EROSION AND RE-DEPOSITION OF LITHIUM AND BORON COATINGS UNDER HIGH-FLUX PLASMA BOMBARDMENT

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Abstract

Lithium and boron coatings have been applied to the walls of many tokamaks to enhance performance and protect the underlying substrates. Li and B-coated high-Z substrates are planned for use in NSTX-U and are a candidate plasma-facing component (PFC) for DEMO. However, previous measurements of Li evaporation and thermal sputtering on low-flux devices [1, 2] indicated that the Li temperature permitted on such devices may be unacceptably low. Thus it is crucial to characterize gross and net Li erosion rates under high-flux plasma bombardment. Additionally, no quantitative measurements have been performed of the erosion rate of a boron-coated PFC during plasma bombardment. A realistic model for the compositional evolution of a Li layer under D bombardment was developed that incorporates adsorption, implantation, and diffusion. A model was developed for temperature-dependent mixed-material Li-D erosion that includes evaporation, physical sputtering, chemical sputtering, preferential sputtering, and thermal sputtering. The re-deposition fraction of a Li coating intersecting a linear plasma column was predicted using atomic physics information and solving the Li continuity equation.

These models were tested in the Magnum-PSI linear plasma device at ion fluxes of $10^{23}-10^{24}$ m$^{-2}$ s$^{-1}$ and Li surface temperatures $\leq 800$ °C. Li erosion was measured during bombardment with a neon plasma that will not chemically react with Li and the results agreed well with the erosion model. Next the ratio of the total D fluence to the areal density of the Li coating was varied to quantify differences in Li erosion under D plasma bombardment as a function of the D concentration. The ratio of D/Li atoms was calculated using the results of MD simulations and good agreement was observed between measurements and the predictions of the mixed-material erosion model, which imply significantly lower erosion rates for a deuterium-saturated Li layer relative to pure Li. These results imply that predicted temperature limits [3] for Li-coated high-Z PFCs in a tokamak are pessimistic. If a Li coating is well-saturated with deuterium, low erosion rates will be maintained even at surface temperatures where the evaporative and sputtered flux
from pure Li would dwarf the incident ion flux. Li coatings were observed to disappear from graphite much faster than from TZM Mo, indicating that fast Li diffusion into the bulk graphite substrate occurred. Li re-deposition fractions very close to unity are observed in Magnum-PSI, consistent with predictions from modeling. In addition, the gross erosion rate of boron coatings was measured for the first time in a high-flux plasma device. Finally, predictions of Li coating lifetimes in the NSTX-U divertor are presented.
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To my grandmother, Carmela Mary Lohrmann

The smartest woman I have ever known
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Chapter 1

Introduction

1.1 Energy use in the 21st century

As global energy consumption steadily rises, it becomes increasingly important to meet this added demand with clean power sources. Averaging over various models, it is predicted that the world’s electrical power production will increase by a factor of six from approximately 2 TWe (Terawatts-electric) in 2000 to about 12 TWe in 2100; see Figure 1.1. It has been estimated that only about 40% of this load can reasonably be generated by renewable sources, and about half of the remainder (30%) could reasonably be generated by nuclear power [4]. Supplanting this 30% fraction with coal power (with no carbon sequestration) for the remainder of the century would result in a long-term increase in atmospheric CO$_2$ concentration by $\sim$80 ppm and a global-average surface temperature rise of about 1 °C, with even more dire predictions for the following century [5] [6]. This motivates the rapid development and expansion of nuclear power, which specific emphasis on fusion power due to the inherent drawbacks associated with fission, which will be discussed below.
1.2. Overview of nuclear power

1.2.1 Nuclear fission

All nuclear power currently distributed to the grid comes from nuclear fission, which consists of splitting heavy elements into lighter elements. The vast majority of fission reactors in operation are light-water reactors (LWRs), which use uranium-235 ($^{235}$U) as the primary fuel, although significant plutonium-239 ($^{239}$Pu) is also bred and burned during operation. An example reaction resulting from nuclear fission of $^{235}$U is as follows:

$$n + ^{235}\text{U} \rightarrow ^{89}\text{Kr} + ^{144}\text{Ba} + 3n \ (215 \text{ MeV}) \quad (1.1)$$

Power production from nuclear fission increased drastically throughout the 1960s and 1970s. However, dating from approximately the time of the Chernobyl disaster in 1986, sociopolitical resistance and increasing cost overruns have led to the total number of operating nuclear power plants re-
1.2. Overview of Nuclear Power

Remaining only constant or even decreasing year-by-year for the last two decades [8]. The recent catastrophic failure of the Fukushima Daiichi nuclear power plant has further exacerbated public tensions and led to more shutdowns in Japan, Germany, and several other nations [9].

Several other significant issues exist with nuclear fission power plants that remain unresolved. For example, nuclear weapons proliferation is a serious threat. The same techniques (such as mass centrifuges) used for enriching natural uranium (∼0.7% $^{235}\text{U}$) to fuel-grade (∼4.5% $^{235}\text{U}$) can be used to enrich the fuel up to weapons-grade (∼90% $^{235}\text{U}$). In addition, no solution has been developed for the long-term storage of nuclear waste. Attempts to create a domestic storage facility, even in remote locations such as Yucca Mountain in Nevada, have been met with strong political resistance. All of these concerns motivate the development of an alternative form of nuclear energy. Nuclear fusion holds this promise.

1.2.2 Nuclear fusion

Nuclear fusion, in direct analogue to fission, refers to the strongly exothermic reactions that occur when light atomic nuclei are placed in extremely close proximity. The primary fusion reaction exploited for the purpose of developing a nuclear reactor is as follows:

$$2^\text{H} + ^3\text{H} \rightarrow ^4\text{He} + \text{n} \ (17.6 \text{ MeV}) \ (1.2)$$

This reaction provides an energy/mass ratio of 3.5 MeV/amu, as opposed to 0.9 MeV/amu in fission and $10^{-7}$ MeV/amu burning fossil fuels. A fusion reactor producing 1 GWe/yr will consume approximately 110 kg of deuterium and 170 kg of tritium annually. For comparison, a coal power plant utilizes approximately $10^9$ kg of coal each year. Deuterium, being a stable isotope of hydrogen, is extremely plentiful in the earth’s oceans. Tritium, however, is radioactive with a decay time of approximately 12.3 years, so it does not appear naturally on earth. It can be produced through
the fission of lithium-6:

\[ n + ^6\text{Li} \rightarrow ^3\text{H} + ^4\text{He} \ (4.8 \text{ MeV}) \]  

(1.3)

The estimated global reserves\[1\] of natural lithium are 12 million metric tons \[10\], of which about 7.5\% is lithium-6. This implies that D-T fusion can produce approximately 2400 TWe-years of electrical energy, or enough to supply all the world’s electricity for 1200 years at current consumption levels.

The abundance of fuel for nuclear fusion, coupled with the lack of each of the three major drawbacks of nuclear fission discussed above (safety, proliferation, and waste) make fusion an extremely attractive prospect. However, unlike fission power where the probability of fission is maximized at thermal energies, nuclear fusion requires the reactants to reach extremely high temperatures—on the order of \( kT =10 \text{ keV} \), where \( k \) is Boltzmann’s constant \((1.38 \cdot 10^{-23} \text{ m}^2\text{kg s}^{-2}\text{K}^{-1})\), or equivalently \( T \approx 120,000,000 \text{ °C} \). At these temperatures, atomic nuclei are stripped of their electrons, becoming positively charged and forming a state of matter known as a plasma.

Intuitively, the requirement for plasmas to become extremely hot for significant nuclear fusion to occur can be understood as follows. Positively charged deuterium and tritium nuclei tend to repel during collisions due to the strong Coulomb potential barrier. However, if the nuclei are sufficiently energetic, a high probability exists of tunneling through this potential barrier and causing a fusion event to occur. Of course, these events also become more probable if there are more ions per unit volume (higher density) or if they spend more time in the plasma before escaping (better confinement). Quantitatively, the requirement for net energy production can be estimated by the Lawson criterion \[11\], which for D-T fusion is approximately given as follows:

\[ n_e \cdot T_e \cdot \tau_e \geq 10^{21} \text{ keV s m}^{-3} \]  

(1.4)

\[1\] The term “reserves” here refers to discovered and undiscovered quantities that are assumed economically viable to mine. If demand for lithium increases and mining becomes more profitable, the lithium reserve could increase significantly, for example, via ocean water extraction.
Here $n_e$ is the electron density, $T_e$ is the electron temperature (assumed equal to the ion temperature in the core of the plasma), and $\tau_e$ is the electron confinement time, which is the characteristic time that electrons tend to stay confined in the plasma. The desire to keep the plasma confined as long as possible motivates placing the plasma within magnetic fields. Because positively and negatively charged particles tend to orbit around and travel along magnetic field lines, the net effect is a large increase in $\tau_e$ relative to an unmagnetized plasma. One of the most promising magnetic confinement schemes, the tokamak, has resulted in a steady increase in $n\tau T$ over the last 50 years; see Figure [1.2].

1.3 The tokamak

A cartoon model of a tokamak is shown in Figure [1.3]. It essentially consists of a magnetic solenoid that has been bent back upon itself to form a doughnut-shaped, or toroidal structure. A second solenoid runs down the center of this device. A current ramp in the central solenoid induces a
current through the conductive tokamak plasma, which produces a \textit{poloidal} field concentric to the current direction. This causes electrons and ions to generally travel in helical orbits through the magnetic field rather than escaping from the plasma. Additional magnetic field coils can bend and stretch the plasma into a more optimal configuration. Electrons and ions thus generally travel along helical field lines in the toroidal region enclosed by the magnetic coils, rather than escaping from the plasma.

The overall efficiency of the tokamak as a fusion reactor can be characterized in terms of the parameter $Q$, the total fusion power output of the tokamak divided by the total power provided to confine and heat the plasma. To date, a maximum value of $Q = 0.62$ has been achieved in the world’s largest tokamak, the Joint European Torus (JET) \cite{14}. However a consortium of seven international partners is currently designing and building the ITER tokamak in Cadarache, France. One of the primary goals of ITER is to demonstrate the capability for “break-even” fusion power ($Q = 1$) and push total fusion gains to $Q = 10$. ITER is currently scheduled to begin operation in 2020 with D-T fusion experiments scheduled for 2027 \cite{15}. However ITER will not actually
supply electricity to the power grid. The first fusion reactor to produce electricity, usually dubbed DEMO, is currently in the design stages and may begin operation in the 2040s.

1.4 Plasma exhaust and the divertor

Plasma particles in large tokamaks are typically confined for several hundred milliseconds, after which they exit the plasma via various mechanisms. Coulomb collisions and plasma turbulence both lead to cross-field transport of the ions and electrons, causing them to escape the region where the magnetic field lines are closed upon each other, known as the core. Once particles enter the region surrounding the core, known as the scrape-off layer, they are quickly lost from the plasma and strike the walls. Most commonly, the magnetic fields are shaped in such a way as to divert the ions and electrons toward toroidally symmetric surfaces on the top and/or bottom of the tokamak. These surfaces are collectively known as the divertor and experience significantly higher heat and particle fluxes relative to the rest of the tokamak walls, which are known as the first wall. A poloidal cross section of the divertor region of a tokamak is shown in Figure 1.4.

Currently most tokamak divertor plasma facing components (PFCs) are composed of either graphite or high-Z metals such as tungsten or molybdenum. These materials have high thermal conductivity and are thus able to swiftly carry heat away from the surface. High-Z materials erode sufficiently slowly on current tokamak devices such that depletion of the divertor material does not become an issue. However, PFCs in the divertor of D-T fusion reactors will experience \~5 orders of magnitude more ion fluence than current-generation experiments. Extrapolating from measurements on present devices, this implies that the erosion rate of the PFCs in a reactor divertor will be > 10 cm/year \[17\]. It has further been estimated \[18\] that for the case of tungsten first walls, \~8000 kg/year of material will be eroded from the first walls. Several tons of re-circulating material are unlikely to be acceptable, and thus addressing the joint issues of first wall and divertor erosion remains a paramount engineering concern for the construction of a DEMO-level reactor.
Figure 1.4: Poloidal cross section of the divertor region. Electrons and ions escape the main plasma (or core), traveling across the separatrix which bounds the core and the scrape-off layer. Particles flow through the scrape-off layer at approximately the ion sound speed \( (T_e/m_i)^{1/2} \) and strike the divertor targets. Image obtained courtesy of [16].
One possible solution to divertor erosion is to operate divertor plasmas in a regime of low temperature ($< 10$ eV) and high density ($> 10^{15} \text{ cm}^{-3}$), which would result in high prompt and local re-deposition, a process by which eroded wall atoms are ionized in the near-surface plasma and return directly to the wall (see Section 3.5). This regime will also minimize gross erosion because of the low sputtering that results at low incident ion energies; see Section 2.5 for more details. However, knowledge gaps still exist in the fundamental processes that govern erosion and re-deposition rates and these must be addressed in current experiments in order to gain predictive capability for how material will migrate in the divertor and on the walls. The U.S. Fusion and Energy Sciences Advisory Committee (FESAC) recognized this task as an “important research thrust” in a 2009 report [19] and again as a “scientific grand challenge” in 2012 [20].

### 1.5 Low-Z coatings for use in fusion devices

While erosion of the bulk wall materials in current-generation tokamak experiments is not a large concern, the walls are often coated with low-Z thin films, which tend to erode very quickly relative to high-Z substrates. For example, the temperature-dependent erosion rate of a lithium layer measured in the PISCES-B linear plasma device [2] is shown in Figure 1.5. Because these films reduce impurity influx into the plasma core and improve confinement, it is crucial that the film does not fully erode until the coating is replenished. Calculations of erosion and re-deposition rates of these films thus becomes important in order to determine how long they last and where they will start to disappear first. Many machines utilize thin-film Li coatings, including NSTX [21], CDX-U [22], LTX [23], HT-7 [24], EAST [25], and FTU [26]. Thin evaporative Li coatings on C substrates are also planned as a PFC for NSTX-U, scheduled to begin operation in early 2015.

The application of thin-film boron (B) coatings on C and Mo substrates is a PFC conditioning technique in use on Alcator C-Mod [27], DIII-D [28], ASDEX-U [29], KSTAR [30], and NSTX [31]. Other thin films that have been applied or proposed for use in tokamaks include beryl-
Figure 1.5: The atomic erosion flux of a Li surface normalized to the incident deuterium ion flux \((8 \cdot 10^{21} \text{ m}^{-2} \text{ s}^{-1})\) measured in the PISCES-B linear plasma device. The predicted erosion flux solely from Li evaporation is given in red. The remaining erosion is due to temperature-dependent Li sputtering, discussed in detail in Section 2.5.4.

Figure 1.5: The atomic erosion flux of a Li surface normalized to the incident deuterium ion flux \((8 \cdot 10^{21} \text{ m}^{-2} \text{ s}^{-1})\) measured in the PISCES-B linear plasma device. The predicted erosion flux solely from Li evaporation is given in red. The remaining erosion is due to temperature-dependent Li sputtering, discussed in detail in Section 2.5.4.

1.6 Thesis Objective

The primary goal of this thesis is to quantitatively investigate the lifetime of low-Z coatings in the tokamak divertor region through measurements in a linear plasma device. The main focus of
this work is on the erosion and re-deposition of lithium-coated plasma-facing components as a function of plasma flux, incident ion energy, and surface temperature. A secondary focus is the erosion of boron-coated materials. Chapter 2 discusses the erosion and diffusion mechanisms of bulk substrates and thin-film coatings in the presence of high-flux plasma bombardment and how to realistically characterize these processes using semi-empirical extrapolations from existing data and the SDTrimSP [35] binary-collision approximation (BCA) sputtering code. Chapter 3 discusses the atomic physics occurring in the near-surface plasma region in the presence of impurity species and analytic/numerical modeling of the evolution of the impurity density using the Atomic Data and Analysis Structure (ADAS) code package [36]. Chapter 4 describes a method of testing these models using the linear plasma device Magnum-PSI [37] to simulate the plasma conditions found in a tokamak divertor. Chapter 5 presents erosion measurements of lithium-coated graphite and TZM molybdenum under high-flux plasma bombardment and compares these measurements to modeling results. Chapter 6 describes observations of lithium re-deposition in Magnum-PSI and comparison to analytic/numerical modeling. Chapter 7 discusses measurements of boron erosion under high-flux plasma bombardment using a novel measurement technique. Chapter 8 provides a synthesis of all these results to determine the feasibility of maintaining a lithium coating on the walls of a fusion device such as NSTX-U or DEMO.
Chapter 2

Theory of Plasma-Induced Erosion

Numerous different interactions can occur when a plasma bombards a low-Z substrate and all those of relevance will be discussed in this chapter. For example, the principal deuterium-lithium plasma-material interactions (PMIs) are shown in Figure 2.1. Plasma ions striking a surface are accelerated by the sheath electric field and strike the surface with an energy ranging from 1 eV to > 50 eV. They can knock atoms off the surface in a process known as sputtering. Incident ions can also excite atoms from their bound states within the material without sufficient energy to sputter, transforming them into mobile surface particles known as adatoms. D atoms can bond to the surface Li atoms and become part of the material, which is called adsorption. This often leads to a chemical change in the layer to lithium deuteride (LiD). Energetic ions can penetrate deeper than the surface layer of the material in a process called implantation. Significant concentrations of D on the near surface can shield Li atoms from ion bombardment, leading to preferential sputtering in which the net Li sputter yield is reduced. D atoms can also diffuse deep into the lithium coating, the rate of which is dependent on temperature and the D impurity concentration. Finally, lithium atoms can be lost from the bulk through conventional sublimation in solid form and evaporation as a liquid, which is also a function of temperature and impurity concentration.
2.1 Adsorption

The process by which a solid or liquid surface interface uptakes free atoms from a gas or plasma is known as adsorption. Further distinct can be drawn between chemisorption, when this surface uptake is the result of a chemical reaction between the particle and the interface, and physisorption, in which no chemical bonding occurs. D adsorption on solid Li surface occurs only through chemisorption, in which a surface Li atom binds to a D atom or ion, forming lithium deuteride. This

Figure 2.1: Cartoon picture of the principal plasma-material interactions occurring when a deuterium plasma contacts a lithium surface.

Many interactions occur within the near-surface plasma as well. A discussion of these processes and how to model them is separated into Chapter 3.
has been directly observed in surface science experiments for several alkali metal systems [38]. Molecular D$_2$ incident on the surface at room temperature or greater is never captured; instead it is reflected, backscattered, or immediately desorbed [39]. Molecular D$_2^+$ can be adsorbed in small quantities [40]. In [41] it was found that liquid Li will also uptake atomic D, although it is likely that implantation (Section 2.2) occurred in addition to chemisorption.

Solid lithium tends to form a body-centered cubic (BCC) lattice structure. There are three likely locations (sites) for a D adsorbdate on this crystal: the “on-top” site where the D atom resides on top of a corner Li atom, “bridge” site in which the D settles halfway between two corner points, and the “hollow” or “open” site where the D atom sits directly above the Li atom at the center of a unit cell. These three possible adsorption locations are shown diagrammatically in Figure 2.2. Various simulations of hydrogen adsorption on to the surface of lithium crystals have been performed using ab initio calculations [42, 43, 44, 45]. The relative depth of each adsorption
energy well, which governs the relative probability of adsorption at each site, varies significantly in each study depending on the chosen simulation method as well as the Li lattice orientation and cluster size. Li layers in fusion devices can be amorphous films (such as when they are liquid) rather than crystalline structures, further increasing the uncertainty. In Section 2.5.3 a sensitivity study of the D→Li preferential sputtering yields to the preferred adsorption site will be presented.

It should be noted that deuterium is also adsorbed on graphite surfaces. The enhancement of this effect in the presence of co-adsorbed oxygen and lithium has been studied in experiment [46] and simulations [47], and the corresponding effect on the Li sputtering yield has also been well characterized [48]. The difficulty of removing retained tritium from a lithium/carbon matrix strongly discourages the use of Li-coated graphite as a PFC in a fusion reactor. Thus this system is not of significant interest in the present work.

2.2 Implantation

In addition to adsorption, sufficiently energetic atoms and ions can implant deeper than the top monolayer of the material [49]. More energetic atoms will take longer to lose energy via collisions with lattice atoms and thus will penetrate deeper into the bulk. The implantation profile is generally dependent on the incident particle species and energy as well as the material composition. Implantation profiles can be calculated probabilistically via the Stopping Range of Ions in Matter (SRIM) code [50]. This code utilizes a Monte Carlo (MC) approach to simulate individual ions impacting a surface and undergoing a series of two-body elastic collisions until their energy falls below some specified value (~1 eV), at which point they are considered at rest within the material. SRIM simulations of 20 eV and 40 eV D implantation profiles in solid Li (Figure 2.3) at normal incidence give a close to skewed Gaussian distribution with a peak several tens of Å below the surface. A lithium monolayer (ML) is ~3 Å, so the majority of low-energy D atoms are implanted within 10-20 ML of the surface. It should be noted that SRIM does not include any chemical ef-
2.3 Diffusion

Diffusion is a process by which material moves from regions of higher concentration to lower concentration. In context of this thesis we will primarily discuss 1-D diffusion of low-Z materials. The 1-D approximation is valid because the layer thicknesses under analysis (< 1 mm) are always much smaller than the length and width of the film (≥ 2.5 mm), and thus any concentration gradients parallel to the surface are negligible relative to the normal direction, assuming isotropic diffusivity. This allows the time evolution of the concentration of low-Z material to be modeled by Fick’s Second Law \[51\]:

\[
\frac{dn}{dt} = \alpha \frac{d^2n}{dx^2} \tag{2.1}
\]
Here \( n \) is the concentration of material (\( m^{-3} \)) and \( \alpha \) is the diffusion coefficient (\( m^2 / s \)). Two diffusion processes are of high interest in this thesis: lithium diffusion into graphite and deuterium diffusion in lithium, each of which will be discussed in turn below.

### 2.3.1 Li diffusion in graphite

Lithium coatings applied to graphite plasma-facing components quickly diffuse into the underlying substrate. While plasma bombardment is not necessary for this process to occur, the plasma causes localized heating of the surface that strongly enhances Li mobility in carbon. The temperature dependence of the Li diffusivity in the direction perpendicular to the basal planes of highly-oriented pyrolytic graphite (HOPG) was measured by Itou [52] using Rutherford backscattering spectrometry (RBS). The derived diffusion coefficient is

\[
\alpha_{\text{Li}}(T) = \left(4.5 \times 10^{-6} \text{ cm}^2 / \text{s}\right) \exp \left(-\frac{0.26 \text{ eV}}{kT}\right) \tag{2.2}
\]

We consider a thin Li film of thickness \( \Delta x \) applied to a graphite substrate. Solving Equation 2.1 for the time \( \tau \) for this Li layer to completely diffuse into the underlying graphite (see, for example, [53]) leads to:

\[
\tau \approx \frac{\pi (\Delta x)^2}{4\alpha_{\text{Li}}} \tag{2.3}
\]

Quantitatively, this implies that a 1000 nm Li layer will completely diffuse into a graphite matrix in \(< 1\) minute. In Ref [52], a 3000 nm layer was observed to disappear after 30 minutes. Equation 2.2 can be considered only an upper bound on the true Li diffusivity since it was conducted in an extremely clean laboratory setting with no other impurities in the graphite matrix. But even a reduction of \( \alpha_{\text{Li}} \) by a factor of 10 still results in complete depletion of the pure Li layer on the graphite surface in \(< 10\) minutes, which is the approximate duty cycle (i.e., time between dis-
charges) for current tokamaks. In addition, diffusion may be enhanced by defects in the structure of the fine grain graphite used in tokamaks, which may allow the Li to intercalate more quickly than in HOPG. Thus it is likely that a Li-C mixed material is always present on the Li-coated graphite walls of fusion devices rather than a pure Li surface coating that could be eroded into the plasma.

Previous analysis of Li-coated graphite tiles from NSTX showed evidence of Li up to 15 µm into the substrate, but not any deeper [54]. The total dose of Li deposited on the tiles is unknown. Depth profiles of the Li and D concentrations in a graphite tile are shown in Figure 2.4. It is evident that significant Li concentrations can accumulate in graphite, with a maximum Li:C concentration greater than 1:2 observed.

### 2.3.2 D diffusion in lithium

Adsorbed deuterium on a lithium surface is capable of penetrating deep into the bulk Li layer via diffusion. The temperature dependence of tritium diffusivity in Li has been measured experimentally for very small concentrations ($10^{-5}$ %) [55]. The best fit curve to these data is given by

$$
\log[\alpha_{\text{TLi}}(T)] = -8.562 + 1.737 \log(T) - \frac{110}{T}.
$$

(2.4)

However, because hydrogen isotopes can absorb into lithium layers in large concentrations [41], it is desirable to have knowledge of the diffusivity as a function of both temperature and hydrogen concentration. Thus the concentration-dependent hydrogen diffusion coefficient is studied using density functional theory (DFT). Deriving an exact solution for the dynamics of many interacting electrons represents an intractable problem using conventional methods. DFT is a formally rigorous theory that provides a framework for calculating particle densities and potentials using density functionals. If an appropriate density functional is known, an analogous system of non-interacting particles can be generated that is significantly easier to solve.
Figure 2.4: Concentrations of D and Li in NSTX graphite tiles in regions directly facing a Li evaporator (above) and shadowed from it (below). The upper panel shows measurements on thin reference samples to indicate depth resolution, which is above 1 μm FWHM at the surface. Plot is a reproduction of Figure 3 in [54].
First-principles molecular dynamics simulations\(^2\) were conducted in the canonical (Nosé-Hoover) ensemble \(^{56}\) using Kohn-Sham density function theory (KSDFT) \(^{57}\). First-principles DFT methods have previously been shown to accurately reproduce the lithium melting temperature and self-diffusion coefficient \(^{58, 59}\). The simulation region is a cubic cell containing 128 lithium atoms and a variable amount of hydrogen isotopes ranging from 4 (3% H/D/T:Li) to 128 (100% H/D/T:Li). D atoms are inserted uniformly into the liquid Li cells at a specified temperature. Because we are using the canonical ensemble, it is necessary to manually tune the ionic density to ensure the external pressure of the system remains zero after entering the equilibrium state. For 25% D:Li at 470 K it was found that the simulation cell tends to shrink to about 90% of its original volume. Next the dynamics of the Li and H/D/T atoms are tracked for a time period of approximately 10 ps. The diffusivity of hydrogen in Li is calculated as

\[
\alpha_{H Li} = \frac{1}{6} \lim_{t \to \infty} \frac{t}{u^2(t) - u^2(0)}
\]

(2.5)

where \(u^2(t)\), the mean-square displacement (MSD), is given by

\[
u^2(t) = \frac{1}{NM} \sum_{i=1}^{N} \sum_{j=1}^{M} [R_j(t) - R_i(0)]^2
\]

(2.6)

where \(R_i(t)\) and \(R_j(t)\) are the positions of lithium atom \(i\) and hydrogen atom \(j\) after time \(t\) of the simulation. The time evolution of the diffusion coefficients \(D(t)\) for 25% H/D/T in Li at 470 K are shown in Figure 2.5. It is evident that after approximately 5-6 ps a suitable equilibrium has been reached because the diffusivity does not continue to evolve strongly in time. Unfortunately, reliable data for smaller concentrations of hydrogen could not be obtained for these MD simulations over the course of several tens of ps, and it would be prohibitively expensive to run computations for significantly longer times.

