Final Report

1. DOE Award #DE-SC0008598

2. Project title: Liquid Metals as Plasma-facing Materials for Fusion Energy Systems: From Atoms to Tokamaks
Principal investigator: Howard A. Stone

3. Date: 06/23/2017; **Period covered:** 8/1/2012 - 7/31/2016

4. A comparison of the actual accomplishments with the goals and objectives established for the period and reasons why the established goals were not met.

Our research grant brought together 6 investigators from Princeton University: Stone [PI], Bernasek, Carter, Debenedetti, Koel, and Panagiotopoulos, and we have three main collaborators: R. Goldston, R. Majeski and C. Skinner from PPPL (R. Kaita and M. Jaworski from PPPL have been also been regular participants in our discussions). B. Koel has a lab at PPPL and we have had joint meetings both at Princeton University and at PPPL. Thus, our research programs have benefitted from advice and suggestions from fusion experts at PPPL, and via the monthly teleconferences with the PFC Steering Committee early on in the grant along with continued external engagements, we learned from the community at large. The multi-investigator effort bridges experiments, modeling and simulations in a coordinated effort that is sketched in Fig. 1.

As described in the following sections, we have met the majority of our goals of developing our simulation and experimental programs and using these tools to address the measurement or simulation of basic material properties and fluid motions relevant to liquid metals in fusion energy applications. We have published papers in the peer-reviewed literature, and most significantly, we have had four graduate students, two postdocs, and a summer undergraduate student join our teams via the official funding to the research groups, and we have several other undergraduate students, graduate students and postdocs participating in the research owing to their common research interests.

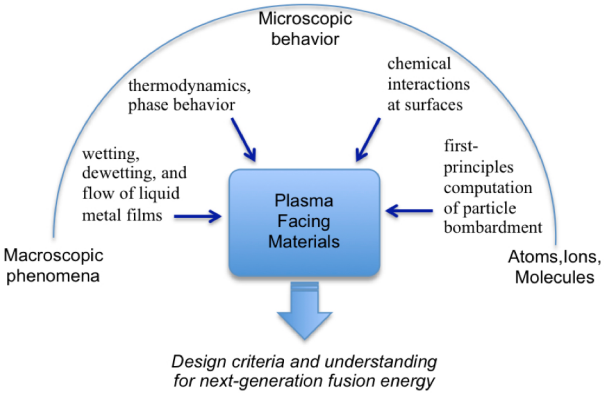

Figure 1: Integrated research effort for liquid metals as plasma-facing materials, including studies from the atomic to the macroscopic scale.

5. A discussion of what was accomplished under these goals during this reporting period, including major activities, significant results, major findings or conclusions, key outcomes or other achievements.

Note: In the summaries below, all references are local to the given subsection.

i) First principles computations of properties of lithium: E.A. Carter

Our efforts focused on atomic scale simulations of the interaction of hydrogen isotopes with liquid lithium (Li) surfaces based on first-principles quantum mechanical theories. The first task was to develop the simulation tools needed. We developed and applied an orbital-free density functional theory molecular dynamics (OFDFT-MD) code in our open-source PRinceton Orbital-Free Electronic Structure Software (PROFESS), which was first used to predict the melting temperature of bulk Li near zero pressure within the isothermal-isobaric (constant NpT) ensemble. Our predicted melting point lies between 434 and 465 K, which is in excellent agreement with the experimental [1] melting temperature of 453 K. This prediction validated the accuracy of our theoretical method.
Further validation came from simulating diffusion coefficients, pair distribution functions, and static structure factors of Li at 470 and 725 K and comparing them to measurements. Overall, we achieved excellent agreement between theory and experiment. We predicted that the diffusion coefficient is 0.63 Angstrom^2/ps for liquid Li at 470 K, identical to the experimental value. For the higher temperature of 725 K, OFDFT-MD yields a value of 2.21 Angstrom^2/ps, larger than the experimental 1.79 Angstrom^2/ps, but still reasonable. Fig. 1 displays the calculated and experimental pair distribution functions and static structure factors for liquid Li. The predicted peak shapes and locations of both pair distribution functions and static structure factors match experimental values exceedingly well at both temperatures. Our results prove that OFDFT is an accurate quantum mechanics method that can characterize properties of both solid and liquid Li, provided that a high quality, nonlocal kinetic energy density functional (KEDF) and an accurate local electron-ion pseudopotential are employed (the two approximate terms in the theory beyond the exchange-correlation (XC) approximations already used in standard DFT).

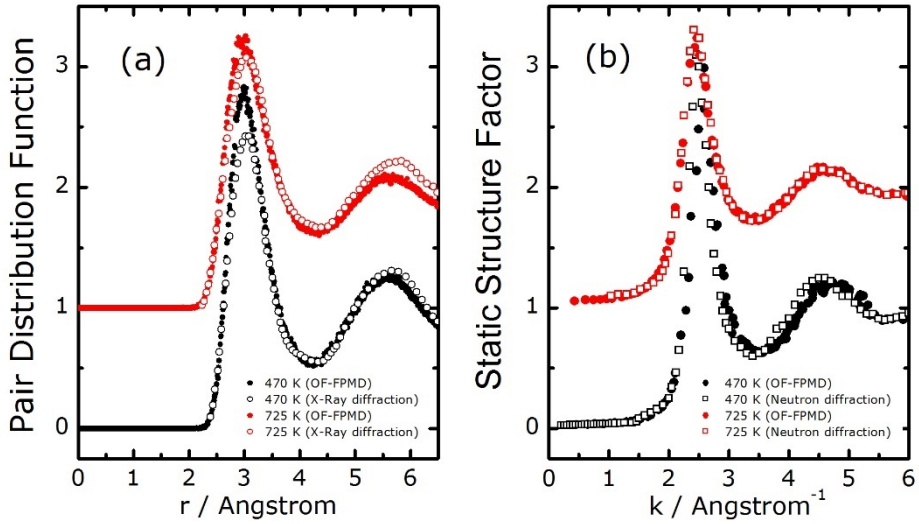

Figure 1: The (a) pair distribution functions and (b) static structure factors of liquid Li at 470 and 725 K. The simulations with 128 atoms were carried out within the canonical ensemble. The results at 725 K were shifted upwards by unity for ease of viewing. Experimental data are from reference [2].

We next studied time-dependent properties of bulk liquid Li to further validate our theory, comparing our results for the dynamic structure factor and the adiabatic sound velocity to experimental values. Fig. 2(a-c) compares experimental [3] to our calculated dynamic structure factors for three different momentum vectors **k**. Our simulations accurately capture all peaks observed in experiments. The adiabatic sound velocity at 470 K for bulk liquid Li was calculated by using peaks in the dynamic structure factors at different **k**. Our result of 4602 m/s compares well with the measured value of 4550 m/s [4].
We additionally studied properties of liquid Li surfaces at different temperatures; the ion density profiles for different temperatures of liquid Li surfaces are shown in Fig. 2(d-f). 1024 atoms were simulated within the canonical ensemble. Blue solid lines represent averaged ion density profiles, while yellow error bars represent fluctuations in the ion density over a 15 ps trajectory. The expected volume expansion of liquid Li surfaces at higher temperature is evident, and the oscillations in the ion density profile when approaching vacuum is also correctly captured [5]. The surface tension was calculated using the method introduced in Ref. [6]. Compared to the experimental value of 398 mN/m at 453 K of a liquid Li surface [7], we predicted 336, 328, and 321 mN/m for 470, 520, and 570 K liquid Li surfaces, respectively. Our predictions exhibit a properly decreasing trend with increasing temperature.

We next carried out tests to validate OFDFT for tin (Sn). We first calculated several solid phases of bulk Sn, including beta-tin, body-centered cubic (bcc), face-centered cubic (fcc), and simple cubic (sc) structures. OFDFT correctly predicts the beta-tin phase as the ground-state structure at ambient conditions. We also carried out canonical ensemble OFDFT-MD simulations for 1000 atoms of liquid Sn at 570 K. The resulting predicted self-diffusion coefficient is 0.30 Angstrom^2/ps for liquid tin at 570 K, which is very close

to the experimental value of 0.28 Angstrom^2/ps [8]. Calculated and experimental [9] static structure factors for liquid tin are displayed in Fig. 3. The predicted shapes and locations of the peaks are in excellent agreement with the experimental values [9]. We especially capture the shoulder structure at around 3 Angstrom^{-1} near the first peak. Our results further prove that OFDFT can characterize both bulk and surface structure and properties of liquid metals (such as Li and Sn) as long as a high quality, nonlocal KEDF and an accurate local electron-ion pseudopotential are employed.

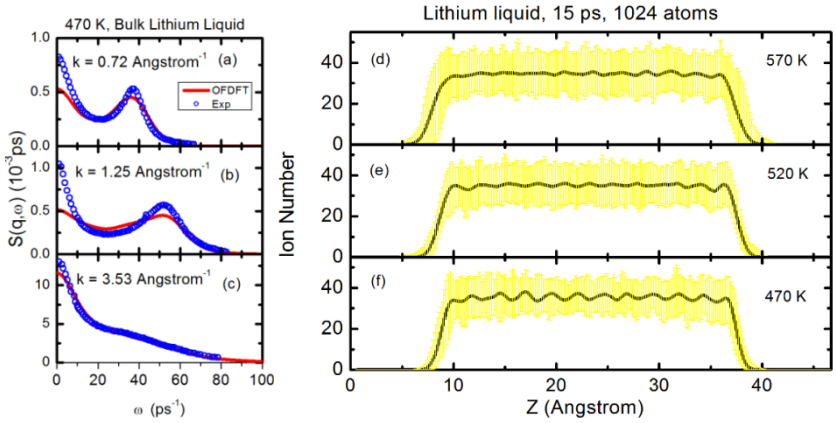

Figure 2: (Left) Dynamic structure factor of bulk liquid Li at 470 K. The experimental data are from reference [3]. (Right) Ion density profiles of liquid Li surfaces along the surface normal of cells simulated at different temperatures. Yellow error bars represent the fluctuations in ion density during 15 ps. The OFDFT-MD simulations involved 1024 Li atoms and were performed within the canonical ensemble.

