a meniscus where the liquid-vapor transition can be nucleated.

5.2.1 Model

Since the pore network provides a hindrance only to drying, the sorbate content during wetting is the same as that in the independent pore model given in equation 5.3. To calculate the sorbate content during drying, we must derive a formula for the probability that a pore is able to empty, as a function of relative pressure. The first step is to turn the volume probability density \( v(r) \) into a number probability density, which requires an assumption about pore shape. Since the model is already built around cylindrical pores, the simplest assumption is that the volume of a pore is proportional to the square of its radius, i.e., pores of different radii have the same length.

At a particular relative pressure \( h \), it is then possible to define the fraction of pores that are below their emptying transition pressure: this fraction \( q \) is given by

\[
q = \frac{\int_{r_K(h)+a(h)}^{\infty} \frac{v(r)}{r^2} \, dr}{\int_{0}^{\infty} \frac{v(r)}{r^2} \, dr}.
\]  

(5.4)

The goal is to calculate the fraction \( Q \) of such pores that has actually emptied. The
total sorbed volume during drying will then be

\[ m_d(h) = \int_0^{r_K(h)+at(h)} v(r) \, dr \\
+ (1 - Q) \int_{r_K(h)+at(h)}^{\infty} v(r) \, dr \\
+ Q \int_{r_K(h)+at(h)}^{\infty} \frac{r^2 - [r - at(h)]^2}{r^2} v(r) \, dr, \]  \hspace{1cm} (5.5)

where the three terms on the right are the contributions of pores that are full due to the pressure being above their emptying pressure, pores remaining full due to the absence of a liquid-vapor interface, and adsorbed water in empty pores, respectively.

To perform this calculation, I model the pore network by a Bethe lattice of connectivity \( z \), where nodes correspond to pores. Although in principle \( z \) is a free parameter describing the material, to avoid overfitting I fix \( z = 4 \), a reasonable value for a random network in three dimensions and typical of values obtained if \( z \) is allowed to vary.

The Bethe lattice has been used previously to describe sorption in a porous material [103, 152]. I introduce an important extension by quantifying the effect of already exposed pores on the drying behavior. Such pores are included through a parameter \( f \), defined to be the fraction of all pores exposed to a liquid-vapor interface as soon as drying commences, so that the pores empty as soon as their equilibrium transition pressure is reached. Figure 5-4 illustrates the model and the principles of the system it represents: the exposed fraction \( f \) accounts for the effect of large pores, which have very different filling behavior and may remain empty throughout an experiment.

There are thus two mechanisms by which a particular pore may have access to the vapor phase. The first is direct exposure, with probability \( f \). The second is that it could be connected to the vapor by a neighbor: I define \( X \) to be the probability that an individual neighbor provides such a connection. This gives

\[ 1 - Q = (1 - f)(1 - X)^z. \]  \hspace{1cm} (5.6)
Figure 5-4: A schematic diagram of a network of small (blue) and large (white) pores formed by a solid skeleton (grey), and its representation by a Bethe lattice, here with \( z = 3 \). The holes in the boundary of some pores, as noted by green arrows, represent an interface between the network of small pores and larger pores.

Taking advantage of the self-similarity of the Bethe lattice, we can further write

\[
X = q[f + (1 - f)(1 - (1 - X)^{z-1})].
\]  

(5.7)

I solve equation 5.7 self-consistently to find \( X \), and then use equation 5.6 to calculate \( Q \). Figure 5-5 shows \( Q \) as a function of \( q \) for \( f = 0.2 \), a typical value.

This percolation model is based on long-established ideas described by Mason and others [105, 103, 152]. In fact, equations 5.6 and 5.7 are equivalent to equations 20 and 21 of the paper by Parlar and Yortsos [125] (there applied to scanning rather than primary isotherms), where \( P_S(q; q_i) \) and \( q_i \) in that paper are equal to \( Qq \) and \( fq \) respectively in this paper.

### 5.2.2 Insertion within the “solid”

Equations 5.3 and 5.5 describe sorption in mesopores. Many porous materials possess a hierarchical pore structure, and sorbate can be found not only in the mesopores, but
Figure 5-5: Probability that a pore below its equilibrium emptying pressure is empty, as a function of the fraction of pores below their equilibrium emptying pressures, for an example case with an initially exposed fraction of 0.2.
also in even smaller spaces within what would be considered the “solid” part of the structure [143] [144]. Simple models that treat the sorbate as a condensing fluid are not applicable to these very small (approximately one nanometer or smaller) spaces, because they neglect strong chemical interactions with the sorbent material, as well as effects arising due to the discreteness of the sorbate molecules [16]. One approach is to use various atomistic simulation techniques [23], but for the purposes of this model a simpler approach is desired. In hardened cement paste, a material in which inserted water is particularly important, the inserted water content as a function of relative humidity is well approximated by assuming no loss of water on drying until 15% relative humidity is reached, linear loss of water below this, and linear reinsertion on wetting [56, 79, 113]. The fluid content is then

\[
\begin{align*}
  m_{\text{ins}} &= m^* \quad h : 1 \to 0.15 \\
  m_{\text{ins}} &= \frac{h}{0.15} m^* \quad h : 0.15 \to 0 \\
  m_{\text{ins}} &= h m^* \quad h : 0 \to 1.
\end{align*}
\]

This leaves only the total inserted water capacity \( m^* \) as an new unknown parameter. If the direction of the pressure change is switched at a point other than 0 or 1, I assume that \( m_{\text{ins}} \) retains its value at the turning point until this is reached by the value predicted by equations 5.8 to 5.10.

### 5.2.3 Homogeneous nucleation

One further effect controls desorption at low relative pressure. This effect has been called cavitation [169] or the tensile strength effect [70]. The cause of desorption is that the condensed fluid becomes unstable at sufficiently low pressure. I assume that the primary result of this desorption mechanism is the homogeneous nucleation of the vapor phase in blocked large pores. In other words, I neglect the effect of the tensile strength on the metastable sorption-desorption isotherm of an isolated single pore.

