

*I propose to develop new theoretical and computational methods for investigating activated chemical processes. Specifically, I will develop a method for calculating derivatives of rate constants, transport properties, and other dynamical timescales with respect to temperature ( $T$ ), pressure ( $p$ ), and chemical potential ( $\mu$ ). I will use these to calculate activation energies ( $E_a$ ) and activation volumes ( $\Delta V^\ddagger$ ) of transport properties in  $\text{CO}_2$ -expanded liquids (CXLs).*

**Motivation:** There is a growing interest in green alternative solvents for use in catalytic reactions.<sup>1</sup> One such alternative media, CXLs, are of particular interest due to their increased safety, cost-effectiveness, and transport properties when compared with traditional organic solvents.<sup>2</sup> Using a CXL can give up to a five-fold reduction in the amount of solvent needed for a reaction compared to the neat solvent, while significantly increasing mass transport important for catalysis where reactions are often diffusion-limited. Diffusion in CXLs has generally been seen to be monotonic with changes in  $p$ ,  $T$ ; however a separate, computationally expensive, vapor-liquid coexistence simulation is currently required at each phase point ( $p, T$ ) before transport calculations can be run with molecular dynamics (MD).

**Introduction:** *Instead, I propose a direct method by which the entire  $T$ -,  $p$ -, and  $\mu$ -dependence of transport properties in CXLs may be evaluated from simulations at a single phase point.* Traditionally, the  $T$ -dependence and activation energies of transport properties are calculated from a series of simulations at different temperatures and evaluating their Arrhenius behavior. While this is generally satisfactory, there are systems in which calculations over large temperature ranges are difficult or inconvenient, as in the case of CXLs where small changes in  $T$  and  $p$  change the composition of the liquid phase.

**Preliminary Work:** A general method has been developed in previous work by which the  $T$ -dependence of transport properties and their activation energies can be extracted from simulations at a single temperature. This is achieved by launching non-equilibrium MD trajectories from different points along a single  $NVT$  trajectory. This was originally applied to the reactive flux correlation functions and was later generalized by our group to work for any rate constant, transport property, or dynamical timescale calculated from a time-correlation function (TCF).<sup>3-4</sup> This also allows for decomposition of  $E_a$  into kinetic and potential energy contributions, providing otherwise unobtainable mechanistic insight into the  $E_a$ .

With this method, the first derivative of transport properties with respect to state variables (*e.g.*,  $T$ ,  $p$ ) can be calculated. This has been successfully applied previously to the diffusion coefficient ( $D$ ) to calculate the  $E_a$  of diffusion of bulk water, as pictured in Figure 1. A typical Arrhenius calculation finds  $E_a$  should be 3.5 kcal/mol while this direct method found a value of 3.48 kcal/mol. The second derivative is also similarly calculable with respect to these variables. For a system with a monotonic dependence on  $T$ , and  $p$ , as in the case of CXLs, these derivatives and a single value of the transport property are all that is needed to determine its value at other state points. This greatly reduces the number of simulations necessary to evaluate the  $T$ -dependence and drastically cuts down the computational expense while also gaining additional insight into the decomposition of the  $E_a$ .

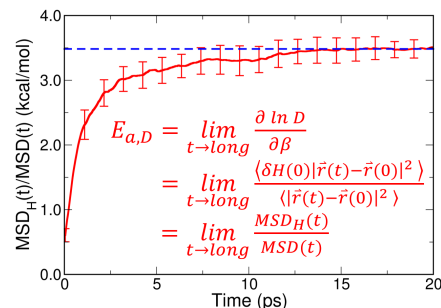


Figure 1: The ratio of the energy-weighted mean-squared displacement ( $MSD_H(t)$ ) to the mean-squared displacement ( $MSD(t)$ ) is presented in red and is equal to  $E_{a,D}$  at the long time limit, presented in blue.