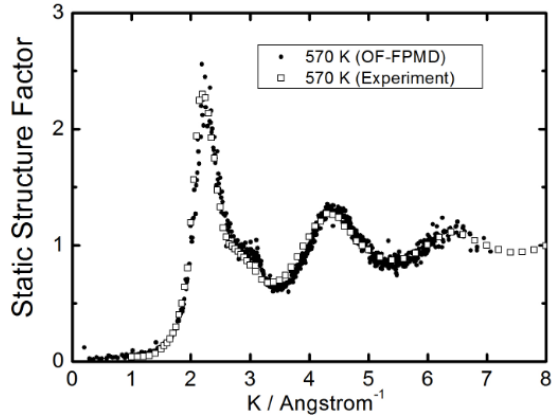

Figure 3: Static structure factors of liquid Sn at 570 K. The OFDFT-MD simulations involved 1000 Sn atoms and were performed within the canonical ensemble. Experimental data are from reference [9].

As a plasma-facing material in fusion reactors, liquid Li may come into contact with deuterium (D). We simulate properties of high D concentrations in liquid Li with DFT-MD simulations; OFDFT-MD was not used as the KEDFs are not yet accurate enough to simultaneously evaluate the kinetic energy of both localized and delocalized electron densities. Liquid Li samples with four concentrations of randomly inserted D atoms (LiD_β, β= 0.25, 0.50, 0.75, and 1.00) were studied at temperatures ranging from 470 to 1143 K. A range of static and dynamic properties were predicted and analyzed.

Importantly, liquid-solid phase transitions forming rock-salt LiD within the liquid Li phase at certain concentrations and temperatures were observed. *Given the much higher melting temperature of LiD compared to liquid Li, we proposed a new design concept: highly deuterated liquid lithium may increase its thermal robustness when exposed to plasma. In fact, high concentrations of D in liquid Li may be the origin of the anomalously low sputter yield observed experimentally under high D flux conditions.* As further validation of these results, the diffusivities predicted as a function of temperature and composition were used in higher length scale simulations of sputter yields, leading to very good agreement with experiment.

Using Li as a plasma facing component on Mo reactor walls will require strong bonding between the two species. In collaboration with Prof. Bruce Koel's experimental group, we studied Li desorption from Mo(110) surfaces theoretically. Our simulated Gibbs free energies agree well with experimentally found Li desorption peaks measured at temperatures ranging from 711 K (1 monolayer, ML) to 1030 K (0.04 ML), with corresponding desorption onsets from 489 to 878 K. Analysis of the electronic structure shows repulsive forces between neighboring Li increase with coverage, reducing the bond strength between Mo and Li and causing the desorption temperature to decrease as the coverage increases. Our simulations further show that Li desorbs at higher temperatures from imperfect surfaces with vacancies than perfect ones. We postulate that steps and kinks present on the Mo(110) surface could behave similarly, causing higher desorption temperatures. *This analysis indicates that roughened Mo surfaces may be beneficial as reactor wall materials since they strengthen Li film adhesion at higher temperatures.*

Another promising material for plasma-facing components in fusion reactors are alloys of Li and Sn by virtue of their high melting points. We used our OFDFT-MD code to study solid and liquid phases of Li-Sn alloys. OFDFT provides an accurate description of Li-rich Li-Sn alloy solid properties, such as their bulk moduli, equilibrium volumes, and cohesive energies. The diffusivities of Li and Sn atoms in the liquid phase are of particular interest. Measurements indicate a partial segregation of the alloy with Li on the surface of the liquid. [10,11] Our simulation of the surface composition of liquid Li-Sn alloys agrees with the experimental findings, and a preliminary analysis indicates that a reduced surface tension of Li compared to Sn may be a cause. Our results are furnishing new, atomic-scale insights into the properties of liquid Li-Sn alloys.

Efficient simulations of plasma-facing components containing molybdenum are also possible using classical interatomic potentials. We have parametrized modified embedded-atom method (MEAM) force fields in collaboration with Prof. Athanassios Panagiotopoulos's group to study wetting of liquid Sn and liquid Li on Mo(110) surfaces. Our parametrizations are based on first-principles DFT reference data, as well as experimental bulk and liquid properties. We have succeeded in both reproducing these training data, as well as independent bulk and liquid benchmark data. Subsequent simulation of the wetting of liquid Li on Mo(110) exhibits perfect wetting, which is in disagreement with previous experimental data finding finite wetting angles. [12] We suspect that oxygen impurities may be the cause for the differences in wetting behavior,

as the experiments were not carried out under ultra-high vacuum conditions. *Noting that perfect wetting may be achievable if oxygen is removed from the Mo substrate could be an important insight for future fusion reactor designs.*

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ii) Surface chemistry of solid and liquid lithium films: S.L. Bernasek and B.E. Koel

Lithium conditioning of plasma facing components has enhanced the performance of several fusion devices, and so the surface chemistry of solid and liquid lithium films is of key interest. We concluded our surface science studies of lithium thin films on graphite investigating oxidation of Li by exposure to O_2, H_2O, and CO gas. [1,2] This work is relevant to understanding oxidation and other chemical reactions that occur from background gas exposures to water and other oxygen-containing molecules on lithiated graphite tiles and lithium thin films used in fusion devices. In order to gain insight into this oxidation process, in these experiments thin (< 3 nm) lithium films on highly oriented pyrolytic graphite (HOPG) were exposed to O_2(g), H_2O(g), and CO(g) in an ultra-high vacuum chamber. As shown in Fig. 1, vibrational spectroscopy from high resolution electron energy loss spectroscopy (HREELS) was used to identify the surface species formed during O_2(g), H_2O(g), and CO(g) exposure.

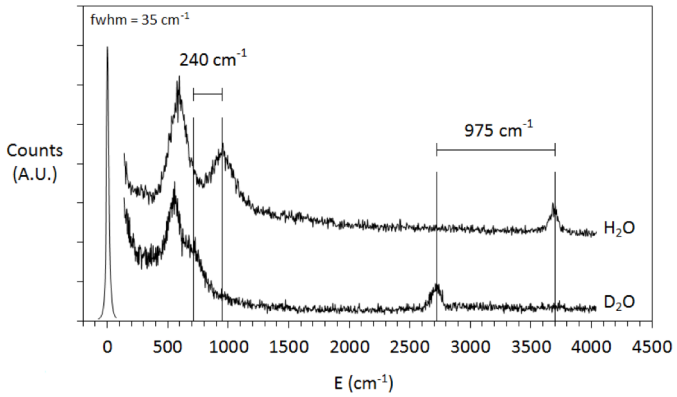

Fig. 1. HREELS spectra of a 15 ML lithium film on HOPG at 100 K exposed to 0.125 L H_2O(g) (top) and D_2O(g) (bottom). Both the H_2O(g) and D_2O(g) partial pressures used during these exposures were 1 x 10^{-8} Torr. [2]

Auger electron spectroscopy (AES) was used to obtain the relative initial sticking coefficients during O_2(g), H_2O(g), and CO(g) exposure. AES experiments showed that as the lithium film thickness decreased from 15 to 5 to 1 ML, the initial sticking coefficients decreased for O_2 (g), H_2O(g), and CO(g). AES measurements showed that a 15 ML lithium film was fully oxidized after 9.7 L of O_2 (g) exposure and Li_2O was formed. Additionally, HREELS spectra showed that, even at 100 K and low exposures (< 0.5 L), O_2(g) fully dissociated upon reacting with the lithium thin films. AES measurements showed that the 15 ML lithium film did not fully oxidize after 15 L H_2O(g) exposure, but the 5 and 1 ML lithium films did fully oxidize. HREELS showed that during initial exposure (< 0.5 L) of H_2O(g), lithium hydride and lithium hydroxide was formed on the surface of a 15 ML lithium film. After 0.5 L H_2O(g) exposure, the H_2O(g) began to physisorb. AES measurements also showed that a 15 ML lithium film was fully oxidized by CO(g) after 11 L CO(g) exposure. Additionally, HREELS measurements have shown no evidence that CO(g) formed either a physisorbed or a chemisorbed Li—CO complex, but showed evidence of Li—O species present at the surface. This suggests that the CO(g) fully dissociated upon reacting with the lithium thin films on HOPG. Finally, O_2(g), H_2O(g), and CO(g) oxygen uptake experiments by 15 ML Li films on HOPG showed that H_2O(g) had the highest relative initial sticking coefficient and CO(g) had the lowest relative initial sticking coefficient.

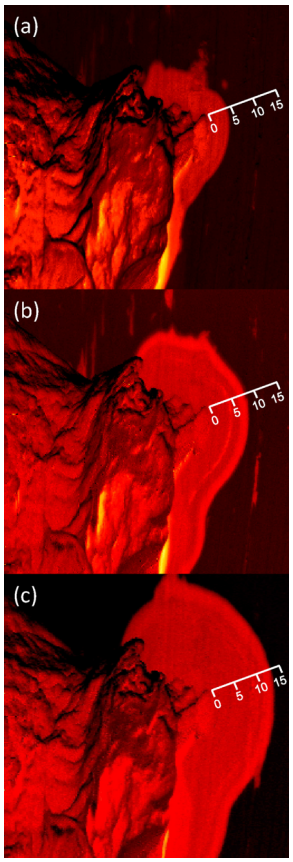

Fig. 2. SAM images showing the spreading of lithium from the particle in the lower left over the stainless steel substrate. Panel (a) was taken 15 d, panel (b) 21 d, and panel (c) 44 d after the lithium was pressed into the stainless steel stub. The scale bar is in microns. [4]

In order to address the fate of lithiated surfaces upon venting the tokamak vessel, as is needed periodically, we investigated the sorption of atmospheric gases by bulk lithium metal. [3] Elemental lithium will react with air during maintenance activities and with residual gases (H_2O, CO, CO_2) in the vacuum vessel during operations. We used a mass balance with microgram sensitivity to measure the mass gain of lithium samples during exposure of a 1 cm^2 surface to ambient and dry synthetic air. For ambient air, we found an initial mass gain of several mg/h declining to less than 1 mg/h after an hour and decreasing by an order of magnitude after 24 h. A 9 mg sample achieved a final mass gain corresponding to complete conversion to Li_2CO_3 after 5 days. Exposure to dry air resulted in a 30 times lower initial rate of mass gain. The results have implications for the chemical state of lithium plasma facing surfaces and for safe handling of lithium-coated components.

