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ABSTRACT
Mo- and S-based lubricant additives reduce friction in boundary lubrication through the formation of molybdenum disulfide (MoS$_2$) during operation. However, the fundamental mechanisms of MoS$_2$ formation are still not fully understood, in part because direct experimental measurement is challenging during the crystallization process. Previously, reactive molecular dynamics simulations were used to model the formation of crystalline MoS$_2$ by compressing and heating amorphous material consisting of Mo and S. Here, the authors test the robustness of these models to capture the crystallization process under different simulation conditions and with different reactive force fields. Lastly, a reactive force field that contains parameters for Mo, S, and O was modified to enable it to capture MoS$_2$ crystallization in the presence of oxygen.

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I. INTRODUCTION
Molybdenum disulfide (MoS$_2$) is a well-known member of transition-metal-dichalcogenide family that has a lamellar structure with hexagonal symmetry. A single layer of MoS$_2$ consists of Mo atoms sandwiched between sulfur atoms. There are strong covalent interactions within the layers of MoS$_2$ and only weak van der Waals interactions between different layers. MoS$_2$ has unique electric and optoelectronic characteristics and has active edge sites for hydrogen evolution reactions, which make it a promising candidate for applications in electronics and catalysis. In addition, MoS$_2$ has been widely used as a solid lubricant that can provide ultralow friction in sliding contacts. As friction modifiers, Mo- and S-containing additives in liquid lubricants have been reported to form crystalline MoS$_2$ films under boundary lubrication to reduce friction and wear. These additives have also been shown to be highly surface active, enabling tribochemical conversion into MoS$_2$. It is known that the degree of crystallinity of MoS$_2$ improves its tribological properties. Therefore, understanding the factors that affect crystallinity and the crystallization process are important to maximizing the performance of MoS$_2$ solid lubricants and Mo- and S-containing additives in liquid lubricants.

Recently, in situ experiments were used to study the nucleation, growth, crystallization, and restructuring of MoS$_2$ from amorphous materials by irradiating them with a laser or electron beam or direct TEM observations of the growth mechanisms via chemical vapor deposition methods. Those studies showed that various MoS$_2$ polymorphs exist during MoS$_2$ formation and that crystallization was influenced by temperature and substrate material. However, in situ techniques for studying the crystallization process are limited because the thick growth substrates impede electron transparency for atomically resolved images and it is difficult to maintain the high temperatures necessary for material growth during in situ measurements. Therefore, the exact mechanisms of the formation of crystalline MoS$_2$ are not yet fully understood.

Experimental studies have been complemented by molecular dynamics (MD) simulations of crystallization of various materials, such as ice, polymers, alkanes, and gold. Such simulations provide atomistic details about the crystallization process and have shown that crystallization depends on temperature, substrate topography, and material. For MoS$_2$ specifically, MD simulations with traditional nonreactive potentials have successfully captured the crystal structure, mechanical properties, and thermal transport behavior of MoS$_2$. However, nonreactive potentials cannot capture the breaking and formation of covalent bonds, which limits the types of processes that can be reproduced in the simulation.
Alternatively, reactive potentials use a bond-order formalism to model chemical reactions as bonds break and form.\textsuperscript{10} For MoS\textsubscript{2}, parameters for the second-generation reactive empirical bond-order (REBO) formulation\textsuperscript{31} have been developed.\textsuperscript{25,33} This potential was shown to be able to predict lattice parameters and other structural properties for the two most common bulk MoS\textsubscript{2} phases with reasonable accuracy and better than several available nonreactive potentials.\textsuperscript{44} Importantly, researchers have used this force field to study the crystallization of MoS\textsubscript{2} under compression, heating, and sliding.\textsuperscript{25} Another bond-order-based potential, ReaxFF,\textsuperscript{36} has also been parameterized for MoS\textsubscript{2}.\textsuperscript{37} This potential has been extended to include oxygen and then used to simulate the synthesis of MoS\textsubscript{2} from MoO\textsubscript{3} and sulfur precursors.\textsuperscript{38,39} At this point, both REBO and ReaxFF potentials have been used to model MoS\textsubscript{2}. However, the relative ability of these different potentials to capture crystallization is still unknown.