\(^2\)Performed by Dr. Mohan Chen, Princeton University.
2.3. **Diffusion**

Figure 2.5: (a) Diffusivity of H, D, and T atoms in liquid Li over the first 10 ps of simulation time for D/Li concentration $\beta = 0.25$ and $T = 470$ K. (b) Lithium self-diffusivity for each isotope case. Plot obtained courtesy of [60].
The calculated temperature-dependent D diffusion coefficients in liquid Li for concentrations ranging from 25% to 100% D saturation are shown in Figure 2.6, along with the experimental result for tritium from [55]. It is evident from Figure 2.5 that the diffusion coefficients are not strongly isotope-dependent and thus the experimental values may be reasonably extrapolated from T to D at low concentrations. It is evident that $\alpha_{DLi}$ decreases strongly as a function of the D/Li concentration- by over an order of magnitude in a certain temperature range. Henceforth we will refer to the ratio of the D concentration to Li concentration as $\beta$. There is even evidence of a lithium deuteride “phase transition” (solidification) in the $\beta = 1$ simulation, as evidenced by a sharp increase in $\alpha_{DLi}$ around the melting temperature of LiD (965 K).
Figure 2.7: The predicted surface D/Li concentration $\beta$ for a 100 µm thick, 400 °C liquid Li layer after a total D fluence of $10^{23}$ m$^{-2}$, calculated by solving Equation 2.1 and using the interpolation method described in Equation 2.7. The D flux range in these experiments and the predictions for a reactor divertor are also shown.

Interpolation between the temperatures and concentrations given in Figure 2.6 are performed in linear-linear-log space:

$$\log [\alpha_{DLi}(\beta, T)] = \sum_{i=0}^{1} \sum_{j=0}^{1} \log [\alpha_{DLi}(\beta_i, T_j)] \frac{|\beta_i - \beta| |T_j - T|}{\Delta \beta \Delta T}$$

where $\beta_0, \beta_1$ and $T_0, T_1$ correspond to the two closest values of $\beta$ and $T$ present in the simulation matrix. $\Delta \beta$ and $\Delta T$ are the absolute differences between the two values.

These profiles allow the time evolution of the D/Li concentration on a Li surface to be performed for any time-varying D implantation rate and Li temperature. Equation 2.1 is solved with the appropriate diffusion coefficients, implantation source term, and boundary conditions. We assume D is implanted uniformly within the top 5 nm of the material; the results are not sensitive to using this assumption rather than the specific implantation profile in Figure 2.3. Boundary condi-
tions $d\beta/dx = 0$ are instituted at each edge to prevent D diffusion out of the Li layer. The surface D/Li concentration of a 100 µm thick, 400 °C liquid Li layer after a total D fluence of $10^{23}$ m$^{-2}$ is shown in Figure 2.7 as the D flux is varied over several orders of magnitude. At low fluxes the Li layer is able to absorb deuterium as fast as it implants into the surface. At high fluxes, however, the deuterium begins to bombard the surface faster than the Li can absorb it. A “runaway” effect is created by the diffusion suppression effect for increasing values of $\beta$. This effect is already evident for reactor divertor-level fluxes even at this relatively low value of fluence. Thus in a reactor the accumulation of deuterium in a lithium layer is expected to be significant even for the case of a flowing Li system. In contrast, on the PISCES-B linear plasma device the total D fluence to the Li sample [61] is approximately $10^{23}$ m$^{-2}$ after the entire Li temperature sweep given in Figure 1.5.

2.4 Sublimation and Evaporation

In a perfect vacuum, any material at a finite temperature will form a vapor cloud with characteristic pressure $p_v(T)$ above its surface. If the material is a solid this process is referred to as sublimation and if it is a liquid it is called evaporation. While plasma bombardment is obviously not necessary for this process to occur, the corresponding increase in temperature under high plasma fluxes strongly enhances $p_v$ and thus merits investigation. Temperature-dependent vapor pressure curves have been measured for nearly every element and many compounds [62]. The curves are typically fit to the following empirical form:

$$\ln(p_v)(\text{Pa}) = AT^{-1} + B\ln(T) + CT + DT^2 + E$$

(2.8)

where $T$ is the temperature in Kelvin and $A, B, C, D, E$ are the vapor pressure coefficients characteristic of specific elements. For lithium the best fit coefficients are $A = -18880$, $B = -0.4942$ and $E = 26.89$. The $C$ and $D$ parameters are not used. The total material flux from a surface due to
2.4. Sublimation and Evaporation

Evaporative flux as a function of temperature for fusion-relevant materials. For the purposes of this plot the ambient pressure \( p_a \) is assumed zero. Data obtained from [62] and references therein.

Evaporation or sublimation is given by the following simple expression derived by Langmuir [63]:

\[
\Gamma_{\text{evap}}(T) = \frac{p_a(T) - p_a(T)}{\sqrt{2\pi mkT}}
\]  

(2.9)

where \( p_a(T) \) is the ambient pressure above the surface of the material and \( m \) is the atomic mass. For a flat surface, the kinetic theory of gases dictates that the angular distribution of evaporated material can be approximated by a cosine distribution in the polar (\( \theta \)) direction and a uniform profile in the azimuthal (\( \phi \)) direction [64].

\(^3\)Henceforth this process will always be referred to as evaporation, with the implicit understanding that it is technically sublimation if the material is a solid.
2.5. Sputtering

The corresponding evaporative fluxes (integrated over all solid angles) for lithium, boron, and other materials in use or proposed for use in fusion devices are shown in Figure 2.8. The evaporation rate of pure lithium is higher than any other material under consideration, which is one of the chief objections raised to using lithium as a PFC. However, the addition of deuterium through adsorption (Section 2.1) and implantation (Section 2.2) into a lithium surface can strongly suppress Li evaporation because the Li vapor pressure curve for LiD \( p_{\text{LiD}}(T) \) is significantly lower than that for pure Li. Measurements of the mixed-material Li/LiD vapor pressure (normalized to that of pure Li) is shown in Figure 2.9 as a function of the D/Li concentration \( \beta \). The Li vapor pressure is strongly reduced at high values of \( \beta \) and this reduction is effectively independent of temperature. Thus this effect is assumed to be characterized by a single mixed-material reduction factor:

\[
\frac{p_{\text{LiD}}(\beta)}{p_{\text{Li}}} = (1 - \beta)^\gamma
\]  

(2.10)

where \( \gamma \) is an empirical fit parameter. Fitting the data in Figure 2.9 gives a value \( \gamma = 0.705 \).

While there are some excursions from this empirical fit in the range of \( \beta = 0.2 - 0.4 \) and no data are available for \( 0.4 < \beta < 0.8 \), we are primarily interested in nearly completely D-saturated lithium (\( \beta \geq 0.9 \)) where Equation 2.10 gives very good agreement with measurements.

2.5 Sputtering

2.5.1 Physical Sputtering of Solid Surfaces

Consider an energetic particle (atom, ion, molecule, etc.) of energy \( E_0 \) incident on a solid surface. When the particle strikes a surface atom, an elastic transfer of momentum and energy will occur. If the energy component normal to the surface transferred to this atom is larger than a value known as the \textit{surface binding energy} (SBE) then the atom will overcome its bound state on the surface and be
2.5. **Sputtering**

Figure 2.9: The Li vapor pressure above a mixed-material Li/LiD surface as a function of the D/Li concentration. Data obtained courtesy of [65]. The best-fit curve described in Equation 2.10 is also shown.

This process is known as **physical sputtering**. There also exists a threshold energy $E_{th}$ for incident particles (higher than the SBE) below which sputtering will not occur. Physical sputtering is a ubiquitous phenomenon that has been observed for a wide variety of incident ion and target substrate combinations at energies ranging from 10 eV up to the MeV range [66], although here we are primarily concerned with low-energy ion sputtering ($< 100$ eV). The rate at which particles are removed from the surface is known as the **sputtering yield** and is defined as

$$ Y = \frac{\text{number of removed atoms}}{\text{number of incident particles}} \quad (2.11) $$

Yields are usually characterized in terms of surface and/or time averages and are typically measured on ion beam experiments at low fluxes ($10^{12}-10^{14} \text{ m}^{-2} \text{ s}^{-1}$). Most measurements of $\text{D} \rightarrow \text{Li}$ sputtering were performed by Allain [1, 67] and $\text{D} \rightarrow \text{B}$ sputter yields were measured by

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Typically the surface binding energy is assumed equal to the heat of sublimation of the material.
2.5. Sputtering

Hecht [68]. In Li sputtering experiments it is found that approximately 2/3 of the Li is sputtered as an ion regardless of the incident D ion energy.

Yields can also be calculated via computer codes that assume either a lattice structure (i.e. MARLOWE [69]) or follow a Monte Carlo approach with an amorphous target (i.e. TRIM.SP [70]). As in the case of implantation simulations described in Section 2.2, these programs follow the collisions and trajectories of incident particles and substrate atoms throughout the material in 3D until they come to rest below some specified energy (∼1 eV). All atom-atom interactions in these codes are approximated by elastic binary collisions characterized by some interaction potential. This is known as the binary-collision approximation (BCA). While the BCA assumption begins to break down at low energies (< 30 eV), reasonable agreement between simulations and experiment at lower energies is found in many cases [66].

Interpolation and extrapolation from existing experiments and simulations can be performed with an empirical formula developed by Bohdansky [71] and later refined by Eckstein [72]:

\[
Y(E_0) = \frac{q s_n^{KrC}(\epsilon)}{\lambda + \left(\frac{E_0}{E_{th}} - 1\right)^\mu} \tag{2.12}
\]

where \(s_n^{KrC}(\epsilon)\) is the nuclear stopping power, the expression for which is given in [73]. Empirical parameters \(q, \lambda, E_{th}\) and \(\mu\) are obtained by fitting to simulation or experimental data. The best-fit lines from Equation 2.12 are shown in Figure 2.10 for TRIM.SP simulations of D→Li and D→B sputtering [66]. Experimental data from [67] and [68] are also overlaid. While these yields do not depend strongly on energy in the 100-1000 eV range, there is a drastic decrease in \(Y\) at energies < 100 eV. Generally TRIM.SP captures the qualitative trends of these sputtering yields but systematically under-predicts absolute value of \(Y\) relative to experiments\(^5\).

\(^5\)It should be noted, however, that all of Allain’s measurements were conducted with ions incident 45° from surface normal, whereas all TRIM.SP simulations were performed at perpendicular incidence. \(Y\) generally tends to increase at more grazing incidence angles.
For normal ion incidence, the angular distribution of sputtered atoms tends to approach a $\cos \theta$ distribution in the polar direction, with symmetry in the azimuthal direction [66]. As shown in Figure 2.11, the distribution calculated via TRIM.SP for 20 eV and 40 eV D ions incident on Li closely follows a cosine curve. Thus this simple formula remains a good approximation.

### 2.5.2 Chemical Sputtering

If incident energetic particles have a tendency to chemically bond with the target substrate, the surface binding energy of the material can be increased or reduced. A reduction in the SBE and the corresponding enhancement in the sputtering yield $Y$ is typically referred to as **chemical sputtering**. The majority of fusion-relevant studies on this subject are focused on chemical sputtering of graphite with hydrogen isotopes, which occurs via hydrocarbon ($C_xH_y$) production [74]. This present work, however, is concerned with the chemical effects of lithium deuteride formation. A reduction of $Y$ is expected because the sublimation energy (or SBE) of LiD (2.26 eV) is higher than that of pure Li (1.67 eV). Thus here we extend the definition of chemical sputtering to include
2.5. Sputtering

Figure 2.11: Angular distribution of sputtered Li atoms for 20 eV and 40 eV D→Li sputtering calculated via the TRIM.SP BCA code. The cosine approximation is also shown.

chemically-induced decreases in $Y$ as well. Reductions in sputtering yields due to compound formation on surface layers has been observed for many materials [75]. While no first-principles model exists to simulate the corresponding D→Li sputtering reduction directly, we will approximate the effect of chemical sputtering by linearly interpolating between the SBEs of Li and LiD:

$$SBE_{\text{eff}} = (1 - \beta)SBE_{\text{Li}} + \beta SBE_{\text{LiD}}$$

(2.13)

where $\beta$ is the D/Li concentration ratio introduced in Section 2.3.2.

2.5.3 Preferential Sputtering

When significant quantities of the incident ion species have implanted/adsorbed within the target substrate, the effective surface density of the original target material is decreased. In addition, the implanted ion species tends to be sputtered more efficiently than the substrate atoms. The net effect is a reduction of the sputter yield of the substrate, referred to as preferential sputtering.
For the D→Li system, a reduction of Li sputtering by a factor of 5-10 was observed after Li surface exposure to a D plasma glow and subsequent irradiation with D ions [1], although no measurements or calculations of the D/Li concentration $\beta$ were performed. Preferential sputtering directly incorporated into the SDTrimSP [35] sputtering code, which is a modified version of TRIM.SP that allows for the dynamic evolution of a material surface. For the purposes of the simulations described below, however, the surface was specified as static and variation of surface parameters was achieved by running multiple simulations.

In order to properly capture preferential sputtering effects, it is necessary to accurately characterize $\beta$ as a function of depth into the surface. Immediately below the first Li/LiD monolayer, the material can be assumed uniform due to the rapid diffusion of deuterium within the Li. The placement of D in the top Li monolayer, however, is dependent on the preferential D adsorption sites discussed in Section 2.1. For $\beta = 1$, (i.e., complete conversion of the Li layer to LiD) population of the on-top adsorption site would imply formation of a full D monolayer on top of a Li layer. Population of the bridge or hollow sites would imply a more homogenous surface with D and Li atoms in the same plane. Upper and lower bounds on preferential sputtering effects can be established by simulating these two limiting cases.

These two cases are incorporated into TRIM.SP as follows. A surface layer of thickness 2.2 Å (the Van der Waals radius of a D atom) is specified. The underlying bulk is 30 nm thick, significantly larger than the penetration depth of a low-energy D atom (Figure 2.3). The bulk is sub-divided into 100 equal partitions of 3 Å each to ensure sufficient depth resolution. For the homogenous case, the atomic fractions of D and Li ($f_D$ and $f_{Li}$) are always equal in both layers. For the non-homogenous case in which adsorbed D is assumed bound in on-top sites, the surface D concentration is enriched with respect to the bulk and simply equal to $\beta$. The relation between $\beta$, $f_D$, and $f_{Li}$ is shown in Table 2.1 for the homogenous and non-homogenous cases.

TRIM.SP simulations of 20 eV D→Li sputtering are performed for values of $\beta$ ranging from 0 to 1, using the relative atomic fractions given in Table 2.1. The surface binding energy of the
2.5. Sputtering

<table>
<thead>
<tr>
<th></th>
<th>Homogenous case</th>
<th>Non-homogenous case</th>
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<tbody>
<tr>
<td>Surface Layer</td>
<td>( f_D = 1/(1 + \beta) )</td>
<td>( f_D = \beta )</td>
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<tr>
<td></td>
<td>( f_{Li} = \beta/(1 + \beta) )</td>
<td>( f_{Li} = 1 - \beta )</td>
</tr>
<tr>
<td>Bulk Layer</td>
<td>( f_D = 1/(1 + \beta) )</td>
<td>( f_D = 1/(1 + \beta) )</td>
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<td>( f_{Li} = \beta/(1 + \beta) )</td>
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Table 2.1: The relation between the \( \beta, f_D, \) and \( f_{Li} \) in the surface and bulk layers for the homogenous and non-homogenous surface cases.

D and Li atoms is determined from Equation 2.13. The results of these simulations are shown in Figure 2.12. It is evident that significant quantities of adsorbed and implanted D in a Li surface results in significant reduction of the sputtering yield. For \( \beta = 1 \), this reduction is about a factor of 10 in the homogenous case and nearly a factor of 40 in the non-homogenous case. A continuous function, which we will refer to as the mixed-material reduction factor \( f(\beta) \), is obtaining by fitting fourth-order polynomials to the data in Figure 2.12 and normalizing to \( Y(\beta=0) = 0.0224 \). It was determined via further simulations that \( f(\beta) \) is effectively independent of ion energy from 20 eV to 100 eV.

2.5.4 Thermal Sputtering

Traditional collisional sputtering from room-temperature surfaces is well-modeled by the binary-collision approximation and can be assumed independent of small variations in temperature. However, when the temperature of the material approaches the melting point, a strong increase in the sputtering yield (thermal sputtering) is observed for many materials, including lithium [11], beryllium [76], tin [77], and tungsten [78]. Measurements of Li erosion in the PISCES-B linear plasma device indicate this enhancement in \( Y \) is dependent on the incident ion species, but not on the ion energy or ion flux [79]. Measurements by Allain [80] also demonstrate thermal He→Li sputtering is independent of ion energy in the range of 200 to 1000 eV, although the absolute yields differ from the PISCES measurements by up to a factor of 5. Two models for the quantitative

---

6Note again the 45° ion incidence angle during IIAX experiments, versus normal ion incidence in the PISCES case, so some discrepancy is expected.
Figure 2.12: TRIM.SP simulations of the 20 eV D→Li sputtering yield as a function of the D/Li concentration $\beta$ in the material. The predictions of both the homogenous (blue) and non-homogenous (red) surface models are shown. The fit formulae $f(\beta)$ for both cases are overlaid with black lines.
dependence of Li thermal sputtering on temperature, the thermal-spike model and the adatom-evaporation/sublimation model, will be discussed below.

2.5.4.1 Thermal-spike model

The theory of the thermal-spike sputtering regime was first developed by Sigmund [81] and has been well established in the high-energy, heavy-ion bombardment limit. Sufficient energy is transferred to a material by an incoming ion as to excite collective motion of all atoms within a certain volume (the thermal spike volume). The local temperature of the material is increased by the thermal-spike temperature $T_{\text{spike}}$ and then decays back to the bulk substrate temperature $T$ with time constant $\tau_{\text{spike}}$. This phenomenon cannot be approximated via the binary-collision approximation because it involves non-linear interactions of a large number of atoms. In Ref [1], this model is extended to light elements at low energies bombarding Li surfaces. The use of this model was justified for D→Li, He→Li and Li→Li bombardment because the deposited energy densities during these interactions are fairly similar to the high-energy, heavy-ion cases [82]. The resulting form for $Y_{\text{thermal}}$ at normal ion incidence is

$$Y_{\text{spike}}(E_0, T^*) = \frac{\kappa T_{\text{spike}} N_{\text{Li}} S_n(E_0)}{\sqrt{\frac{9\pi}{2} m_{\text{Li}} kT^*}} \exp\left(\frac{-S_{\text{BE, Li}}}{kT^*}\right) \tag{2.14}$$

Here $\kappa$ is a dimensionless number dependent on the mass ratio $m_2/m_1$ of the target atom mass (6.941 amu for Li) divided by the incident ion mass (2.014 for D$^+$). Sigmund [83] calculates $\alpha$ to be in the range of 0.2 - 0.25 for $m_2/m_1 < 0.5$ and $E_0$ less than several hundred eV, which is the regime considered here. $N_{\text{Li}}$ is the lithium density in atoms/m$^3$ and $T^* = T + T_{\text{spike}}$. $S_n(E_0)$, referred to as the “elastic stopping power,” is given in [83] as:

$$S_n(E_0) = \frac{1}{1 - m} C \gamma^{1-m} E_0^{1-2m} \tag{2.15}$$
where $m$ is a dimensionless number between 0 and 1. The observed lack of dependence of $Y$ on $E_0$ measured in experiments argues for a value of $m \approx 0.5$. $C$ is a constant on the order of several Å$^2$ and $\gamma = 4m_1m_2/(m_1 + m_2)^2$ is the maximum energy fraction that can be transferred in a head-on collision. While there is some precedent \cite{84} for the estimation of $T_{\text{spike}}$ and $\tau_{\text{spike}}$ for certain materials through semi-analytic modeling or MD simulations, here we follow the treatment of Allain and leave both as fitting parameters.

We use Equation 2.14 to fit the sputtering data presented in \cite{2} for 50 eV D incident on liquid Li (re-produced in Figure 1.5). The procedure for this is as follows. First, while no error analysis is discussed in the aforementioned work, we assume error bars of ±30%, which is typical of sputter yield measurements. Next, the evaporative component of the erosive Li flux (Figure 2.8) is subtracted from the data. Then the room-temperature physical sputtering yield for 50 eV D → Li (Figure 2.10) $Y = 0.040/3 = 0.013$ is subtracted from this result. The factor of of 3 is present because PISCES-B uses a biased target and thus all sputtered Li ions do not escape from this potential well. The fitted values are $\tau_{\text{spike}} \approx 3.1 \mu$s and $T_{\text{spike}} \approx 350$ K and the resulting fit curve is shown in Figure 2.13. This model predicts drastic increases in the Li sputtering yield at elevated temperatures. It should be noted, however, that typical values for $T_{\text{spike}}$ and $\tau_{\text{spike}}$ are on the order of 0.1-1 ps and 2000-10000 K, respectively \cite{84}. This suggests that the thermal spike model may not provide a realistic description of the physics of thermal Li sputtering.

### 2.5.4.2 Adatom evaporation/sublimation model

An alternative model of thermal Li sputtering involves the production and subsequent evaporation of surface adatoms \cite{76, 85}. As depicted in Figure 2.1, an adatom is essentially an atom that has been excited from its bound state on the surface of the material but does not possess sufficient energy to actually be sputtered. Adatoms have been directly observed on solid crystal surfaces using scanning-tunneling-microscopy after ion beam irradiation \cite{86}, and the generation of adatoms on a liquid surface formed by ion bombardment has been observed in MD simulations \cite{87}. Once an
Figure 2.13: Measured thermal sputtering yields for 50 eV D→Li bombardment on PISCES-B as a function of Li temperature. The fit curves to the predictions of the thermal-spike model (Equation 2.14) and adatom evaporation/sublimation model (Equation 2.18) are also shown.
adatom is created, it is highly mobile and quickly either diffuses across the surface to an appropriate recombination site or it sublimates/evaporates. These two processes have time constants \( t_{\text{rec}} \) and \( t_{\text{evap}} \), respectively. The time rate of change of the areal density of surface adatoms \( \rho_{\text{ad}} \) is given by Equation 1 in [85]:

\[
\frac{d\rho_{\text{ad}}}{dt} = Y_{\text{ad}}\Gamma_i - \frac{\rho_{\text{ad}}}{t_{\text{rec}}} - \frac{\rho_{\text{ad}}}{t_{\text{evap}}} \tag{2.16}
\]

where \( \Gamma_i \) is the incident ion flux and \( Y_{\text{ad}} \) is the adatom yield, i.e., the average number of adatoms created per incident ion. The rate of adatoms ejected off the surface will be given by \( \rho_{\text{ad}}/t_{\text{evap}} \). We assume the steady-state \( (d\rho_{\text{ad}}/dt = 0) \) and that the time constants \( t_{\text{rec}} \) and \( t_{\text{evap}} \) can be modeled by an Arrhenius-type behavior:

\[
t_{\text{rec}} = A_0\exp\left(\frac{E_D}{kT}\right) \quad t_{\text{evap}} = B_0\exp\left(\frac{E_{\text{ad}}}{kT}\right) \tag{2.17}
\]

where \( E_{\text{ad}} \) is the adatom surface binding energy (lower than the bulk material SBE) and \( E_D \) is the activation energy associated with diffusion to a surface recombination site. \( A_0 \) and \( B_0 \) are constants. Combining Equations 2.16 and 2.17 we obtain the expression (Equation 5 in [85]) for the effective thermal sputtering yield due to surface adatoms:

\[
Y_{\text{adatom}}(T) = \frac{Y_{\text{ad}}}{1 + A\exp\left(\frac{E_{\text{eff}}}{kT}\right)}. \tag{2.18}
\]

Here \( E_{\text{eff}} = E_{\text{ad}} - E_D \) and the constant \( A = B_0/A_0 \). Treating \( Y_{\text{ad}} \), \( A \), and \( E_{\text{eff}} \) as fitting parameters, we can fit the predictions of Equation 2.18 to the PISCES-B measurements of thermal Li sputtering using the same procedure described in Section 2.5.4.1. The best-fit values are \( Y_{\text{ad}} = 2.9 \), \( A = 9.6 \cdot 10^{-6} \), and \( E_{\text{eff}} = 0.70 \) eV. This implies a ratio of the adatom yield to the physical sputtering yield \( Y_{\text{ad}}/Y_{\text{sp}} \approx 70 \). MD simulations of Li adatom formation have not been performed, but calculations for ion bombardment of platinum predict \( Y_{\text{ad}}/Y_{\text{sp}} \) up to 30 [88]. The surface diffusion activation energy \( E_D \) of multilayer lithium films has been measured to be 0.75 eV [89], implying
an adatom binding energy $E_{ad}$ of 1.45 eV, reduced from the Li surface binding energy (1.67 eV) as expected. The similarity of these fit parameters to previous measurements and calculations suggests the adatom evaporation/sublimation model provides a more realistic physical picture of the thermal sputtering of lithium than the thermal-spike model.