A key factor in the performance of liquid lithium components, which are of interest since lithium conditioned plasma facing surfaces have lowered recycling and

enhanced plasma performance on many fusion devices and liquid lithium plasma facing components are under consideration for future machines, is the wetting by lithium of its container. We investigated Li wetting by observing the surface spreading of lithium from a mm-scale particle to adjacent stainless steel surfaces using a scanning Auger microprobe (SAM) that has surface sensitivity and elemental discrimination. [4] An example of the data obtained is shown in Fig. 2. The spreading of lithium occurred at room temperature (when lithium is a solid) from one location at a speed of 0.62 mm/day under ultrahigh vacuum (UHV) conditions. Separate experiments using temperature programmed desorption (TPD) investigated bonding energetics between monolayer-scale films of lithium and stainless steel. While multilayer lithium desorption from stainless steel begins to occur just above 500 K (with a desorption activation energy, E_{des} = 1.54 eV), sub-monolayer Li desorption occurred in a TPD peak at 942 K (E_{des} = 2.52 eV) indicating more energetically favorable lithium-stainless steel bonding (in the absence of an oxidation layer) than lithium-lithium bonding.

The effect of temperature on the desorption of lithium from refractory metal surfaces has important implications for a class of potential fusion reactor first wall materials. In particular, determining the strength of Li binding to molybdenum is critical to assessing the survivability of Li on Mo as a potential first wall material. We have presented the results of a joint experimental and theoretical investigation into how Li desorbs from single-crystal Mo(110) surfaces, used to eliminate the influence of grain boundaries, based on what can be deduced from temperature-programmed desorption measurements and density functional theory (DFT). [5] As shown in Fig. 3, Li desorption peaks measured at temperatures ranging from 711 K (1 monolayer, ML) to 1030 K (0.04 ML), with corresponding desorption onsets from 489 to 878 K, follow a trend similar to predicted Gibbs free energies for Li adsorption. Bader charge analysis of DFT densities reveals that repulsive forces between neighboring positively charged Li atoms increase with coverage and thus reduce the bond strength between Mo and Li, thereby lowering the desorption temperature as the coverage increases. Additionally, DFT predicts that Li desorbs at higher temperatures from a surface with vacancies than from a perfect surface, offering an explanation for the anomalously high desorption temperatures for the last Li to desorb from Mo(110). Analysis of simulated local densities of states indicates that the stronger

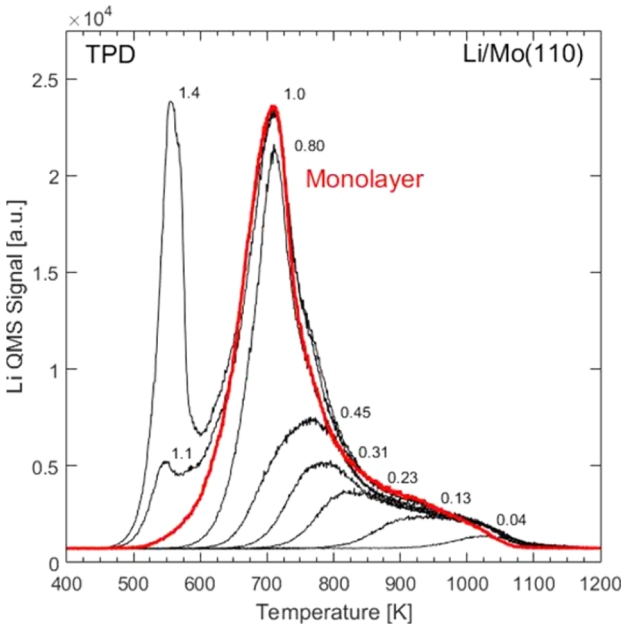

Fig. 3. Li TPD traces from Mo(110) for Li coverages ranging from 1.4 to 0.04 ML. The red curve is defined as arising from a Li coverage of 1.0 ML. [5]

binding to the defective surface is correlated with enhanced interaction between Li and Mo, involving the Li 2s electrons and not only the Mo 4d electrons as in the case of the pristine surface, but also the Mo 5s electrons in the case with surface vacancies. We suggest that steps and kinks present on the Mo(110) surface behave similarly and contribute to the high desorption temperatures. These findings imply that roughened Mo surfaces may strengthen Li film adhesion at higher temperatures.

A key property of Li films is their ability to retain hydrogen. We investigated deuterium retention at the Mo–Li interface by studying thin Li films three monolayers thick on a TZM Mo alloy, exploring the effects of temperature and surface contamination on D retention in these films. [6] Li films at temperatures between 315 and 460 K were exposed to a deuterium ion beam and D retention was measured using temperature programmed desorption, giving the results shown in Fig. 4. In the absence of oxygen, D is retained as LiD, and the relative amount of retained D decreases with increasing substrate temperature. In three-monolayer thick lithium oxide films, the amount of D retained was 2.5 times higher than the amount retained as LiD in the metallic Li film. However, oxygen reduces the thermal stability of D in the film, causing D2O and D2 to be released from the surface at temperatures 150–200 K below the LiD decomposition temperature. These results highlight the importance of maintaining a metallic Li layer for high D retention in Li films on TZM at elevated temperatures.

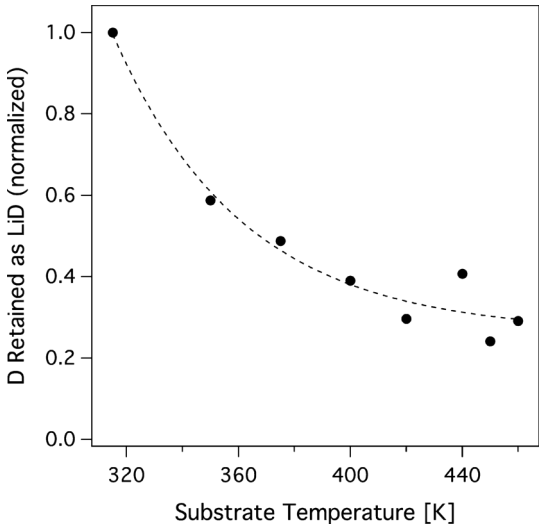

Fig. 4. The amount of deuterium retained as LiD in a 3 ML Li film was measured at different substrate temperatures using TPD. The decrease in relative D retention with increasing substrate temperature is described well by an exponential fit. [6]

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iii) Simulations of liquid metals as plasma-facing materials for fusion energy systems: P.G. Debenedetti and A.Z. Panagiotopoulos

The goals and objectives established for this project in the area of atomistic simulations

of liquid metal properties and phase behavior were met. Specifically, we tested existing force fields for pure liquid Li and Sn with respect to the diffusivities, viscosity, surface tension, and phase behavior, developed a new force field for liquid Sn, and studied the wetting properties of liquid Li on solid Mo. The force field development was performed in collaboration with the group of Prof. Carter. These accomplishments are described in more detail below.

Six lithium force fields from the literature were tested by examining their ability to predict a variety of liquid and coexistence properties. It was found that the force field developed by Cui et al. [Modell. Simul. Mater. Sci. Eng. 20, 015014 (2012)] is the most robust due to its accurate prediction of the melting temperature and liquid-phase data. Further studies of liquid lithium were thus performed with this force field. A new liquid tin force field was also developed in this work. It was found that the Ravelo and Baskes force field [Phys. Rev. Lett. 79, 2482 (1997)] was suitable for the solid phases of tin, but not the liquid phase. Therefore, a simulated annealing
procedure is used to construct the new force field by primarily fitting to experimental liquid-phase data. The new force field accurately reproduces a majority of the experimental data used in the fitting procedure and also accurately predicts liquid data not used in the optimization.

The wetting properties of liquid lithium on solid molybdenum were also examined. A lithium-molybdenum force field was developed by fitting to first-principles data. It was found that liquid lithium perfectly wets the (110) surface of molybdenum, in contrast with experimental data. This suggests the presence of oxygen and surface structure can significantly affect the ability of lithium to wet molybdenum. It was also found that the lithium atoms close to the molybdenum surface behave solid-like as evidenced by their low mobility and ordered structure, even at temperatures well above the bulk melting temperature of lithium. This shows that lithium strongly adheres to the molybdenum surface. These results suggest that if the solid walls of the reactor are primarily composed of molybdenum, liquid lithium would be a strong candidate for
liquid plasma-facing material due to its ability to wet and adhere to the solid surface.

The Ph.D. student that worked on this project, Joseph R. Vella, completed his dissertation and successfully defended his thesis in February, 2017. He will be joining ExxonMobil Research and Engineering in Houston, TX later this year.

iv) Fluid dynamics of thin films on curved surfaces: H.A. Stone

For the fluid dynamics part, we met all or most of our objectives, as we established a description of thin film flows on curved boundaries, analyzed the Rayleigh-Taylor instability, identified critical conditions for instability, and extended the work from two dimensions (cylinders) to three dimensions (spheres, tori). The final part of our work aimed to include magnetohydrodynamic effects and is something we are currently

working on with colleagues at PPPL. This is discussed in more detail below.

A liquid film on the underside of a planar or inclined planar surface is unstable due to gravitational effects, which is referred to as the Rayleigh-Taylor instability. Neglecting intermolecular interactions with the substrate, the liquid film is always unstable no matter what is the film thickness. This topic is very well studied in the fluid dynamics literature but it has largely been studied only for planar substrates.

In plasma fusion applications, we expect to have liquid films on the underside of curved substrates (because of the typical geometries of the tokamaks). Hence, we have studied, using experiments, theory and numerical simulations the influence of substrate curvature on the Rayleigh-Taylor instability. To the best of our knowledge this problem has never been investigated. For a two-dimensional example, we have shown that there is a critical film thickness below which the curvature can suppress the instability (Trinh et al. [1]): effectively the liquid can flow along the surface at about the same rate as which interfacial instabilities tend to grow. We have used experiments to identify the different kinds of film dynamics, including determining the approximate film thickness above which instability occurs. Similar ideas apply to the case of a liquid film on the underside of a spherical surface, which is a result we are completing now and is illustrated in a few figures below.