The vapor phase will nucleate in homogeneous bulk liquid when turning a small
quantity of liquid to vapor decreases the free energy: this will happen at some characteristic chemical potential. I denote the relative pressure in the vapor phase corresponding to this chemical potential by \( h_n(\infty) \). Now when vapor is nucleated in a pore of finite size, the same free energies are involved, but also the surface energy resulting from emptying the pore, which may be accounted for most simply by dividing it equally among all the molecules, exactly as was done when considering pore filling or emptying at equilibrium. The chemical potential difference between nucleating vapor in a pore of width \( r \) and in the bulk is therefore (approximately) the same as the chemical potential difference between condensation/evaporation in the pore and in the bulk. In terms of pressures in the vapor phase, this can be written

\[
h_n(r) = h_n(\infty) e^{-\frac{2\gamma v}{KV}}
\]

The value of \( h_n(\infty) \) should depend on the sorbate and temperature but not on the sorbent.

Equation 5.11 gives a relationship between relative pressure and the width above which all pores must be empty. Defining

\[
q_n = \frac{\int_{r_n}^{\infty} \frac{v(r)}{r^2} \, dr}{\int_{0}^{\infty} \frac{v(r)}{r^2} \, dr},
\]

we can then write

\[
X = q_n + (q - q_n)[f + (1 - f)(1 - (1 - X)^{z-1})]
\]
and

\[ m_d(h) = \int_0^{r_K(h)+at(h)} v(r) \, dr + (1 - Q) \int_{r_K(h)+at(h)}^{r_n} v(r) \, dl + Q \int_{r_K(h)+at(h)}^{r_n} \frac{r^2 - [r - at(h)]^2}{r^2} v(r) \, dr + \int_{r_n}^{\infty} \frac{r^2 - [r - at(h)]^2}{r^2} v(r) \, dr. \] (5.14)

The four terms on the right are the contributions of pores that are full due to the pressure being above their equilibrium emptying pressure, pores remaining full due to the absence of a liquid-vapor interface, adsorbed water in pores that could have been kept full by the network but happen to have been emptied through propagation of a meniscus, and adsorbed water in pores that must have emptied due to cavitation.

Figure 5-6 plots an illustrative prediction of this theory for a pore size distribution with \( \mu = 1.5, \sigma = 0.8 \) and \( f = 0.3 \). The figure divides the contributions to hysteresis from single pore and network effects, and also shows the adsorbed quantity predicted by the BET and Langmuir equations with no influence of the finite pore size.

### 5.2.4 Application of the model to experimental data

Figure 5-7 compares the model results with experimental observations for various systems [92, 98, 61, 12]. The model parameters were determined in each case by a least squares fit. Figure 5-8 shows the calculated pore size distributions for these materials. The median radius of 13 nm found for the case of carbon nanotubes is consistent with the transmission electron microscope image of these nanotubes (figure 12 of Frackowiak and Béguin [61]).

Values of \( f \) and \( z \) calculated for various materials are presented in table 5.1. Uncertainty ranges are calculated by comparing isotherms of samples produced with different specifications (hardened cement paste), or taken at different temperatures (dental enamel) or using different sorbates (porous silica glass and Vycor). This is
Figure 5-6: An example sorption and hysteresis prediction of the model presented here, showing the contributions to hysteresis of single pore and network effects, along with the adsorbed quantity predicted by the BET and Langmuir equations.
Figure 5-7: Experimental (points or dashed lines) and modeled (solid lines) sorption isotherms on wetting (blue) and drying (red) for (a) water in hardened cement paste [12], (b) water in Vycor [92], (c) nitrogen in carbon nanotubes [61] and (d) xenon in silica glass [98].
Figure 5-8: Pore size distributions, obtained by applying the model of this work to published experimental data, for hardened cement paste [12], Vycor [92], carbon nanotubes [61] and silica glass [98].
Table 5.1: Initial fraction of exposed pores, \(f\), calculated by applying the model presented here to a variety of published experimental data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sorbate/s</th>
<th>Reference</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>Nitrogen</td>
<td>[61]</td>
<td>0.4</td>
</tr>
<tr>
<td>Cement</td>
<td>Water</td>
<td>[59, 12]</td>
<td>0.33 ± 0.06</td>
</tr>
<tr>
<td>Enamel</td>
<td>Water</td>
<td>[187]</td>
<td>0.54 ± 0.05</td>
</tr>
<tr>
<td>Silica glass</td>
<td>CCl(_2)F(_2), C(<em>4)H(</em>{10}), Xe, O(_2)</td>
<td>[98]</td>
<td>0.13 ± 0.09</td>
</tr>
<tr>
<td>Vycor</td>
<td>(\text{N}_2), H(_2)O, C(<em>6)H(</em>{14})</td>
<td>[28, 92, 121]</td>
<td>0.06 ± 0.01</td>
</tr>
</tbody>
</table>

statistical uncertainty only and does not account for model uncertainty.

5.2.5 Scanning isotherms

The principles of the model can be applied directly to the case of scanning isotherms, where the partial pressure is cycled over some subsection of the possible range.

If the decrease in partial pressure is halted at \(h_{\text{min}}\) and the partial pressure then increased to \(h\), the total sorbed volume will be

\[
m_{\uparrow\text{scan}}(h) = \int_{0}^{r_{K}(h_{\text{min}})+a(t(h_{\text{min}}))} v(r) \, dr \\
+ [1 - Q(h_{\text{min}})] \int_{r_{K}(h_{\text{min}})+a(t(h_{\text{min}}))}^{r_{n}(h_{\text{min}})} v(r) \, dr \\
+ Q(h_{\text{min}}) \int_{r_{K}(h_{\text{min}})+a(t(h_{\text{min}}))}^{r_{n}(h_{\text{min}})} \frac{r^2 - [r - a(t)]^2}{r^2} v(r) \, dr \\
+ \int_{r_{n}(h_{\text{min}})}^{\infty} \frac{r^2 - [r - a(t)]^2}{r^2} v(r) \, dr,
\]

where any non-zero integral bound must be replaced by \(r_{K}(h)/2 + a(t)\) when the latter surpasses the former.

If the increase in partial pressure is halted at \(h_{\text{max}}\) and the partial pressure then decreased to \(h\), the total sorbed mass can be calculated using equations 5.12 and 5.14, but using the smaller of \(r_{n}(h)\) and \(r_{K}(h_{\text{max}})/2 + a(t_{\text{max}})\) in place of \(r_{n}(h)\), i.e. the radius of the largest pores that could be filled.