The resulting best-fit curve for the adatom-evaporation model is shown in Figure 2.13. The predictions of this model are similar to the thermal-spike model at low Li temperatures because both are fit to the same PISCES-B data. For Li temperatures greater than 500 °C, the adatom model predicts a plateau in the sputtering yield near $Y = 2.7$ while $Y_{\text{spike}}(T)$ continues to increase dramatically. Physically, this plateau corresponds to the adatom evaporation rate becoming limited by their rate of creation. PISCES-B is only able to perform thermal sputtering measurements at temperatures up to 500 °C before the Li erosion becomes dominated by evaporative flux. There is some evidence of a plateau in $Y$ at the high end of this temperature range, but measurements at higher D fluxes are necessary to truly distinguish between the two models. Such experiments will be described in Chapter 5 of this thesis.

### 2.6 A realistic model for lithium erosion

A synthesis of Sections 2.1 through 2.5 of this chapter suggest that a realistic model of lithium erosion under high-flux deuterium plasma bombardment is necessarily a function of the Li temperature, incident D ion energy $E_{D^+}$ and flux $\Gamma_{D^+}$, and the D/Li concentration $\beta$ at the surface. The complete formulation of the Li erosion flux can be written as follows:

$$
\Gamma_{\text{Li}}(T_{\text{Li}}, \beta, \Gamma_{D^+}) = \Gamma_{\text{Li}}f(\beta) \left[ \frac{Y_{\text{phys}}(E_{D^+})}{3} + \frac{Y_{\text{ad}}}{1 + A\exp \left( \frac{E_{\text{eff}}}{kT} \right)} \right] + \frac{p_v(T, \beta) - p_a(T)}{\sqrt{2\pi m_{\text{Li}} kT}}
$$

(2.19)
2.6. A REALISTIC MODEL FOR LITHIUM EROSION

where \( f(\beta) \) is the mixed-material reduction factor introduced in Section 2.5.3, \( Y_{\text{phys}} \) is the physical Li sputtering yield given in Figure 2.10, and \( Y_{\text{ad}}, A, \) and \( E_{\text{eff}} \) the adatom-evaporation model parameters discussed in Section 2.5.4.2. We assume that \( Y_{\text{phys}} \) and \( Y_{\text{ad}} \) are reduced by \( f(\beta) \). The last term represents the contribution from Langmuir Law evaporation for a mixed-material Li/LiD layer (Section 2.4). The Li vapor pressure and ambient pressure are given by \( p_v \) and \( p_a \), respectively.

Figure 2.14 displays the cumulative Li erosion yield \( Y_{\text{Li}} = \Gamma_{\text{Li}}/\Gamma_{\text{D}^+} \) for a D ion flux \( \Gamma_{\text{D}^+} = 10^{24} \text{ m}^{-2} \text{ s}^{-1} \) and \( \text{D}^+ \) energy 20 eV. At low temperatures, Li erosion is dominated by physical sputtering. At moderate temperatures, the Li erosion yield increases due to thermal sputtering, before plateauing again when the evaporation rate of the adatoms becomes limited by their rate of creation. At high temperatures, the erosive Li flux begins increasing again as it becomes dominated by evaporation. Measurements to test the predictions of this Li erosion model are presented in Chapter 5.

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\(^7\)For the purposes of this formulation, an average of the homogenous and non-homogenous cases in Figure 2.12 is taken.
2.6. A realistic model for lithium erosion

Figure 2.14: The predicted atomic Li erosion yield vs. $T$ and the D/Li concentration ratio $\beta$ for D plasma bombardment at $\Gamma_{D^+} = 10^{24} \text{ m}^{-2} \text{ s}^{-1}$ and $E_{D^+} = 20 \text{ eV}$, incorporating the effects chemical sputtering, preferential sputtering, thermal sputtering, and mixed-material evaporation as modeled by Equation 2.19.
Chapter 3

Modeling the Near-Surface Plasma

In Chapter 2 we discussed mechanisms by which impurity species may be ejected off the surface into the plasma. These impurities can undergo numerous processes once they are inside the plasma itself; see Figure 2.1 for the D-Li example. The dynamics of these processes determine the equilibrium density \( n_0 \) of a neutral impurity species in the plasma through the continuity equation:

\[
\frac{\partial n_0}{\partial t} + \nabla \cdot (n_0 \mathbf{v}_0) = -n_0 n_e S + n_+ n_e R + n_+ n_n C_{+0} - n_0 n_i C_{0+}
\]  

(3.1)

where \( \mathbf{v}_0 \) is the impurity species velocity, \( n_+ \) is the density of the singly-ionized impurity, \( n_i \) is the main ion density, and \( n_n \) is the neutral density of the main ion species. \( S, R, \) and \( C_{+0}/C_{0+} \) represent the effective rate coefficients (\( \text{cm}^3 / \text{s} \)) due to the atomic physics processes of ionization, recombination, and charge-exchange, respectively. Quantitative characterization of these effects as a function of \( n_e \) and \( T_e \) will be discussed in the sections below. Impurity atoms can also be excited by a passing electron and then decay back to the ground state emitting line radiation. Impurity ions will become entrained in the plasma flow and may eventually be deposited back on the surface (re-deposition). These effects will be also be discussed in the ensuing sections.
Because impurity re-deposition can induce further erosion and surface modification, the processes discussed in Chapter 2 and Chapter 3 are highly intertwined.

### 3.1 The collisional-radiative model

Consider a plasma ion or neutral atom that is collisionally excited from its ground state to some excited state. For very low plasma densities, the probability that an atom is de-excited via a second collision is negligible in comparison with spontaneous decay via a radiative transition. This state is known as **coronal equilibrium**. The regime of validity of coronal equilibrium has been derived [90] and is given as

\[
n_e \lesssim 5.6 \cdot 10^8 (Z + 1)^6 T_e^{1/2} \exp \left( \frac{1.162 \cdot 10^3 (Z + 1)^2}{T_e} \right)
\]

where \( n_e \) is the electron density in \( \text{cm}^{-3} \), \( Z \) is the ion charge state, and \( T_e \) is the electron temperature in K. Above this critical value of \( n_e \), collisions are sufficiently frequent such that collisional de-excitation needs to be taken into account. This regime is known as the **collisional-radiative model**. The plasma is assumed comprised of two dominant ion populations: a recombined ion ground state and a recombining ion ground state. It is further assumed that all excited level populations equilibrate much faster than the rate at which the density of the ground state changes (which happens on the transport time scale), and thus their time derivatives can be neglected. This approximation is valid up until the plasma is sufficiently dense and collisional such that the population of excited states of ion charge \( Z + 1 \) is similar to the population of ground state ions of charge \( Z \).

The threshold for the validity of this assumption was computed by Bates [91]. Above this value of \( n_e \), the plasma may be treated in **local thermodynamic equilibrium (LTE)** limit as long as collisional processes dominate over spontaneous radiative decay, which for hydrogenic plasmas can be

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1 These derivations assume that only principal quantum numbers \( n \leq 6 \) are sufficient to describe the evolution of the collisional/radiative behavior of the plasma. A justification for this value is given in [90].
3.1. THE COLLISIONAL-RADIATIVE MODEL

Figure 3.1: The boundaries in $n_e$ and $T_e$ between the coronal equilibrium, collisional-radiative, and local thermodynamic equilibrium regimes for hydrogenic plasmas. The parameter range of interest in this thesis is also shown.

expressed as the condition \[ n_e \gtrsim 1.6 \cdot 10^{12} T_e^{1/2} (\Delta E_{mn})^3 \] \hspace{1cm} (3.3)

where $\Delta E_{mn}$ is the excitation potential (in eV) from level $m$ to level $n$. The ranges of validity for coronal equilibrium, the collisional-radiative model, and LTE for hydrogenic plasmas ($Z = 1$) are shown in Figure 3.1. It is apparent that the collisional-radiative model is needed to describe atomic physics processes in plasmas over a wide range of densities and temperatures. The parameters of interest in this thesis ($0.5 \text{ eV} \leq T_e \leq 5 \text{ eV}$, $10^{12} \text{ cm}^{-3} \leq n_e \leq 10^{15} \text{ cm}^{-3}$) lie within the collisional-radiative regime.
3.2 Atomic Data and Analysis Structure (ADAS)

ADAS is a set of interconnected computer codes and collections of data that allows for modeling atomics physics processes in plasmas using the collisional-radiative model [36]. At its core, ADAS contains a number of physics routines for calculating fundamental atomic data such as energy levels, transition probabilities, and electron impact collision cross sections. Such information is then used as input into a number of subroutines which process these data into more useful formats, such as ionization rate coefficients, recombination rate coefficients, photon emissivity coefficients, and fractional ion abundances as a function of electron density \(n_e\) and electron temperature \(T_e\). These post-processed data have been incorporated into many codes used to model impurity transport in plasmas such as B2-EIRENE [92] or DEGAS2 [93]. This present work, however, utilizes ADAS data directly in order to develop an “as-simple-as-possible” representation of the physics. This allows for the functional dependence of the impurity species erosion and re-deposition rates on various physical parameters to be systematically investigated in a manner that is not computationally intensive. A full description of all the information utilized from the ADAS database is described below.

3.2.1 Electron-impact ionization and recombination

Electron-impact ionization (henceforth referred to as simply ionization) is the process by which a bound electron is excited via a series of Coulomb collisions with free electrons until it escapes into the continuum. The inverse process, in which a free electron is captured by a passing ion and decays down to the ground state through collisionally-induced or spontaneous transitions, is known as recombination. The ionization and recombination rates for neutral lithium have been computed over a wide range of \(n_e\) and \(T_e\) using the ADAS collisional-radiative model [94] and are considered to be highly accurate [36]. These rate coefficients for boron ionization and recombination are also available, although these results are considered less accurate [36]. Interpolation between existing
values of $S$ and $R$ in the $n_e$ and $T_e$ grid are performed in logarithmic space using the following formula:

$$
\log [S(n_e, T_e)] = \sum_{i=0}^{1} \sum_{j=0}^{1} \log \left[ S(n_{i e}, T_{j e}) \right] \frac{\log \left( \frac{n_i^{n_e}}{n_{i e}} \right)}{\Delta n_e} \frac{\log \left( \frac{T_j^{T_e}}{T_{j e}} \right)}{\Delta T_e} \quad (3.4)
$$

where $n_{i e}^0$, $n_{i e}^1$ and $T_{j e}^0$, $T_{j e}^1$ correspond to the two closest values of $n_e$ and $T_e$ present in the ADAS database and $\Delta n_e$ and $\Delta T_e$ are the absolute differences between the two values (in logarithmic space). Note that this is effectively the same procedure utilized in Section 2.3.2 except here the interpolation is performed in fully logarithmic space rather than linear-linear-log space.

The resulting values of $S_{Li}(n_e, T_e)$ and $R_{Li}(n_e, T_e)$ are plotted in Figure 3.2 and values of $S_B(n_e, T_e)$ and $R_B(n_e, T_e)$ are shown in Figure 3.3. It is evident that these rate coefficients (particularly ionization) are strongly dependent on $T_e$. The $n_e$ dependence of $S_{Li}$ is fairly strong, with an increase of an order of magnitude over this parameter range. No ionization or recombination data are available for boron for $T_e < 1$ eV and the given ionization rates are not $n_e$-dependent, so they are plotted as a single black curve. Assuming a typical ratio $n_0/n_+ \geq 10$, it is evident that the ionization source term $n_0n_eS$ dominates over recombination down to electron temperatures as low as 0.5 eV for Li and 1.0 eV for B. This simplifies the modeling approach at sufficiently high $T_e$ because the recombination term in Equation 3.1 can be neglected.

### 3.2.2 Line Radiation

The process where a bound electron de-excites via photon emission is known as line radiation. Such transitions occur spontaneously with some constant rate and can also be collisionally induced. The resulting photon emission is extremely useful for obtaining information about impurity species in the plasma. There are two transitions that are of particular interest for this work. The first is the $1s^22p \rightarrow 1s^22s$ transition for neutral Li (Li-I) which emits a photon of characteristic frequency.
3.2. Atomic Data and Analysis Structure (ADAS)

Figure 3.2: Ionization and recombination rate coefficients for neutral Li atoms.

Figure 3.3: Ionization and recombination rate coefficients for neutral B atoms.

wavelength $\lambda = 670.8$ nm. The second is the $1s^22s^23s \rightarrow 1s^22s^22p$ transition for neutral B (B-I) with wavelength $\lambda = 249.7$ nm. The intensity of this line radiation in a plasma is given by

$$I(\text{photons/ m}^3\text{s}) = n_e n_0 P(n_e, T_e)$$

where $P$ is known as the photon emissivity coefficient (PEC) and can be obtained from the ADAS database. The PEC values for the two transitions described above are given in Figure 3.4 as a function of $n_e$ and $T_e$. The PEC values for the Li-I transition include both electron-impact excitation and electron de-excitation during recombination. The recombination term becomes significant for $T_e < 1$ eV. The PEC values for the B-I transition include electron-impact excitation only. Interpolation between existing values on the $n_e$ and $T_e$ grid are performed as described in Equation 3.4 above. These PEC values can be used to infer the density of the neutral impurity species in the plasma given experimental values of $n_e$, $T_e$ and the line-integrated photon flux on to a camera with the appropriate wavelength filter. The procedure for this process is described in Chapter 4.
For sufficiently high impurity concentrations, the resulting impurity cloud can become opaque to a certain range of wavelengths. Physically this corresponds to radiated photons undergoing resonant collisions with impurity ions, causing them to be re-absorbed rather than emitted from the plasma. This phenomenon is referred to as radiation trapping. The photon absorption mean free path $\lambda_{abs}$ is given by [95]:

$$
\lambda_{abs} = \left( \frac{2kT_0}{m_0} \right)^{0.5} \frac{8\pi^{1.5}}{\lambda^3} \frac{g_l}{g_u A_{ul} m_0} 
$$

where $\lambda$ is the radiation wavelength, $g_u, g_l$ are the statistical weights of the upper and lower states, $A_{ul}$ is the Einstein coefficient (s$^{-1}$) for the transition, $m$ is the impurity ion mass, and $T$ is the impurity ion temperature. To avoid radiation trapping the width of the impurity species layer (characterized by the ionization mean free path $\lambda_{iz} = v_0/n_e S$) must be significantly smaller than $\lambda_{abs}$. The
magnitude of the effect of radiation trapping will be considered during analysis of experimental data.

3.3 Charge Exchange

Charge exchange (CX) is the process by which a positively charged ion collects an electron from a neutral atom during a collision. The initial charge of the ion is given by \( q_e \), where \( e \) is the elementary charge and \( q \) is an integer less than or equal to the atomic number of the ion. Since like-particle charge exchange has no net effect on \( n_0 \) or \( n_+ \), the processes of interest are collisions between unlike particles, namely the impurity and main plasma ion species. For Li colliding with D, the CX reactions involving neutral Li can be written as

\[
\text{Li}^+ + \text{D} \rightarrow \text{Li} + \text{D}^+ \quad (3.7)
\]

and for the inverse process

\[
\text{Li} + \text{D}^+ \rightarrow \text{Li}^+ + \text{D} \quad (3.8)
\]

These two reactions are characterized by rate coefficients \( C_{+0}(n_e, T_e) \) and \( C_{0+}(n_e, T_e) \), respectively. If either the third or fourth terms on the left side of Equation 3.1 are significant relative to the ionization term, this additional source or sink of neutral impurities must be accounted for. The relevant charge exchange data contained in ADAS assumes a constant cross section (for Li) or is missing altogether (for B). However, calculations of Li\(^+\)-H(1s) charge exchange cross sections have recently been performed using an \textit{ab initio} quantal treatment \[96\] for \( E/\mu \geq 25 \text{ eV/amu} \), where \( E \) is the system energy in the center-of-mass (COM) reference frame and \( \mu \) is the reduced mass. These simulations show good agreement with the experimental data available at high energies \[97\]. The calculations have been extrapolated up to the higher-\( n \) excited states\(^3\) using an existing empir-

\(^3\)As in the case of Section 3.1, this calculation only utilizes principal quantum numbers \( n \leq 6 \).
Figure 3.5: The charge exchange rate coefficients for Li\(^{q+}\) and neutral H, where \(q = 1, 2, 3\), as a function of electron temperature \(T_e\). Extrapolations obtained courtesy of [99]. For comparison, the Li ionization rate in a plasma with \(T_e = 1\) eV, \(n_e = 10^{14}\) cm\(^{-3}\) is about \(10^{-8}\) cm\(^3\)/s.

The results of this calculation are shown in Figure 3.5, along with a similar extrapolation for the Li\(^{3+}\)-H CX reaction. Rates for the Li\(^{2+}\)-H (also shown in Figure 3.5) display very different behavior due to a strong resonance between Li\(^{2+}(n=3)\) and H(1s) [100]. It is evident that the \(q = 1\) Li CX rate coefficients are many orders of magnitude below those of ionization and recombination at low \(T_e\) and thus can be neglected in Equation 3.1.

For the boron case, charge exchange calculations have only been performed using semiclassical atomic orbital expansions [101]. For Li charge exchange, the results in [96] indicate that semiclassical calculations can be off by an order of magnitude or more at low energies. But strong species dependence in CX reactions is generally not observed for impurity ions of the same charge state (see, for example [102]). Since the boron-hydrogen CX rate coefficients would need to be
3.4 Modeling the eroded neutral impurity species

3.4.1 Neutral-ion collisions

The density of lithium or boron atoms that have eroded from a material surface into the plasma can be determined via Equation 3.1. In Sections 3.2 and 3.3 we have demonstrated that the recombination and charge exchange terms in this equation can be neglected for most of the high-density, low-temperature regime considered here. In addition, the typical ionization time of an eroded impurity atom \( \tau_{iz} = v_0/\lambda_{iz} \) is \(< 1 \mu s\) for Li atoms and \(< 1 \text{ ms}\) for B atoms. Thus as long as the time evolution of plasma parameters (typically on the order of seconds) is long on average relative to these time scales, the steady state \( (\partial n_0/\partial t \approx 0) \) can be assumed. This simplifies Equation 3.1 to the following form:

\[
\nabla \cdot (n_0 v_0) = -n_0 n_e S(n_e, T_e). \tag{3.9}
\]

We consider solutions of this equation for the case of neutral atoms ejected with velocity \( v_0 \) into a quasi-neutral plasma \((n_e = n_i)\). To determine the ejected impurity velocity \( v_0 \) we make the assumption \([35]\) that sputtered atoms are ejected with about half of the surface binding energy (SBE), which is 1.45 eV for Li adatoms and 5.76 eV for B atoms. This initial Dirac delta function velocity distribution \( f(v) = \delta(v - v_0) \) can be modified via collisions with plasma ions. We assume that atom-ion collisions can be approximated by “hard-sphere” elastic scattering. In this limit the collisional cross-section is given by the sum of the atomic radii \( \sigma_c = \pi(r_{\text{VDW},0} + r_{\text{VDW},i})^2 \) where \( r_{\text{VDW},0} \) and \( r_{\text{VDW},i} \) are the Van der Waals radii of the eroded atom and plasma ion, and the collisional collisions.

\[4\]Note that this approximation breaks down during the ramp-up phase of a plasma discharge or during transient events, which are not addressed in this work.
3.4. Modeling the eroded neutral impurity species

The ratio of the ionization MFP $\lambda_{iz}$ to the neutral-ion collision MFP $\lambda_c$ for Li and B atoms in a deuterium plasma is shown in Figure 3.6. A horizontal line indicates where this ratio is equal to unity, below which neutral-ion collisions can be ignored. The ratio $\lambda_{iz}/\lambda_c$ for Li and B atoms is shown in Figure 3.6. It is apparent that neglecting neutral-ion collisions for Li is acceptable down through electron temperatures $T_e < 1$ eV, implying that the neutral atom distribution in velocity space is not significantly altered by collisions. In the B case, the ionization MFP is longer than the collisional MFP only for $T_e < 5$ eV. Thus neglecting collisions in the case of boron impurities is only valid for plasma scale lengths $L < \lambda_c$. For context, in a plasma with density $n_e = 10^{14}$ cm$^{-3}$, $\lambda_{c,B}$ is approximately equal to 5 cm.
3.4.2 Modeling Approach

With the assumptions described above, Equation 3.9 can be solved for any distribution of ejected impurity atoms and arbitrary inhomogeneous D plasma background. For this work we are primarily interested in a linear plasma column such as Magnum-PSI (see Chapter 4) with a roughly Gaussian $n_e$ and $T_e$ distribution in the radial ($r$) direction and approximately uniform plasma profiles in the azimuthal ($\phi$) and axial ($z$) directions. This plasma column intersects the surface normal to the axial direction of the beam. The plasma column is simulated by a 3D grid with spacing $\Delta r = 0.5$ mm, $\Delta z = 0.5$ mm, and $\Delta \phi = \pi/18$ ($10^\circ$) in the radial, axial, and azimuthal directions, respectively. Finer grid spacing in any dimension does not result in appreciable differences in the solution.

Impurity erosion is simulated at axial location $z = 0$ by placing an impurity-emitting point source of strength $R$ at every radial/azimuthal grid point. The strength of this point source ($s^{-1}$) is equal to

$$R = Y \Gamma_{D^+} \frac{\Delta \phi}{2\pi} \left[ \left( r + \frac{\Delta r}{2} \right)^2 - \left( r - \frac{\Delta r}{2} \right)^2 \right]$$

(3.10)

where $Y$ is the radially-dependent impurity erosion yield and $\Delta \phi$ is in radians. Following the treatment of [16] the ion flux to the target is given by $\Gamma_{D^+} = \frac{1}{2} n_e c_s$, where $c_s = (2T_e/m_{D^+})^{1/2}$ is the ion sound speed. The factor of 2 is present in the definition of the ion sound speed because the plasma is assumed sufficiently collisional such that $T_e = T_i$.

For ease of calculation we transform to a spherical coordinate system $\langle \rho, \theta, \phi' \rangle$ with the origin at the point source location $\langle r_0, 0, \phi_0 \rangle$ and the $\phi' = 0$ direction given by the vector between the point source and the center axis of the column. Both coordinate systems are diagrammed in Figure 3.7 and the complete transformations between $\langle r, z, \phi \rangle$ and $\langle \rho, \theta, \phi' \rangle$ are given in Appendix A.1. The numerical grid in spherical coordinates contains resolution $\Delta \theta = \pi/36$ in the polar direction and

---

The presence of the factor of $\frac{1}{2}$ is derived with the assumption that no net ion flow exists far upstream from the wall region. If the bulk plasma ion flow is non-zero, the density drop in the pre-sheath region is reduced, leading to a larger sheath-edge density.
Figure 3.7: Depiction of the cylindrical (blue) and spherical (green) coordinate systems utilized during the process of numerically solving for the neutral impurity density.
3.4. Modeling the Eroded Neutral Impurity Species

\( \Delta \phi' = \pi/18 \) in the azimuthal direction. The radial direction \( \rho \) consists of 100 grid points with spacing \( \Delta \rho = \rho_0/100 \), where \( \rho_0 \) is the distance from the impurity ejection location \( (\rho = 0) \) to the boundary of the plasma column along the polar and azimuthal ejection angles \( \theta \) and \( \phi' \). The expression for \( \rho_0 \) is derived in Appendix A.2. The specified spherical coordinate system is useful because in Sections 3.2-3.4.1 it was shown that under a certain range of plasma conditions an ejected impurity atom traverses the plasma column in a straight line with constant velocity \( v_0 \) until it is ionized, i.e. \( \vec{v}_0 = v_0 \hat{\rho} \). In this case, Equation 3.9 reduces to a simple form:

\[
\frac{2v_0n_0}{\rho} + v_0 \frac{\partial n_0}{\partial \rho} = -n_0n_eS(n_e, T_e) \tag{3.11}
\]

where \( n_0 \), \( n_e \) and \( T_e \) are all functions of \( \rho \), \( \theta \), and \( \phi' \). We specify a cosine flux distribution for the point source in the polar direction and symmetry in the azimuthal direction, as is typical for sputtering and evaporation (see Sections 2.4 and 2.5). With this boundary condition, the solution to Equation 3.11 (derived in Appendix A.3) is given by:

\[
n_0 = \frac{R}{\pi \rho^2 v_0} \cos \theta \exp \left[ -\frac{1}{v_0} \int_0^\rho n_eS(n_e, T_e) d\rho \right]. \tag{3.12}
\]

The coefficients \( n_0^{ijk\iota'} \), which reflect the contribution to the impurity density at coordinates \( \langle r_i, z_j, \phi_k \rangle \) due to impurity erosion from the target at coordinates \( \langle r'_i, 0, 0 \rangle \), are calculated numerically by transforming Equation 3.12 back to cylindrical coordinates. It is only necessary to calculate \( n_0 \) at one value of \( \phi \) due to the azimuthal symmetry of the problem. Finally, a 2D \( \langle r_i, z_j \rangle \) grid is obtained for \( n_0 \) by summing over the \( k \) and \( \iota' \) indices:

\[
n_0(r_i, z_j) = \sum_k \sum_{\iota'} n_0^{ijk\iota'} \tag{3.13}
\]

\(^{6}\)Obviously the exact grid points of a spherical and cylindrical coordinate system will not overlap, so in practice values of \( n_0 \) from the spherical coordinate grid points are assigned to the corresponding closest grid point of the cylindrical coordinate system.
3.5. Modeling the singly ionized impurity species

A diagram of this solution grid is shown in Figure 3.8. As a simple example we choose a plasma beam with peak density $n_e(z = 0) = 10^{14}$ cm$^{-3}$ and temperature $T_e(z = 0) = 2$ eV. The radius of the plasma column $r_0$ is equal to 12.5 mm and the half-width at half-maximum (HWHM) $\sigma = R_0$ for both the electron density and temperature. Thus the number of radial grid points $N_i = 25$ and the number of axial grid points $N_j$ is specified as 100 such that the near-surface cutoff distance $z_0 = N_j \Delta z = 50$ mm. The erosion yield of the Li layer is given a constant value $Y = 0.1$, typical of a LiD layer at temperatures around 500 °C (see Figure 2.14). The erosion yield of the boron layer is specified as $Y = 0.004$, the value for 20 eV D→Li physical sputtering calculated with TRIM.SP (see Figure 2.10).