Experiments: We study the flow and possible instability of a liquid film on the underside of a curved substrate (Figure 1a). To make a uniform thin liquid film, we first coat silicone oil on top of the substrate by using a spin coater. Then, the liquid film layer is maintained on a horizontal table until the film thickness is uniform, which is validated by measurements with a confocal laser scanning microscope with fluorescent dye and an optical interferometry device (Figure 1b). The error in the position of the horizontal axis of the aligned table is less than 0.1 degrees, which is calibrated by a digital protractor (PRO3600). When a uniform thin liquid layer is obtained, we impose a curvature to the substrate and turn it upside down. By varying the initial film thickness, h_i, of silicone oil and the curvature ($1/R$) of the substrate, we vary the aspect ratio. To measure the evolution of the film thickness, we use an optical interferometry device, which is integrated with a light source and a CCD array-based spectrometer.

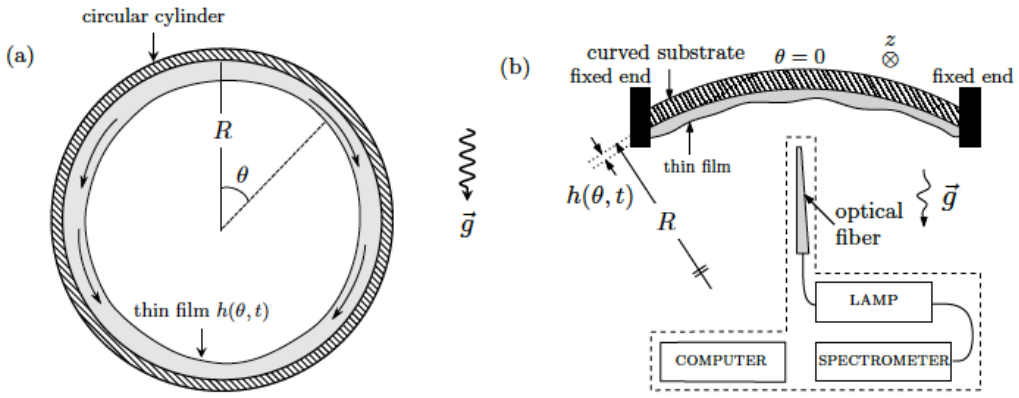

Figure 1: (a) Thin film flow on the inside of a circular cylinder and (b) schematic of the experimental setup. For the experiments sketched in (b) the substrate is formed from a curved sheet with the axial direction (z) directed into the page.

Theory and simulations: We use the thin-film equations, well-known from viscous ow theory, to provide a description of the role of substrate curvature on the gravitationally driven flow of the film on the underside of a circular cylinder (Figure 1a). These equations are solved analytically in the crucial regime near the top of the cylinder. The analytical predictions are confirmed by numerical solutions of the full equations. Based upon the governing partial differential equations and boundary conditions, we identify a single dimensionless parameter $B = \rho g R h_i/\gamma$, a modified Bond number, that governs the behavior of the flow and incorporates the surface tension γ, initial film thickness h_i, and substrate curvature $1/R$, where ρ is the density of the fluid and g is the gravitational acceleration.

Typical results from the experiments, theory and simulations; Below a critical value of B, the film is stable to perturbations with a thickness that decreases monotonically in time. For larger values of B, i.e. thicker films (or flatter substrates), the dynamics exhibit either transient perturbation growth followed by decay, or instability via drop formation. These results are shown in Figure 2a; experiments showing an initial perturbation that convects away is shown in Figure 2b and thick films that lead to (unstable) dripping are shown in Figure 2c. A direct comparison of the analytic (labeled asymptotic) and experimental results with two different ways to characterize the full numerical simulations are shown in Figure 3.

In recent work we have extended these studies to more general curved substrates. The case of a liquid film flowing due to gravity on the inside of a sphere is shown in Figure 4 and 5. We have solved this problem numerically (including development of a new numerical method, referred to as the closest point method; see the PhD thesis by N. Hammoud [2]) and analyzed the instability analytically. In addition, we developed results for the typical wavelength of the fingering instability. Also, we note that contrary to the flow shown in Figure 4, the film remains stable for these parameter values when the flow is outside the sphere.

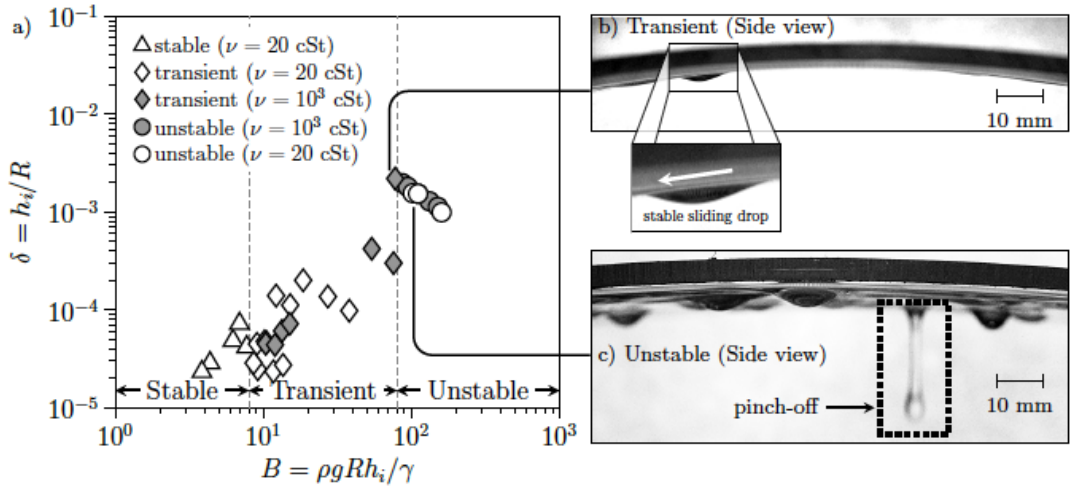

Figure 2: (a) Experimental results in the (B, δ)-plane and classified as stable, transient, or unstable. Two critical values of the Bond number are indicated: B=8 and B=80. Experimental images of the side view in the case of (b) transient and (c) unstable flows, where actual dripping of liquid drops is evident.

We believe that the combination of theory and experiments provides a relatively complete characterization of the Rayleigh-Taylor instability of a liquid layer under a curved surface, and the manner in which substrate curvature can stabilize the film.

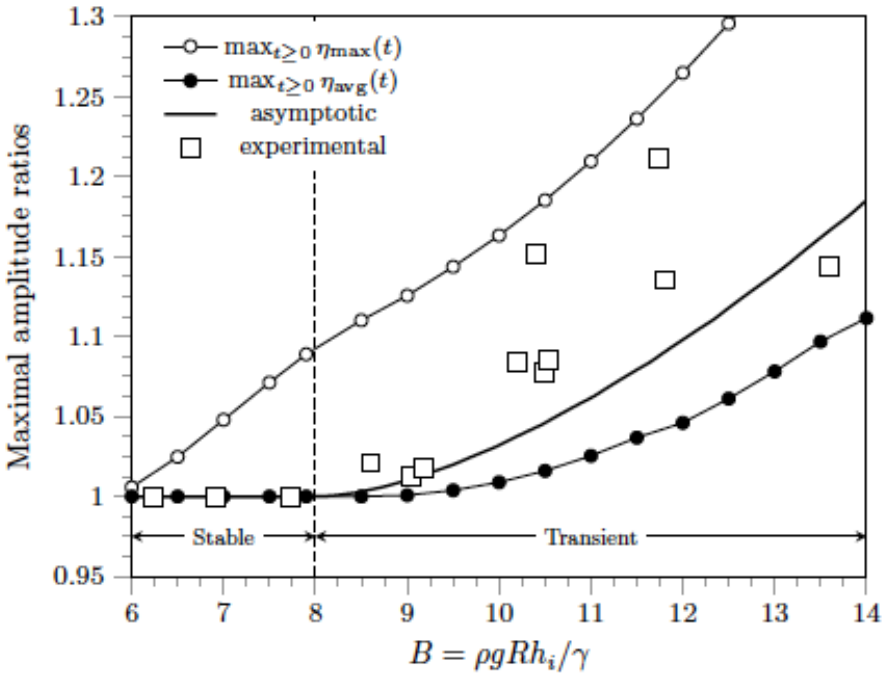

Figure 3 Comparison of two different measures of the numerical simulations with the analytical (asymptotic) and numerical results.

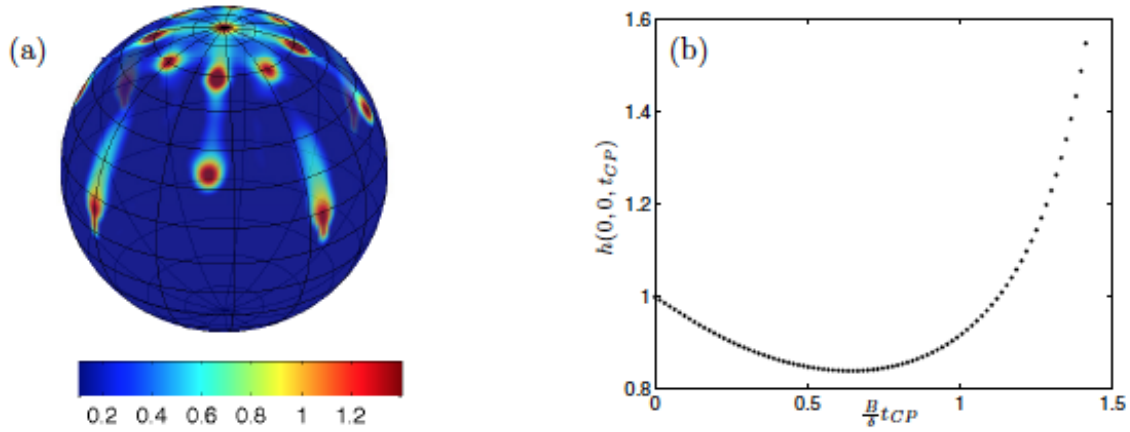

Figure 4: Example of a thin film inside a sphere for $Bd = 130$ ($B = 1300$, $\delta = 0.1$). (a) Surface plot of the film shows both a fingering instability and growth of the film thickness at the top of the sphere ($f = 0$), which indicates the possibility of a Rayleigh-Taylor instability. (b) Exponential growth in film thickness at the top of the sphere suggests the possibility of a Rayleigh-Taylor instability.