In this paper, we compare the crystallinity of MoS\textsubscript{2} formed from heating and compressing an amorphous material using two parameter sets of the REBO potential [REBO1 (Ref. 34) and REBO2 (Refs. 32 and 33)], which differ in their parameterization of the bond-order coordination terms, and two parameter sets of the ReaxFF potential [ReaxFF1 (Ref. 37) and ReaxFF2 (Ref. 38)], where ReaxFF2 is reparameterized to more accurately describe the interaction of S\textsubscript{2} molecules and incorporate parameters for oxygen. First, the results of Ref. 35 are reproduced using the REBO1 potential with different model sizes. Then, the effect of the wall used for compression is tested, based on observations from previous studies that surface structure\textsuperscript{2,23} and interaction strength\textsuperscript{11} affect the crystallization process. Next, the ability of the four potentials to capture crystallization is directly compared. Lastly, the ReaxFF2 potential that contains parameters for oxygen is tested and then modified to simulate the formation of crystalline MoS\textsubscript{2} from an oxygen-containing amorphous material, which is relevant to crystallization processes that occur under ambient conditions.

II. METHODS

The model system is shown in Fig. 1. Molecular dynamics simulations with this model were carried out using the LAMMPS package\textsuperscript{40} and Ovito\textsuperscript{41} was used for visualization.\textsuperscript{42} Dynamics was simulated for the same model system with two different empirical potential formulations, REBO (Ref. 31) and ReaxFF.\textsuperscript{36} Two parameterizations of the REBO potential, REBO1 (Ref. 34) and REBO2\textsuperscript{32,33}, were used with a time step of 0.1 fs, and two parameterizations of the ReaxFF potential, ReaxFF1 (Ref. 37) and ReaxFF2\textsuperscript{38}, were used with a time step of 0.25 fs.

The crystallization process was modeled using the same procedure as reported previously.\textsuperscript{35} First, amorphous material was created by heating a single layer of crystalline MoS\textsubscript{2} to 5300 K and then rapidly quenching to room temperature. The system was then equilibrated at room temperature, and a pressure of 50 GPa was applied in the surface-normal direction using a Parrinello-Rahman barostat. After reaching stable potential energy, the amorphous system was inserted between two crystalline MoS\textsubscript{2} layers, as shown in Fig. 1. The crystalline layers were rigid, and a normal force was applied at the top layer to maintain a pressure of 50 GPa. The bottom MoS\textsubscript{2} layer was fixed in all directions. Periodic boundaries were applied in the x- and y-directions and a fixed boundary was applied in the z-direction. The size of the simulation box at this stage was 10.3 × 9.8 × 3.8 nm\textsuperscript{3} in x-, y-, and z-directions, respectively, with 10368 atoms in total and 3456 atoms in the middle amorphous layer. Next, this sandwiched system was equilibrated for 0.2 ns at room temperature with a Nosé-Hoover thermostat. After equilibration, the temperature of the system was increased from room temperature to 4000 K using a Langevin thermostat with a damping parameter of 100 fs. The simulation was then run at 4000 K for 1 ns, where the high temperature was used to accelerate the crystallization process such that it could be observed within the short duration of the simulation. Note that 4000 K is above the melting temperature of MoS\textsubscript{2} grown by chemical vapor deposition at ambient pressure.\textsuperscript{45} However, the melting temperature is dependent on the pressure\textsuperscript{43} and our simulations at different pressures indicated that 4000 K was below the melting temperature at the 50 GPa used here to model crystallization.