**Aim-1 Application to the  $NpT$  Ensemble:** With the  $NpT$  ensemble, fluctuations occur in both energy and volume that allow for the calculation of both  $E_a$  and  $\Delta V^\ddagger$ . Using a similar derivation to our previously published works, we have been able to show that  $\Delta V_D^\ddagger = k_B T \frac{\partial \ln(D)}{\partial p} = \lim_{t \rightarrow \text{long}} \frac{\langle \delta V(0)[r(t) - r(0)]^2 \rangle}{\langle [r(t) - r(0)]^2 \rangle}$ . Experiments and simulations have previously used an "Arrhenius-like" plot of  $\ln(D)$  vs  $p$  to calculate  $\Delta V^\ddagger$ ; however, these calculations require that measurements be taken across an enormous range of pressures (1- 10,000 bar) to distinguish a measurable change in  $D$  with respect to  $p$ . Yet in some cases  $\ln(D)$  is not linear in  $p$ . This should allow us to probe this non-linearity which is generally inaccessible using traditional methods. Additionally, cross-derivatives, such as  $\frac{\partial E_a}{\partial p}$ , can be calculated, allowing us to extract the  $p$ -dependence of  $E_a$  from simulations at a single  $p$ .

**Aim-2 Application to the  $\mu VT$  ensemble:** In the  $\mu VT$  ensemble, the first derivative of a transport coefficient or other dynamical timescale with respect to the chemical potential can be written as  $\frac{\partial C_{AB}(t)}{\partial \mu} = \beta \langle \delta N(0) A(0) B(t) \rangle_{\mu VT}$ . In practice, this derivative can be calculated by running an  $NVT$  simulation in which a sub-volume has been defined, allowing the number of molecules in the sub-volume to fluctuate. This provides a means by which changes in rate constants, diffusion coefficients, or other dynamical timescales with respect to the chemical potential can be calculated without separate simulations at different compositions.

**Aim-3 Application to CXLS:** I propose to apply this method to a variety of CXLS of industrial importance, including CO<sub>2</sub>-expanded ethylene oxide (EO) and methanol (MeOH) which are involved in a non-phosgene route for the industrial commodity chemical, dimethyl carbonate.<sup>6</sup> The methods described in the previous aims will be used to probe the  $T$ -,  $p$ -, and  $\mu$ -dependence of their transport properties and other relevant dynamical timescales from simulations at a single point. Ideally, this will allow for the calculation of the entire surface of diffusion coefficients, reorientation times, and other dynamic timescales for these CXLS without requiring more than a single phase coexistence simulation.

**Intellectual Merit:** The methods proposed within this work are simple to apply, significantly decrease computational costs, and provide deeper insight into the mechanisms of transport properties. Additionally, they provide a convenient means by which first (and higher-order) derivatives with respect to  $T$ ,  $p$ , and  $\mu$  may be calculated. This will allow for entire dependence of these properties on these macroscopic variables to be calculated without requiring expensive phase coexistence calculations at each phase point.

**Broader Impacts:** The EO-CO<sub>2</sub> and MeOH-CO<sub>2</sub> system is a green alternative solvent considered for the production of dimethyl carbonate, an important precursor in polyurethane production and will be investigated in collaboration with chemical engineers at the Center for Environmentally Catalysis.<sup>6</sup> I will also be co-organizing the 2019 Liquid Gordon Research Seminar for graduate and postdoctoral students. I will continue to mentor undergraduate students throughout the course of my studies. Furthermore, I will pursue the outreach program proposed in my personal statement. The methods proposed in this work can be extended to solve a wide variety of chemical problems.

[1] P. Anastas and N. Eghbali. *Chem. Soc. Rev.*, **39**, pp. 301-312 (2010). [2] P. Jessop, and B. Subramaniam *Chem. Rev.*, **107**, pp. 2666-2694 (2007). [3] O.O. Mesele and W.H. Thompson. *J. Chem. Phys.*, **145**, 134107 (2016). [4] Z.A. Piskulich, O.O. Mesele and W.H. Thompson. *J. Chem. Phys.*, **147**, 134103 (2017). [5] K. Krinicki, C. Green, and D. Sawyer. *Faraday Discuss. Chem. Soc.*, **66**, pp. 199-208 (1978). [6] Z.A. Piskulich, B.B. Laird and W.H. Thompson. *Fluid Phase Equilib.*, Submitted, (2017).