The resulting 2D profile of the atomic Li and B densities is shown in Figure 3.9. It is evident that due its strong ionization rate, the Li impurity density in the plasma tends to decrease very rapidly as a function of distance from the target. In the B case, however, the impurity density is fairly flat since the ionization MFP is on the same order as the plasma scale length. This implies that nearly all Li tends to be ionized within such a plasma whereas much of the boron tends to escape. In addition, in both the Li and B cases $n_0$ tends to be higher near the edge of the plasma due to the Gaussian decrease in $n_e$ and $T_e$, which leads to higher values of $\lambda_{iz}$ at larger radius.

3.5 Modeling the singly ionized impurity species

3.5.1 Determination of the impurity ion density

Consider the impurity ion species of density $n_+(r, z)$ in the quasineutral, axisymmetric plasma column with electron density $n_e(r)$ and axial magnetic field $B$. The full continuity equation for the ion density is given by:

$$\frac{\partial n_+}{\partial t} + \nabla \cdot (n_+ v_+) = n_0 n_e S - n_+ n_e R - n_+ n_n C_{+0} + n_0 n_i C_{0+}$$ (3.14)
Figure 3.8: Depiction of the resulting 2D grid geometry used to determine the spatially resolved impurity density in the plasma column. Note that this is a cartoon depiction only and does not indicate the full grid point resolution.
Figure 3.9: 2D radial and axial neutral impurity density profiles for Li and B in a plasma column. The density contours are outlined in black in the B case to distinguish between the small variations in $n_B$. The density fluctuations are not due to turbulence or any physical effect, they are simply small amounts of noise introduced via the numerical integration procedure.
Here we have neglected terms involving $n_{2+}$ because the doubly ionized Li population in these plasmas is negligible \[94\]. In addition, as has been discussed above, all terms other than the divergence term on the left and the ionization source term on the right can also be neglected.

These impurity ions are assumed to thermalize quickly with the background plasma, and stream through the plasma column along the magnetic field lines at the deuterium sound speed $c_s = (T_e/m_{D^+})^{1/2}$ until they arrive back at the target surface. This process is referred to as re-deposition. This assumption of thermalization of impurities has been verified in simulations for carbon and hydrocarbon ions \[103\], and has been measured in experiments with B$^+$ and Al$^{2+}$ impurities in He plasmas on the PISCES-B linear plasma device \[104\]. We also make the assumption that $v_+ = -c_s \hat{z}$, i.e., all motion of the ion gyrocenter is in the axial direction and diffusive motion perpendicular to the magnetic field $\vec{B} = B\hat{z}$ is small. An estimate of the perpendicular diffusive velocity is determined in Appendix B.1 and found to be small ($<10\%$) relative to parallel motion. Note that the same approximations break down in the case of boron impurities because the ionization MFP is significantly longer, implying boron ions have significant time to diffuse before re-deposition on the surface. Thus boron re-deposition fractions will not be calculated here.

With these assumptions, Equation 3.14 simplifies to:

$$v_+ \frac{\partial n_+}{\partial z} = n_e n_0 S(n_e, T_e) \quad (3.15)$$

and the solution to this equation is given by

$$n_+(r, z) = \frac{2n_e S(n_e, T_e)}{c_s} \int_{z_0}^z n_0(r, z') \partial z'. \quad (3.16)$$

Note that this model assumes fast thermalization of impurities, i.e., the thermalization time of the Li impurity ion is negligible relative to its total residence time in the plasma.
where \( z_0 = 5 \text{cm} \) is the near-surface cutoff distance. These bounds of integration are chosen because the Li density is effectively zero out at \( z_0 \) (see Figure 3.9) and thus the constant of integration vanishes. The integration in Equation 3.16 is performed numerically.

### 3.5.2 Lithium re-deposition profiles

The lithium ion flux returning to the surface is given by \( \Gamma_+(r, 0) = n_+(r, 0)v_+ \). This quantity can be determined directly from Equation 3.16. But the true quantity of interest is the re-deposition fraction \( R(r) = \Gamma_+(r, 0)/\Gamma_0(r, 0) \),

\[
R(r) = \frac{\Gamma_+(r, 0)}{\Gamma_0(r, 0)} = \frac{n_+(r, 0)v_+}{n_0(r, 0)v_0}
\]  

(3.17)
i.e., the re-depositing flux of Li ions divided by the eroded flux of Li neutrals. In Figure 3.10 we plot \( R(r) \) for a plasma column with a Gaussian profile of HWHM \( \sigma = r_0 = 12.5 \text{ mm} \) with peak electron density \( n_e = 10^{14} \text{ cm}^{-3} \) and electron temperatures \( T_e \) varying from 0.5 eV to 2.0 eV.

Several features of this plot are immediately evident. First, the re-deposition fraction is a very strong function of electron temperature. This is because the ionization MFP \( \lambda_{iz} \) varies from 25 cm at \( T_e = 0.5 \text{ eV} \) to 0.5 mm for \( T_e = 2.0 \text{ eV} \). At the low end of this temperature range, \( \lambda_{iz} \) is much longer than the plasma scale length \( L \sim 1.25 \text{ cm} \) and most eroded atoms escape from the column. At the high end of this range, \( \lambda_{iz} \ll L \) and thus nearly all eroded Li atoms are ionized and correspondingly re-deposited. Second, the re-deposition fractions can actually exceed unity at high \( T_e \) near the center of the target, implying a build-up of Li material. This is predicted because atoms are preferentially ionized closer to the axis of the plasma column where \( n_e \) and \( T_e \) are highest. Finally, \( R \) dips sharply near outer edge of the plasma because any atom that is ejected outward and escapes the column without ionizing is lost. Experimental measurements of the Li re-deposition fraction to test this model will be presented in Chapter 6.
Figure 3.10: The re-deposition fraction of eroded Li atoms in a plasma column as a function of radial position and electron temperature $T_e$. 
Chapter 4

The Magnum-PSI linear plasma device

The divertor plasma in a tokamak is characterized by high electron densities \( n_e > 10^{20} \text{ m}^{-3} \) and low electron temperatures \( T_e < 5 \text{ eV} \) leading to high particle fluxes \( \Gamma_i > 10^{23} \text{ m}^{-2} \text{ s}^{-1} \). Thus it is important to carefully study the plasma-material interactions (PMI) described in Chapters 2 and 3 under these divertor-relevant plasma conditions. This motivates experiments in linear plasma devices, where PMI can be studied with better diagnostic access and more controlled experimental conditions than those present in a tokamak. The Magnum-PSI linear plasma device \([37, 105]\) is capable of obtaining the plasma conditions described above and provides detailed information about the near-surface plasma and surface itself. Thus it provides a useful testing ground for the theory of temperature-dependent erosion and re-deposition described in the preceding chapters. A top-down photograph of Magnum-PSI is displayed in Figure 4.1 and schematic diagram is shown in Figure 4.2. An overview of the machine hardware and diagnostic capabilities will be described in this chapter.
Figure 4.1: A top-down photograph of the Magnum-PSI linear plasma device.

Figure 4.2: Schematic side-view diagram of the Magnum-PSI linear plasma device. A high-density plasma is generated in the cascaded-arc source (a) and streams down the magnetic field lines generated by oil-cooled copper magnetic coils (b). The plasma column (c) is stripped of neutral atoms by a skimmer system (d) before impacting on the target holder (e). Image obtained courtesy of [105].
4.1 Experimental Apparatus

4.1.1 Plasma Source

The Magnum-PSI discharge is produced by a cascaded-arc plasma source \[106\] capable of producing extremely high electron densities \((> 10^{21} \text{ m}^{-3})\). A schematic diagram of the source is shown in Figure 4.3. Between magnetic field pulses, argon gas flows through the source at approximately 6 Pa \(\cdot\) m\(^3\)\(\cdot\)s. During the discharge itself this gas can be switched to H\(_2\), D\(_2\), He, or Ne at flow rates ranging from 4-9 Pa \(\cdot\) m\(^3\)\(\cdot\)s. In the present work the gases utilized were argon, deuterium, and neon. Gas is ionized between the cascaded plates consisting of a series of water-cooled copper rings and boron nitride spacers. Plasma current flows between the cathode needle at the far end of the plates and a conductive ring nozzle at the gas outlet that serves as the anode. The anode is electrically grounded to the main vessel. The plasma current inside the source is adjustable from approximately 80 to 220 A. Control of the gas flow rate and source current serve as two primary mechanisms for controlling plasma parameters \(n_e\) and \(T_e\) at the target. Generally the plasma density and temperature increase as a function of source current and decrease as a function of gas flow rate, but these trends can be reversed for certain gas species in specific parameter ranges. Degradation of the source materials over time can also lead to unexpected changes in plasma performance, which lead to the source being replaced every few weeks. In practice an empirical approach involving small adjustments of the source current and gas flow rate is necessary to obtain specific desired values of \(n_e\) and \(T_e\).

4.1.2 Magnetic field coils

The original design of Magnum-PSI called for the implementation of superconducting magnetic field coils to allow for long pulse lengths at magnetic fields of \(~3\ T\) \[37\]. Due to significant manufacturing delays, however, oil-cooled copper magnetic coils were temporarily installed on
the device, shown as the set of structures labeled (b) in Figure 4.2. The pulse length and duty cycle of plasma discharges is primarily limited by ohmic heating of the coils. Four different coil current/magnetic field settings have been developed to allow for a trade off between pulse duration and $n_eT_e$ [108]. These experiments used primarily the so-called Magnet Setting 3 (MS3), which results in a magnetic field in the source $B_{\text{source}} = 1.30$ T. Due to the divergence of the magnetic field lines outside of the coils themselves, the field at the target drops by approximately a factor of 5 to $B_{\text{target}} = 0.25$ T. For comparison, NSTX typically operated with a toroidal magnetic field on-axis of $\sim 0.45$ T, and with NSTX-U this value will increase to $\sim 1.0$ T [109]. At this magnetic field setting, Magnum-PSI plasma pulses are limited to a maximum of 12 s, although in practice shorter durations are often used to allow for a higher duty cycle. The $B$ field gradually decreases throughout the plasma discharge (see Figure 4.4), leading to a slowly varying $n_e$ and $T_e$. The typical shot cycle varies from 10-20 minutes depending on the pulse length and corresponding cool-down time of the copper magnets.
4.1.3 Differential pumping

Due to a desire to minimize the fraction of neutral gas present at the target, a differential pumping system \[110\] was developed in which the vessel is separated into three distinct sections. Each portion of the vessel is separated by independently pumped “skimmers” which serve to eliminate neutral gas emanating from the source. In this configuration the dominant source of neutrals in the near-surface plasma is recycling from the target itself. It has been verified in simulations of the Pilot-PSI plasma beam \[111\] that the ionized plasma fraction remains very high (> 90%).

4.1.4 Target manipulator

The Magnum-PSI device is capable of employing several interchangeable target holders \[112\]. Of primary interest in this work is the multi-target holder capable of exposing circular disk-shaped samples, shown schematically in Figure 4.5. For samples smaller than the 64 mm maximum, a TZM (Titanium-Zirconium-Molybdenum alloy) clamping ring fixes the targets in place. The target holder is capable of rotation via a rotary feed-through and can expose up to five separate samples without breaking vacuum. In practice only three of these five holders are typically used, each spaced 90° apart. The samples remain in physical contact with a water-cooled copper backing.
4.1.1 Experimental Apparatus

Figure 4.5: The rotary target holder used in Magnum-PSI. Samples are mounted on top of five possible copper base plates (shown in yellow). The red tube (aluminum/bronze alloy) is both the water supply and axis of rotation. A clamping ring is shown mounted on the central target, allowing for exposure of a 30mm diameter sample. Image obtained courtesy of [112].

No external heaters are present in the target holder, and thus the sample temperature rise during experiments is solely due to the plasma heat flux. The cooling rate to the sample can enhanced to some extent by increasing the torque on the clamping ring bolts. The cooling can also be mitigated by using thicker samples or by placing one or more grafoil® (flexible graphite foil) spacers between the clamped target and copper backing. Information on sample preparation for particular experiments will be provided in subsequent chapters.

4.1.5 Target Exchange and Analysis Chamber (TEAC)

The sample manipulator arm is mounted on a 5-meter long linear motion feed-through and bellows system that allows the target holder to be retracted into the Target Exchange and Analysis Chamber (TEAC). A photograph of the TEAC interior and target holder shown in Figure 4.6. This chamber is independently pumped from the rest of the vessel and thus allows for samples to be exchanged
and analyzed without breaking vacuum in the main chamber. The TEAC is \( \sim 1 \) m in diameter and contains over 30 ports that provide numerous diagnostic and viewing capabilities. The top lid of the chamber is completely removable, enabling full access to the target manipulator. The sample arm can be retracted and extended between the TEAC and main chamber in approximately 1 minute. Venting the TEAC takes \( \sim 15 \) minutes, exchanging samples takes about 10 minutes, and pumping the chamber back down to pressures of \( \sim 5 \cdot 10^{-7} \) torr requires approximately 30 minutes. Thus the complete sample exchange process can be completed in about 1 hour. The main diagnostics present in the TEAC are laser induced desorption (LID) and laser induced breakdown spectroscopy (LIBS), but these were not used in the present work. The TEAC also contains a lithium evaporation system utilized for applying thin lithium coatings to target samples; see Section 4.2 for details.

4.2 Lithium Evaporation System

4.2.1 Alvatec Evaporation Source

The initial lithium evaporation system on Magnum-PSI (installed May 2012) consisted of an Alvatec Alvasource\textsuperscript{\textregistered} Type V Li vapor source. A photograph of the Alvatec source is shown in Figure 4.7. The source consists of a small stainless steel tube that is filled with Li metal under an argon atmosphere and then pugged with an indium (In) sealant. Two different source sizes with diameters \( d = 2.5/4 \) mm and a total Li inventory of 25/45 mg were used. The tube is electrically connected to a current supply via two copper rods that allow the source to be resistively heated. At a temperature of \( \sim 200-250 \) °C, the In seal melts and heated Ar gas expels the sealant from the tube. The source then begins emitting Li vapor when a given activation current (several amps) is reached.

The lithium deposition rate on to target samples was monitored via a quartz crystal microbalance (QCM) system [113] with an Inficon Q-pod\textsuperscript{TM} transducer. The source evaporation rate in-
Figure 4.6: Photograph of Magnum-PSI machine operator John Scholten accessing the target manipulator arm inside the Target Exchange and Analysis Chamber (TEAC), circa June 2012. The target holder is inserted into the main chamber via the large port visible on the far left. The top lid of the TEAC has been removed via an overhead crane.
creased linearly with current (Figure 4.8) until the Li in the reservoir was depleted, which occurred after a total deposition of $\lesssim 500$ nm. In addition these sources were plagued by inconsistent operation, possibly due to either clogging of the source nozzle with residual indium or shorting in the source’s electrical connections. These unreliability issues, in addition to a desire to deposit significantly larger quantities of lithium on to sample targets, motivated the installation of a more robust and powerful lithium evaporation system that will be described below.

### 4.2.2 The LIThium EvaporatoR (LITER)

The LIThium EvaporatoR (LITER) is a lithium evaporation system originally designed for coating the divertor tiles in NSTX [114]. A prototype LITER unit known as LITER-1C was shipped to Magnum-PSI and installed on the TEAC in April 2013. It has a 90 g lithium capacity, although overflow events due to Li wetting/creep at high fill fractions in addition to the finite packing fraction of solid Li granules limit this capacity to about 45 g in the present work. The unit consists of a Li reservoir that is heated up to a maximum temperature of 650 °C. Evaporated Li atoms reflect off a heated back plate and stream down a heated exit tube or “snout” into the vacuum chamber.
4.2. Lithium Evaporation System

Each component of the LITER system (reservoir, back plate, snout) is separately resistively heated and the temperature of each component is monitored via Type K thermocouples. A cartoon diagram of the LITER-1C unit indicating the thermocouple locations is shown in Figure 4.9 and a schematic diagram of the LITER-1C interface with the TEAC chamber is shown in Figure 4.10. The current draw to the heaters is controlled via a central variac™ and a set of sliding switches. The temperature of each LITER-1C component was calibrated as a function of heater current.

The evaporation procedure for the LITER-1C unit was as follows. The snout, reservoir, and back plate were pre-heated to temperatures of approximately 350, 280, and 250 °C, respectively. Next the appropriate target sample was placed within line-of-sight of the evaporator. A quartz crystal microbalance (QCM) was extended in front of the snout and the LITER temperature was slowly ramped upward until evaporation began. When a reliable deposition rate was established, the QCM was retracted, allowing Li to begin coating the sample surface. The total evaporation
4.2. Lithium Evaporation System

Figure 4.9: Cartoon diagram of the LITER-1C evaporation source indicating the location of each Type K thermocouple.

Figure 4.10: Schematic diagram of the LITER-1C interface with the Magnum-PSI TEAC chamber.
Figure 4.11: LITER-1C deposition rate on the quartz crystal microbalance (QCM) over the course of three separate days. An exponential fit to this data is overlaid to guide the eye.

required approximately 15-30 minutes depending on the coating thickness desired. Total coating thickness ranged from 100 nm to 1000 nm. Every 5 minutes during the evaporation process, the QCM was extended in front of the sample for 60 seconds to verify the current deposition rate. A calibration of the resulting deposition rate vs. snout temperature for three separate days of Li evaporation is shown in Figure 4.11. It is evident that the LITER-1C evaporation rates were fairly consistent and show a roughly exponential increase with temperature. Although some variation was observed, no systematic trend was evident on a day-to-day basis. In addition, because the Li deposition rate was directly measured during each evaporation session, this variation did not introduce any additional uncertainty in determining the amount of lithium on the target.
4.3 Diagnostic Setup

The Magnum-PSI diagnostic suite was utilized to obtain detailed measurements of both the plasma and target surface. A depiction of the experiment and diagnostic setup during exposures of Li-coated samples is shown in Figure 4.12. Radial electron density and temperature profiles $n_e(r)$ and $T_e(r)$, where $r$ is the radial distance from the center of the plasma column, were obtained using a Thomson scattering (TS) system. Spatially resolved neutral Li emission profiles were derived from a Phantom camera with a Li-I (670.8 nm) filter. For experiments involving boron-coated targets, the Phantom camera was replaced with a Princeton Instruments PIXIS 2040B camera with a B-I (249.7 nm) filter. A FLIR systems infrared (IR) camera was calibrated against a spectrally resolved pyrometer to obtain emissivity-independent measurements of the target surface temperature, which ranged from room temperature up to approximately 800 °C. The setup and calibration of each of these diagnostics is described in more detail below.

4.3.1 Thomson Scattering

The Magnum-PSI Thomson Scattering (TS) system [115, 116] consists of a 532 nm Nd:YAG laser and a 35 m long laser beam path that intersects the center of plasma column from bottom to top, perpendicular to the central axis. The resulting beam has a spot size of approximately 0.7 mm at the plasma center and can be pointed at one spot for several hours with an accuracy of about 0.15 mm. The absolute distance from the target surface to the TS beam path can be adjusted to as close as 3-4 mm, but generally the surface is placed 10-20 mm from the laser beam to minimize stray light. Extensive efforts are also taken to minimize reflection and scattering of light within the optics system. The TS laser window is mounted at the Brewster angle to eliminate reflections. Several apertures collimate the stray light originating from the input windows. A new background subtraction is performed every time the target changes position. To monitor the absolute sensitivity of the TS system, Rayleigh scattering is performed on a daily basis.
Figure 4.12: Overview of the Magnum-PSI experiment and diagnostic setup. During experiments on B-coated targets, the Phantom camera was replaced by the PIXIS 2040B camera with a B-I filter.
4.3. Diagnostic Setup

The resulting TS light is imaged onto an array of 59 fibers with a nominal magnification $M = 0.267$. This light is collected by a transmission grating spectrometer equipped with a Princeton Instruments PI-Max ICCD camera. The spectral resolution of the complete system is about 0.137 nm (18 pixel FWHM), which corresponds to a minimum measurable temperature of $\sim 0.07$ eV, assuming a thermal (Maxwellian) distribution and a minimum measurable density of $\sim 10^{11}$ cm$^{-3}$. The spectral range of the spectrometer is 17.9 nm, implying that temperatures as high as $T_e = 34$ eV can be measured, but the peak plasma temperature never exceeded 5 eV in these experiments. Each fiber has a diameter of 400 µm but due to inherent limits of the viewing system resolution and magnification, the spatial resolution of plasma $n_e$ and $T_e$ measurements is $< 2$ mm. The procedure for the post-processing of the raw TS signals is described in [117] and post-processed data $n_e(r)$ and $T_e(r)$ for a typical Magnum-PSI pulse are shown in Figure 4.13 along with error bars.

Figure 4.13: Example electron density and temperature profiles in the Magnum-PSI plasma column, obtained from a single chord 20 mm from the target.
4.3.2 Pyrometry

The infrared radiation (IR) spectrum emitted from the target sample is measured using a commercially available FAR Associates Model FMPI SpectroPyrometer. This system has demonstrated accurate temperature measurements even for liquid metal surfaces [118] where the emissivity is often very uncertain. For highly reflective surfaces such as Li or TZM Mo, reliable pyrometry measurements can generally only be obtained for temperatures \( \gtrsim 600 \, ^\circ\text{C} \) due to the low amounts of infrared radiation emitted by the metal. The time resolution of the pyrometer is temperature-dependent and varies from \( \sim 1 \) Hz near 600 \(^\circ\text{C}\) and up to \( \sim 10 \) Hz far above this temperature.

IR emission in the wavelength range \( \lambda = 1000\text{-}1700 \, \text{nm} \) is focused via an optics system consisting of a series of mirrors and lenses onto an optical fiber cable and carried to a “black box” containing the spectroscopy, imaging, and data analysis hardware/software. Two high pass filters provide strong attenuation of all visible light, including the intense \( \text{D}_\alpha \) and \( \text{D}_\beta \) spectral lines. The system can be aligned by backlighting the fiber with a laser and moving the incident laser beam spot with the tuning knobs on a mirror mount. Typically the beam spot is focused on the center of the target sample, but if the plasma center is mis-aligned relative to the sample center the beam spot can be readjusted to capture the maximum surface temperature. The data analysis software automatically applies a background substraction to the raw intensity profiles and outputs a corrected intensity spectrum. The resulting corrected intensity spectra from a liquid Li surface during a typical Magnum-PSI discharge is shown in Figure 4.14.

4.3.2.1 Data Analysis

It is assumed that the surface functions as a “gray-body,” i.e., the surface emissivity \( \epsilon \) is not strongly wavelength dependent and thus the emission is expected to follow Planck’s law:

\[
B_\lambda(T) = \Omega \tau \epsilon(T) \frac{2hc^2}{\lambda^5} \exp\left(\frac{hc}{\lambda kT}\right) - 1
\]  

(4.1)
where $B$ denotes spectral radiance (W / sr m$^3$), $T$ is the surface temperature, $\Omega$ is the solid angle subtended by the optics system, $\tau$ is the transmission factor, $h$ is Planck’s constant, and $c$ is the speed of light. It is evident in Figure 4.14 that this spectrum contains many peaks due to line radiation from the plasma, particularly for $\lambda < 1300$ nm. Sometimes the SpectroPyrometer software successfully filters these peaks from the raw data, but often the wavelength region of these peaks must be manually removed. The resulting best-fit curve to Equation 4.1 is overlaid in Figure 4.14 along with the sections of the curve that are fitted and removed. Because the coefficients $\Omega$ and $\tau$ are not measured precisely, the numerical coefficient $\Omega \tau \epsilon$ is treated as a single free parameter. Although there is some temperature dependence to $\epsilon$, it is apparent that the gray body assumption results in a fairly good fit to the data. The inferred surface temperature for the spectrum in Figure 4.14 is 885 K (612 °C).
4.3. Diagnostic Setup

4.3.2.2 Error Analysis

The two dominant sources of error in this measurement are uncertainty in the fitting parameters themselves and uncertainty introduced by the gray-body assumption. The formal 1-sigma standard error of the fit parameter $T$ is typically around 2-3 °C. For an estimate of the error introduced by the gray-body assumption, separate fits are performed to the top half of the spectrum and bottom half of the spectrum, then compared to the value obtained fitting the entire spectrum. For the data shown in Figure 4.14, this analysis results in error bars $T = 612^{+85}_{-62}$ °C.

4.3.3 Infrared thermography

The sample temperature is also monitored using a FLIR Systems SC7500-MB IR camera operating at 100 Hz with a spatial resolution of approximately 0.5x0.5 mm. This camera is useful in addition to pyrometry because it has faster time resolution, provides measurements down to room temperature, and records a 2D thermal profile across the sample rather than a single data point. The camera is capable of operating in either a broad-band mode where it collects all light in the wavelength range 3.5-5.0 µm or with a narrow-band filter from 3.97-4.01 µm for higher-temperature operation. In nearly all the present experiments the narrow-band filter was used. The diagnostic setup is shown in Figure 4.12. IR light emitted from the surface reflects off an in-vacuo stainless steel mirror and passes through a barium fluoride (BaF$_2$) window before being collected by the camera. This results in the camera viewing the sample at an angle of approximately 20°-30° relative to surface normal.