Figure 5-9 compares the model with experimental scanning isotherms for dental enamel [187].
Figure 5-9: Primary and scanning sorption isotherms calculated using the model of this work (solid lines), along with experimental sorption isotherms for water in dental enamel at 298 K [187] (points).
5.3 Potential for further developments

The model presented provides an overall description of hysteresis sorption in mesoporous media, especially in materials in which macropores are also present. Nevertheless, there remain some complications that increase the uncertainty in the level to which the model can quantitatively describe pore size and network structure.

First, the model as formulated assumes cylindrical pores, and a particular amount of single-pore hysteresis due to differences in the shape of the liquid-vapor interface. Other assumptions, such as slit pores with larger hysteresis or equilibrium filling and hence no hysteresis, could have been made instead and built into the model in a straightforward way. Agreement with TEM observations for the case of carbon nanotubes gives some confidence that the assumption of cylindrical pores is reasonable. However, the assumption still influences the obtained results. Specifically, if cylindrical pores are assumed when the system is really made up of slit pores, the obtained pore sizes will be larger and obtained value of $f$ smaller than in reality (the discrepancies are opposite if in fact the pores are able to reach local equilibrium on filling).

Second, the model uses a very simple model of surface adsorption. The effect of this can be seen in some discrepancy between model and experimental results at low pressure. Where the data are available, this could be rectified by using experimental $t$ curves [156], at the loss of some generality.

Third, the assumption of a fixed value of $z$ precludes distinguishing between systems based on their connectivity. For example, we might expect carbon nanotubes to have $z \approx 2$, while disordered porous systems such as glasses and cement paste have higher $z$. Sorption data alone are not sufficient to allow such an identification to be made. Also, it seems to be $f$ rather than $z$ that is most influential in determining the sorption behavior.

One tantalising prospect is the use of experiments like those cited in this work to measure $h_n(\infty)$ for various fluids as a function of temperature. In only two distinct cases: water around 25 °C and at 50 °C, was the characteristic knee observed. $h_n(\infty)$
was larger at higher temperature as expected. A systematic study could allow this quantity to be measured as a function of temperature, providing insight into the nature of forces between molecules in a liquid.

Values of $h_n(\infty)$ can be calculated for some simple models of interacting fluids. For example, the regular solution model predicts

$$h_n(\infty) = e^{-2\sqrt{1-\tau/\tau}(1 + \sqrt{1-\tau}) \over 1 - \sqrt{1-\tau}},$$  

(5.15)

where $\tau = T/T_c$ is temperature divided by the critical temperature of the sorbate. A solution can also be found for a van der Waals fluid, though not in closed form. Writing

$$p(v) = {8\tau v^2 - 27v + 27 \over 27(v - 1)v^2},$$  

(5.16)

which is the van der Waals equation of state in units where the parameters are both 1, we have

$$h_n(\infty) = {p(v_{cav}) \over p_{eq}},$$  

(5.17)

where $v_{cav}$ is the root of

$$4\tau v^3 - 27v^2 + 54v - 27 = 0$$  

(5.18)

that lies between 1 and 3 and $p_{eq}$ is found by applying the Maxwell equal area rule,

$$\int_{v_1}^{v_2} p(v) \, dv = p_{eq}(v_2 - v_1)$$  

(5.19)

with

$$p(v_1) = p(v_2) = p_{eq}. $$  

(5.20)

Figure 5-10 compares these equations with the two existing data points. Although these simple models are not necessarily good approximations of a sorbing fluid, the independence of the curves on material specifics suggests that there might be a general trend across sorbates, though there is no reason to expect a strictly universal curve.
Figure 5-10: Relative pressure at which homogeneous nucleation occurs in the bulk in the regular solution and van der Waals models, along with two experimental data points.
Chapter 6

Drying shrinkage in hardened cement paste

The content of this chapter is based heavily on the article in preparation “Hysteresis from multiscale porosity: water sorption and shrinkage in cement paste” by the author, Masoero et al. [134].

In chapter 5, I showed that although sorption hysteresis can make it more difficult to interpret sorption isotherms, it can also allow the calculation of an additional parameter describing the pore system, namely the connectedness of the mesopores to larger pores. The situation is similar for drying shrinkage in hardened cement paste: an understanding of the processes leading to hysteresis helps to understand the overall shrinkage process.

6.1 Overview of hardened cement paste

6.1.1 Structure

The primary constituent of cement paste is calcium-silicate-hydrate (C–S–H), a semi-crystalline and non-stoichiometric solid with a layered molecular structure [167, 166, 143, 130], which is formed by hydration reactions between cement clinkers (calcium silicate minerals) and water during the setting of cement paste. The C–S–H precipi-
tation process produces a solid network containing many pores several nanometers in size: the overall material comprising both solid and pore is referred to as C–S–H gel [167, 171]. Water can be (and, in normal environmental conditions is) located within these pores, both adsorbed on pore walls and condensed into a liquid state. Additionally, the solid network itself contains water within its layered molecular structure, in spaces smaller than a nanometer [79].

The water found in cement paste is important because it influences important mechanical properties such as drying shrinkage [18, 175, 147]. This influence arises due to forces exerted on the solid structure by the water itself and ions dissolved in it. Shrinkage plays a fundamental role in cracking of cement and concrete, and so a model of shrinkage could contribute to efforts to perform quality controle, assess degradation, and design new cement-based materials that are more resilient against damage due to shrinkage and cracking. To understand and predict shrinkage and its effect on cracking, it is necessary to know where water is located as a function of humidity [12, 79, 140], what forces are present and most significant in pores of a particular size, and how the pore structure of hardened cement paste influences bulk transport of water [64].

6.1.2 Shrinkage hysteresis

In many mesoporous materials, such as Vycor, a porous borosilicate glass, shrinkage during drying is greater than at the same relative humidity during wetting. Furthermore, hysteresis is not present at low humidity, when water is not condensed in the pores but only adsorbed on pore walls. These observations are easily explained using Kelvin-Laplace theory: there is a negative pressure in the water in the pores, and since there is more water present at the same humidity on drying than wetting (as explained in chapter 5), the shrinking effect is greater [19, 142].