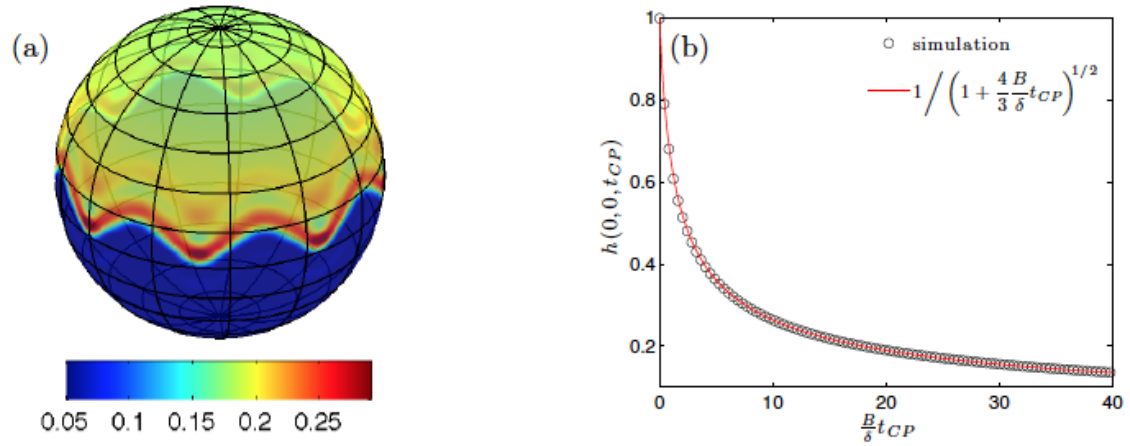

Figure 5: Example of a thin film outside a sphere for $B\delta = 130$ (same parameter values as Fig. 4). (a) Surface plot shows that for a film outside the sphere, the fingering instability is inhibited. (b) Decay in film thickness at the top of the sphere in agreement with theory.

Finally, inspired by the capillary porous surfaces often discussed for handling liquid metals in fusion applications, we have studied wetting of a uniform mesh. Such meshes, and mesh-like structures, are described in the literature on capillary porous surfaces. We performed experiments for wetting liquids and developed theoretical arguments for rate of penetration of the liquid into a regular mesh that was originally dry. The wetting patterns varied from polygonal to circular, which we explained with theoretical arguments [3]. Future work could consider transient insults or perturbations of initially liquid-filled meshes to understand how significant energy pulses could disrupt the liquid film and cause exposure of the underlying solid mesh.

References

[1] P. Trinh. H. Kim, N. Hammoud, P.D. Howell, S.J. Chapman and H.A. Stone, *Phys.*

Fluids, Curvature suppresses the Rayleigh-Taylor instability. *Phys. Fluids* **26**, 051704.
[2] N. Hammoud, On Instabilities in Thin-Film Flows, Ph.D. thesis, Princeton University (2016).
[3] H. Kim, Z. Zheng, H.A. Stone 2015 Noncircular stable displacement patterns in a meshed porous layer. *Langmuir* **31**, 5684-5688

6. Cost Status: Show approved budget by budget period and actual costs incurred.

We applied for and received a one-year no-cost extension to the original grant award, and this is reflected in our budget below. Additional personnel and expenditures were added during that period to accomplish the work described in the proposal and expend all of the allocated funds.

	Budget	**Report Period** 8/1/2012 - 7/31/2016	**Balance**
Salaries	$ 474,599.50	$454,129.80	$20,469.70
Personnel Benefits	$ 60,770.86	$ 95,004.95	$(34,234.09)
Materials & Services	$ 84,216.00	$101,402.17	$(19,647.57)
Publication, Reprints, Pages	$-	$ 45.00	$0
Maintenance & Repair	$-	$ 2,259.00	$0
Total Freight Costs	$-	$ 7.40	$0
Total Food & Entertainment	$-	$ 150.00	$0
Subcontracts up to $25K	$-	$	$0
Domestic Travel	$ 19,543.00	$24,661.27	$(5,118.27)
Foreign Travel	$-	$-	$0
Recharge Center Use	$-	$2,812.40	$(2,812.40)
Modified Total Direct Costs	$ 639,129.36	$ 680,471.99	$(41,342.63)
Assistant Tuition	$189,393.44	$120,654.06	$68,739.38
Other Student Aid/Support	$-	$-	$0
Subcontracts over $25K	$-	$-	$0
Other Departmental Charges	$-	$-	$0
Equipment	$-	$-	$0
Indirect Costs	$362,204.97	$389,601.72	$(27,396.75)
TOTAL COSTS	**$1,190,727.77**	**$1,190,727.77**	**$0**

7. Schedule Status.

Most of our goals have been met by continuing work developing our simulation and experimental programs to address our research objectives. We made good progress on accomplishing the research activities for the project according to the schedule provided in the Gannt chart in the proposal, as outlined below for activities through 2015 and the no-

cost extension year 2016:

- Experiments on flows of liquid Li walls
- Models of flows of liquid Li walls
- Deuterium adsorption and retention in Li film experiments
- Liquid lithium investigations
- Li-Sn alloy studies
- Molecular dynamics: wetting
- Monte Carlo simulations: solubility limits
- Dynamics of deuterium bombardment of liquid Li
- Li-Sn alloy studies
- Reports

Our research plan outlined specific studies and specific questions to be answered that serve as technical milestones. Tackling these questions requires working somewhat in parallel, carrying out experiments and theoretical calculations and simulations at several length scales, with feedback from one course of study to another. We accomplished significant progress on the following milestones during the last grant period:

I. Flows of Lithium in Fusion-Relevant Geometries: Experiments and Simulations with Model Systems

(1) Surface-tension-driven flows.

(2) Flows relevant to liquid films on the inner surface of a curved substrate.

II. Experimental Investigations of the Surface Science of Liquid Metal Films on Solid Substrates

(1) Structure and energetics of deuterium (D, D_2, and D^+) adsorption, absorption, desorption, and deuteride formation and thermal stability in Li films.

(2) Influence of contaminants on deuterium adsorption and retention by Li films.

III. Molecular dynamics and Monte Carlo simulations of phase behavior in liquid metals

(1) Selection and validation of force fields for solid Li.

(2) Molecular dynamics calculations for diffusivities, viscosity and surface tension for liquid Li, Sn and Li-Sn mixtures using effective or EAM potentials.

IV. First-principles computations of liquid metal films exposed to particle bombardment

(1) Structure of liquid Li and Sn surfaces computed and validated against available experimental data structure; key data used to constrain classical force fields.

(2) Structure and energetics of ordered and disordered Li surfaces and films on Mo, and deuterium adsorption, diffusion, and absorption into Li surfaces.

8. Any changes in approach or aims: No.

9. Actual or anticipated problems: None anticipated at this time.

10. Any absence or changes of key personnel or changes in consortium/teaming management: No.

11. A description of any product produced or technology transfer activities accomplished during this reporting period

a. Publications (list journal name, volume, issue); conference papers; or other public releases of results. Attach or send copies of public releases to the DOE Program Manager identified in Block 15 of the Assistance Agreement Cover Page;

J. R. Vella, M. Chen, F. H. Stillinger, E. A. Carter, A. Z. Panagiotopoulos, and P. G. Debenedetti, "A modified embedded-atom method (MEAM) force field for liquid tin", in preparation (2016).

Abstract: Liquid tin is a promising material as a plasma-facing component in tokamak fusion reactors. In the present work, classical molecular dynamics simulations are performed using a new modified embedded atom (MEAM) force field parametrization developd for the simulation of liquid tin. Previous MEAM parametrizations such as Ravelo and Baskes' (RB) were designed for solid phases of tin. Starting from their parameters, we use a simulated annealing optimization procedure to fit a MEAM expression against experimental properties of liquid tin. The predictive capabilities of our new and the RB force field are evaluated by comparing to a wide range of first-principles quantum mechanics and experimental data. These properties include crystal properties, melting temperature, liquid structures, liquid density, self-diffusivity, viscosity, and vapor-liquid surface tension. We find the RB force field to generally provide better agreement with the solid properties of tin, however, better liquid tin properties emerge from our new MEAM force field, suggesting its appropriateness for future simulations of liquid tin films relevant to fusion reactor conditions.

J. R. Vella, M. Chen, F. H. Stillinger, E. A. Carter, A. Z. Panagiotopoulos, and P. G. Debenedetti, "Wetting of molybdenum surfaces by liquid Li: Classical dynamics simulations," in preparation (2016).

Abstract: The wetting properties of Li on Mo substrates are relevant to the efficacy of Li as a plasma facing component in fusion reactors. In this work, we present a new modified embedded-atom method (MEAM) force field parametrized to describe the interactions between Mo and Li. Previous parametrizations for pure Mo and Li exist, which we extend by tuning cross-term parameters between Mo and Li. Our new MEAM force field reproduces well a range of benchmark properties obtained from first-principles quantum mechanics simulations, including binding curves for Li at different adsorption sites on Mo (110). With this new force field, wetting angles of liquid Li on Mo (110) were derived from molecular dynamics simulations. We find that liquid Li tends to completely wet the perfect Mo (110) surface, in contradiction with previous measurements finding finite wetting angles for liquid Li on polycrystalline Mo surfaces. However, these experiments were not carried out under ultra-high vacuum conditions, suggesting that impurities such as oxygen or the roughness of Mo surfaces may play a crucial role in this wetting process.