4.3.3.1 Data Analysis

A 2D profile of the target surface temperature can be inferred from measurements of the IR intensity. Following the discussion in [119], the measured value of the IR emission $Q_{\text{meas}}$ can be written
4.3. Diagnostic Setup

\[ Q_{\text{meas}}(T) = \tau [\epsilon W_{\text{obj}}(T) + (1 - \epsilon) W_{\text{refl}}] + W_{\text{other}} \]  

(4.2)

where \( \tau \) is the transmission of the optics system, \( \epsilon \) is the object emissivity, \( W_{\text{obj}} \) is the radiative intensity of the object itself, \( W_{\text{refl}} \) is IR light from the surroundings that is reflected by the target, and \( W_{\text{other}} \) is light originating from other sources within the optics system itself, such as mirrors, windows, and lenses. It is assumed that \( \tau, \epsilon, W_{\text{other}}, \) and \( W_{\text{refl}} \) are independent of the object temperature \( T \). To eliminate \( W_{\text{refl}} \) and \( W_{\text{other}} \) a background subtraction at base temperature \( T_0 \) is performed, typically at the beginning of the discharge when \( T_0 = 20 \) °C. Subtracting \( Q_{\text{meas}}(T_0) \) from \( Q_{\text{meas}}(T) \), Equation 4.2 simplifies to

\[ Q_{\text{meas}}(T) - Q_{\text{meas}}(T_0) = \tau \epsilon [W_{\text{obj}}(T) - W_{\text{obj}}(T_0)] \]  

(4.3)

The quantity \( \tau \epsilon \) can be determined by obtaining the surface temperature at the center of the target \( T_{\text{center}} \) from pyrometry measurements (see Section 4.3.2). Assuming \( W_{\text{obj}}(T) \) follows Planck’s law, we have

\[ W_{\text{obj}}(T_{\text{center}}) = f_{\text{planck}}(T_{\text{center}}) = \int_{\lambda=3.97 \text{nm}}^{\lambda=4.01 \text{nm}} B_{\lambda}(T_{\text{center}}) d\lambda. \]  

(4.4)

The integral in Equation 4.4 cannot be evaluated analytically, but it can be approximated very accurately by \( f_{\text{planck}}(T) = B_{\lambda=3.99 \text{nm}}(T) \Delta \lambda \) where \( \Delta \lambda = 0.04 \) µm because \( B_{\lambda}(T) \) varies insignificantly over this very small range of \( \lambda \). The only remaining unknown is a single parameter \( A_0 = \tau_{\text{IR}} \epsilon_{\text{IR}} \Omega_{\text{pyro}} \epsilon_{\text{pyro}} \), the expression for which is given by

\[ A_0 = \frac{Q_{\text{meas}}(T_{\text{center}}) - Q_{\text{meas}}(T_0)}{f_{\text{planck}}(T_{\text{center}}) - f_{\text{planck}}(T_0)}. \]  

(4.5)

Note that this method assumes the object emissivity \( \epsilon_{\text{IR}} \) is spatially uniform across the surface.
Once $A_0$ is determined, the surface temperature can be inferred directly by combining Equations 4.3-4.5:

$$T(Q_{\text{meas}}) = \frac{hc}{\lambda k} \ln \left[ \frac{\frac{2hc^2}{\lambda^5} \Delta \lambda}{\frac{Q_{\text{meas}}}{A_0} - f_{\text{planck}}(T_0) + 1} \right]^{-1}$$

(4.6)

where $\lambda = 3.99 \, \mu m$.

### 4.3.3.2 Error Analysis

The dominant sources of error in the analysis of IR camera data come from the two assumptions of wavelength-independent pyrometer emissivity $\epsilon_{\text{pyro}}$ (the gray body approximation) and temperature-independent IR camera emissivity $\epsilon_{\text{IR}}$. The temperature uncertainty introduced by a constant $\epsilon_{\text{pyro}}$ can be estimated by calculating the corresponding values of $T$ obtained by replacing $T_{\text{center}}$ with the value at the bottom and top of the error bar on the pyrometry measurements. For bare TZM samples, this introduces an error of about $\pm 20 \, ^\circ C$.

The uncertainty introduced by a constant $\epsilon_{\text{IR}}$ can also be estimated. Although the $T$-dependent spectral emissivity of Mo or TZM Mo has not been well characterized, extensive measurements exist for the case of tungsten [120] and for $\lambda \geq 0.8 \, \mu m$ this data is well fit by the linear relations [121]

$$\epsilon_{W}(T, \lambda) = \epsilon_0(\lambda) + \epsilon_1 \lambda \cdot T$$

(4.7a)

where

$$\epsilon_0(\lambda) = 0.4205 \left( \frac{1.88949\lambda^3 + 0.24191}{\lambda^4 + 1.90197} \right)^{-1}$$

(4.7b)

and

$$\epsilon_1(\lambda) = 5.55537 \cdot 10^{-5} + 1.777171 \cdot 10^{-6} \epsilon_0 - 8.43353 \cdot 10^{-4} \epsilon_0^2 + 9.82596 \cdot 10^{-4} \epsilon_0^3.$$

(4.7c)
4.3. Diagnostic Setup

Figure 4.15: Error bars on the horizontal temperature profile across the surface of a bare TZM Mo sample inferred from IR camera measurements from 1 s, 2 s, and 4 s into a Magnum-PSI discharge.

Assuming that the $\epsilon_W(\lambda, T)$ is a reasonable proxy for $\epsilon_{TZM}(\lambda, T)$, the uncertainty introduced by a temperature-independent $\epsilon_{IR}$ is determined by creating a $T$-dependent $A_0$:

$$A_0(T) = A_0(T_{\text{center}}) \frac{\epsilon_W(T)}{\epsilon_W(T_{\text{center}})}.$$  (4.8)

The uncertainty is calculated as the difference between the inferred values of $T$ obtained by using $A_0(T)$ instead of $A_0(T_{\text{center}})$ in Equation 4.6. This uncertainty is introduced into the positive error bar only and varies from 1-25 °C, growing larger with the difference between $T$ and $T_{\text{center}}$. Note that Equations 4.7a-4.7c are valid for $\lambda > 800$ nm, which is the range considered here. The formulae are assumed valid for all $T$ below the tungsten melting temperature (3410 °C).
A horizontal temperature profile through the center of a bare TZM Mo sample is shown in Figure 4.15 for three separate times in the same discharge. It is evident that while the profile starts out fairly Gaussian, “hot spots” develop at later times. This may be due to asymmetric thermal contact with the copper backing and cooling water or reflected light from elsewhere in the chamber. In either case, typically only the central 1 cm region of the sample or smaller is utilized for data analysis, so these hot spot regions are not considered. The time evolution of the temperature at the center of the sample, averaged over a 3x3 pixel grid in each frame, is shown in Figure 4.16 along with temperatures measured on the SpectroPyrometer. The IR camera is not capable of measuring surface temperatures \( \lesssim 100 \, ^\circ C \) with the 3.97-4.01 \( \mu m \) filter because the signal strength \( Q_{\text{meas}} \) is too low. The magnitude of the IR data at the end of the discharge is in good agreement with the SpectroPyrometer, which is of course expected because the pyrometry data is utilized in the IR camera calibration. In addition, both pyrometry and IR data show a relatively constant temperature over the last second of the discharge, providing another level of confirmation that the diagnostics remain consistent.

### 4.3.4 Fast camera imaging

Radiation from Li-coated sample surfaces was monitored via a Vision Research Phantom v12.1 fast camera with a complementary metal-oxide semiconductor (CMOS) image sensor. Although this camera is capable of frame rates up to \( 10^6 \) Hz, videos were typically acquired at 100 Hz to optimize disk usage and capture the entire plasma pulse. The spatial resolution of the Phantom camera is \( \sim 0.5 \times 0.5 \, mm \) and the exposure time \( \Delta t_{\text{exp}} \) varied from 0.5 \( \mu s \) to 100 \( \mu s \) depending on the level of Li radiation emitted. A current session reference (CSR) is acquired before every discharge in order to eliminate background light and avoid digital artifacts. A narrow-band filter was placed in front of the camera lens in order to eliminate all radiation other than the \( 2p \to 2s \) Li-I transition (670.8 nm). The location of the Phantom camera in the diagnostic setup is shown in Figure 4.12.
4.3. Diagnostic Setup

Figure 4.16: The error band on the temperature at the center of a bare TZM Mo sample vs. time in a Magnum-PSI discharge. Temperatures measured on the SpectroPyrometer are also shown.

Radiation from the surface passes through a BaF$_2$ window, reflects off a silvered-glass mirror, and finally passes through the Li-I filter before begin collected by the camera. The camera views the sample at an angle of $\sim 45^\circ$ from surface normal.

4.3.4.1 Data Analysis

The raw counts $N_{\text{counts}}$ collected by each pixel of the CMOS sensor are linearly related to the line-integrated radiation intensity $I$ (photons/cm$^2$/s) by the following equation:

$$ I = N_{\text{counts}} \frac{S_{\text{CMOS}}}{\Delta t_{\text{exp}} \cdot f_{\text{geo}} \cdot f_{\text{opt}}} $$

The factor $S_{\text{CMOS}}$, the sensitivity (photons/count) of the CMOS sensor, was measured using a LabSphere™ Uniform Source Sphere with an absolutely calibrated spectral radiance (W / cm$^2$·s·sr·m) in the spectral range 0.3-2.4 µm. The geometric factor $f_{\text{geo}}$ is the fraction of solid
angle subtended by the Phantom camera lens

\[ f_{\text{geo}} = \frac{\Omega_{\text{lens}}}{4\pi} = \frac{\pi r_{\text{lens}}^2}{4\pi L_{\text{opt}}^2} \]  

(4.10)

where \( r_{\text{lens}} \) is the radius of the lens aperture and \( L_{\text{opt}} \) is the optical path length between the sample and the lens. The optical factor \( f_{\text{opt}} \) is given by

\[ f_{\text{opt}} = R_{\text{mirror}} T_{\text{window}} T_{\text{filter}} \]  

(4.11)

where \( R_{\text{mirror}} \) is the reflectivity of the mirror, \( T_{\text{window}} \) is the transmission of the BaF\(_2\) window, and \( T_{\text{filter}} \) is the transmission of the Li-I filter. The transmission spectrum of this filter was also directly measured via the LabSphere\textsuperscript{TM} and is shown in Figure C.1 in Appendix C. This spectrum is integrated over the shape of the Li spectral line determined via optical emission spectroscopy (see Section 4.3.6) to derive the overall transmission of the filter. The typical shape of the Li spectral line, along with a Gaussian fit, are also shown in Figure C.1.

Typical values of each calibration factor discussed above are given in Table 4.1. The transmission \( T_{\text{window}} \) was acquired both before and after each experimental run campaign and did not degrade noticeably, indicating that Li coatings did not significantly change the window transmission. These factors allow determination of the photon flux \( I \) from the surface of the sample. A 2D false-color image of the Li-I photon flux from the surface of a 25 mm diameter Li-coated sample is shown in Figure 4.17. This photon intensity is used to infer the eroded atomic Li flux \( \Gamma_{\text{Li}} \) using a procedure that will be described in the next chapter.

### 4.3.4.2 Error Analysis

The uncertainties of each calibration factor are also listed in Table 4.1. The CMOS counts are assumed to follow Poisson statistics and thus the error bar varies as \( \sqrt{N} \). The error bar in the CMOS
Figure 4.17: False color image of the calculated total photon flux $I$ from the surface of a Li-coated sample 1.5 s into a Magnum-PSI discharge.
4.3. Diagnostic Setup

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Calibration Factor</th>
<th>Typical value</th>
<th>Error</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{counts}})</td>
<td>CMOS counts</td>
<td>&lt; 4096</td>
<td>±(\sqrt{N_{\text{counts}}})</td>
<td></td>
</tr>
<tr>
<td>(S_{\text{CMOS}})</td>
<td>CMOS sensitivity</td>
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<td>±5</td>
<td>photons / pixel</td>
</tr>
<tr>
<td>(\Delta t_{\text{exp}})</td>
<td>Exposure time</td>
<td>0.5-100</td>
<td></td>
<td>µs</td>
</tr>
<tr>
<td>(r_{\text{lens}})</td>
<td>Lens aperture radius</td>
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<td>±1</td>
<td>mm</td>
</tr>
<tr>
<td>(L_{\text{opt}})</td>
<td>Optical path length</td>
<td>110-140</td>
<td>±5</td>
<td>cm</td>
</tr>
<tr>
<td>(R_{\text{mirror}})</td>
<td>Mirror reflectivity</td>
<td>0.95</td>
<td>±0.05</td>
<td></td>
</tr>
<tr>
<td>(T_{\text{window}})</td>
<td>BaF(_2) window transmission</td>
<td>0.45</td>
<td>±0.05</td>
<td></td>
</tr>
<tr>
<td>(T_{\text{filter}})</td>
<td>Li-I filter transmission</td>
<td>0.36</td>
<td>±0.02</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Table of typical values and error bars for each of the calibration factors present in Equations 4.9-4.11.

sensitivity originates from the uncertainty in the object distance and transmission factors of the optics set-up used for the calibration. No error bar is listed for the exposure time because it is assumed negligible. Because the sample is tilted at 45° relative to surface normal, the optical path length can vary slightly depending on whether a photon is emitted at the near side or far side of the sample. Errors in \(R_{\text{mirror}}\) and \(T_{\text{window}}\) stem primarily from differences in measurements conducted before and after the run campaign. Errors in \(T_{\text{filter}}\) come from small differences between the measured values and those given by the manufacturer specifications. For a value of \(N_{\text{counts}} = 1000\), error propagation yields a relative uncertainty in the line-integrated radiation intensity \(\Delta I/I \approx 29\%\).

4.3.5 Slow camera imaging

Because neutral boron does not have any strong radiation lines in the visible spectrum, it was decided to utilize the \(2s^23s \rightarrow 2s^22p\) B-I (249.7 nm) transition in the near-ultraviolet (UV) range for the purposes of measuring boron erosion. The quantum efficiency (photoelectrons/photon) of the Phantom v12.1 camera is negligible in the UV spectrum, and thus a Princeton Instruments PIXIS 2040-B camera with CCD sensor was utilized instead. This camera was capable of frame rates of about 4 Hz at a spatial resolution of \(\sim 1\times1\) mm. The exposure time is primarily limited
by the camera shutter speed, which was empirically determined to be 59 ms. It is assumed that
the shutter moves at a constant speed as it opens and closes. The PIXIS camera does not have
the capability to acquire a current session reference, so instead a background measurement was
acquired before each discharge and then subtracted from the measured data. The background was
always a factor of 10 or lower below the signal level.

No appropriate UV lens mount was available for the PIXIS camera, and thus a custom-built UV
optics system was installed (Figure 4.18). Radiation from the surface passes through the same BaF₂
window, reflects off a UV-enhanced aluminum mirror, passes through a pair of plano-convex UV
fused silica lenses to collimate and focus the light, and finally through a pair of UV filters. The first
filter is a UV ‘shortpass’ filter that blocks all visible light. The second filter is a UV bandpass filter
with a ~251 nm center wavelength and HWHM of ~5 nm. A small aperture 5 mm in diameter
was also placed between the lenses to further attenuate the UV signal. Numerous efforts were
undertaken to ensure that it was UV light, and not residual visible light, reaching the PIXIS CCD.
When broadband light from the LabSphere™ was directed through the optics pathway and imaged
onto a spectrometer, a peak was present at 250 nm and no other peaks were visible. In addition,
when a piece of BK7 optical glass (completely opaque to UV light) was placed in the optical path,
the signal entirely disappeared.

4.3.5.1 Data Analysis

Determining the line-integrated photon intensity $I$ due to B-I emission was performed via a similar
procedure to that described in Section 4.3.4.1 with Equation 4.9. Here the factor $f_{\text{geo}}$ is given by

$$f_{\text{geo}} = \frac{\Omega_{\text{aper}}}{4\pi} = \frac{\pi r_{\text{aper}}^2}{4\pi L_{\text{opt}}^2}$$  (4.12)
Figure 4.18: The custom-built UV optics system (not to scale) installed along the line of sight of the PIXIS camera in order to measure B-I emission from the near-surface Magnum-PSI plasma.

where $r_{\text{aper}}$ is the radius of the optical aperture shown in Figure 4.18. The optical calibration factor also contains several extra terms:

$$f_{\text{opt}} = R_{\text{mirror}} T_{\text{window}} T_{\text{bp}} T_{\text{sp}} T_{\text{lens}}^2$$

(4.13)

where $R_{\text{mirror}}$ is now the transmission of the UV-enhanced Al mirror, $T_{\text{window}}$ is the transmission of the BaF$_2$ window at 250 nm, $T_{\text{bp}}$ is the transmission of the 250 nm bandpass filter, $T_{\text{sp}}$ is the transmission of the shortpass filter, and $T_{\text{lens}}$ is the transmission of each plano-convex UV lens. The values of each factor needed for the optical calibration are given in Table 4.2. The factors $R_{\text{mirror}}$, $T_{\text{bp}}$, $T_{\text{sp}}$, and $T_{\text{lens}}$ are obtained from manufacturer specifications. The transmission curves of the shortpass and bandpass filters are provided in Figure C.2 of Appendix C and the reflectivity of the Al mirror is shown in Figure C.3. The product $T_{\text{bp}} T_{\text{sp}}$ was also directly measured via calibration with a Acton MS-416 Mercury Pen-Ray Light Source (253.7 nm) and found to be within 15% of
### 4.3. Diagnostic Setup

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Calibration Factor</th>
<th>Typical value</th>
<th>Error</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{counts}}$</td>
<td>PIXIS CCD counts</td>
<td>$&lt; 65536$</td>
<td>$\pm \sqrt{N_{\text{counts}}}$</td>
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<tr>
<td>$S_{\text{CCD}}$</td>
<td>PIXIS CCD sensitivity</td>
<td>23</td>
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<td>photons / pixel</td>
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<tr>
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<tr>
<td>$r_{\text{aper}}$</td>
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<td>mm</td>
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<tr>
<td>$L_{\text{opt}}$</td>
<td>Optical path length</td>
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<td>$\pm 5$</td>
<td>cm</td>
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<tr>
<td>$R_{\text{mirror}}$</td>
<td>UV mirror reflectivity</td>
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<td>$\pm 0.03$</td>
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<tr>
<td>$T_{\text{window}}$</td>
<td>BaF$_2$ window transmission</td>
<td>0.36</td>
<td>$\pm 0.03$</td>
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<tr>
<td>$T_{\text{sp}}$</td>
<td>Shortpass filter transmission</td>
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<td>$\pm 0.05$</td>
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<td>$T_{\text{bp}}$</td>
<td>Bandpass filter transmission</td>
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<td>UV lens transmission</td>
<td>0.99</td>
<td>$\pm 0.01$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Table of typical values and error bars for each of the calibration factors for 250 nm UV emission imaged on the PIXIS camera.

Specifications. The window transmission $T_{\text{window}}$ was measured in a separate *ex-situ* calibration, also using the MS-416 light source.

#### 4.3.5.2 Error Analysis

Error bars on each UV optics parameter are also shown in Table 4.2. Again the CCD counts are assumed to follow Poisson statistics so that the error bar is equal to $\sqrt{N_{\text{counts}}}$. The PIXIS CCD sensitivity was determined via direct calibration using the Acton MS-416 Mercury Pen-Ray Light Source, so the error bar represents the actual measurement uncertainty. The error bar in the mirror reflectivity is the difference in $R_{\text{mirror}}$ between 240 nm and 260 nm. The BaF$_2$ window transmission at 250 nm was also determined directly from calibration data, and the error bar reflects the measurement uncertainty. Error bars on the two UV filter transmissions are derived from the difference ($\sim 15\%$) between a calibration measurement and the manufacturer specifications. The uncertainty in the lens transmission is the difference in $T_{\text{lens}}$ between 240 nm and 260 nm from manufacturer specifications. For a typical count rate $N_{\text{counts}} = 5000$, error propagation yields a relative uncertainty in the line-integrated radiation intensity $\Delta I/I \approx 39\%$. 
### 4.3. Diagnostic Setup

#### 4.3.6 Optical emission spectroscopy

Visible light from the plasma is also imaged onto six separate fibers connected to a 2-channel and a 4-channel optical emission spectrometer. Some of these fibers are located on the same line of sight as the TS system, and some are located 15 cm upstream from this position to characterize the plasma closer to the source. The names, locations, spectral range, and spectral resolution of each spectrometer fiber is shown in Table 4.3. The acquisition rate of the 2-channel system is $\sim 7$ Hz and the acquisition rate of the 4-channel system is $\sim 3$ Hz. The exposure time was varied from 1 ms to 100 ms depending on the strength of the lines of interest.

A background subtraction was performed by subtracting the minimum counts present on each channel. The resulting spectrum from all six channels is shown in Figure 4.19. The count rates of the 2-channel and 4-channel OES spectra were normalized with respect to each other such that the height of the deuterium Balmer peaks fall into the ratio predicted by the NIST Atomic Spectra Database [122]. In these experiments the OES system was utilized primarily to check for impurity lines such as oxygen (O-I, 777 nm) or hydroxide (OH, 308-310 nm) emission originating from the surface of the samples. Such measures were necessary because the results of [123] predict that the top several monolayers of the Li surface will be completely transformed to lithium hydroxide (LiOH) in about 30 seconds due to the residual background pressure of H$_2$O in the vacuum cham-

<table>
<thead>
<tr>
<th>Fiber name</th>
<th>Spectral range (nm)</th>
<th>Spectral resolution (nm)</th>
<th>Sight line location</th>
</tr>
</thead>
<tbody>
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<td>2ch-1</td>
<td>295-455</td>
<td>0.090</td>
<td>TS laser position</td>
</tr>
<tr>
<td>2ch-2</td>
<td>444-580</td>
<td>0.080</td>
<td>TS laser position</td>
</tr>
<tr>
<td>4ch-1</td>
<td>378-472</td>
<td>0.057</td>
<td>15 cm upstream</td>
</tr>
<tr>
<td>4ch-2</td>
<td>485-557</td>
<td>0.049</td>
<td>15 cm upstream</td>
</tr>
<tr>
<td>4ch-3</td>
<td>599-642</td>
<td>0.035</td>
<td>15 cm upstream</td>
</tr>
<tr>
<td>4ch-4</td>
<td>600-949</td>
<td>0.19</td>
<td>TS laser position</td>
</tr>
</tbody>
</table>

Table 4.3: Names, locations, spectral range, and spectral resolution of each fiber in the optical emission spectroscopy (OES) system.
4.3. Diagnostic Setup

Figure 4.19: The emission spectra from all six channels of the Magnum-PSI OES system from \( \sim 1.25 \) s into a discharge.

ber. Generally no evidence of these lines was observed in the OES spectra. This suggests that if formation of LiOH monolayers did occur, they eroded from the Li-coated samples during the first several milliseconds of each Magnum-PSI plasma discharge, exposing an oxygen-free Li surface underneath for the remainder of the plasma exposure.
Chapter 5

Temperature-dependent lithium erosion under high-flux plasma bombardment

As discussed in Chapter [1], lithium coatings are applied to the walls of many current plasma confinement devices to enhance performance and protect the underlying solid walls. Li-coated graphite and high-Z substrates are planned for use in NSTX-U and liquid metals such as lithium are candidate plasma facing materials for a DEMO reactor. However Li evaporation (Section [2.4]) and the strong enhancement of the Li sputter yield at elevated temperatures (Section [2.5]) implies that the maximum Li temperature permitted on such devices may be unacceptably low [3]. Thus it is crucial to characterize gross Li erosion rates under high-flux plasma bombardment. Thin (< 1 µm) Li films on TZM molybdenum and graphite substrates were studied in the Magnum-PSI linear plasma device (Chapter [4]) at ion fluxes > 10^{24} m^{-2} s^{-1} and Li surface temperatures ≤ 800 °C. Measured Li erosion rates were found to be reduced from the predictions given in Section [2.6]. This is hypothesized to be due to the effects of interactions between the thin Li layer and the underlying TZM Mo substrate [124, 125], which could affect behavior of the lithium under bombardment with hydrogenic species.
To eliminate potential thin-film effects, a procedure was developed to expose macroscopically thick (≥ 100 µm) Li coatings to the Magnum-PSI plasma. The ratio of the total D fluence to the areal density of the Li coating was varied to quantify the differences in the Li erosion behavior between the low-fluence regime where little D is present in the Li film ($\beta \ll 1$), and high-fluence regime where the top Li layer is almost completely saturated with D ($\beta \approx 1$). The time-dependent ratio of D to Li atoms on the target surface $\beta(t)$ was calculated using the results of the MD simulations of hydrogen diffusion in lithium via the procedure described in Section 2.3.2. Good agreement is observed between the measured Li erosion and the predictions in Section 2.6 if a fast reduction of the Li thickness via macroscopic melt motion and droplet ejection is assumed. Li erosion behavior was also measured during bombardment with a neon plasma that will not chemically react with Li. It was found that the measurements agree well with the predictions of evaporation and thermal sputtering with no yield reduction due to preferential sputtering (Section 2.5.3) or chemical sputtering (Section 2.5.2). Finally, Li coatings are observed to disappear from graphite long before the total eroded Li fluence equals the initial areal density of the evaporative Li coating. This is a strong indicator that fast Li diffusion into the bulk graphite substrate occurred, as predicted in Section 2.3.1.

5.1 Sample Preparation

5.1.1 Thin Li films

Disk-shaped samples 1 mm thick and 30 mm in diameter were machined from a Titanium-Zirconium-Molybdenum alloy (TZM) and ATJ fine-grain graphite to act as substrates for the thin Li films. TZM molybdenum was purchased in 1 mm thick sheets from Goodfellow USA (www.goodfellowusa.com) and ATJ graphite was acquired from existing excess stock utilized in the machining of the NSTX wall tiles. The typical elemental concentrations (obtained
5.1. Sample Preparation

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>&gt; 99.3</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.5</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.07</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.05</td>
</tr>
<tr>
<td>Tungsten</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron</td>
<td>0.005</td>
</tr>
<tr>
<td>Barium</td>
<td>0.002</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.002</td>
</tr>
<tr>
<td>Others</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

Table 5.1: Typical elemental concentrations present in the TZM molybdenum alloy. Data obtained courtesy of Goodfellow USA (www.goodfellowusa.com).

from manufacturer specifications) of TZM molybdenum are shown in Table 5.1. Samples were fabricated using a computer numerical control (CNC) machine. After fabrication the TZM samples were immersed in an acetone-filled beaker for cleaning. This beaker was placed in an ultrasonic bath for 30-60 s to agitate the solvent. The beaker was drained, re-filled with ethanol, and the process of agitating the beaker in the ultrasonic bath was repeated. Then both the TZM and graphite samples were baked in an oven at 100-150 °C for approximately 20 minutes. Images of clean TZM and graphite samples are shown in Figures 5.1 and 5.2 respectively. Finally the samples were wrapped in chem-wipes™ and stored in airtight plastic bags for shipment to Magnum-PSI.