Hardened cement paste has the opposite behavior: shrinkage is greater during wetting than during drying, and the hysteresis extends over the entire range of relative humidity. This hysteresis behavior is also found in clays [128, 35]. In both cement paste and clay, evaporable water can be found in molecular-scale spaces between layers
Figure 6-1: Water sorption and shrinkage isotherms for (a, d) Portland cement paste [58], (b, e) raw clay with calcium ions in the molecular layers [36], and (c, f) Vycor glass [73]. Notice that the drying (red) and wetting (blue) strain paths for cement paste and clay (d, e) are upside-down compared with those of Vycor (f). Figure courtesy of Enrico Masoero.

of the solid skeleton, suggesting that it is the removal and reinsertion of this water that causes the “upside-down” shrinkage hysteresis. Figure 6-1 compares sorption (in which hysteresis is in the same direction, though quantitatively different) and shrinkage isotherms for cement paste, clay and Vycor. Figure 6-2 illustrates the water content of hardened cement paste over a drying and wetting cycle.

In this chapter, I present an overall picture of the pore spaces in which water may be found, and a model of how water sorption in these spaces determines shrinkage. Section 6.2 outlines the different types of water found within hardened cement paste. Section 6.3 explains how ideas from chapter 5 can be used to deduce the quantity of water present in each location as a function of relative humidity, while section 6.4 uses the division by type to develop a continuum model of shrinkage.
Figure 6-2: (a) Backscattered scanning electron micrograph of a polished cement paste surface. (b) Experimental water sorption isotherm [59]. (c) Schematic diagrams illustrating the C–S–H water content at the six points marked on the isotherm. A: saturated state with large capillary pores empty. B, F: configurations at the same relative humidity, but different water content, on drying and wetting. C, E: same, at a lower humidity. D: an almost completely dried configuration. Figure courtesy of Enrico Masoero and Hamlin Jennings.
This work was performed in collaboration with Enrico Masoero et al. I developed the quantitative model of shrinkage, as well as contributing to the development of the overall ideas regarding the importance of water present in different locations.

6.2 Classification of water in cement paste

Water can be divided into four categories based on its local environment within the cement paste microstructure.

6.2.1 Interlayer water

Interlayer water is found in spaces with width less than about one nanometer. It is bound strongly and removed only at low relative humidity. If C–S–H is considered to have a particulate or granular structure [79], interlayer water includes both that between layers within a single particle, and that between particles where they are in close contact. It is well documented [126, 79] that there is substantial collapse and swelling of the interlayer space as water is removed and re-inserted, respectively.

6.2.2 Gel pore water

The C–S–H gel formed during cement hydration is inevitably porous, as the product density is higher than the average density of the reactants. The gel porosity is defined in the cement literature as the minimum porosity achievable: that resulting when reaction products uniformly (on a large enough length scale) fill the originally water-filled space, leaving no capillary pores [136]. Gel pores have width between approximately 1 and 10 nanometers.

6.2.3 Capillary pore water

Capillary pores are the voids left in regions not filled by C–S–H during hydration. They range in size from 10 nanometers up to hundreds of micrometers. The smaller end of this range may include some pores intrinsic to the C–S–H gel [12, 114], but
since pore properties depend fundamentally on size, we include these pores in the capillary pore category.

### 6.2.4 Surface adsorbed water

When gel and capillary pores are empty of condensed water, they retain an adsorbed layer of water on their pore walls due to the hydrophilic nature of the C–S–H surface. This adsorbed water is influential in determining shrinkage because it affects the surface energy of the solid/pore interface.

### 6.3 Water sorption isotherm of hardened cement paste

#### 6.3.1 Interlayer water

The Kelvin equation (equation 4.3) implies that water will not be removed from the interlayer space until low relative humidity, around 14%. This is supported by molecular simulations [24, 25] and nuclear magnetic resonance (NMR) experiments, which are able to determine the size of the pore in which water is located [113]. The removal of water at lower humidities is a complex process which depends on chemical and electrostatic interactions between water, ions and the C–S–H surface. I make the very simple approximation that water is removed from the interlayer space linearly between 15% and 0% relative humidity.

Modeling the reinsertion of water requires more care. Direct measurements of interlayer water content on wetting are not yet available, so I use Jennings’ analysis [79] of the experimental data of Feldman [56]. To experimentally determine the interlayer water content on the adsorption branch at a particular relative humidity, the sample is first fully dried, then equilibrated at the desired humidity. This procedure ensures that the interlayer water content reaches (local) equilibrium at that humidity, and for sufficiently high relative humidity will also result in some water being present in the gel pores. The humidity is then decreased from the level of interest down to a level at which the gel pores are empty of condensed water: in this case, 11%
From the water that remains, the quantity adsorbed on pore walls must be subtracted: this was estimated as 0.25 moles per mole of C–S–H [79]. The result is the interlayer water content at the turning point on adsorption. Possessing an estimate of the interlayer water content on adsorption and desorption, the remainder of the water must be adsorbed and condensed in the gel and capillary pores.

6.3.2 Gel and capillary pore water

The total water content of the gel and capillary pores is the experimentally observed water content minus the interlayer water content. Equations 5.3, 5.6 and 5.14 can then be used to rationalize this observed pore water content in terms of a pore size distribution and connectivity to the largest pores. In particular, these equations allow the calculation of the quantity of adsorbed and condensed water at any particular humidity. These quantities, along with the interlayer water content, are shown in figure 6-3 and used in the model of drying shrinkage presented in section 6.4.

6.4 Continuum modeling of reversible drying shrinkage

Knowing the quantity of water in each category as a function of humidity on wetting and drying, it is possible to model reversible drying shrinkage due to the changing water content. “Reversible” as a descriptor of drying shrinkage means that a bulk sample returns to its original dimensions when fully resaturated: there is still extensive hysteresis in the strain at intermediate humidity values. Irreversible drying shrinkage, when the sample does not return to its original dimensions on resaturation, is observed primarily on the first cycle of drying and rewetting, and the mechanisms for this are not part of the models discussed here. We assume throughout that shrinkage is isotropic, so the linear strain measured in experiment is one third of the volumetric strain.

Several continuum models of deformations induced by humidity changes have been
Figure 6-3: Contributions to the water sorption isotherm from (a) water adsorbed on pore walls, (b) water present in filled gel and capillary pores, and (c) water present in the interlayer space, along with (d) the overall model result (red) obtained by adding the three curves at left, along with the experimental isotherm (black) for bottle-hydrated Portland cement [58]. Figure courtesy of Enrico Masoero, from data calculated by the author.
proposed [18, 175, 147]. These models are based on poromechanics and relate the volumetric strain to the Laplace pressure in the pore water (also known as capillary stress). We extend such modeling to account also for the effects of surface energy, and swelling caused by water in the interlayer space [129].