M. Chen, B. G. del Rio, and E. A. Carter "Orbital-free density functional theory study of Li-Sn alloys", in preparation (2016).

Abstract: Alloys of lithium and tin are promising candidates for plasma-facing

components in fusion reactors due to their high melting points. We use orbital-free density functional theory (OFDFT), a quantum-mechanics simulation method, to study solid and liquid phases of Li-Sn alloys. OFDFT accurately describes properties of Li-rich Li-Sn alloy crystals. Properties of Li-Sn alloys, Li, and Sn liquids are also examined. Previous measurements suggest that Li tends to segregate to the surface of liquid Li-Sn alloys. To assess this claim, we analyze the surface compositions of liquid Li-Sn alloys at different temperatures, revealing new insights into properties of liquid Li-Sn alloys.

M. Chen, J. Roszell, E. V. Scoullos, C. Riplinger, B. E. Koel, and E. A. Carter, "Effect of temperature on the desorption of lithium from molybdenum (110) surfaces: implications for fusion reactor first wall materials," *J. Phys. Chem. B*, in press (2016).

Abstract: Determining the strength of Li binding to Mo is critical to assessing the survivability of Li as a potential first wall material in fusion reactors. We present the results of a joint experimental and theoretical investigation into how Li desorbs from Mo(110) surfaces, based on what can be deduced from temperature-programmed desorption measurements and density functional theory (DFT). Li desorption peaks measured at temperatures ranging from 711 K (1 monolayer, ML) to 1030 K (0.04 ML), with corresponding desorption onsets from 489 to 878 K, follow a trend similar to predicted Gibbs free energies for Li adsorption. Bader charge analysis of DFT densities reveals that repulsive forces between neighboring positively charged Li atoms increase with coverage and thus reduce the bond strength between Mo and Li, thereby lowering the desorption temperature as the coverage increases. Additionally, DFT predicts that Li desorbs at higher temperatures from a surface with vacancies than from a perfect surface, offering an explanation for the anomalously high desorption temperatures for the last Li to desorb from Mo(110). Analysis of simulated local densities of states indicates that the stronger binding to the defective surface is correlated with enhanced interaction between Li and Mo, involving the Li 2s electrons and not only the Mo 4d electrons as in the case of the pristine surface, but also the Mo 5s electrons in the case with surface vacancies. We suggest that steps and kinks present on the Mo(110) surface behave similarly and contribute to the high desorption temperatures. These findings imply that roughened Mo surfaces may strengthen Li film adhesion at higher temperatures.

T. Abrams, M. A. Jaworski, M. Chen, E. A. Carter, R. Kaita, D. P. Stotler, G. De Temmerman, T. W. Morgan, M. A. van den Berg, and H. J. van der Meiden, "Suppressed gross erosion of high-temperature lithium via rapid deuterium implantation," *Nucl. Fusion*, **56**, 016022 (2016).

Abstract: Lithium-coated high-Z substrates are planned for use in the NSTX-U divertor and are a candidate plasma facing component (PFC) for reactors, but it remains necessary to characterize the gross Li erosion rate under high plasma fluxes ($>10^{23}$ m^{-2} s^{-1}), typical for the divertor region. In this work, a realistic model for the compositional evolution of a Li/D layer is developed that incorporates first-principles molecular dynamics (MD) simulations of D diffusion in liquid Li. Predictions of Li erosion from a mixed Li/D material are also developed that include formation of lithium deuteride (LiD). The erosion rate of Li from LiD is predicted to be significantly lower than from pure Li.

This prediction is tested in the Magnum-PSI linear plasma device at ion fluxes of 10^{23}–10^{24} m^{-2} s^{-1} and Li surface temperatures ≤800 °C. Li/LiD coatings ranging in thickness from 0.2 to 500 μm are studied. The dynamic D/Li concentrations are inferred via diffusion simulations. The pure Li erosion rate remains greater than Langmuir Law evaporation, as expected. For mixed-material Li/LiD surfaces, the erosion rates are reduced, in good agreement with modelling in almost all cases. These results imply that the temperature limit for a Li-coated PFC may be significantly higher than previously imagined.

M. Chen, T. Abrams, M. Jaworski, and E. A. Carter, "Rock-Salt Structure Lithium Deuteride Formation in Liquid Lithium with High-Concentrations of Deuterium: A First-Principles Molecular Dynamics Study," *Nucl. Fusion*, **56**, 016020 (2016).

Abstract: Because of lithium's possible use as a first wall material in a fusion reactor, a fundamental understanding of the interactions between liquid lithium (Li) and deuterium (D) is important. We predict structural and dynamical properties of liquid Li samples with high concentrations of D, as derived from first-principles molecular dynamics simulations. Liquid Li samples with four concentrations of inserted D atoms (LiD_β, β= 0.25, 0.50, 0.75, and 1.00) are studied at temperatures ranging from 470 to 1143 K. Densities, diffusivities, pair distribution functions, bond angle distribution functions, geometries, and charge transfer between Li and D atoms are calculated and analyzed. The analysis suggests liquid–solid phase transitions can occur at some concentrations and temperatures, forming rock-salt LiD within liquid Li. We also observe formation of some D_2 molecules at high D concentrations.

M. Chen, J. R. Vella, F. H. Stillinger, E. A. Carter, A. Z. Panagiotopoulos, and P. G. Debenedetti, "Liquid Li Structure and Dynamics: A Comparison Between OFDFT and Second Nearest-Neighbor Embedded-Atom Method," *AIChE Journal*, **6**, 2841 (2015).

Abstract: The structure and dynamics of liquid lithium are studied using two simulation methods: orbital-free (OF) first-principles molecular dynamics (MD), which employs OF density functional theory (DFT), and classical MD utilizing a second nearest-neighbor embedded-atom method potential. The properties studied include the dynamic structure factor, the self-diffusion coefficient, the dispersion relation, the viscosity, and the bond angle distribution function. Simulation results were compared to available experimental data when possible. Each method has distinct advantages and disadvantages. For example, OFDFT gives better agreement with experimental dynamic structure factors, yet is more computationally demanding than classical simulations. Classical simulations can access a broader temperature range and longer time scales. The combination of first-principles and classical simulations is a powerful tool for studying properties of liquid lithium.

M. Chen, L. Hung, C. Huang, J. Xia and E.A. Carter 2013 The melting point of lithium: An orbital-free first principles molecular dynamics study. *Molecular Physics* **111**, 3448.

Abstract: The melting point of liquid lithium near zero pressure is studied with

large-scale orbital-free first-principles molecular dynamics (OF-FPMD) in the isobaric-isothermal ensemble. We adopt the Wang-Govind-Carter (WGC) functional as our kinetic energy density functional (KEDF) and construct a bulk-derived local pseudopotential (BLPS) for Li. Our simulations employ both the "heat-until-melts" method and the coexistence method. We predict 465 K as an upper bound of the melting point of Li from the "heat-until-melts" method, while we predict 434 K as the melting point of Li from the coexistence method. These values compare well with an experimental melting point of 453 K at zero pressure. Furthermore, we calculate a few important properties of liquid Li including the diffusion coefficients, pair distribution functions, static structure factors, and compressibilities of Li at 470 K and 725 K in the canonical ensemble. Our theoretically-obtained results show good agreement with known experimental results, suggesting that OF-FPMD using a nonlocal KEDF and a BLPS is capable of accurately describing liquid metals.

"Effects of temperature and surface contamination on D retention in ultrathin Li films on TZM", A.M. Capece, J.P. Roszell, C.H. Skinner, B.E. Koel, *J. Nucl. Mat.,* **463**, 1177–1180 (2015).

Abstract: In this work, we investigate deuterium retention at the Mo–Li interface by studying thin Li films three monolayers thick on a TZM Mo alloy. Li films at temperatures between 315 and 460 K were exposed to a deuterium ion beam and D retention was measured using temperature programmed desorption. In the absence of oxygen, D is retained as LiD, and the relative amount of retained D decreases with increasing substrate temperature. In three-monolayer thick lithium oxide films, the amount of D retained was 2.5 times higher than the amount retained as LiD in the metallic Li film. However, oxygen reduces the thermal stability of D in the film, causing D2O and D2 to be released from the surface at temperatures 150–200 K below the LiD decomposition temperature. These results highlight the importance of maintaining a metallic Li layer for high D retention in Li films on TZM at elevated temperatures.

"High performance discharges in the Lithium Tokamak eXperiment with liquid lithium walls", J. C. Schmitt, R. E. Bell, D. Boyle, Ben Esposti, R. Kaita, T. Kozub, B. LeBlanc, M. Lucia, R. Maingi, R. Majeski, E. Merino, S. Punjabi-Vinoth, G. Tchilinguirian, A. M. Capece, B. E. Koel, J. Roszell, T. M. Biewer, T. K. Gray, S. Kubota, P. Beiersdorfer, K. Widmann, K. Tritz, Phys. of Plasmas, 22, 056112-1–056112-8 (2015).

Abstract: The first-ever successful operation of a tokamak with a large area (40% of the total plasma surface area) liquid lithium wall has been achieved in the Lithium Tokamak eXperiment (LTX).These results were obtained with a new, electron beam-based lithium evaporation system, which can deposit a lithium coating on the limiting wall of LTX in a five-minute period. Preliminary analyses of diamagnetic and other data for discharges operated with a liquid lithium wall indicate that confinement times increased by 10compared to discharges with helium-dispersed solid lithium coatings. Ohmic energy confinement times with fresh lithium walls, solid and liquid, exceed several relevant empirical scaling expressions. Spectroscopic analysis of the discharges indicates that oxygen levels in the discharges limited on liquid lithium walls were

significantly reduced compared to discharges limited on solid lithium walls. Tokamak operations with a full liquid lithium wall (85% of the total plasma surface area) have recently started.

"Sorption of Atmospheric Gases by Bulk Lithium Metal", C.A. Hart, C.H. Skinner, A.M. Capece, B.E. Koel, J. Nucl. Mat., 468, 71–77 (2016).