The atomic position of each atom was used to determine if it was part of crystalline or amorphous material, and the degree of crystallinity of the system was characterized by the percent of crystalline Mo atoms. For each molybdenum atom, first, we calculated its distance from all sulfur atoms. If the distance was within a predetermined distance range, then the S atom was considered to be a
neighbor of the Mo atom. If the number of neighbor atoms was six, we then calculated the angles between the Mo atom and its neighbor S atoms. If all angles were within the neighbor angle range, then this Mo atom was defined as a crystal atom. The same calculation was applied to the sulfur atoms using three neighbor atoms as the criterion for crystallinity. The neighbor distance and angle ranges for REBO were taken from the previous study\(^3\) and calculated for ReaxFF here using the same approach as reported previously. Specifically, a simulation of three layers of crystalline MoS\(_2\) was run for 1 ns at 4000 K. At the end of the simulation, the minimum and maximum values of the distances and angles were calculated, as reported in Table I. Using these values, the degree of crystallinity of an MoS\(_2\) sheet was quantified as the number of crystalline Mo atoms plus the number of Mo neighbors of crystalline S atoms divided by the total number of Mo atoms in the system. This calculation yielded the same result if S atoms were considered instead of Mo atoms.

### III. RESULTS AND DISCUSSION

First, we reproduced the crystallization of MoS\(_2\) from an amorphous material by compression and heating using the REBO1 potential, as done in Ref. 35. The time profile of the crystallinity is reported in Fig. 2(a). The crystallinity of the material, quantified by the percent of crystalline Mo atoms, increased immediately after the temperature increase began and rapidly approached the maximum value. Snapshots of the middle layer taken from the trajectory of the simulation at various times in Fig. 2(b) show the atoms reordered from amorphous to crystalline phase. At the initial stage, a number of small crystals nucleated and these crystals proceeded to grow with time. The growth rate was initially very fast due to the availability of an amorphous material. The crystalline domains continued to grow and coalesce to form larger domains until the growth slowed down due to a lack of available amorphous atoms. The increase of crystallinity \(c\) with time \(t\) was fit to an exponential function: 
\[
c(t) = A(1 - e^{-rt}),
\]
where \(A\) is a prefactor and \(r\) is the rate constant for the process.\(^4\) For the case shown in Fig. 2(a), this reaction rate was calculated to be 18.0 ns\(^{-1}\). Note that the data can be fit equally well to an alternative form of this equation, 
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high temperature and pressure of the model, this simulation was extended another 2 ns with the temperature and pressure decreased to ambient and the crystallinity shown in Fig. 2 did not change.

As mentioned above, the nucleation and growth rate of the MoS$_2$ crystals depends on the availability of amorphous atoms in the system. This suggests that the simulation size may affect the crystallization rate observed in the simulation. To test the effect of the simulation size, two more models were created, with in-plane dimensions of $20.6 \times 19.6$ and $30.9 \times 29.4$ nm$^2$. As shown in Fig. 3, the three models with side lengths of approximately 10, 20, and 30 nm exhibited the same trends in the nucleation and growth rate. The crystallinity of all three models increased at approximately the same rate (with a reaction rate from 17.2 to 19.2 ns$^{-1}$), reaching between 93.7% and 95.4% crystallinity by 1 ns. The number of nucleation sites was also characterized for the three models, where a nucleation site was defined based on the distance between crystalline atoms. It was found that the number of nucleation sites scaled with the cross-sectional area of the model, indicating that the smallest model system was large enough to capture crystallization dynamics. Based on this observation, and the fact that the rates of crystallization and steady state crystallinity were comparable for the three systems, all subsequent analyses were performed with the 10 nm model.

Previous research has shown that the structure$^{12,23}$ and interaction strength$^{15}$ of the substrate can affect the crystallization process. Also, it is known that the precursor materials from which MoS$_2$ is formed in lubricated contacts may be confined between various surface materials and structures. To capture this, first, the interactions between the rigid MoS$_2$ walls and the amorphous material were modified to include only van der Waals interactions, i.e., no covalent bonding with the walls was allowed. Second, the rigid MoS$_2$ walls were replaced by rigid walls with atoms in a diamond and gold crystal lattice; in both cases, interactions between the amorphous material and the walls were only via van der Waals. The crystallization rate for the model system with four different wall types is reported in Fig. 4(a), and side-view snapshots of the simulations after 1 ns are shown Fig. 4(b). The nucleation rate is similar in all four cases, but the percent crystallinity is slightly lower for the model with covalent bonding allowed; for example, at 0.15 ns, the average crystallinity for the three models...
with only van der Waals interactions is 91.6% while that with the covalent bonding is 87.5%. Based on these results, neither the bond interactions nor the structure of the confining walls had a significant effect on the formation of MoS$_2$ using the REBO1 potential.