Immediately before insertion in the Magnum-PSI target holder, the TZM samples were given one final wiping with acetone and ethanol. Graphite samples were not treated in order to avoid diffusion of hydrocarbons into the carbon matrix. These samples were placed inside a 64 mm diameter TZM or tantalum clamping ring and mounted on the Magnum-PSI target manipulator. As discussed in Section 4.1.4, the cooling rate to the sample can be adjusted to some extent by changing the torque on the clamping ring bolts or by placing one or more grafoil® (flexible graphite foil) spacers between the clamped target and copper backing. Sometimes a hole was cut in the center of the grafoil spacer to further decrease the target cooling rate. Once the TEAC had been
pumped down, lithium coatings were applied to the samples utilizing the LITER-1C evaporator and the procedure discussed in Section 4.2.2. For the purposes of measurements of Li erosion, typically coatings 200 nm thick were applied to the substrates\(^1\).

### 5.1.2 Thick Li coatings

After experiments on thin Li films it was inferred via modeling (Section 2.3.2) that these layers tended to saturate with deuterium extremely quickly. In order to measure the Li erosion rate as a function of the D/Li surface concentration \(\beta\), a procedure was developed to expose macroscopically thick (\(\geq 100\ \mu m\)) Li coatings to Magnum-PSI plasmas. 64 mm diameter, 3 mm thick TZM disks (also from Goodfellow USA) were machined with a shallow 25 mm diameter well in center of the sample. The depth of this well varied from 0.1 to 1.0 mm among different samples. The well was

---

\(^1\)When evaporatively coating ATJ graphite targets with Li, fast intercalation of the Li into the carbon matrix occurs, as discussed in Section 2.3.1. Thus the specified thicknesses represents the nominal equivalent thickness of a Li coating on an impermeable substrate.
filled with lithium *ex-situ* and then the samples were mounted directly on the Magnum-PSI target holder without the need for a clamping ring.

The lithium filling procedure for these samples was as follows. First, the machined TZM disks were cleaned via the same procedure discussed in Section 5.1.1. Next, the samples were placed inside an argon glove box at PPPL containing both N$_2$ and O$_2$ scrubbers. The glove box pressure was typically maintained at about +2 mbar to ensure that impurity concentrations of N$_2$, O$_2$, and H$_2$O remained in the range of < 50 ppm. This impurity-free environment resulted in minimal oxidation of the lithium during the filling process. A stainless steel base plate was placed on top of a hot plate, and the sample was loaded on top of the SS base plate. A single lithium piece approximately 5 mm long and 10 mm in diameter was cut from a Li rod and placed in the center of the sample cup. A photograph of four Li samples melted into wells on a SS prototype plate is shown in Figure 5.3. The hot plate was heated up to a temperature of ~ 450 °C. A metal spatula was used to spread the Li uniformly throughout the sample well. The melted Li was leveled within the cup with a knife edge. The hot plate was turned off and a 0.002 inch thick piece of SS shim stock was placed over the Li metal after it cooled to a temperature of ~ 250 °C. This shim stock piece bonded with the top Li layer and acted as a sealing mechanism to prevent oxidation of the Li layer as long as the SS piece remained in place. When the sample cooled to room temperature, it was placed inside a heat-seal aluminized mylar bag. This heat-seal bag was placed inside a second bag along with a dessicant to eliminate any accumulated moisture.

After transportation of the samples from PPPL to Magnum-PSI, no visible damage to the bags or samples was apparent. When preparing to mount a Li-wetted sample on the Magnum-PSI target holder, the SS shim stock cover was not removed until immediately before sealing up and pumping down the vacuum vessel. A photograph of a mounted Li-filled target before the SS cover was removed is shown in Figure 5.4. The Li was only exposed to atmosphere for approximately 20-30 s during this process. When the SS piece was removed the Li surface was extremely reflective, but after 10-20 s a black oxide coating could be observed to develop. After pumpdown of the
Figure 5.3: Image of four Li samples melted into wells in a SS prototype plate inside an argon-filled glove box. Two of these wells have been covered with SS shim stock.
Figure 5.4: Photograph of a Li-filled TZM sample mounted on the Magnum-PSI target holder with the SS shim stock cover still in place.

TEAC, the Li sample (viewed through a window) was observed to be completely black in color. Thus before exposure to D plasma, the Li layers were exposed to several Ar plasma discharges to sputter away impurities from the surface, during which the Li reached a temperature of $\sim 350 \, ^\circ\text{C}$. After these Ar pulses the Li layer had transformed back to the highly reflective state characteristic of a metallic surface with an oxide layer only several monolayers thick.

5.2 Experimental Procedure

5.2.1 Measuring temperature-dependent Li erosion on TZM Mo

As discussed in Section 4.1.4, the Magnum-PSI sample holder contains no external heaters, and thus all temperature rise of the Li-coated samples was accomplished through plasma heat flux.
Following the discussion in [16], the heat flux to a plasma-facing surface can be estimated by

\[ \Gamma_{\text{heat}} = \frac{1}{2} \gamma n_e T_e c_s \]  

(5.1)

where \( \gamma \) is the sheath heat flux transmission coefficient and \( c_s \) is the ion sound speed. In [126] a value \( \gamma \approx 3 \) near the center of the plasma column was calculated for hydrogen plasma. Thus the rate and total magnitude of thermal increase can be controlled by varying the plasma heat flux as well as the cooling rate to the sample (also discussed in Section 4.1.4). The temperature-dependent erosion rate of thin Li films on TZM molybdenum under deuterium plasma bombardment was measured for three separate samples. A summary of the experimental conditions for each discharge is given in Table 5.2. Before each experiment, a D plasma discharge with identical machine settings was performed on a bare TZM substrate. This discharge provided a good estimate of the resulting thermal evolution of the Li-coated sample, with the assumption that a \(< 1 \) \( \mu \)m thick film has negligible impact on the sample temperature.

The diagnostic setup is shown in Figure 4.12. The thermal evolution of the sample was monitored with infrared thermography (Section 4.3.3) and pyrometry (Section 4.3.2) throughout each discharge. It was verified that the center sample temperature (measured by the pyrometer) was very similar during plasma exposures on bare and Li-coated TZM samples. Li-I emission was monitored via a Phantom camera covered with a 670.8 nm band-pass filter. Estimates of the plasma density and temperature were obtained via the TS system. Because these Li films were extremely thin and were experiencing very high plasma flux, Li depletion was generally observed in the center of these samples after 1-2 s. This depletion was characterized by a “roll-over” and subsequent sharp decrease in the magnitude of the Li-I emission measured on the Phantom camera. This depletion was confirmed by several more plasma pulses on the sample, which exhibited progressively lower Li-I photon count rates characteristic of additional depletion of the Li layer; see Figure 5.5. However, because the majority of the thermal rise of the sample occurred during the first 1-2 seconds of
### Table 5.2: Table of experimental settings used during each Magnum-PSI discharge to measure temperature-dependent Li erosion from a TZM Mo substrate. The values of $n_e$, $T_e$, ion flux, and heat flux are their peak values at the center of the plasma column. Values of heat flux assume a value $\gamma = 3$ for deuterium plasmas, while $\gamma$ was unknown for the Ne plasmas and thus a heat flux is not given. The Li thicknesses are the initial Li thicknesses before plasma exposure begins. Each row represents plasma exposure of a separate Li-coated sample.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Target Bias (V)</th>
<th>Li thickness (µm)</th>
<th>$n_e$ ($10^{14}$ cm$^{-3}$)</th>
<th>$T_e$ (eV)</th>
<th>$\Gamma_i$ ($10^{24}$ m$^{-2}$s$^{-1}$)</th>
<th>$\Gamma_{\text{heat}}$ (MW/m$^2$)</th>
<th>$T_{\text{Li,peak}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$</td>
<td>-20</td>
<td>0.019</td>
<td>2.7</td>
<td>1.7</td>
<td>1.7</td>
<td>17</td>
<td>740</td>
</tr>
<tr>
<td>D$_2$</td>
<td>-20</td>
<td>0.019</td>
<td>2.3</td>
<td>1.7</td>
<td>1.5</td>
<td>14</td>
<td>660</td>
</tr>
<tr>
<td>D$_2$</td>
<td>-20</td>
<td>0.019</td>
<td>3.0</td>
<td>1.6</td>
<td>1.9</td>
<td>18</td>
<td>1100</td>
</tr>
<tr>
<td>Ne</td>
<td>-20</td>
<td>0.020</td>
<td>4.4</td>
<td>1.6</td>
<td>0.86</td>
<td>18</td>
<td>560</td>
</tr>
<tr>
<td>Ne</td>
<td>-40</td>
<td>0.020</td>
<td>2.2</td>
<td>2.5</td>
<td>0.53</td>
<td>13</td>
<td>560</td>
</tr>
<tr>
<td>D$_2$</td>
<td>-20</td>
<td>500</td>
<td>2.4</td>
<td>1.3</td>
<td>1.3</td>
<td>13</td>
<td>620</td>
</tr>
<tr>
<td>D$_2$</td>
<td>-40</td>
<td>500</td>
<td>1.1</td>
<td>1.2</td>
<td>0.60</td>
<td>11</td>
<td>590</td>
</tr>
</tbody>
</table>
Figure 5.5: Li-I count rates vs. time for three consecutive discharges on the center of a Li-coated sample, as imaged via a Phantom camera. Depletion of the Li layer (initially 190 nm thick) was evident approximately 1.5-2 s into the first discharge, with count rates decreasing strongly during subsequent shots.

the plasma discharge, it was still possible to accurately measure high-temperature Li erosion rates before depletion occurred.

As discussed above, Li erosion behavior was also measured during bombardment with a neon plasma that will not chemically react with Li. The experimental settings for these discharges are also provided in Table 5.2. The sample bias was varied from 20 V to 40 V to investigate the dependence of the Li erosion rate on the incident ion energy. Although $\gamma$ has not been measured for neon plasmas in Magnum-PSI, it was evident that the incident heat flux to the samples was lower because it was not possible to obtain peak temperatures as high as the D$\rightarrow$Li case. This was to be expected because for a given $n_e$ and $T_e$, the equivalent neon ion flux is lower than the D ion flux by the square root of the mass ratio $\sqrt{m_D/m_{Ne}}$.

Additional experiments were conducted to expose macroscopically thick ($\geq 100$ µm) Li coatings to the Magnum-PSI plasma to eliminate the possibility of thin-film effects. While thin Li films
tend to completely transform to lithium deuteride (LiD) in < 1 ms under D plasma bombardment in Magnum-PSI, this process takes > 5 s for macroscopically thick films. Thus as discussed in Section 5.1.2, the ratio of the total D fluence to the surface to the areal density of the Li coating can be varied in order to measure differences in the Li erosion rate between the low-fluence regime where little D is present in the Li film (\( \beta \ll 1 \)), and high-fluence regime where the top Li layer is almost completely saturated with D (\( \beta \approx 1 \)). Unlike the thin-film case where Li depletion occurred after 1-2 seconds, the Li did not deplete from these targets even after one or more 8 s D plasma discharges. This allowed for measurement of the Li erosion rate over the course of an entire pulse. Settings for these discharges are also shown in Table 5.2. In addition, TS data was acquired at 1 Hz for these discharges (rather than just once) in order to characterize the time evolution of \( n_e \) and \( T_e \). The values provided in the data table represent a time average.

### 5.2.2 Comparison of Li-coated TZM Mo and graphite

Similar plasma exposures were also conducted on Li-coated graphite samples. As discussed in Section 2.3.1, it is expected that even at room temperature thin layers of Li evaporated onto a graphite substrate will completely diffuse into the carbon matrix within a matter of seconds or minutes. Thus it is anticipated that the total fluence, \( \Phi \), of lithium from the surface of the Li-coated graphite sample will not reach the initial thickness of the Li layer because the vast majority of the Li will intercalate into the carbon substrate rather than erode away. To test this hypothesis, a series of plasma discharges were conducted on a Li-coated graphite sample to determine the total Li fluence \( \Phi_{Li} \) that could be extracted from this sample. If \( \Phi_{Li} \) is significantly lower than the initial areal density \( \rho_{Li} \), this indicates that most of the Li diffused into the graphite substrate. Plasma exposures were conducted at lower \( \Gamma_{D+} \) in order to prevent \( T_{Li} \) from getting overly high (\( \Gamma_{D+} \leq 10^{23} \text{ m}^{-2} \cdot \text{s}^{-1}, T_{Li,peak} < 400 ^\circ \text{C} \)).
5.3 Data Analysis

The yield of neutral Li atoms $Y_{Li}$ was indirectly inferred from measurements of the line-integrated neutral lithium emission. As discussed in Section 3.2.2, the Li emission intensity (photons/cm$^3$·s) is equal to $n_{Li} n_e P_{Li}$ where $P_{Li}$ is the Li photon emissivity rate coefficient (PEC). The neutral Li density $n_{Li}$ was modeled in the Magnum-PSI plasma column using the procedure described in Section 3.4. The coefficients $n^{ij}_{Li}$, the contribution to the Li density at radial grid point $i$ and axial grid point $j$ due to Li erosion from the target at radial grid point $i'$, were calculated by numerically solving the continuity equation over the entire $i,j$ grid with boundary condition $\Gamma_{Li}^{i'} = Y_{Li}^{i'} \Gamma_{D+}^{i'}$.

A model for the line-integrated Li-I emission $I^{ii'}$ from radial grid point $i'$ due to Li erosion from radial grid point $i'$ was then obtained by summing in the axial direction over all $j$ subscripts:

$$I^{ii'} = \sum_j n^{ij}_{Li} n_e^{ij} P^{ij}$$

where $n_e^{ij}$ and $P^{ij}$ are the electron density and PEC at each grid point. It is evident from Equations 3.10, 3.12, and 5.2 that the quantities $I^{ii'}$ are linearly dependent on $Y^{i'}$. We will refer to this constant of proportionality as $\alpha$ such that $I^{ii'} = \alpha^{ii'} Y^{i'}$. This separates $I^{ii'}$ into known quantities $\alpha^{ii'}$ and unknown quantities $Y^{i'}$ that we wish to determine in these experiments. The total line-integrated emission $I^i$ from each radial grid point $i$ is modeled by the following system of equations:

$$
\begin{bmatrix}
I^1 \\
I^2 \\
\vdots \\
I^{N_i}
\end{bmatrix} =
\begin{bmatrix}
\alpha^{1,1} & \alpha^{1,2} & \cdots & \alpha^{1,N_i} \\
\alpha^{2,1} & \alpha^{2,2} & \cdots & \alpha^{2,N_i} \\
\vdots & \vdots & \ddots & \vdots \\
\alpha^{N_i,1} & \alpha^{N_i,2} & \cdots & \alpha^{N_i,N_i}
\end{bmatrix}
\begin{bmatrix}
Y^1 \\
Y^2 \\
\vdots \\
Y^{N_i}
\end{bmatrix}
$$

where $N_i$ is the number of radial grid points.
A model for $I^i$ is useful because it can be compared with experimental observations of line-integrated Li-I emission. Measurements of line-integrated Li-I photons / m²·s recorded on the Phantom camera were radially averaged in 1 mm wide rings concentric with the center of the plasma column to create the $I^i$ inputs for Equation 5.3. In other words, $I^i$ is the average line-integrated Li-I intensity in radial bin $i$, where $i-1$ mm < $r$ < $i$ mm. In practice the center of the column and target differed by up to 5 mm; thus emission measurements for $r \geq 7.5$ mm originated partially on the clamping ring rather than the sample itself. To mitigate this source of error, measurements of $I$ outside of $r = 7$ mm were discarded so the number of radial grid points $N_i = 7$. For measurements of macroscopically thick Li films, it was observed that the Li radiation and temperature were effectively constant vs. radius near the center of the plasma column. Thus it was only necessary to use the center radial grid point $N_i = 1$. Equation 5.3 was then solved for $Y^i$ by inverting the $\alpha^{ii'}$ matrix and multiplying it by the measured values of $I^i$.

As discussed in Section 4.3.4, the Phantom camera was tilted ~45° from the surface normal. However the ratio of the decay length of the Li-I radiation intensity to the plasma column radius $\lambda_{iz}/R_0 \leq 0.1$. This implies that Li radiation was strongly localized near the target and the tilted line of sight of the camera did not introduce significant uncertainty into the measurements. But during the plasma exposures on Li-coated graphite targets at lower plasma settings, $\lambda_{iz}/R_0 > 1$ and the radiation profile was significantly altered by the tilted viewing angle of the Phantom camera. Thus measured values of $I^i$ as a function of radial bin $i$ could not easily be deduced. As an alternative we summed the total Li-I emission $I$ from the target and replaced $Y^{ii'}$ the “average” Li yield $\langle Y \rangle$ that is independent of $r$:

$$I = \sum_i \sum_{i'} I^{ii'} = \langle Y \rangle \sum_i \sum_{i'} \alpha^{ii'}$$

(5.4)

This is a single equation that was solved for $\langle Y \rangle$ rather than the system of equations in 5.3 that was solved for $Y^i$ for all $i$. This method allows one to calculate the accumulated Li fluence from the
substrate as a function of time:

$$\Phi_{\text{Li}}(t) = \int_0^t \langle Y(t') \rangle \langle \Gamma_{D+}(t') \rangle dt'$$ (5.5)

where here the quantities $\langle Y(t') \rangle$ and $\langle \Gamma_{D+}(t') \rangle$ are now averaged over the target surface.

5.4 Results

5.4.1 Temperature-dependent Li erosion

5.4.1.1 D bombardment of thin Li films

A plot of the inferred neutral Li yields $Y_{\text{Li}}$ as a function of the Li temperature for the first three discharges in Table 5.2 are shown in Figure 5.6. Li temperatures were obtained from IR and pyrometer data using the procedure described in Section 4.3.3 and are averaged in the same concentric ring geometry described above for the Phantom camera videos. Erosion yields from each of the three discharges showed fairly consistent trends, suggesting that the data analysis described above provides a robust method of inferring temperature-dependent Li erosion yields independent of the specific ion fluxes, heat fluxes, and surface temperatures present during each exposure. Inferring Li yields by the more straightforward ionizations/photon (SXB) technique that has been used in other studies [127] provided almost identical results. The SXB technique makes the assumptions that atomic excitation during ionization is the only source of photon emission and the Li impurity species is completely ionized along the line of sight of the diagnostic. These approximations were strongly satisfied in this particular experiment, and thus agreement with the SXB method was expected. If these same Li-I emission measurements originated from plasma more typical of detached divertor conditions ($n_e = 10^{15}$ cm$^{-3}$, $T_e = 0.5$ eV), the yields inferred by these methods would differ by roughly a factor of two.
Figure 5.6: Atomic Li erosion yields vs. temperature during deuterium plasma bombardment inferred from three different sets of experimental measurements of Li-I emission in Magnum-PSI. The predictions of the adatom-evaporation mixed-material model (Section 2.6) for D/Li concentration $\beta = 1$ (expected) and $\beta = 0$ are also overlaid.
Because these evaporated Li films were so thin, calculations using the procedure described in Section 2.3.2 predict that the D/Li concentration ratio is effectively unity ($\beta = 1$) within several ms into the plasma discharge. Thus overlaid in Figure 5.6 are the predictions for the mixed-material Li erosion rate (Section 2.6) with $\beta = 1$. Also overlaid are Li erosion predictions with no deuterium adsorption or implantation in the Li coating, i.e., $\beta = 0$ for the entire discharge. The error band represents the difference between the homogenous and non-homogenous models of D adsorption on the Li surface. Inferred yields at Li temperatures $< 700^\circ$C are lower than the predictions of Equation 2.19 but measurements agree with theory at higher temperatures. In particular it is clear that the Li evaporation term has been completely suppressed by the presence of deuterium in the film as predicted by theory (Section 2.4). At low temperatures, the collisional sputtering term obtained from TRIM.SP underestimates the measured Li erosion yield by approximately a factor of three.

One novel Li erosion suppression effect that may be present in this particular experiment is interaction between the Li and the underlying TZM substrate. During previous experiments on other devices [1, 2], the Li layer was several mm thick, while in these measurements the initial thickness of the layer was about 190 nm and rapidly decreased through the first several seconds of the discharge. An effect was hypothesized in [128] by which Li-Mo bonding leads to an effective binding energy on the Li surface that exceeds the surface binding energy of pure Li. In addition to chemical cohesion, Li is also capable of penetration into molybdenum along grain boundaries [124] and formation of Li-Mo-O compounds [125]. Recent surface science laboratory experiments [129] have demonstrated that material mixing occurs between Li and TZM Mo at a depth exceeding 10 monolayers (3 nm) as inferred from thermal desorption spectroscopy (TDS) measurements. While the exact reason for the low Li erosion yields from these thin Li films remains unclear, results from surface science experiments suggests that modifications to the Li binding energy may be occurring via material mixing.
Figure 5.7: Atomic Li erosion yields vs. temperature during neon plasma bomardment at Ne ion energies of (a) 20 eV and (b) 40 eV. The predictions of the adatom-evaporation model are overlaid, along with a second curve in which the collisional sputter yield (obtained from TRIM.SP) was increased by a factor of 3. Predictions from Langmuir Law evaporation alone are also shown.
5.4. RESULTS

5.4.1.2 Ne bombardment thin Li films

The temperature-dependent Li erosion yields measured during 20 eV and 40 eV Ne ion bombardment are shown in Figure 5.7. The predicted contribution to the erosion yield from Langmuir Law evaporation alone is overlaid, along with a fit curve that also includes both collisional sputtering and thermal sputtering from the adatom-evaporation model. As predicted by the model, there was no suppression of Li evaporation under Ne plasma bombardment because the Li films remained hydrogen-free. Note that was not possible to distinguish between the thermal-spike model and the adatom model of thermal Li sputtering in these cases because the evaporation term dominated before Li temperatures were high enough for predictions to diverge. Thus plots of the thermal-spike model would produce near-identical curves to the the adatom-evaporation case. Since no previous measurements exist for temperature-dependent Ne→Li sputtering, the unknown constants $Y_{ad}$, $A$, and $E_{eff}$ were treated as fit parameters. The thermal sputtering term was significantly larger in the 40 eV case relative to the 20 eV case. This was in contrast with previous measurements on a low-flux device that give nearly identical thermal sputtering behavior independent of ion energy [1, 76].

The temperature dependence of the 40 eV yields were fairly similar to previous measurements [2] of Ne→Li sputtering and evaporation at 50 eV. This suggests that thermal sputtering may only be reduced by thin-film Li-Mo effects very close to the energy threshold. In addition, the TRIM predictions again underestimated the Li sputtering yield by a factor of about 3. The fit curves obtained using $3 \cdot Y_{coli}$ are overlaid in Figure 5.7.

5.4.1.3 D bombardment of thick Li coatings

During argon plasma bombardment of thick Li layers to sputter off impurity coatings, significant macroscopic melt motion of the liquid Li was observed. Li droplet ejection also occurred during some Ar and D plasma discharges. These two effects altered the Li thickness from its initial value of 500 µm before D plasma exposures began. Post-mortem analysis, i.e. analysis after the samples
had been removed from the TEAC, could not be performed on these Li layers because the samples were exposed until the layer fully depleted from the center of the sample prior to removal from the TEAC. Instead analysis was performed on a Li-coated TZM sample that was only exposed to a single neon plasma shot where the Li temperature did not exceed 400 °C. The initial Li thickness was 500 µm but significant macroscopic melt motion was observed throughout the discharge.

The final Li thickness profile on this sample was inferred via confocal microscopy. First two small holes were bored in the lithium carbonate (Li$_2$CO$_3$) coating in order to expose the underlying TZM substrate and establish a depth baseline. These holes are located at points A and B in Figure 5.8. The sample was placed under an optical microscope at 20x magnification and the stage was raised until the underlying TZM substrate at Point A was in focus. Then the stage was translated 0.5 mm to the left and the stage was lowered until the Li$_2$CO$_3$ came into focus. The difference in the stage z-axis positions during these two observations corresponded to the depth of the Li$_2$CO$_3$ layer. The resolution of this technique was primarily limited by the stage motor that can only move in 1 µm increments. Five measurement points with 0.5 mm spacing were obtained by scanning horizontally to the left from both Point A and Point B. In inferring the corresponding Li thickness from measurements of the lithium carbonate thickness, the relative Li atomic densities in the two materials were taken into account. The ratio of atomic Li density to Li$_2$CO$_3$ density $n_{Li}/n_{Li_2CO_3} \approx 1.33$. It was assumed that the z direction was the only dimension along which the oxidizing Li layer was free to expand, and thus the measured thickness were divided by a factor of 1.33. The resulting confocal microscopy measurements are provided in Table 5.3. Although there was a fair amount of variation in the inferred thicknesses, they were all significantly below the initial Li depth of 500 µm. Therefore the visual observations of fast lithium thinning during plasma bombardment were confirmed by this post-mortem analysis.

These results motivated modeling of the time-dependent D/Li concentration $\beta(t)$ using the 1-D diffusion model described in 2.3.2 both for the initial Li thickness of 500 µm as well as nominal decreases in the Li thickness to 50 µm or 25 µm. The modeled evolution of $\beta(t)$ for three different
Figure 5.8: Photograph of a Li-coated TZM sample acquired during post-mortem analysis. The Li layer is assumed completely transformed to lithium carbonate. The baseline locations for confocal microscopy scans are labeled as points A and B.

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Point A thickness (µm)</th>
<th>Point B thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>25</td>
<td>56</td>
</tr>
<tr>
<td>1.0</td>
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</tr>
<tr>
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<td>39</td>
<td>125</td>
</tr>
<tr>
<td>2.0</td>
<td>40</td>
<td>132</td>
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<tr>
<td>2.5</td>
<td>7</td>
<td>156</td>
</tr>
</tbody>
</table>

Table 5.3: Inferred post-mortem Li thickness profile obtained via confocal microscopy from two different scans across a Li-coated sample. These scans originated at points A and B, respectively, which are shown in Figure 5.8.
Li thicknesses is provided in Figure 5.9. The D/Li concentration increased quickly on a solid Li surface because D diffusion in the layer is extremely slow, as shown in Figure 2.6. There was a sharp dip in $\beta$ at the Li melting point as the Li liquefied and a sudden increase in the D diffusivity occurred (see Section 2.3.2). For the remainder of the discharge $\beta$ continued to increase, reaching nearly unity after several seconds in the 25 µm and 50 µm cases. These values of $\beta(t)$ provided one of the inputs for the predicted Li erosion rate $\Gamma_{Li}(t)$ as described in Section 2.6.