Abstract: Lithium conditioning of plasma facing components has enhanced the performance of several fusion devices. Elemental lithium will react with air during maintenance activities and with residual gases (H_2O, CO, CO_2) in the vacuum vessel during operations. We have used a mass balance (microgram sensitivity) to measure the mass gain of lithium samples during exposure of a ~1 cm2 surface to ambient and dry synthetic air. For ambient air, we found an initial mass gain of several mg/h declining to less than 1 mg/h after an hour and decreasing by an order of magnitude after 24 h. A 9 mg sample achieved a final mass gain corresponding to complete conversion to Li_2CO_3 after 5 days. Exposure to dry air resulted in a 30 times lower initial rate of mass gain. The results have implications for the chemical state of lithium plasma facing surfaces and for safe handling of lithium coated components.

"Spreading of lithium on a stainless steel surface at room temperature", C. H. Skinner, A. M. Capece, J. Roszell, B. E. Koel, J. Nucl. Mat., 468, 26–30 (2016).

Abstract: Lithium conditioned plasma facing surfaces have lowered recycling and enhanced plasma performance on many fusion devices and liquid lithium plasma facing components are under consideration for future machines. A key factor in the performance of liquid lithium components is the wetting by lithium of its container. We have observed the surface spreading of lithium from a mm-scale particle to adjacent stainless steel surfaces using a scanning Auger microprobe that has elemental discrimination. The spreading of lithium occurred at room temperature (when lithium is a solid) from one location at a speed of 0.62 mm/day under ultrahigh vacuum conditions. Separate experiments using temperature programmed desorption (TPD) investigated bonding energetics between monolayer-scale films of lithium and stainless steel. While multilayer lithium desorption from stainless steel begins to occur just above 500 K (E_{des} = 1.54 eV), sub-monolayer Li desorption occurred in a TPD peak at 942 K (E_{des} = 2.52 eV) indicating more energetically favorable lithium-stainless steel bonding (in the absence of an oxidation layer) than lithium-lithium bonding.

"The low temperature oxidation of lithium thin films on HOPG by O_2 and H_2O", S. M. Wulfsberg, B. E. Koel, and S.L. Bernasek, Surface Sci., 651, 120–127 (2016)

Abstract: Lithiated graphite and lithium thin films have been used in fusion devices. In this environment, lithiated graphite will undergo oxidation by background gases. In order to gain insight into this oxidation process, thin (<15monolayer (ML)) lithium films on highly ordered pyrolytic graphite (HOPG) were exposed to O_2(g) and H_2O(g) in an ultra-high vacuum chamber. High resolution electron energy loss spectroscopy (HREELS) was used to identify the surface species formed during O_2g) and

H_2O(g) exposure. Auger electron spectroscopy (AES) was used to obtain the relative oxidation rates during O_2 (g) and H_2O(g) exposure. AES showed that as the lithium film thickness decreased from15 to 5 to 1 ML, the oxidation rate decreased for both O_2 (g) and H_2O(g). HREELS showed that a 15 ML lithium film was fully oxidized after 9.7 L (L) of O_2 (g) exposure and $Li_2O$was formed. HREELS also showed that during initial exposure (<0.5 L) H_2O(g), lithium hydride and lithium hydroxide were formed on the surface of a 15 ML lithium film. After 0.5 L of H_2O(g) exposure, the H_2O(g) began to physisorb, and after 15 L of H_2O(g) exposure, the 15 ML lithium film was not fully oxidized.

"Effect of Temperature on the Desorption of Lithium from Molybdenum (110) Surfaces: Implications for Fusion Reactor First Wall Materials", M. Chen, J. Roszell, E.V. Scoullos, C. Riplinger, B.E. Koel, and E.A. Carter, J. Phys. Chem. B, 120(26), 6110–6119 (2016).

Abstract: Determining the strength of Li binding to Mo is critical to assessing the survivability of Li as a potential first wall material in fusion reactors. We present the results of a joint experimental and theoretical investigation into how Li desorbs from Mo(110) surfaces, based on what can be deduced from temperature-programmed desorption measurements and density functional theory (DFT). Li desorption peaks measured at temperatures ranging from 711 K (1 monolayer, ML) to 1030 K (0.04 ML), with corresponding desorption onsets from 489 to 878 K, follow a trend similar to predicted Gibbs free energies for Li adsorption. Bader charge analysis of DFT densities reveals that repulsive forces between neighboring positively charged Li atoms increase with coverage and thus reduce the bond strength between Mo and Li, thereby lowering the desorption temperature as the coverage increases. Additionally, DFT predicts that Li desorbs at higher temperatures from a surface with vacancies than from a perfect surface, offering an explanation for the anomalously high desorption temperatures for the last Li to desorb from Mo(110). Analysis of simulated local densities of states indicates that the stronger binding to the defective surface is correlated with enhanced interaction between Li and Mo, involving the Li 2s electrons and not only the Mo 4d electrons as in the case of the pristine surface, but also the Mo 5s electrons in the case with surface vacancies. We suggest that steps and kinks present on the Mo(110) surface behave similarly and contribute to the high desorption temperatures. These findings imply that roughened Mo surfaces may strengthen Li film adhesion at higher temperatures.

"The low temperature oxidation of lithium thin films on graphite by O_2, H_2O, and CO", S. M. Wulfsberg, Ph.D. Dissertation, Princeton University, January 2016.

Lithiated graphite and lithium thin films are used in fusion devices. In fusion devices, lithiated graphite will undergo oxidation by background gases. In order to gain insight into this oxidation process, thin (< 3 nm) lithium films on highly oriented pyrolytic graphite (HOPG) were exposed to O_2(g), H_2O(g), and CO(g) in an ultra-high vacuum chamber. High resolution electron energy loss spectroscopy (HREELS) was used to identify the surface species formed during O_2(g), H_2O(g), and CO(g) exposure. Auger electron spectroscopy (AES) was used to obtain the relative initial sticking coefficients during O_2(g), H_2O(g), and CO(g) exposure. AES experiments showed that as the lithium

film thickness decreased from 15 to 5 to 1 ML, the initial sticking coefficients decreased for O_2(g), H_2O(g), and CO(g). AES measurements showed that a 15 ML lithium film was fully oxidized after 9.7 L of O_2(g) exposure and LivO was formed. Additionally, HREEL spectra showed that, even at 100 K and low exposures (< 0.5 L), O_2(g) fully dissociated upon reacting with the lithium thin films. AES measurements showed that the 15 ML lithium film did not fully oxidize after 15 L of H_2O(g) exposure, but the 5 and 1 ML lithium films did fully oxidize. HREELS showed that during initial exposure (< 0.5 L) of H_2O(g), lithium hydride and lithium hydroxide was formed on the surface of a 15 ML lithium film. After 0.5 L of H_2O(g) exposure, the H_2O(g) began to physisorb. AES measurements also showed that a 15 ML lithium film was fully oxidized by CO(g) after 11.0 L of CO(g) exposure. Additionally, HREELS measurements have shown no evidence that CO(g) formed either a physisorbed or a chemisorbed Li—CO complex, but showed evidence of Li—O species present in the surface. This suggests that the CO(g) fully dissociated upon reacting with the lithium thin films on HOPG. Finally, O_2(g), H_2O(g), and CO(g) oxygen uptake experiments by 15 ML Li films on HOPG showed that H_2O(g) had the highest relative initial sticking coefficient and CO(g) had the lowest relative initial sticking coefficient.

J.R. Vella, F.H. Stillinger, A.Z. Panagiotopoulos and P.G. Debenedetti, "A Comparison of the Predictive Capabilities of the Embedded-Atom Method and Modied Embedded-Atom Method Potentials for Lithium." *The Journal of Physical Chemistry B*, **119**: 8960-8968 (2015).

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J.R. Vella, M. Chen, S. Fürstenberg, F.H. Stillinger, E. A. Carter, A. Z. Panagiotopoulos, and P.G. Debenedetti, "Characterization of the Liquid Li-Solid Mo (110) Interface from a Second-Nearest Neighbor Modied Embedded-Atom Method Force Field" (submitted, 2017).

P.D. Howell, H. Kim, M. Popova and H.A. Stone 2016 Rivulet flow over a flexible beam. *J. Fluid Mech.* **796**, 285-305.

H. Kim, Z. Zheng and H.A. Stone 2015 Non-circular stable displacement patterns in a meshed porous layer. *Langmuir* **31**, 5864-5868.

P.H. Trinh, H. Kim, N. Hammoud, P.D. Howell, S.J. Chapman and H.A. Stone 2014 Curvature suppresses the Rayleigh-Taylor instability. *Phys. Fluids* **26**, 051704.

N. Hammoud, On Instabilities in Thin-Film Flows, Ph.D. thesis, Princeton University (2016).

N. Hammoud, C.B. Macdonald, T. Marx, H.A. Stone and P.H. Trinh, Thin film flows on general curved surfaces with gravity and surface tension. In preparation.

