Technical Summary

Single-layer graphene membranes and other 2D membranes can realize very high gas permeation fluxes due to their atomic or unit cell thickness. Established modeling approaches for membrane transport consider transport through a finite and continuum thickness, and therefore they do not apply to the emerging field of 2D membranes, motivating the development of new theoretical treatments. In this thesis, I first developed an analytical theory for the transport of gases through single-layer graphene membranes, from the perspective of using pores in the graphene layer as a means for separation. I considered two pathways for the transport. The first being direct gas phase impingement on the pore, for which the large-pore separation factors are dictated by Knudsen selectivity, inversely proportional to the molecular weight; selectivity exceeding Knudsen is possible with smaller pores that reach a size commensurate with the size of the molecule, enabling separation by molecular sieving. The second pathway involves adsorption and transport on the graphene surface, similar to mechanisms in heterogeneous catalysis, which becomes more relevant for larger, strongly-adsorbing molecules. These models and pathways are applied for an estimate of a $\text{N}_2/\text{H}_2$ separation and as an explanation for results observed in the molecular dynamics literature.

I applied our understanding of nanopore mechanisms and developed analysis of gas transport through graphene with approximately one selective nanopore etched into it, using experimental data from Bunch et al at Boston University for transport of He, H$_2$, Ne, Ar, and CO$_2$ through a small area graphene membrane with a single or few pores. The transport was measured by collaborators via monitoring the deflection of a graphene flake sealing a pressurized, 5μm diameter microcavity on the surface of a Si/SiO$_2$ wafer. For this experimental system, I report on a mathematical formalism that allows one to detect and analyze stochastic changes in the gas phase fluxes from graphene membranes, extracting activation energies of pore rearrangements, 1.0 eV, and even identifying contributions from multiple, isolated pores.

One opportunity that I identified is the use of a molecularly sized nanopore to ‘direct write’ the flux using a translatable platform. I performed an exploratory investigation of this concept of using a “nanonozzle,” a nanometer scale pore that can deliver a flow of material locally, to grow nanoscale features. The model application was the growth of a graphene nanoribbon on a surface. I explored a variety of analytical mathematical models to understand the parameters and limitations of such a system. I developed a simple simulation of the nanoribbon growth and compared the results to the models for a range of parameters, considering the reasons for differences between the simulated and calculated results. This analysis provides considerations for the experimental design of such a system.

Overall, the theories in this thesis and the analysis in they enable should aid the development of 2D membranes for separations applications and a novel direct write method for nanoscale patterning.