Since cement paste is isotropic at the bulk scale, and there is no external load, drying shrinkage is isotropic and hence the linear strain is one third of the volumetric strain. The linear strain (which is less than 0.5%) is sufficiently small that the constitutive equation for cement paste is linear, so the strain can be decomposed into three contributions: $\varepsilon_L$ from Laplace pressure in the gel and capillary pores, $\varepsilon_S$ due to surface energy, and $\varepsilon_I$ from swelling caused by the interlayer water. These contributions can be associated with three categories of water described in section 6.2 (gel and capillary pore water considered together since water has bulk properties in both; surface-adsorbed water; and interlayer water). The low strain magnitude also means that there is negligible change in gel and capillary pore widths. I also neglect the effect of any gradient in saturation, as this will be small when the relative humidity is changed in steps and the system allowed to equilibrate.

### 6.4.1 Macroscopic length change due to Laplace pressure

A simple and widely-used constitutive model describing the strain of a porous material due to Laplace pressure in the gel pore water is [19, 175]

$$\varepsilon_L = \frac{1}{3} \frac{kT}{a^3} \ln h S \left( \frac{1}{K_b} - \frac{1}{K_s} \right). \quad (6.1)$$

Here $kT \ln h/a^3$ is the Laplace pressure in the pore water, $K_b = 19$ GPa is the bulk modulus of the macroscopic sample, $K_s = 50$ GPa is the bulk modulus of the solid part of the C–S–H gel [99] and $S$ is the filling fraction of the gel and capillary pores.

### 6.4.2 Macroscopic length change due to surface energy

To calculate the macroscopic length change associated with a change in surface energy, the Bangham equation [8, 138, 74] must be modified to account for additional surface
area as pores empty. The linear strain due to surface energy is then

\[ \varepsilon_S = -\frac{\Delta(\sigma\gamma)}{3K(1-2\nu)}, \]  

(6.2)

where \( \sigma \) is the surface area of empty pores per volume of porous material and \( \gamma \) is the total surface tension of the pore wall with its adsorbed layer (note that “empty” pores retain a layer of water adsorbed on their walls). Consequently \( \Delta(\sigma\gamma) \) is the change in the total surface energy; \( \nu \) is Poisson’s ratio of the bulk macroscopic volume, approximately 0.2 (see e.g. [150]). At 100% RH all pores are full, with the possible exception of some very large pores with low surface area, so \( \Delta(\sigma\gamma) = \sigma\gamma \).

The surface tension is given by Gibbs’ equation [57, 138]:

\[ \gamma = \gamma_0 - \frac{kT}{a^2} \int_{h_0}^{h} \frac{dh}{\frac{t}{h}}, \]

(6.3)

where \( \gamma_0 \) is the surface tension at \( h_0 \). It is convenient to use complete drying, 0% relative humidity, as the reference point. The solid-air surface tension at this humidity must be assumed: I estimate a value twice that of water-air.

6.4.3 Macroscopic length change due to loss of interlayer water

It is well established that many layered materials experience expansion when a substance is intercalated into them [49, 46, 185, 90], but the details of this expansion can be complex. An accurate model of the relationship between the quantity of interlayer water in C–S–H and the associated length change of the macroscopic cement paste sample will be rather difficult to develop. The presence of dissolved ions produces a repulsive osmotic pressure, but this is small: a mean field treatment with walls separated by 0.5 nm gives a pressure around 1 MPa or less, regardless of ion concentration [4]. More important are effects arising due to the discreteness of ions: correlation effects can even result in a force that is joining instead of disjoining [129].

In the absence of a detailed model that accurately predicts length changes due
to changes in interlayer water content, useful progress can be made with the simple assumption that the strain of the bulk cement paste is isotropic and is linearly proportional to the quantity of interlayer water, such that

$$\varepsilon_I = \frac{\lambda}{3} v_I$$

(6.4)

where $v_I$ is the volume of interlayer water (which can be calculated using the method described in the previous section: see figure 6-3), and $\lambda$ is a proportionality constant. Although $\lambda$ is found empirically in this work and thus may be considered a fitting parameter, it has an important physical meaning: it measures the proportion of microscopic strain that is translated into bulk strain, rather than simply being accommodated by the porous material. The value calculated here could potentially be used to assess a microscopic model linking microscopic and macroscopic strains in cement paste. The quantity may also be estimated from experimental measurements. X-ray diffraction experiments have found 20% shrinkage of interlayer space while the macroscopic shrinkage of the bulk was only 3\% [72]. Similarly, digital image-based deformation mapping has found local deformations around 10\% while overall strain was less than 0.5\% [116]. These observations suggest that the heterogeneous structure of cement paste is capable of taking up most of the microscopic length change, and only a small fraction is transmitted to overall strain. $\lambda$ should therefore have a value around 0.1.

### 6.4.4 Comparison with experiment

Figure 6-4 shows the overall predicted shrinkage calculated using this model, along with the contributions from each of the three sources, and experimental data measured by Feldman [58]. The unknown parameter $\lambda$ is used as the only fitting parameter: the best-fit value obtained is 0.07. The combined model successfully reproduces the magnitude and general shape of the hysteresis in the reversible drying strain across the entire range of humidity.

The model explains the sources of the observed shrinkage and its hysteresis. There
Figure 6-4: Predicted shrinkage due to water (a) on the surface of C–S–H, (b) in the gel pores, and (c) in the interlayer spaces, along with (d) total predicted and experimentally measured [58] shrinkage. Figure courtesy of Enrico Masoero, from data calculated by the author.

is little hysteresis in the shrinkage caused by surface tension, and the hysteresis in the shrinkage caused by Laplace pressure is in the opposite direction to the overall shrinkage hysteresis. Only by accounting for the swelling effect of interlayer water can the observed hysteresis in the shrinkage be understood. For this reason, models based exclusively on Laplace pressure have been unable to explain experimental results [175]. The importance of interlayer water also means that if a sample is not dried below approximately 15% relative humidity, much of the shrinkage hysteresis will disappear, and the remaining hysteresis will be in the opposite direction. That is, shrinkage as a function of relative humidity will be greater during desorption than adsorption, as is observed in many other porous materials such as Vycor. This claim is partly confirmed by the data of Feldman and Sereda, who observed that the upside-down shrinkage hysteresis disappears when re-wetting is started before drying below 25% RH [57].
6.5 Potential future extensions

The model presented here used indirect methods to determine the water content of each type of space, and thence calculate shrinkage. Since NMR techniques are able to more directly measure the water content of the various spaces [114], if NMR data were available over a full wetting and drying cycle, a more confident prediction of shrinkage could be made. Nevertheless, this work has shown that classifying the water in cement paste according to its location and then modeling the physical behavior of each of these water types separately allows the overall behavior of the paste to be better understood.