The time-dependent D ion flux $\Gamma_{D+}$ for the -20 V bias discharge is also shown in Figure 5.9. These values were obtained by measuring $n_e$ and $T_e$ profiles with 1 Hz frequency and linearly interpolating between each time point. Prior to the first Thomson scattering (TS) measurement
point at \( t = 1 \) s, \( n_e \) and \( T_e \) were assumed proportional to the magnet current \( I_B \). After the last measurement point at \( t = 6 \) s, \( n_e \) and \( T_e \) were assumed constant. The measured thermal evolution of the Li layer is overlaid. Error bars on this data (not shown) were obtained as described in Section 4.3.3.2, with uncertainty due to the temperature dependence of the Li emissivity calculated from results in [130].

The measured temperature-dependent erosion yields \( \Gamma_{\text{Li}}/\Gamma_{\text{D+}} \) for 20 eV and 40 eV D bombardment of thick Li layers is shown in Figure 5.10. The predictions of the adatom-evaporation mixed-material model are overlaid assuming both a 500 µm Li coating and a reduced value of this coating at the beginning of the plasma discharge. For the 20 eV case, the data matches best with a reduced Li thickness of 25 µm, while in the 40 eV case a thickness of 5 µm provides the best agreement. It should be emphasized that while the reduction of the Li thickness was considered as a fit parameter, it is a static scalar value. Adjusting only this single parameter provides good agreement between measurements and predictions from modeling over a range of 600 °C in Li temperature and two orders of magnitude in the Li erosion rate.

Collisional sputtering and evaporation (strongly reduced via LiD formation) provided negligible contributions to the erosion rate between 300 °C and 650 °C, so the curves in Figure 5.10 are effectively plots of the thermal sputtering term only at high temperatures. According to theory (Section 2.5.4) thermal sputtering is independent of ion energy. The error band on the predicted Li yields represents the difference between the homogenous and non-homogenous models of D adsorption on the Li surface discussed in Section 2.1. The factor of \( \sim 3 \) discrepancy in the collisional sputtering yield with TRIM.SP calculations is consistent with previously described results (Figures 5.6 and 5.7).
Figure 5.10: Atomic Li erosion yields vs. temperature during deuterium plasma bombardment at D ion energies of (a) 20 eV and (b) 40 eV. The predictions of the adatom-evaporation model are overlaid, assuming both a 500 µm Li coating and a reduced value of this coating at the beginning of the plasma discharge.
5.4. Results

5.4.2 Li diffusion in graphite

A plot of the time-dependent Li fluence $\Phi_{Li}$ from a Li-coated graphite sample is shown in Figure 5.11 relative to the initial coating areal density $\rho_{Li}$, as determined from QCM measurements described in Section 4.2.2. Reference measurements from a Li-coated TZM sample are also shown. The condition $\Phi_{Li}/\rho_{Li} = 1$ corresponds to a Li layer that has completely eroded into the plasma - the “worst-case scenario” of zero Li re-deposition. Both Li-coated samples demonstrated a decrease in erosion yield after the first 5-10 seconds. Because ion flux and Li surface temperature were fairly constant throughout the majority of each plasma discharge, no decrease in erosion yield was expected as long a Li coating continued to exist on the surface of the sample. Thus a decreasing erosion rate indicates that a pure Li coating no longer exists to be eroded into the plasma. This Li depletion was verified by post-mortem visual inspection for both samples.

It is evident that the Li coating disappeared from a graphite substrate much faster than expected from the measured Li erosion rate into the plasma. This indicated that fast diffusion of Li into graphite occurred. Previous analysis of Li-coated graphite tiles from NSTX showed evidence of Li up to 15 microns into the substrate, but not deeper than this [54]. As discussed in Section 2.3.1 solving the 1-D equation for Li diffusion perpendicular to the basal planes of graphite predicts that a 200 nm Li layer at room temperature will completely diffuse into the graphite substrate in $< 5$ s. Nearly 30 minutes elapsed between the conclusion of Li evaporation onto graphite and the resumption of plasma exposures. Thus it is likely that a Li-C mixed material was present in the graphite target substrate as opposed to a pure Li surface coating available for erosion into the plasma. In contrast, the Li fluence from the Li-coated TZM sample strongly exceeded unity, indicating that significant re-deposition of eroded Li atoms occurred. This effect is discussed and measurements are described in Chapter [6]
Figure 5.11: Time-dependent Li fluence $\Phi_{Li}$ from a Li-coated graphite and Li-coated TZM sample normalized to the initial areal density of the coating $\rho_{Li}$ over 30-60 s of exposure time.

5.5 Discussion

Because the Li erosion yields inferred in these experiments represented such strong reductions from measurements on other devices, mechanisms unrelated to the material composition that could affect the observed intensity of Li-I emission were also investigated. The ratio of the Li-I photon mean free path $\lambda_{absorb}$ remained larger than the Li density decay length $\lambda_{iz}$, indicating that radiation trapping (see Section 3.2.2) was not a significant effect in this experiment. Li-I emission intensity was also strongest in the center of the target where the highest Li densities were present, further indicating that the Li vapor cloud was not optically thick. Resonances do exist in the Li-Li$^+$ charge exchange cross sections, but only at higher Li velocities than present here [131]. If Li recombination or charge exchange were significant additional sources of neutral Li atoms, a given Li-I emission rate would correspond to an even lower Li yield. Thus neglecting the recombination and CX gives an upper bound on the Li erosion rate. Finally, the processes of dielectronic recom-
bination and collision-induced quenching of Li excitation were both accounted for in the ADAS collisional-radiative model [36].

As depicted in Figure 5.10 the mixed-material Li erosion model developed in Chapter 2 accurately predicted the measured erosion yield of macroscopically thick Li coatings under high-flux deuterium plasma bombardment in Magnum-PSI. Because this erosion model made no assumptions about the experimental geometry, it can also be applied to D ion bombardment in tokamak divertors. A synthesis of these results with the re-deposition measurements provided in Chapter 6 enable the predictions for the Li material lifetime in the NSTX-U divertor, which are discussed in Chapter 8. These results also imply that predicted temperature limits [3] for Li-coated high-Z PFCs in a tokamak are pessimistic. If a Li coating is well-saturated with deuterium, low erosion rates will be maintained even at surface temperatures where the evaporative and sputtered flux from pure Li would dwarf the incident ion flux.

In contrast, disappearance of the Li coating from the surface of Li-coated graphite was observed after 1-2 seconds even at D fluxes $\Gamma_{D+} \approx 10^{23} \text{ m}^{-2} \text{s}^{-1}$ and Li temperatures not exceeding 400 °C. This is a strong indicator that fast Li diffusion into the bulk graphite substrate occurred. These results are consistent with the empirical formula for Li diffusion [52], as well as the results of experiments on Li-coated graphite from NSTX [54]. If these results are parameterized in terms of the gross Li fluence $\Phi_{Li}$ divided by the initial areal density $\rho_{Li}$, a Li coating on TZM Mo was over 200 times more persistent than it is on Li-coated graphite. This implies that pure Li coatings on high-Z substrates will last significantly longer than Li on graphite in the NSTX-U divertor.

Finally it should be noted that the theoretical calculations of the time-dependent D/Li ratio assume that $\beta$ cannot exceed unity. If a non-equilibrium situation exists such that the surface is temporarily over-saturated with D atoms, the effective Li yield could be further reduced via preferential sputtering. While such a condition has never been directly observed in experiment, it could be measured in the future with surface-sensitive diagnostics. Electron energy loss spectroscopy (EELS) or low-energy electron diffraction (LEED) could measure hydrogen content near the sur-
face, but not during plasma discharges while strong magnetic fields exist. The surface could also be probed in real time during plasma exposures with ion beam diagnostics such as nuclear reaction analysis (NRA) or elastic recoil detection (ERD). No such diagnostics were available during these studies, however.
Chapter 6

Lithium re-deposition in high-density, low-temperature plasmas

As discussed in Sections 1.4 and 1.5, one possible solution to the issue of high levels of divertor erosion (due to high particle fluxes and elevated wall temperatures) is to operate in a regime of low-temperature, high-density divertor plasmas. This state has been theorized to lead to high re-deposition fractions of eroded atoms, but it is necessary to test these predictions (Section 3.5.2) under realistic divertor-like plasma conditions ($T_e < 10$ eV, $n_e > 10^{14}$ cm$^{-3}$). Such measurements have been performed for carbon re-deposition [103, 132] but not for lithium. Experiments described in this chapter indicate that extremely high re-deposition fractions ($R > 0.99$) can be achieved in high-density, low temperature plasmas, as predicted by modeling efforts.

It should be noted that the specific process of local re-deposition studied here refers to eroded atoms that are ionized in the near-surface plasma and return directly to a nearby wall location. This can be distinguished from material migration, which more broadly refers to eroded wall atoms that re-deposit anywhere on the tokamak divertor or first wall. The latter studies are outside the scope of the present work, but carbon migration is also under active investigation for NSTX-U [133].
6.1 Experimental Setup and Procedure

Sample preparation involved evaporatively coating 30 mm diameter, 1 mm thick TZM molybdenum disks with approximately 200 nm of lithium, similar to some of the experiments described in Chapter 5. The experimental and diagnostic setup were the same as depicted in Figure 4.12. After the evaporation was complete, each Li-coated sample was exposed to a series of deuterium plasma discharges. A chart of the settings for each plasma pulse in these experiments is provided in Table 6.1. All tests were conducted at a target bias of -20 V. The Li-I emission rate was monitored during the first discharge of each series to determine at what point the Li coating was depleted from the center of the sample. As shown in Figure 5.5, this time point was characterized by a fast “roll-over” and sharp decrease in the Li-I emission rate from the target location corresponding to the center of the plasma beam.

After the series of discharges was complete, the Li samples were removed and immediately photographed. An example photograph acquired during post-mortem analysis is shown in Figure 6.1. It is apparent that Li was absent from a circular region of the sample concentric with the plasma beam center but was still present at larger radii. The radius of this circle (referred to as $r_{\text{min}}$) is the minimum radius of the plasma column where Li did not completely erode during the plasma discharges. This radius was determined for each of the three Li-coated sample in Table 6.1 and is equal to $5.5 \pm 0.5$ mm, $7.0 \pm 0.5$ mm, and $5.5 \pm 0.5$ mm, for samples TZM-Li-1, TZM-Li-2, and TZM-Li-3, respectively. Li was absent from the outer 2.5 mm of the sample because this edge was shielded by the clamping ring during Li evaporation.

6.2 Data and Error Analysis

The time $\tau$ it takes for a Li film to be completely eroded from any given point on the surface of a Li-coated metal substrate is referred to as the coating lifetime. This quantity is related to
### 6.2. Data and Error Analysis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Initial Li thickness (nm)</th>
<th>$n_e$ ($10^{14}$ cm$^{-3}$)</th>
<th>$T_e$ (eV)</th>
<th>$\Gamma_i$ ($10^{24}$ m$^{-2}$s$^{-1}$)</th>
<th>Duration (s)</th>
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<td>1.6</td>
<td>1.6</td>
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</table>

Table 6.1: Table of Magnum-PSI experimental settings used to measure Li re-deposition. The values of $n_e$, $T_e$, and ion flux are their peak values at the center of the plasma column. The Li thicknesses are the initial Li thicknesses before plasma exposure begins.
the Li erosion yield, $Y_{\text{Li}}$, deuterium ion flux, $\Gamma_{\text{D}^+}$, and re-deposition fraction, $R$, by the following equation:

$$R = 1 - \frac{\rho_{\text{Li}}}{\int_0^\tau Y_{\text{Li}} \Gamma_{\text{D}^+} dt}$$  \hspace{1cm} (6.1)

where it is assumed that $Y_{\text{Li}}$, $\Gamma_{\text{D}^+}$, and $R$ were azimuthally symmetric and thus have only radial dependence. $R$ is assumed to be time-independent. The quantity $\int_0^\tau Y_{\text{Li}} \Gamma_{\text{D}^+} dt$ is defined as $\Phi_{\text{Li}}$, the total Li fluence from the surface of the sample. The coating lifetime at the center of the plasma column was determined by the time when the Li-I emission from the center of the sample reach its highest value. The coating lifetime at radius $r_{\text{min}}$ was taken equal to the entire duration of plasma exposure on the particular Li coated sample. The time-dependent Li erosion yields $Y_{\text{Li}}(t)$ were indirectly inferred from Li-I emission measurements on the Phantom camera as described in Section 5.3. The deuterium ion flux was determined from Thomson Scattering measurements (Section 4.3.1).
Error analysis of Li erosion yield data has been previously described in Section 4.3.4.2 and was typically about 30%. The uncertainty in the Li coating lifetime $\tau$ at the center of the plasma column was determined to be $\pm 0.1$ s. This typically introduced an additional 15% uncertainty into the total Li fluence $\Phi_{Li}$. Uncertainty in the initial Li thickness was assumed to be $\pm 10$ nm based on linear fits performed on data obtained from the quartz crystal microbalance (QCM) system.

6.3 Results

Using these quantities, it was possible to determine the time-averaged re-deposition fraction $R$ at radial locations $r = 0$ and $r = r_{\text{min}}$ on each sample. Inferred values of $R$ are provided in Table 6.2 along with the calculated Li fluences and initial Li areal densities. The measured re-deposition fractions from $r = 0$ and $r = r_{\text{min}}$ on each of the three samples in Table 6.1 are also plotted in Figure 6.2. The measured values of $R$ were also extremely close to unity. These values of $R$ can be directly compared with the modeling results described in Section 3.5.2.

Predicted re-deposition profiles across the surface of each sample were calculated with 0.1 mm resolution by solving the continuity equations for eroded neutral Li (Section 3.4) and ionized Li (Section 3.5). These predicted re-deposition fractions for each Li-coated sample were calculated based on the measured $n_e$ and $T_e$ profiles for the first discharge of each series in Table 6.1. The results of these calculations are overlaid in Figure 6.2. The displayed $R$ profiles have been smoothed from the raw data, which show fluctuations on the order of 0.01-0.03 due to errors introduced in the numerical integration procedure. Smoothing was performed in a region $\pm 1$ mm and the given error bands represent the standard deviation of the results in this region. It is predicted that $R$ should be very close to unity in all three cases; note the difference in the scale of the vertical axis between the top and bottom plots. Near the edge of the sample $R$ decreased rapidly because any Li atom that eroded off the outer radius of the sample was assumed permanently lost from the plasma.
Figure 6.2: Predicted re-deposition fractions in Magnum-PSI with error bands for the three samples given in Table 6.1. The top plot displays the full vertical axis and the bottom plot contains a suppressed zero. Measured re-deposition fractions are also overlaid. In some cases error bars are smaller than the symbol size.
Table 6.2: Measurements of Li re-deposition in Magnum-PSI deuterium plasmas for three different Li-coated samples.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li lifetime ( (r = 0) ) (s)</th>
<th>( \Phi_{Li} (r = 0) ) ( (10^{24} \text{ m}^{-2}) )</th>
<th>( \Phi_{Li} (r_{min}) ) ( (10^{24} \text{ m}^{-2}) )</th>
<th>Redep. fraction ( (at \ r = 0) )</th>
<th>Redep. fraction ( (at \ r = r_{min}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZM-Li-1</td>
<td>1.9±0.1</td>
<td>5.2 ± 1.8</td>
<td>34 ± 10</td>
<td>0.9983^{+0.0005}_{-0.0010}</td>
<td>0.9998^{+0.0001}_{-0.0001}</td>
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<tr>
<td>TZM-Li-2</td>
<td>2.1±0.1</td>
<td>1.8 ± 0.6</td>
<td>14 ± 4</td>
<td>0.9952^{+0.0014}_{-0.0028}</td>
<td>0.9994^{+0.0002}_{-0.0003}</td>
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<tr>
<td>TZM-Li-3</td>
<td>1.6±0.1</td>
<td>2.4 ± 0.9</td>
<td>22 ± 6</td>
<td>0.9964^{+0.0010}_{-0.0023}</td>
<td>0.9996^{+0.0001}_{-0.0002}</td>
</tr>
</tbody>
</table>

6.4 Discussion

While measured re-deposition fractions agree well with modeling, it should be noted that a fundamental difference exists between re-deposition fractions \( R < 1 \) and \( R > 1 \). If \( R \) is below unity, this was a region of net erosion while \( R > 1 \) corresponds to a region of net deposition. Thus if \( R \) was truly above unity near the center of the sample, the model predicts that Li material will accumulate near the center while eroding near the edge. As is evident from the photograph in Figure 6.1, such accumulation near the target center was not observed. Similar results were obtained in a study of carbon re-deposition. Simulations using the ERO transport code predicted rapid carbon build-up near the center of carbon-coated Mo samples due to ionization and re-deposition in Pilot-PSI plasmas, but the observed re-deposition efficiency in experiments was significantly lower [103].

There are several effects not incorporated into this model that could lead to the samples transitioning from regions of net deposition \( (R > 1) \) to net erosion \( (R < 1) \). Ions in the plasma tend to diffuse to larger radii via Coulomb collisions; see Appendix B.1 for more details. While the typical Li atom tends to diffuse < 50 \( \mu \)m outward in the radial direction before re-depositing, incorporating collisions into the model would cause a slight decrease in the true re-deposition efficiency. In addition, the Magnum-PSI magnetic field was assumed perfectly axial (normal to the surface of the sample), but in reality there was a slight divergence of the field lines that could also...
lead to outward motion of Li ions as they traverse the magnetic field lines. Finally, because $R$ was assumed time-independent, the model does not incorporate the ramp-up phase at the beginning of every discharge where $n_e$ and $T_e$ have yet to reach a steady state value. As shown in Figure 3.10, the predicted re-deposition efficiency decreases sharply at values of $T_e$ below 1 eV.

Despite the approximations present in the modeling, agreement within 5% between theory and experimental measurements of Li re-deposition fractions in Magnum-PSI indicates that the re-deposition model described in Section 3.5.2 is capable of accurate estimates of Li coating lifetimes in high-density, low-temperature plasmas such as those found in a tokamak divertor. Accurate estimates of the re-deposition efficiency are important because for a given Li erosion yield and D$^+$ ion flux, the lifetime of a thin film is proportional to $1/(1 - R)$. Thus a thin Li film exposed to a plasma with re-deposition fraction $R = 0.99$ will last ten times longer than in a plasma where $R = 0.9$. Predictions of Li coating lifetimes for the divertor parameters expected in NSTX-U are discussed in Chapter 8.
Chapter 7

Boron erosion under high-flux deuterium plasma bombardment

As discussed in Section 1.5, coating metal PFCs with thin B films has also improved plasma performance in a number of tokamak devices. Thin boron coatings on high-Z substrates are a candidate plasma-facing component for NSTX-U. While measurements [68] and simulations [66] of physical B sputtering have been conducted down to ion energies of 20 eV, the temperature dependence of B sputtering has not been investigated. Boron erosion during plasma bombardment has previously been qualitatively inferred from observations of B-I spectral lines [134], but the absolute gross erosion rates were not determined. It has generally been observed [1, 76, 78] that thermal sputtering does not dominate over physical sputtering until the surface temperature exceeds $0.5 T_{\text{melt}}$, where $T_{\text{melt}}$ is the melting point of the material. The melting temperature of boron is 2076 °C and thus little temperature dependence of the B sputtering yield is expected in the temperature range $< 800$ °C of these investigations.
7.1 Sample Preparation

64 mm diameter, 3 mm thick TZM molybdenum disks were machined and cleaned for vacuum using the same procedure described in Section 5.1 but with no circular well bored into the top surface. These TZM samples were then mounted inside a vacuum chamber at PPPL, and thin boron coatings were applied using a circular magnetron sputtering source commercially available from Kurt J. Lesker Company (www.lesker.com). A photograph of the experimental setup is provided in Figure 7.1. The deposition rate was monitored via a dual-crystal quartz crystal microbalance (QCM) system. The typical deposition rate was 0.3-0.6 Å/s and the total boron thickness deposited on the QCM approximately 300 nm. Assuming a $\cos \theta$ sputtering distribution from the source and considering the relative positions of the QCM and TZM samples, an average thickness of 210 ± 10 nm was deposited on the TZM sample itself. After the deposition was complete, the chamber was vented and the TZM samples were removed and sealed in plastic bags for transportation to Magnum-PSI.

A boron-coated sample immediately following sputter deposition and removal from the vacuum chamber is shown in Figure 7.2. While a 300 nm pure B film should be completely opaque to visible light \[135\], the film shown in Figure 7.2 appears to be somewhat transparent, which could indicate transformation from a pure boron film to a boron oxide (B$_2$O or B$_2$O$_3$). This is in contrast with previous surface science experiments \[136\], which showed that while boron is a fairly strong getter of O$_2$ at elevated temperatures (> 600 K), the oxygen uptake is negligible at room temperature. It is also evident from the thin film interference fringes on the sample that the B coating is not perfectly uniform. No further investigation into the film composition or thickness profile was performed.
7.1. Sample Preparation

Figure 7.1: Depiction of the hardware setup for sputter deposition of thin boron films on TZM molybdenum samples.

Figure 7.2: Photograph of a TZM Mo target with 300 nm of boron deposited on the surface.
7.2 Experimental Apparatus and Procedure

The experimental setup for measurements of B erosion in Magnum-PSI is shown in Figure 4.12, with the Phantom camera replaced with the UV optics system shown in Figure 4.18. As discussed in Section 4.3.5, this optical system enables measurement of the 249.7 nm B-I emission line in the near-UV range. The experimental procedure was very similar to that discussed in Section 5.2. First a test discharge was performed on a bare TZM substrate to acquire a baseline for the thermal evolution of the sample via infrared thermography and pyrometry. Then the B-coated sample was exposed to deuterium plasma bombardment while recording the B-I emission rate with the PIXIS camera (Section 4.3.5) and measuring the plasma $n_e$ and $T_e$ via the Thomson Scattering system to determine the plasma flux. As in the case of thin Li films, this thin boron layer was observed to completely erode from the sample after several seconds. Subsequent discharges and post-mortem visual analysis confirmed that little boron remained on the surface of the sample.

7.3 Data and Error Analysis

Because the ratio of the boron ionization mean free path $\lambda_{iz}$ to the plasma column radius $R_0$ was equal to unity or higher during these experiments, the tilted line of sight of the PIXIS camera introduced significant uncertainty into any type of localized erosion measurement. Thus as in the case of plasma exposures on Li-coated graphite, the total B-I emission $I_{B,\text{meas}}$ from the target was summed and a single “average” boron yield $\langle Y_B \rangle$ that is independent of $r$ was calculated. Henceforth we drop the brackets and refer to this quantity as simply $Y_B$. This surface-averaging procedure represents an even better approximation in this experiment because no temperature dependence was expected for the B erosion rate, so the thermal profile across the surface of the sample was unimportant. The spatially integrated count rates from the PIXIS camera were compared with predictions
7.4. **Results and Discussion**

of the total B-I 249.7 nm emission rate:

\[
I_{\text{B,model}} = \int_0^{z_0} \int_0^{r_0} n_0(r, z, Y_B) n_e(r) P_B(r) dr dz \tag{7.1}
\]

where the neutral boron densities \(n_0(r, z, Y_B)\) were obtained by solving the continuity equation (Figure 3.9). The photon emissivity coefficients \(P_B\) for boron were obtained from the ADAS database and are plotted in Figure 3.4. The boron yield from the sample was inferred by setting \(I_{\text{B,meas}} = I_{\text{B,model}}\) and solving for \(Y_B\). Values of \(n_e\) and \(T_e\) were only acquired once at time \(t = 1\) s into the discharge, but these were extrapolated to earlier and later times by assuming that they were proportional to the magnet current \(I_B\).

As discussed in Section 4.3.5.2, the relative uncertainty of measurements of the B-I photon count rates obtained via the PIXIS CCD was approximately 40%. This dominated the error propagation in the analysis. Other sources of uncertainty such as TS data \(n_e(r)\) and \(T_e(r)\) had only a 5-10% error bar.

### 7.4 Results and Discussion

The surface-averaged boron erosion yield vs. time is shown in Figure 7.3, along with the time-dependent peak surface temperature. As discussed in Section 2.5.1, the sputtering yield for 20 eV D→B bombardment has been measured to be \(Y_B = 0.004\) in ion beam experiments [68], significantly lower than was measured here. It is evident that depletion of the boron layer began to occur around \(t \approx 1.7\) s, with a progressive decrease in \(Y_B\) for the remainder of the discharge.

The low measured boron yield, however, was not consistent with the observed short lifetime of the boron coating on the TZM substrate. Assuming the “worst case scenario” of zero boron re-deposition, a lower bound on the erosion yield can be obtained from a simplified version of
Figure 7.3: The surface-averaged erosion yield $Y_B$ from a boron-coated TZM sample during deuterium plasma bombardment in Magnum-PSI. The thermal evolution at the center of the sample is also shown.
Equation 6.1

\[ Y_B = \frac{\rho_B}{\tau I_{D^+}} \]  

(7.2)

where \( \rho_B \) was the initial areal density of the boron coating and \( \tau = 1.7 \) s was the coating lifetime. Even neglecting the ramp-up phase of D plasma flux, Equation 7.2 implies a boron yield \( Y_B = 0.034 \), which is about a factor of 3 higher than the erosion yield inferred via measurements of B-I radiation. It should be noted that it was not possible to measure the absolute mass change of the B-coated TZM sample before and after plasma exposure because of the large mass of the TZM Mo sample (~1 kg). The sample mass was significantly higher than the weight limit of any mass balance capable of microgram-level resolution.