Invited lectures

March 14, 2016 "Quantum Solutions for a Sustainable Energy Future," The Fred Kavli Innovations in Chemistry Lecture at the 251st ACS Spring National Meeting, San Diego, CA; by E. A. Carter

Jan. 21, 2016 "Materials for Sustainable Energy," keynote lecture at The Academy of Medicine, Engineering & Science of Texas (TAMEST) 2016 Annual Conference, Dallas, TX; by E. A. Carter

July 7, 2015 "How Quantum Mechanics Can Help Provide a Sustainable Energy Future," plenary lecture at the SCF'15 Conference on Chemistry and Energy Transition, Lille, France; by E. A. Carter

May 30, 2015 "Ab Initio Molecular Dynamics for Sustainable Energy: From Fuel Cells to Fusion," at the Chemical Dynamics and the Rabinovitch Legacy: A Symposium in Memory of B. S. Rabinovitch, University of Washington, Seattle, WA; by E. A. Carter

March 20, 2015 "Quantum Mechanical Simulations of Millions of Atoms and Its Application to Fusion Energy," at the NAI Fellows Induction Ceremony, Pasadena, CA; by E. A. Carter

Feb. 14, 2015 "How Quantum Mechanics Can Help Solve the World's Energy Problems," at the 2015 AAAS Meeting, San Jose, CA; by E. A. Carter

July 13, 2014 "First Principles Quantum Simulations of Renewable Energy Phenomena," at the Gordon Research Conference on Atomic Molecular Interactions, Easton, MA; by E. A. Carter

Nov. 4, 2013 "Quantum Mechanics and the Future of the Planet," Mathematics of Planet Earth 2013 Simons Public Lecture at the Institute for Pure and Applied Mathematics Workshop III: Batteries and Fuel Cells, Los Angeles, CA; by E. A. Carter

Aug. 27, 2013 "How Quantum Mechanics Can Help Solve the World's Energy Problems," plenary lecture at the Applied Mathematics, Modeling and Computational Science (AMMCS) 2013 International Conference, Waterloo, ON, Canada; by E. A. Carter

Aug. 14, 2014 "Surface Science of Plasma-Wall Interactions for Liquid Metal Plasma Facing Components", *General Atomics*, San Diego, CA, DIII-D Boundary/PMI Center; by B. E. Koel

June 2, 2015 "Deuterium Ion Retention in Clean and Oxidized Lithium Films", 2015 IEEE/NPSS Symposium on Fusion Engineering (SOFE): Session SO14 PMI and Plasma Edge Physics, Austin, TX; by **J.P. Roszell**, A.M. Capece, B.E. Koel

Jan. 11, 2016 "Molecular Simulation of Phase Equilibria: Progress and Challenges," Keith E. Gubbins Lecture, North Carolina State U., (A.Z. Panagiotopoulos)

May 2014 Department of Applied Mathematics and Theoretical Physics, Cambridge University, G.K. Batchelor Lecture, (H. A. Stone)

January 2016 Invited speaker, 5th Northwest Complex Fluids and Soft Matter Workshop, NYU Tandon School of Engineering. (H. A. Stone)

May 2016 Lacey Lectures, Division of Chemistry and Chemical Engineering, Caltech. (H. A. Stone)

May 2016 Stanford S. and Beverly P. Penner Distinguished Lecture, Mechanical and Aerospace Engineering, UC San Diego (H. A. Stone)

November 2016 Fluid Dynamics Prize, Otto Laporte Lecture, APS-DFD Annual Meeting, Portland OR. (H. A. Stone)

Contributed talks and presentations by PIs, postdocs, graduate students and undergraduate students

"Rock-Salt Structure Lithium Deuteride Formation in Liquid Lithium with High-Concentrations of Deuterium: A First-Principles Molecular Dynamics Study," poster at the *4th Annual Meeting of the Princeton E-ffiliates Partnership*, Princeton, NJ; presented by Mohan Chen, Nov. 20, 2015.

"Predictive Power of Embedded-Atom Method (EAM) Force Fields for Lithium," talk at the *2015 AIChE Annual Meeting*, Salt Lake City, UT; presented by Joseph R. Vella, Nov. 12, 2015.

"First-principles molecular dynamics simulations of high-concentration deuterium implantation in liquid lithium," talk at the *APS March Meeting 2015*, San Antonio, TX; presented by Mohan Chen, March 4, 2015.

"First-Principles Molecular Dynamics of Liquid Metals," talk at the *"Where No Materials Dares To Go" Workshop*, Leiden, the Netherlands; presented by Mohan Chen, Jan. 9, 2014.

"Towards a Better Understanding of Plasma-Surface Interactions in a Fusion Reactor: an Orbital-Free First-Principles Molecular Dynamics Study of Liquid Lithium," poster at the *2nd Annual Meeting of the Princeton E-ffiliates Partnership*, Princeton, NJ; presented by Mohan Chen, Nov. 15, 2013.

"The melting point of lithium: an orbital-free first-principles molecular dynamics study," poster at the *66th Gaseous Electronics Conference*, Princeton, NJ; presented by Mohan Chen, Oct. 3, 2013.

"Multiscale, integrated divertor plasma-material simulation"
P. Krstić, I. Kaganovich, D. Stotler, B.E. Koel
DOE Fusion Energy Science Advisory Board, Washington, DC, June 2014

"Surface chemistry analysis of boron conditioned RFX-mod graphite samples correlated to plasma operation"
B. Rais, A. Canton, P. Innocente, C.H. Skinner, B.E. Koel, J. Fu
41st European Physical Society (EPS) Conference on Plasma Physics, Berlin, June 2014

"A Liquid Metal PFC Initiative"
R. Maingi, J.P. Allain, D. Andruczyk, D. Currelli, R. Goldston, M. Jaworski, R. Kaita, B. Koel, R. Majeski, D. Ruzic, C. Skinner, D. Stotler
DOE Fusion Energy Science Advisory Board (FESAC) Strategic Planning Panel Meeting, Gaithersburg, MD, July 2014

"Establishing the surface science and engineering of liquid-metal PFCs"
J.P. Allain and B.E. Koel
DOE Fusion Energy Science Advisory Board (FESAC) Strategic Planning Panel Meeting, Gaithersburg, MD, July 2014

"Absorption of Atmospheric Gases by Bulk Lithium Metal"
C. A. Hart, A. M. Capece, B. E. Koel, and C. H. Skinner
Annual Student Poster Session, Princeton Plasma Physics Laboratory, Princeton, NJ, August 2014

"SEE Properties of Plasma-Facing Components for Fusion Applications"
K. Pardinas and B. E. Koel
PEI Summer of Learning Symposium, Princeton, NJ, October, 2014

"Lithium wetting of stainless steel for plasma facing components"
C.H. Skinner, A.M. Capece, J.P. Roszell, B.E. Koel
56th Annual Meeting of the APS Division of Plasma Physics, New Orleans, LA, October 2014

"Sputtering rates of lithium and lithium hydride due to low energy ion impact"
J.P. Roszell, A.M. Capece, C.H. Skinner, B. Koel
56th Annual Meeting of the APS Division of Plasma Physics, New Orleans, LA, October 2014

"Measurements of the Absorption of Atmospheric Gases in Bulk Lithium Metal using a Mass Balance"
C.A. Hart, C.H. Skinner, A.M. Capece, B.E. Koel
56th Annual Meeting of the APS Division of Plasma Physics, New Orleans, LA, October 2014

"Overview of results from the Lithium Tokamak eXperiment (LTX)"
R. Majeski, R. Bell, D. Boyle, A. Capece, A. Diallo, E. Granstedt, C.M. Jacobson, R. Kaita, B. Koel, T. Kozub, B. Leblanc, M. Lucia, R. Maingi, E. Merino, J. Schmitt, D. Stotler, G. Tchilingurian, T.M. Biewer, T.K. Gray, S. Kubota, W.A. Peebles, P. Beiersdorfer, K. Tritz, J.P. Allain, F. Bedoya
56th Annual Meeting of the APS Division of Plasma Physics, New Orleans, LA, October 2014

"Predictive Abilities of Embedded-Atom Method (EAM) Potentials Developed for Lithium," J. R. Vella, M. Chen, F. H. Stillinger, E. A. Carter, A. Z. Panagiotopoulos, and P. G. Debenedetti, poster presentation at the FOMMS 2015 Conference, Mt Hood, OR, July 12-16, 2015.

"Predictive Power of Embedded-Atom Method (EAM) Force Fields for Lithium," J. R. Vella, M. Chen, E. A. Carter, F. H. Stillinger, A. Z. Panagiotopoulos, and P. G. Debenedetti, AIChE Annual Meeting, Salt Lake City, UT, Nov. 8-13, 2015.

"A Liquid Tin Force Field for the Computational Investigation of Liquid Metal Plasma-Facing Materials," J. R. Vella, M. Chen, E. A. Carter, F. H. Stillinger, A. Z. Panagiotopoulos, and P. G. Debenedetti, poster presentation at the Andlinger Center Symposium, May 17, 2016.

"Liquid interface instabilities in tokamak, oil, and whisky," Pohang University of Science and Technology, South Korea. September 2016

"Hydrodynamic Instabilities and Complex Fluids," Korea Advanced Institute of Science and Technology, South Korea. September 2016 (H. Kim)

"Control of fluid-fluid interface instabilities," University of Hong Kong, Hong Kong. August 2016. (H. Kim)

"Control of interfacial instabilities by using geometry and surface-active components," Ulsan National Institute of Science and Technology, South Korea. February 2016 (H. Kim)

"Control of pattern formation by using geometry and surface-active components," Kumoh National Institute of Technology, South Korea. February 2016 (H. Kim)

"Rayleigh-Taylor instability under a curved substrate," the 66th Annual Meeting of the APS Division of Fluid Dynamics, Pittsburgh, Philadelphia, USA. November 2013 (Oral) (H. Kim)

"Tomographic PIV towards a complex free surface," the 8th KSME-JSME Thermal and Fluids Engineering Conference, Incheon, South Korea. March 2012 (Oral) (H. Kim)

b. Web site or other lnternet sites that reflect the results of this project: We have a password-protected internal website for sharing slides from talks, papers of interest, and other collaborative information.

c. Networks or collaborations fostered: Collaboration with PPPL: (i) Koel was funded via an NSTX-U Collaboration proposal that leveraged results from work on this project; and (ii) Panagiotopoulos and Debenedetti are participating in a SCIDAC pending proposal entitled "Center for Advanced Simulations of Plasma-Liquid Metal Interactions" that will leverage results from the present project. Also we have established several collaborations beyond the Princeton-PPPL collaborations that this proposal enabled. In particular, Stone has established a collaborative research study on theory and simulations for thin film flows on curved substrate with Applied Mathematicians at Oxford University. This work has led to one joint paper and several related on-going projects stimulated by the topics of the research grant. Also, we continue to interact substantively with J.P. Allain (University of Illinois) and R.D. Kolasinski (Sandia National Laboratories, Livermore, CA).

d. Technologies/Techniques: Our various experimental, theoretical and simulation approaches are using existing methods, or, where necessary, introducing new techniques that we are refining and will report in journal articles in the future.

e. lnventions/PatentApplications: None to date.

f. Other products, such as data or databases, physical collections, audio or video, software or netware, models, educational aid or curricula, instruments or equipment: None to date.