The understanding of the fundamental importance of the difference between water in different locations, and of the different humidity ranges over which these locations empty and fill, opens the door to a new perspective for designing experiments that extract information about the microstructure of cement based materials. For example, the gel pores can be probed without interference from interlayer space by only drying to about 25\% RH. The size distribution of the gel pores can then be analyzed from the adsorption isotherm, and their connectivity to the larger pores by analysis of the hysteresis. This could be used, for example, to assess the gel pore ratio and initial water to cement ratio of an existing sample of cement. The structure of gel pores can change due to drying, load, or even deliberate alteration such as by filling these 10-100 nanometer-scale spaces with polymer [108]. Since such a change in structure will greatly influence properties, this technique for assessing the gel pore structure would be a valuable research tool. In addition, it can complement and support the validation of a growing body of mesoscale coarse-grained simulations aimed at elucidating the mechanisms of formation, the nanoscale structure, and the mechanical properties of the C–S–H gel [69, 107, 101, 68, 102, 77, 53]. There is also much scope for interesting research on the kinetics of water leaving each kind of space. Chapter 7 examines water dynamics in the larger pores, but the problem of dynamics in the interlayer space remains open.
Chapter 7

Modeling of transport with hysteresis in porous materials

I now turn to the problem of transport of a sorbing fluid through a porous material. One reason that such transport is important is that it plays a role in the degradation of many porous materials [158, 106], such as creep, corrosion and contamination in concrete [55, 149, 20, 65]. Other important areas of application include carbon dioxide sequestration in sorbents such as zeolites or activated carbon [39], and shale gas extraction [78].

7.1 Model formulation

For a sorbing fluid, Darcy’s law (equation 4.5) must be written as

\[ q = -\frac{c \kappa}{\tau \mu} \nabla p, \]  

(7.1)

where \( c \) is the saturation of fluid (that is, its coarse-grained concentration relative to the maximum possible), since flow only happens where there is fluid. \( \tau \) is a correction for tortuosity: a typical model, known as the Bruggeman relation, is that it is proportional to \( c^{-1/2} \) [31]. Since the pore network itself has a tortuous structure in the porous material, there should be an additional constant factor: I use a factor of 3
as suggested by Gruener et al. [71]. The other fundamental principle describing flow
is conservation of mass, which can be written as

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{q}$$

(7.2)

To close this system of equations, it is necessary to know the relationship between
pressure and saturation, and obtaining a suitable relationship is the most important
step in the development of the model presented here.

First, I note that there is a well-defined relationship between relative pressure $h$
in the vapor phase and pressure $p$ in the liquid phase, given by

$$p = \frac{kT}{v} \ln h,$$

(7.3)

where $v$ is the average molecular volume in the liquid phase. Air pressure may be
ignored because it is so much smaller than liquid pressures at partial pressures below
saturation. Since the adsorption isotherm gives saturation as a function of relative
pressure, it gives an upper bound for liquid pressure as a function of saturation.

A general expression relating liquid pressure and saturation relies on assumptions
about the processes that govern sorption. The assumption I use is that the adsorp-
tion isotherm, which marks the minimum quantity that can be sorbed at a particular
partial pressure, gives the stable quantity of fluid based on local considerations. Any
additional sorption must be trapped due to non-local considerations such as network
effects. Note that the term “trapped” simply refers to the absence of any monoton-
ically decreasing path on a free energy landscape from the full to the empty state.
There is no kinetic blocking and the sorbate is free to move through the region oc-
cupied by trapped water. The measured saturation at some partial pressure can be
divided into stable and trapped parts $c_s$ and $c_t$:

$$c(h, ...) = c_s(h) + c_t(h, ...),$$

(7.4)

where $c_s(h)$ is given by the adsorption isotherm and is an empirical input to the
model. The form of the functions $c$ and $c_t$ denotes that they depend on more than just the current local partial pressure.

I propose as a reasonable assumption that the maximum fraction of the pore space not filled with stable fluid that can be filled with trapped fluid is a function of the total fluid content, and denote this function as $\bar{g}(c)$. An experimental desorption isotherm $c^\downarrow(h)$ then allows the calculation of $\bar{g}$:

$$c^\downarrow(h) = c_s(h) + \bar{g}[c^\downarrow(h)][1 - c_s(h)].$$  \hspace{1cm} (7.5)

Likewise, for any state $(h, c)$, not necessarily accessed by a desorption isotherm, it is possible to define an analogous fraction $g$ by

$$c = c_s(h) + g[1 - c_s(h)].$$  \hspace{1cm} (7.6)

Since we know the relationship between $c_s$ and $h$, our description of the problem will be complete if we determine a method for allocating changes in total saturation to $c_s$ and $c_t$. I do this by making the approximation that the probability that a pore is full of trapped water is independent of the radius of the pore and hence the partial pressure at which it will fill (assuming of course that the partial pressure is above the filling pressure). In this case, increasing $c$ will not affect $g$, and the ratio of trapped fluid turned into stable fluid to new fluid added will be $g/(1 - g)$, so

$$\delta c_s = \delta c + \frac{g}{1 - g}\delta c.$$  \hspace{1cm} (7.7)

When sorbate pressure is decreased, stable fluid will be turned into trapped fluid and lost from the local region in proportion $\bar{g}$ to $1 - \bar{g}$. Additionally, the loss of fluid will cause $g$ to decrease. The assumption that trapping is independent of pore size implies that

$$\frac{1}{g} \frac{dg}{dc} = \frac{1}{\bar{g}} \frac{d\bar{g}}{dc},$$  \hspace{1cm} (7.8)
\[ \delta c = (1 - \bar{g}) \delta c_a + \frac{c_t}{\bar{g}} \frac{d\bar{g}}{dc} \delta c. \] (7.9)

Using equations 4.5-7.3, 7.7 and 7.9, it is now possible to simulate transport in a porous medium with arbitrary initial and boundary conditions.