This suggests that one or more of the calibration factors utilized for measurements of B-I emission (Table 4.2) may be inaccurate. Additional uncertainty may be introduced into the measurements by the assumption of constant opening and closing speed of the shutter on the PIXIS camera. As discussed in Section 4.3.5, the shutter opening and closing phases dominated the total CCD exposure time. Absolute calibration of the PIXIS CCD sensivity (photons/count) was performed with an ex-situ setup using a separate light source and an appropriate error bar was placed on this measurement. This suggests that there may have been some additional source of attenuation in the optical path that was not accounted for in the data analysis. Although the boron ionization rate coefficients obtained from the ADAS database are considered “low” quality and may, in reality, be significantly larger at these high electron densities, this did not introduce any major uncertainties into the measurements. Even a factor of 10 increase in \( SCD_B \) still resulted in minimal boron ionization within the Magnum-PSI plasma column, and thus only small changes in the neutral boron density profile (Figure 3.9).

Assuming that value \( Y_B = 0.034 \) represents a conservative lower bound on the boron erosion yield in this experiment, it stands a factor of 8-9 higher than an existing measurement on ion beam devices [68]. This discrepancy may be accounted for by deuterium or background oxygen gas
reacting with the boron layer to form compounds such as boron trioxide ($\text{B}_2\text{O}_3$) or deuterated diborane ($\text{B}_2\text{D}_6$). Compound formation could lead to higher B sputter yields via chemical sputtering because the surface binding energy of $\text{B}_2\text{O}_3$ (3.84 eV) and $\text{B}_2\text{D}_6$ (∼0.17 eV) is lower than that of pure boron (5.76 eV). Calculations of D→$\text{B}_2\text{O}_3$ sputtering with the TRIM.SP code predict that the sputter yield of boron oxide is about 15 times higher than that of pure boron, and the D→$\text{B}_2\text{D}_6$ yield is over 50 times higher than pure B. It should be noted, however, that the absolute yields predicted by TRIM.SP are off by more than an order of magnitude for low-energy D→B bombardment (Figure 2.10).

Another possibility is that thermal sputtering was actually significant for boron even at the relatively low temperatures obtained in this discharge, resulting in the erosion rate at the center of the sample exceeding that near the edge due to the temperature profile across the target. This is considered unlikely, however, since the peak sample temperature did not approach $0.5T_{\text{melt}}$ even by the end of the plasma pulse. The possibility that boron material is re-depositing on the target and then eroding at a significantly higher rate was also discarded. While such effects have been observed in experiments for beryllium [137], the long boron ionization mean free path implies that minimal re-deposition was occurring. Thus all available evidence indicates that the reason for the high measured boron erosion rates was chemical sputtering via boron oxide or deuteride formation.
Chapter 8

Discussion and Conclusions

8.1 Suppressed gross erosion of lithium

In Chapter 2, it was hypothesized that a high incident flux of deuterium ions on a lithium-coated PFC could lead to fast saturation of the Li surface with D:Li ratio of up to 1:1. Such saturation had previously been obtained [41] by bombarding a Li layer with low fluxes of deuterium for tens of minutes. In this case, however, the diffusion rate of D in Li was sufficiently high that an equilibrium D:Li concentration could be maintained throughout the entire depth of the sample (several mm). For the situation in high-flux devices such as Magnum-PSI or a tokamak divertor, it was shown in simulations that deuterium will bombard the surface faster than the Li layer can absorb it, leading to larger D:Li concentrations near the surface relative to the bulk of the Li layer (Figure 2.7). This fast saturation of the Li surface with D leads to suppression of evaporation and sputtering via the formation of lithium deuteride (LiD). Suppression of Li evaporation has been demonstrated in chemistry experiments [65] and suppression of Li sputtering was predicted via the TRIM.SP Monte Carlo sputtering code (Section 2.5).

These predictions were tested on the Magnum-PSI linear plasma device using both thin (<500 nm) and thick (≥100 µm) Li coatings on TZM molybdenum. Lithium erosion yields were
inferred from Li-I emission measured with a fast filtered camera. Li temperatures were obtained through IR and pyrometry measurements. On thin Li films under neon plasma bombardment, the Li layer eroded at the rate predicted for pure Li via evaporation, collisional sputtering, and thermal sputtering (Section 5.4.1.2). On thin Li films under D plasma bombardment, the erosion rate was significantly suppressed due to Li/D mixed-material effects, in addition to possible monolayer-level interactions with the underlying TZM Mo substrate (Section 5.4.1.1). To eliminate the latter effects, the erosion yield of thick Li films was measured and found to be in agreement with the adatom-evaporation mixed-material model of Li erosion for both 20 eV and 40 eV D plasma bombardment, assuming that the Li thickness was reduced from 500 µm to 5-25 µm during plasma exposure via melt motion and droplet ejection (Section 5.4.1.3). This suggests that existing temperature limits for Li-coated PFCs in a tokamak divertor may be highly pessimistic.

8.2 High lithium re-deposition efficiencies

The re-deposition fraction of a Li coating under plasma bombardment on Magnum-PSI was predicted using atomic physics information from the ADAS database and solving the continuity equation for the neutral and ionized Li impurity species. It was predicted that the Li re-deposition fraction $R$ should be extremely close to unity everywhere in Magnum-PSI plasmas except very close to the sample edge. These predictions were tested on Magnum-PSI by bombarding Li-coated TZM Mo samples with a series of D plasma discharges and determining the Li coating lifetime $\tau$ at two different radii on each sample. Measurements indicated that the Li re-deposition fraction $R > 0.99$ in the high-density, low-temperature regime characteristic of tokamak divertors (Section 6.3). Since the coating lifetime is proportional to $1/(1 - R)$, this suggests that the net erosion rate of a Li-coated divertor will be reduced by a factor $> 100$ relative to gross erosion.
8.3 Boron erosion under high-flux plasma bombardment

The gross erosion rate of boron coatings was measured for the first time in a high-flux plasma device (Chapter 7). The erosion yield was measured using two different techniques: (i) inferences based on measurements of B-I radiation and (ii) by dividing the areal density of the boron coating by the total deuterium ion fluence at the time the coating begins depletion. Although discrepancies of a factor of 3-4 were observed between these two measurements, both inferred erosion rates were significantly larger than the sputtering yield measured on ion beam devices. It was proposed that this enhancement was due to chemical sputtering effects via the formation of boron compounds, such as boron oxide or deuterated diborane. It was verified with TRIM.SP sputtering calculations that a significant increase in the boron sputter yield is expected from a $\text{B}_2\text{O}_3$ or $\text{B}_2\text{D}_6$ film relative to pure boron.

8.4 Predictions of Li lifetimes in the NSTX-U divertor

Realistic models for lithium erosion and re-deposition rates were developed in Chapters 2 and 3, respectively. Experiments were designed to test these models and the results, presented in Chapters 5 and 6, were found to agree well with predictions. Thus in this section we present predictions for low long a Li coating on TZM film will last in the NSTX-U divertor as a function of $n_e$, $T_e$, and the initial Li thickness. The current flat-top of an NSTX-U discharge is expected to reach 5 s [109]. Using a 1D treatment of thermal diffusion, one can model the temperature evolution of a TZM Mo surface under a constant heat flux by

$$T_{\text{Mo}}(t) = T_0 + q \left( \frac{4 \alpha_{\text{Mo}} t}{\pi k_{\text{Mo}}^2} \right)^{1/2}$$

(8.1)
8.4. Predictions of Li lifetimes in the NSTX-U divertor

where $\alpha_{Mo} = 5.43 \cdot 10^{-5}$ m$^2$/s and $k_{Mo} = 138$ W/m·K are the thermal diffusion coefficient and thermal conductivity, respectively, for molybdenum\textsuperscript{1}. The initial divertor temperature $T_0$ is assumed equal to 20 °C. The thin Li coatings are assumed to have negligible impact on the thermal evolution of the PFC. The heat flux $q$ is calculated using Equation 5.1 with an additional factor of $\sin \theta$, where $\theta$ is the magnetic incidence angle in the divertor. A value of $\theta = 3^\circ$ is assumed and the sheath heat flux transmission coefficient $\gamma$ is assumed equal to 8.

Under a constant plasma flux, the Li lifetime $\tau$ can be obtained via the following equation:

$$\int_0^\tau Y_{Li}[T_{Li}(t), \beta(t), \Gamma_{D^+}] \, dt = \frac{\rho_{Li}(1-R)\Gamma_{D^+}}{(1-R)\Gamma_{D^+}}$$

(8.2)

where the time-dependent Li temperature is obtained from Equation 8.1 and the D/Li concentration $\beta(t)$ is calculated as discussed in Section 2.3.2. It is assumed that sufficient time exists between plasma shots for the D/Li concentration $\beta(z)$ to become uniform throughout the Li film. Also note that oxidation of the first several monolayers of the Li surface\textsuperscript{123} is neglected during this analysis. The thickness of the Li film is dynamically adjusted within the diffusion calculations each time it drops below 90% of its current value. The expression for $Y_{Li}$ is given by Equation 2.19, with the mixed-material reduction factor $f(\beta)$ calculated by averaging the predictions of the homogenous and non-homogenous models of D adsorption on a Li surface (Section 2.1). In calculating collisional sputter yields, it assumed that all incident D ions have energy $3kT_e$ and impact the surface at a 45° angle. The resulting collisional yields (calculated with TRIM.SP) are $Y = 0.014$ and $Y = 0.033$ for the $T_e = 5$ eV and $T_e = 10$ eV cases, respectively. No angular dependence is assumed for the thermal sputter yield.

For typical divertor parameters expected in NSTX-U ($n_e \geq 5 \cdot 10^{13}$ cm$^{-3}$, $T_e \geq 3$ eV), the gyroradius of a lithium ion is significantly longer than the ionization MFP, implying that the Li ion will be re-deposited within one gyro-period. This is referred to as prompt re-deposition. Thus

\textsuperscript{1}For these estimates, the temperature dependence of $\alpha_{Mo}$ and $k_{Mo}$ are ignored, as are any differences in the material properties of TZM Mo and pure Mo.
specifying that the Li ion re-deposits at the surface location directly below its point of ionization is a reasonable approximation in the NSTX-U divertor. Additionally, because the Li ionization MFP ($<1$ mm) is significantly shorter than the typical divertor plasma scale lengths ($\sim3.5$ cm), the differences in plasma geometry between the linear device and the tokamak are not important close to the strike point. Still, as a conservative approximation that acknowledges possible reductions in re-deposition efficiency due to grazing magnetic incidence, the maximum value of the re-deposition fraction $R$ is assumed equal to 0.99. Calculated re-deposition fractions are displayed in Table 8.1 as a function of $n_e$ and $T_e$.

The resulting predictions for Li coating lifetimes in a tokamak divertor are given in Figure 8.1. For very long lifetimes, diffusion simulations were only run until the D/Li concentration on the surface reaches a value $\beta = 0.99$; then the evolution of film thickness is linearly extrapolated to the depletion time $\tau$. The maximum values of $\tau_{Li}$ are predicted at electron densities between $10^{13}$ and $5 \cdot 10^{13}$ cm$^{-3}$. At lower values of $n_e$, the lifetimes decrease because the re-deposition efficiency $R$ begins to drop. At very high densities, the higher incident flux and increased surface temperatures lead to increases in the erosion rate and corresponding decreases in $\tau_{Li}$. The same trend is observed (for the same reason) as a function of electron temperature. For a given $n_e$ and $T_e$, the Li lifetime is not completely linear with initial thickness. Because a thin Li coating saturates

<table>
<thead>
<tr>
<th>$n_e$ (cm$^{-3}$)</th>
<th>$T_e = 5$ eV</th>
<th>$T_e = 10$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{12}$</td>
<td>0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>$3 \cdot 10^{12}$</td>
<td>0.55</td>
<td>0.70</td>
</tr>
<tr>
<td>$10^{13}$</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>$3 \cdot 10^{13}$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$10^{14}$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$3 \cdot 10^{14}$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$10^{15}$</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 8.1: Predicted Li re-deposition fractions in tokamak divertor plasmas. A maximum value of $R = 0.99$ has been assumed.
with D very quickly, the erosion rate will be reduced relative to the thick coating that does not approach D saturation before fully eroding.

8.5 Future Work

As discussed in Section 5.5, future experiments could directly measure the hydrogen and oxygen concentration in lithium coatings with a surface diagnostic such as electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), nuclear reaction analysis (NRA), or elastic recoil detection (ERD). Such diagnostics could either be directly installed on Magnum-PSI, or if this proves impractical, on a low-energy ion beam facility. Macroscopic melt motion and droplet ejection of the Li layer could be eliminated by utilizing a capillary-porous system (CPS) rather than the free surface used in these experiments. Such investigations are planned on Magnum-PSI in the near future. The erosion yield of Li at grazing magnetic incidence could also be measured, although only about a factor of 2 increase in the collisional sputtering yield is expected (and no increase in evaporation). The Li re-deposition fraction could be measured at lower \( n_e \) and \( T_e \), where \( R \) is not very close to unity. To model re-deposition is such plasmas, however, a full kinetic transport code such as ERO [138] will likely be needed because neglecting Coulomb collisions will no longer be a good approximation. Finally, measurements of erosion and re-deposition could be repeated for other liquid metals such as Sn, Ga, and Sn-Li eutectics. Preliminary measurements of temperature-dependent Sn erosion have already been conducted [77].
Figure 8.1: Predicted Li coating lifetimes in a tokamak divertor as a function of electron density, electron temperature, and initial Li coating thickness.
Appendix A

A.1 Coordinate transformations in Section 3.4

Consulting Figure 3.7, a triangle is formed in the plane of the target with side lengths $r$, $r_0$, and $\rho \sin \theta$ with angle $\phi'$ between the latter two sides. Thus the radial coordinate can be calculated directly via the law of cosines:

$$r^2 = r_0^2 + (\rho \sin \theta)^2 - 2r_0 \rho \sin \theta \cos \phi'$$ (A.1)

The axial coordinate is trivially related to $\rho$ and $\theta$:

$$z = \rho \cos \theta$$ (A.2)

To determine the azimuthal coordinate, we use the law of cosines on the same triangle, but instead with the angle between $r$ and $r_0$:

$$(\rho \sin \theta)^2 = r_0^2 + r^2 - 2r_0 r \cos(\phi_0 - \phi)$$ (A.3)
A.2. DISTANCE FROM IMPURITY EJECTION LOCATION TO EDGE OF PLASMA

Figure A.1: Modified version of Figure 3.7 that diagrams the triangles used (via the law of sines) to determine $d_{\text{side}}$.

Solving for $\phi$, substituting for $r$, and simplifying, we obtain:

$$
\phi = \phi_0 - \cos^{-1} \left[ \frac{r_0 - \rho \sin \theta \cos \phi}{\sqrt{r_0^2 + (\rho \sin \theta)^2 - 2r_0\rho \sin \theta \cos \phi'}} \right]
$$

(A.4)

Note that Equation (A.4) is only applicable for $0 \leq \phi' \leq \pi$. A similar derivation can be performed for $\pi \leq \phi' \leq 2\pi$, which results in a plus (+) sign after $\phi_0$ term instead.
A.2 Distance from impurity ejection location to edge of plasma

To begin, we note that any vector $\vec{\rho}_0$ from the source ejection location with a positive $\hat{z}$ component will intersect exactly once with both the cylindrical wall of the plasma column and the cross-sectional plane defined by the near-surface cutoff location $z_0$. The true value of $\rho_0$ is the closer of the two intersection points, which we define as $d_{\text{side}}$ and $d_{\text{top}}$, respectively. Consider the triangle formed in the plane of the target with side lengths $R_0$, $r_0$, and $d_{\text{side}}$ as shown in Figure A.1. Using the law of sines, we have the relation:

$$\frac{R_0}{\sin \phi'} = \frac{r_0}{\sin \omega}$$  \hspace{1cm} (A.5)

Solving for $\omega$ yields

$$\omega = \arcsin \left( \frac{r_0 \sin \phi'}{R_0} \right)$$  \hspace{1cm} (A.6)

Using the law of sines a second time leads to

$$\frac{d_{\text{side}} \sin \theta}{\sin(\pi - \omega - \phi')} = \frac{R_0}{\sin \phi'}$$  \hspace{1cm} (A.7)

and finally solving for $d_{\text{side}}$ gives

$$d_{\text{side}} = \frac{R_0}{\sin \phi' \sin \theta} \sin \left[ \pi - \phi' - \arcsin \left( \frac{r_0 \sin \phi'}{R_0} \right) \right].$$  \hspace{1cm} (A.8)

The value of $d_{\text{top}}$ is simply given by

$$d_{\text{top}} = \frac{z_0}{\cos \theta}.$$  \hspace{1cm} (A.9)

Thus $\rho_0$ is given by the minimum of these two values, i.e.,

$$\rho_0 = \min \left\{ \frac{R_0}{\sin \phi' \sin \theta} \sin \left[ \pi - \phi' - \arcsin \left( \frac{r_0 \sin \phi'}{R_0} \right) \right], \frac{z_0}{\cos \theta} \right\}.$$  \hspace{1cm} (A.10)
A.3 Derivation of Equation 3.12

We desire to solve the continuity equation in spherical coordinates \((\rho, \theta, \phi')\) for a point source of total strength \(R\) centered on the origin with flux distribution proportional to \(\cos \theta\) in the polar direction and uniform in the azimuthal \((\phi')\) direction. The normalized flux of the point source into a vacuum is given by:

\[
\vec{\Gamma}_{\text{point}} = \frac{R}{\pi \rho^2} \cos \theta \hat{\rho} \tag{A.11}
\]

Using this normalization, we next introduce Equation 3.11:

\[
\frac{2v_0 n_0}{\rho} + v_0 \frac{\partial n_0}{\partial \rho} = -n_0 n_e S(n_e, T_e) \tag{A.12}
\]

where \(n_0, n_e\) and \(T_e\) are generally all functions of \(\rho, \theta,\) and \(\phi'\). Solving for \(n_0\), we obtain

\[
\frac{\partial \ln n_0}{\partial \rho} = -\frac{n_e S(n_e, T_e)}{v_0} - 2 \frac{\rho}{\rho}. \tag{A.13}
\]

Multiplying by \(\partial \rho\) and integrating results in

\[
\ln n_0 = -2 \ln \rho - \int \frac{n_e S(n_e, T_e)}{v_0} \partial \rho + \ln A_0 \tag{A.14}
\]

where \(\ln A_0\) is the constant of integration. Taking the logarithmic inverse of both sides, we obtain an expression for \(n_0\) such that

\[
n_0(\rho, \theta, \phi') = \frac{A_0}{\rho^2} \exp \left[ -\frac{1}{v_0} \int_0^\rho n_e S(n_e, T_e) \partial \rho' \right] \tag{A.15}
\]

where the integration variable has been replaced by \(\rho'\) to avoid confusion with the actual radial coordinate \(\rho\). Using the fluid approximation \(\Gamma = n_0 v_0\) and applying the boundary condition Equa-

In the limit $\rho \to 0$, we obtain

$$\lim_{\rho \to 0} \frac{R}{\pi \rho^2} \cos \theta = \lim_{\rho \to 0} \frac{A_0 v_0}{\rho^2} \exp \left[ -\frac{1}{v_0} \int_0^\rho n_e S(n_e, T_e) \partial \rho' \right].$$  \hspace{1cm} (A.16)

Applying the $\rho \to 0$ limit, the exponential term becomes unity and we solve for the constant of integration $A_0$ to yield

$$A_0 = \frac{R}{\pi v_0} \cos \theta$$ \hspace{1cm} (A.17)

Thus the final expression for $n_0$ becomes

$$n_0 = \frac{R}{\pi \rho^2 v_0} \cos \theta \exp \left[ -\frac{1}{v_0} \int_0^\rho n_e S(n_e, T_e) d\rho' \right]$$ \hspace{1cm} (A.18)

which is identical to Equation 3.12.
Appendix B

B.1 Test ion diffusion in a plasma column

We are interested in the characteristic velocity \( v_\perp \) at which impurity ions in a plasma column will diffuse in the radial direction. Solving for the perpendicular component of the fluid equation of motion [139], we obtain:

\[
v_\perp = \mu_\perp E - \frac{D_\perp}{n_+} \frac{dn_+}{dr}
\]  

(B.1)

where \( \mu_\perp \) and \( D_\perp \) are the perpendicular mobility and diffusion coefficients, respectively, defined as

\[
\mu_\perp = \frac{\mu_+}{1 + \Omega_+^2 \tau_{+i}^2} \quad \text{and} \quad D_\perp = \frac{D_+}{1 + \Omega_+^2 \tau_{+i}^2}
\]

(B.2)

(B.3)

Note that in Equation [B.1] \( v_\perp \) is the *diffusive* perpendicular velocity of the ion gyrocenter. In Equation [B.2], \( \tau_{+i} = \nu_{+i}^{-1} \) is the collision time between an impurity test ion and the background ion species in the plasma, and \( \Omega_+ = eB/m_+ \) is the gyrofrequency, where \( e \) is the elementary charge. The mobility and diffusion coefficients \( \mu_+ \) and \( D_+ \) are given by \( e\tau_{+i}/m_+ \) and \( c_s^2\tau_{+i} \), respectively, where \( c_s \) is the deuterium ion sound speed. With a singly-charged background plasma and impurity
ion, the Coulomb collision frequency $\nu_{+i}$ reduces to

$$\nu_{+i} = 1.4 \cdot 10^{-13} \frac{m_i^{1/2} n_i}{m_+ T_i^{1/2} E_+} \ln \Lambda$$  \hspace{1cm} (B.4)$$

where $n_i$ is the main plasma ion density ($\text{m}^{-3}$), $T_i$ is the main ion temperature (eV), $m_i$ is the main ion mass (amu), $m_+$ is the impurity ion mass (amu), $E_+$ is the impurity ion energy (eV), and $\ln \Lambda$ is the Coulomb logarithm\footnote{The weak $n_e$ and $T_e$ dependence of the $\ln \Lambda$ is ignored throughout this derivation.}. Of particular interest is the case of a population of lithium impurity ions in a deuterium background plasma. An estimate of the impurity ion density $n_+$ can be obtained by first assuming no perpendicular diffusion, then turning diffusion “on” at some initial time and seeing whether $v_\perp$ becomes large. This method is an approximation but provides an estimate of the diffusive velocity without solving a time-dependent impurity distribution function using a plasma transport code.

A typical radial electric field profile in a plasma column can be obtained from measurements on the Pilot-PSI linear plasma device\footnote{1}. The plasma conditions are $T_e = T_i = 1.7$ eV, $n_i = n_e = 2.4 \cdot 10^{14}$ cm$^{-3}$, and $E_+ = 1$ eV. Figure B.1 shows the resulting ratio $v_\perp/v_\parallel$ of the perpendicular to parallel velocities of the impurity ion species, with $v_\parallel = c_s$. Also included are the separate contributions to this ratio from both the mobility and diffusion coefficients. It is evident that diffusive motion perpendicular to the magnetic field is small relative to parallel motion everywhere in the plasma column.

In order to determine the total perpendicular distance an ion travels, on average, before redepositing on the target, we must find the time-dependent parallel Li velocity $v_\parallel(t)$, where $t = 0$ corresponds to the time of ionization. Solving the 1-D differential equation for frictional slowing down\footnote{1} we obtain

$$v_\parallel(t) = (v_0 + c_s)\exp(-\nu_{+i,\text{slow}} t) - c_s \hspace{1cm} (B.5)$$

where $v_0$ is the initial parallel velocity, $c_s$ is the characteristic speed of sound, and $\nu_{+i,\text{slow}}$ is the slow Coulomb collision frequency. The weak $n_e$ and $T_e$ dependence of the $\ln \Lambda$ is ignored throughout this derivation.
where \( v_{0\parallel} \) is the initial parallel velocity of the lithium ion and \( \nu_{i,i,\text{slow}} \) is the collisional frequency associated with slowing down due to ion-ion collisions. Integrating, we obtain an expression for the axial ion position as a function of time:

\[
d_{\parallel} = \frac{1}{\nu_{\text{slow}}} (v_{0\parallel} + c_s)[1 - \exp(-\nu_{i,i,\text{slow}}t)] - c_st + d_{iz}
\]  

(B.6)

where \( d_{iz} \) is the axial ionization location, which is assumed (on average) equal to the ionization MFP \( \lambda_{iz} \). Setting \( d_{\parallel} = 0 \) and solving for \( t \) determines the typical time \( \tau \) at which the Li ion re-deposits on the surface of the target. Then the total perpendicular distance \( d_{\perp} \) traveled by a lithium ion before re-depositing is

\[
d_{\perp} = \int_0^\tau v_{\perp}(t) \, dt
\]  

(B.7)

where the expression for \( v_{\perp} \) is given in Equation B.1. A plot of \( d_{\perp} \) versus the radial position where a Li atom is ionized is shown in Figure B.2. It is evident that a Li atom ionized nearly anywhere in the plasma column will travel (on average) < 50 \( \mu \)m in the perpendicular direction before it re-deposits on the Li-coated target. This is smaller than the Li ion gyroradius (\( \sim 1.5 \) mm) as well as the grid spacing \( \Delta r = 0.5 \) mm of the modeled impurity distribution. It is also significantly smaller than the plasma scale length (12.5 mm) and thus perpendicular diffusion via Coulomb collisions does not significantly affect the Li re-deposition profile.
B.1. Test ion diffusion in a plasma column

Figure B.1: The ratio of the average perpendicular to parallel Li ion velocity in a linear plasma column.

Figure B.2: Total perpendicular distance traveled by a Li ion between ionization and re-deposition on the target surface.
Appendix C

C.1 Optical Filter/Mirror Transmission Spectra

The transmission spectrum of the Li-I filter was obtained directly via experimental measurements and agrees closely (< 5%) with manufacturer specifications provided by SpectroFilm (www.spectrofilm.com). The transmission spectrum of the UV shortpass filter was obtained from manufacturer specifications by Omega Optical (www.omegafilters.com). The transmission of the 250 nm bandpass filter and the reflectance of the Al UV-enhanced mirror were obtained via manufacturer specifications from ThorLabs (www.thorlabs.com).
Figure C.1: Transmission spectrum of the narrow-band Li-I filter utilized for these experiments (blue). OES measurements of the Li-I spectral line (red squares) and a Gaussian fit to this data (dashed red line) are also shown.

Figure C.2: Transmission spectra of the shortpass and bandpass UV filters utilized during measurements of the 249.7 nm B-I spectral line.
Figure C.3: Transmission spectrum of the Al UV-enhanced mirror utilized during measurements of the 249.7 nm B-I spectral line.
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