The crystallization simulation was next repeated with the three other available reactive potentials: REBO2, ReaxFF1, and ReaxFF2. The time profiles of the crystallization are reported in Fig. 5(a) along with snapshots of the models after 1 ns in Fig. 5(b). REBO2 effectively captured the crystallinity, but this was not exhibited by either of the ReaxFF potentials. To understand the differences exhibited by these potentials, we analyzed the parameters in the REBO and ReaxFF potentials. One notable difference was a much larger minimum energy distance between Mo and S atoms in the REBO potentials ($\approx 0.411$ nm) than in the ReaxFF potentials ($\approx 0.210$ nm). This shorter distance could cause Mo atoms in the amorphous material to preferentially bond with the S atoms in the walls as opposed to forming crystalline MoS$_2$, as shown in the inset of Fig. 5(a). Alternatively, preferential bonding of Mo with S atoms could also be linked to how the energy penalty associated to overcoordination of sulfur is implemented in ReaxFF. Underestimating this energy penalty could also affect the ability of the material to crystallize. It is, however, unknown which of these factors is responsible. Regardless, the goal of this study is to capture crystallization of MoS$_2$ from precursor materials that may be confined between various surface materials and structures. Therefore, we repeated the simulations with ReaxFF after restricting the interactions between the middle layer and walls to van der Waals, as done with REBO above.

Simulations were run with both ReaxFF1 and ReaxFF2 without covalent bonding between the middle layer and walls. As
shown in Fig. 6, the percent crystallinity increased and approached the limiting value with the ReaxFF1 potential, while only $\frac{1}{3}$ of the atoms became crystalline with the ReaxFF2 potential. The inability of ReaxFF2 to capture crystallization is an issue because this is the only one of the four potentials that includes oxygen. In many applications, MoS$_2$ is exposed to ambient conditions where water vapor and oxygen have been shown to drastically affect the performance of electronic devices and lubrication.$^{8,45-48}$ This effect could not be studied with the existing, oxygen-containing ReaxFF2 potential because it was unable to capture the crystallization process.

To address this, further modifications of the potential were needed. We first compared the van der Waals parameters of ReaxFF1 (Ref. 37) (that captured crystallization with wall interactions modified) and ReaxFF2 (Ref. 38) (that did not capture crystallization). We found that the van der Waals interactions for Mo–S and S–S were stronger in ReaxFF2 than in ReaxFF1, while the Mo–Mo interactions were the same. Therefore, the dissociation energies in the distance-corrected Morse potential used by ReaxFF to capture van der Waals forces were changed for Mo–S and S–S in ReaxFF2 to match those in ReaxFF1. Specifically, $D_{Mo-S}$ was changed from 0.1876 kcal/mol to 0.1 kcal/mol and $D_{S-S}$ was changed from 0.4937 to 0.3236 kcal/mol. Then, we confirmed that the changes made to the ReaxFF2 potential did not affect its ability to reproduce the correct crystal structure of 2H MoS$_2$. We found that the modifications had a minimal effect on the atomic distances (within 4%) and angles (within 3%) of the MoS$_2$ crystal. Also, as shown in Fig. 6, the new ReaxFF2 was able to reproduce the crystallization of MoS$_2$. The modified version of ReaxFF2 is provided as supplementary material.$^{54}$ However, it should be noted that the changes made to ReaxFF2 may adversely affect the ability of the potential to capture some material properties and full reparameterization would be required to develop a more broadly applicable potential.