7.2 Results

As an interesting example of transport of a sorbing fluid through a porous medium, I look at water sorption in hardened cement paste. Experimental adsorption and desorption curves are taken from the work of Baroghel-Bouny [12]. Simulations are performed for a prismatic slab 50 cm in thickness, assuming an intrinsic permeability of \((2 \text{ nm})^2\), since 2 nm is a typical pore radius.

7.2.1 Time-dependent hysteresis curves

One problem that can be tackled with this method is the identification of the contribution of transport effects to dynamic hysteresis curves, obtained when the atmospheric humidity is changed too rapidly to be equilibrated across the sample. To simulate these curves, the humidity at the surface of the sample was allowed to oscillate between 0 and 1 with period ranging from 1 hour to 1 month. The total mass of water sorbed in the cement is plotted in figure 7-1 as a function of the instantaneous humidity (in the limit of long time, when the response is periodic). The mass change can be seen to shrink as the humidity variation becomes too fast to be transmitted through the sample.

Very different results are obtained if the sample is dried from complete saturation to 2% relative humidity over a time equal to half of each of the periods tested and allowed to equilibrate at this humidity for a month, then humidity is increased back to 100% over the same timespan. In this case, faster humidity changes lead to wider hysteresis curves: figure 7-2

These two tests are simply examples of the conditions that can be simulated with
Figure 7-1: Average saturation as a function of instantaneous relative humidity when humidity is cycled with a period of 1 month (pink), 1 week (green), 1 day (blue) and 1 hour (red).
Figure 7-2: Average saturation as a function of instantaneous relative humidity when humidity is cycled with a period of 1 month (pink), 1 week (green), 1 day (blue) and 1 hour (red), with a month’s equilibration at 2% relative humidity between drying and wetting.
7.2.2 Saturation-dependent apparent diffusivity

A different approach to the analysis of transport through porous materials has been to assume that a diffusion equation,

\[ q = -D \nabla c, \tag{7.10} \]

can be written, with an effective diffusivity \( D \) that depends on \( c \) [100, 13]. Although this approach does not offer insight into the physical processes governing transport, it can be a convenient way of expressing experimental observations. Using equation 7.1, we can write the effective diffusivity as

\[ D = \frac{\kappa k T}{\tau \mu \nu h} \frac{dc}{dh}. \tag{7.11} \]

Using the above value for \( \kappa \), the term \( \kappa k T/(\mu \nu) \) has value \( 6 \times 10^{-7} \) m² s⁻¹. The calculated effective diffusivity as a function of saturation for a particular sample of hardened cement paste [12] is shown in figure 7-3.

7.3 Humidity-dependent permeability

Although this method seems to be a useful approach to modeling transport in a porous material with sorption hysteresis, there remains the fundamental problem that it substantially overpredicts transport rates. The intrinsic permeability of hardened cement paste is not around \( 10^{-17} \) m² as may be expected, but around \( 10^{-20} \) m² [9, 174, 184]. It may be that a more detailed treatment of where water is present and absent in the porous material can correct this discrepancy. I propose here two stages of development by which this could be incorporated into the transport model. Although the current version of the model does not include this development, continuing work in the Bazant research group, especially by Tingtao Zhou, is focused on
Figure 7-3: Calculated effective diffusivity along the wetting (blue) and drying (brown) isotherms for a sample of hardened cement paste [12].
its implementation.

7.3.1 Pore size

The current version of the transport model uses an intrinsic permeability that is, apart from a simple model for tortuosity, independent of humidity. Since smaller pores fill at lower humidity than larger pores, this independence is certainly an approximation and perhaps an unreasonable one. A simple first step towards including the effect of filling pores of different sizes would be to keep track of the size of pores filled, which can be determined by applying the model of chapter 5 to the adsorption isotherm. Taking a weighted average over the full pores, it will then be possible to calculate an intrinsic permeability.

One immediately apparent consequence of such a technique is that we can expect higher permeability during drying than wetting, as larger pores remain full due to pore blocking. The technique is, however, unlikely to fully account for the discrepancy between predicted and observed intrinsic permeabilities, as a permeability of $10^{-20}$ could naively be associated with pores of width smaller than a molecule, clearly an unreasonable proposition.

7.3.2 Pore connectedness

A potential solution to this difficulty would come from a consideration of the connectedness of pores. Throughout this thesis, pores of various sizes have been considered without any discussion of the configuration of the solid skeleton that forms these pores. A proposed model of the structure of hardened cement paste suggests that it may be thought of as a colloidal or granular material with grains of a few nanometers in size [79]. In such a case, the first water to condense as humidity is increased will be located in thin bridges near the contact points of grains. Such bridges will not be connected, and if the adsorbed water is held in place by strong forces from the grain surfaces, there will be no flow. The permeability will thus be much lower than expected, especially at low humidity.
A percolation model will be needed to allow the calculation of permeability of configurations approximating the actual distribution of water. A network with pore sizes assigned randomly from an appropriate distribution would be insufficient, because the true porous material most likely enhances the probability that small pores are disconnected, due to the alternating arrangement of tiny bridges and larger interstices surrounded by more than two particles.

A better model can be built by beginning with a random packing of particles: identical spheres are probably sufficient. The Young-Laplace equation can be used to find a stable configuration of condensed water in the material, as a function of humidity. Some suitable measure of permeability can then be found on this system.

Below some saturation, which could be found with this model, there will be no connected path of condensed water spanning the system and hence no possibility of fluid flow. In this case, Knudsen diffusion in the vapor phase may be the dominant transport mechanism.