Using the modified ReaxFF parameters, the effect of oxygen on the crystallization of MoS$_2$ could be tested. For this, 10% and 20% oxygen atoms were added to the amorphous materials by replacing Mo and S atoms at a ratio of 1 to 2. As shown in Fig. 7(a), oxygen decreased the degree of crystallinity during MoS$_2$ formation. The crystallinity after 1 ns are 98%, 84%, and 63% for models without oxygen, and with 10% and 20% oxygen, respectively. Snapshots of the 10% and 20% cases at 1 ns are shown in Fig. 7(b). Oxygen clearly inhibits crystallization. Further analyzing the simulations, we observed the formation of oxysulfides and MoO$_3$; examples of these species are shown in Fig. 7(c). For the 10% oxygen case, there were 3 MoO$_3$ and 28 oxysulfides at 1 ns; for the 20% oxygen case, the number of MoO$_3$ and oxysulfides increased to 6 and 77. Oxidation of MoS$_2$ is expected in oxygen-sufficient environments$^{49}$ and previous studies have reported both oxysulfides$^{50-52}$ and MoO$_3$, consistent with the species observed in present simulations.

IV. CONCLUSIONS

In this study, we evaluated the ability of four reactive empirical force fields to capture the crystallization of MoS$_2$ from amorphous material. First, we modeled crystallization using a compression and heating simulation with the REBO1 potential, as done in a previous study.$^{35}$ Then, the sensitivity of this approach to simulation conditions was tested by varying the size of simulation and the structure and interaction strength of confining walls. It was found that the simulation captured crystallization of the material to over 95% with
any size system as well as using walls with modified structure and interatomic interactions. The crystallization simulation was repeated with the REBO2, ReaxFF1, and ReaxFF2 force fields. With the interactions between the middle layer and walls restricted to van der Waals, the REBO2 and ReaxFF1 potentials yielded results similar to REBO1, but the ReaxFF2 potential was unable to capture crystallization. This limitation was an issue because, of the four force fields tested, only ReaxFF2 contains parameters for oxygen.

So, to address the issue with ReaxFF2, van der Waals interactions for Mo and S were adjusted to match those in the ReaxFF1 and this modified ReaxFF2 potential was able to capture the crystallization of MoS2. Finally, the new ReaxFF2 potential was used to study the effect of oxygen on the formation of crystalline MoS2. It was found that the degree of crystallinity decreased with increasing presence of oxygen due to oxidation of the edges of crystalline domains, which impeded their growth and the formation of amorphous molybdenum oxysulfide as opposed to crystalline MoS2.

Overall, this study demonstrated that reactive molecular dynamics simulations can capture crystallization of MoS2 using heating and compression, but modifications have to be made to van der Waals interactions for some empirical potentials. Further, the modified ReaxFF2 potential can be used to study crystallization in the presence of oxygen, which is highly relevant to many applications of MoS2 where the material has to function in ambient conditions. Future work may include a comprehensive reparameterization of the Mo/S/O potential such that it can capture both MoO3, as it was originally designed to do, and the crystallization of MoS2, as demonstrated here. Further, simulations performed under lower temperature and pressure conditions may explore conditions closer to those expected in applications such as a tribological interface.

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37 See supplementary material at https://doi.org/10.1116/1.5128377 for the modified ReaxFF2 potential.
Ashlie Martini is a Professor of Mechanical Engineering at the University of California Merced. She obtained her BS and PhD in Mechanical Engineering from Northwestern University in 1998 and 2007, respectively, with a stint in IT consulting between the two degree programs. Professor Martini's research expertise lies in the field of tribology, with specific focus on understanding the fundamental mechanisms of the physical processes underlying friction, wear, and lubrication. She is currently an Editor of the journal Tribology Letters and an Associate Editor of the journal Tribology Transactions. Professor Martini's research impact has been recognized by ASME's Burt L. Newkirk and Lloyd Hamilton Donnell Awards and the AFOSR Young Investigator Award. Her teaching contributions have been recognized by campus-wide awards at UC Merced including the Senate Faculty Distinguished Undergraduate Teaching and the Senate Faculty Distinguished Graduate Teaching/Mentorship Awards.

Rimei Chen is a PhD candidate in Mechanical Engineering at the University of California Merced, working with Professor Ashlie Martini. Her research focus is on the fundamental understanding of tribological behaviors at the atomic scale. Rimei earned her Bachelor's degree in Mechanical Engineering at the University of Science and Technology of China in 2012 and obtained her Master's in 2014 at the University of Hawaii at Manoa.