7.4 Inclusion of detailed modeling of hysteresis mechanisms

The transport model of this chapter is largely independent of the sorption model of chapter 5. There are simplifications in the model that could be refined using the sorption model. For example, the transport model assumes at every time that the trapped water is distributed uniformly across all pore sizes above those filled with stable water. In some situations, this is manifestly false. Consider, for example, a system that is uniformly brought from humidity $h_3$ to $h_1$, then returned to $h_2$, where $h_1 < h_2 < h_3$, and humidity then decreased again from $h_2$. Those pores that filled just below $h_2$ will now contain trapped water with probability $\bar{g}$ calculated at $h_2$, while those that fill above $h_2$ were never refilled during rewetting, and contain trapped water only with probability $\bar{g}$ calculated at $h_1$. This difference is ignored in the model here. A model could be developed that keeps track of $g$ as a function of
pore size, and indeed the model of Mualem is set up in this way [112]. For simplicity, however, I chose not to include this feature, assuming that for many typical applied humidity protocols it would be unimportant.
Chapter 8

Conclusions and outlook

8.1 Battery degradation

We have developed a general theoretical framework to model capacity fade and lifetime statistics in rechargeable batteries, focusing on the mechanism of SEI formation at the anode. We have shown that a very simple single particle reaction model is sufficient to quantitatively understand SEI formation on graphite, since it provides a good fit to observed capacity fade. Moreover, computational results with a more complicated porous electrode model of capacity fade show that no significant spatial variations form at the cell level. The temperature dependence of the diffusivity of the limiting reacting species through SEI can be modeled using an Arrhenius dependence. This model can be used to model the degradation of rechargeable batteries in a variety of thermal conditions, to guide and interpret accelerated aging experiments, and to understand the statistics of battery lifetime. The model can also be extended to account for rapid SEI growth due to area changes and SEI loss, which occur, for example, in nanostructured silicon anodes.

Although we have focused on SEI formation in Li-ion batteries, some of our models and conclusions may have broader relevance to other battery technologies, not involving ion intercalation. It is important to emphasize that, although SEI growth leads to capacity fade, it also plays a crucial role in rechargeable battery engineering. The formation of a stable SEI layer protects the anode at large negative potentials.
and allows the design of high-voltage batteries operating outside the voltage window for electrochemical stability of the electrolyte. The same general principle enables the stable operation of lead-acid rechargeable batteries (at a voltage of over 2 V), where the half-cell reactions at the lead anode and the lead oxide cathode both form amorphous lead sulfate films, which allow active ions to pass, while suppressing water electrolysis outside the voltage window of the sulfuric acid electrolyte (approximately 1 V) [137]. In that case, capacity fade can also occur by irreversible reactions involving active species via lead sulfate crystallization ("sulfation") [43, 182, 111, 148]. Although this capacity fade mechanism differs from SEI formation in Li-ion batteries in the microscopic details, the engineering consequences are the same (increased interfacial resistance and loss of active material), and it may be possible to apply and extend our models of capacity fade and lifetime prediction to this and other rechargeable battery systems.

8.2 Sorption and transport in porous materials

The latter portion of this thesis has presented modeling covering various aspects of sorption in porous media, with particular relevance to water in cement paste. Chapter 5 showed that a simple model can explain sorption and its hysteresis in a range of porous materials. This model accounts for some degree of hysteresis at the single-pore level, as well as the effect of the porous network in suppressing nucleation of the vapor phase by a liquid-vapor interface. The model allows calculation of the pore size distribution as well as a measure of the connectedness of the mesopores to larger pores in the material.

Some more detailed questions related to this model remain open. The assumed single-pore sorption behavior, in particular the hysteresis between filling and emptying, was validated only for carbon nanotubes, through comparison of the peak in the pore size distribution found by the model with the nanotube size measured by transmission electron microscopy. In other cases, especially materials with pores of a very different shape, it may be that a different single-pore isotherm is more appropriate.
This would not harm the general principles of the model, but would change the relative contribution of single-pore and network effects to hysteresis, and the calculated pore size.

Also, the assumed surface adsorption is based on a very simple model, lacking both interactions between molecules within an adsorbed layer, and interactions of the surface with molecules beyond the first adsorbed layer. A more accurate quantification of surface adsorption, which may need to be specific to each sorbate-sorbent pair, could improve the agreement of the model with experimental data at lower relative pressure.

The model accounts, in an empirical way, for the existence of fluid in spaces at a scale smaller than the mesopores in which a continuum description of condensation is sufficient. This is especially important for water in hardened cement paste. Molecular simulation techniques such as grand canonical Monte Carlo [25] may be able to explain the observed quantity of water as a function of humidity, based on first principles. Even without such an explanation, the recognition of the role of this water enables substantial progress in the modeling of drying shrinkage, as shown in chapter 6.

Chapter 7 describes a simple model of transport through a porous material that accounts for sorption hysteresis. The model is able to capture dynamic hysteresis, and can be used to simulate arbitrary applied humidity (or more generally, sorbate partial pressure) conditions.

Although the principles of the model seem sound, it does not yet agree quantitatively with experimental results: specifically, it predicts faster transport of water through cement paste than is actually observed. This could be due to the porous structure producing a disconnected or poorly-connected configuration of water at all but rather high humidities. I have proposed some ways to extend the model to account for this.

Other important extensions of the models presented here will be aimed at applying the models to applications of particular relevance to engineering. An example of such an application is moisture-buffering materials [119]. These materials take up water from, and release water to, the atmosphere and moderate humidity changes, and are
used in construction for purposes such as to increase comfort or reduce damage to fragile objects. If the design of such materials is to be optimized, it is important to understand what factors influence water sorption. Also, a dynamical model that accounts for the link between sorption and transport is needed to assess the effectiveness of materials in proposed operating conditions.

Another situation where transport modeling is very important is understanding the degradation of porous materials such as concrete. Important degradation processes in concrete include corrosion of reinforcements [1], reactions between ions dissolved in the pore water and the concrete itself [65], and the freezing and thawing of pore water [54]. All of these degradation mechanisms rely on the presence of water, so an understanding of its transport through the material is an important ingredient in the modeling of degradation. The transport model will need to be extended when it is not directly the water that causes damages, but ions dissolved in the water. In this case, convection of ions carried by flowing water as well as diffusion of ions must be considered, as well as electrostatic effects that may influence the relative prevalence of ions in pores of different sizes and reactions that consume or produce ions.

Another degradation process is cracking due to differential shrinkage on non-uniform drying [17]. Modeling of this process will require a combination of transport and shrinkage models such as those presented here. Additionally, since cracking occurs predominantly during first drying, when the hydration reactions that lead to cement setting are still proceeding, a complete model must account for the consumption of water and changes in the pore structure due to chemical reactions. The complex interaction of several physical processes is a reason why models that elucidate the underlying mechanisms are needed, and why scientific and engineering research in these areas will continue.
Bibliography


[38] Candace K. Chan, Riccardo Ruffo, Seung Sae Hong, and Yi Cui. Surface chemistry and morphology of the solid electrolyte interphase on silicon nanowire lithium-ion battery anodes. *Journal of Power Sources*, 189(2):1132–1140, April 2009.


