The effect of defect geometry on the melting of crystal lattices

Timothy McHenry
Mentored by Dr. Brian Barnes

SMA Science and Mathematics Academy

ARL

Introduction

The melting of materials may appear to be a simple, everyday process; however, it remains a complex phenomenon that is not fully understood despite decades of progress in physics and chemistry. This project investigated how the shape and distribution of defects within a crystal lattice influence melting behavior. In this study, a face-centered cubic (FCC) crystal lattice was used as the model system (Figure 1).

To capture atomic-scale behavior, molecular dynamics (MD) simulations were used to model atomic motion and interactions. MD is a well-established and widely used technique for simulating melting and generating melting curves (Karavaev et al., 2016).

Previous research has shown that introducing defects lowers a material's melting temperature (Agrawal et al., 2003); however, these studies have largely focused on simplified defect geometries, such as spherical voids or uniform defect distributions. This study investigated how the shape and distribution of more complex defects within a crystal lattice influenced its behavior during melting.

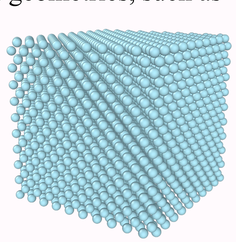


Figure 1 (right): Example of an ideal face-centered cubic (FCC) lattice, showing atoms arranged in a box-like structure.

Methods and Materials

All simulations were performed with Sandia National Laboratories' Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). A Python script using Pandas and the LAMMPS Python library was written to automate simulation execution and data analysis.

The simulations modeled a crystal lattice with introduced defects of varying geometry and distributions (Figure 2). Seven different defect types were investigated, with porosity values ranging from 0.00 to 0.05 (dimensionless), representing the fraction of removed atoms.

Melting temperatures of the lattices were measured with the Z-method, in which the crystal lattice was simulated many times across a broad range of temperatures, and the results of the simulations were used to provide an estimate of the melting temperature.

This was repeated for progressively smaller ranges of temperatures to refine the final estimate of melting temperature (Figure 3), which was recorded.

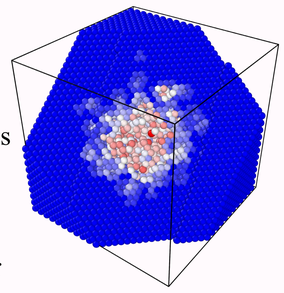


Figure 2 (above): A crystal lattice with normally-distributed monovacancy defects.

Methods and Materials (continued)

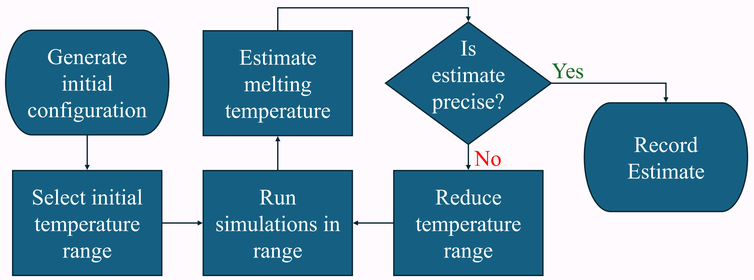


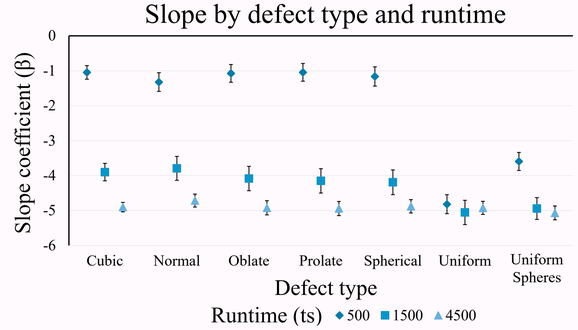
Figure 3 (above): Z-method for determining the melting temperature of a lattice. Estimates are considered precise when they are within 0.01 temperature units.

This process was repeated 25 to 30 times for each defect geometry with different initial configurations (velocities and choice of deleted atoms) and porosity values. Measurements of melting temperature were obtained at three different times within the simulations: 500, 1500, and 4500 timesteps (ts) after start.

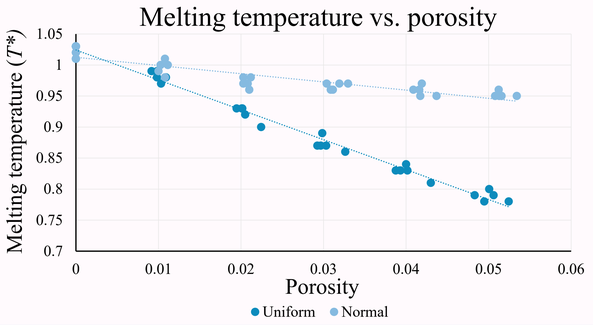
Temperatures were recorded in Lennard-Jones reduced temperature units (T^*), which are scaled by the bond energy of the atoms being simulated, to allow the results to be generalized.

Results

Graph 1 (right): Graph of the regression slopes for melting temperature vs. porosity, by defect type and runtime. Error bars represent ±2*SE*.



Graph 2 (right): Melting temperatures plotted against porosity values, for uniformly and normally-distributed monovacancy defects, for a runtime of 500 ts.



Results (continued)

Observation time (ts)	*df*	*F*	*p*	η^2_p
500	(13, 191)	291.34	<.001	.901
1500	(13, 197)	20.21	<.001	.381
4500	(13, 191)	2.34	.033	.068

Table 1 (left): Table of ANCOVA results for different observation times. η^2_p is a measure of effect size a given factor has on the model.

Running ANCOVA with an interaction term revealed significant interactions between defect geometry and porosity on melting temperature at 500, 1500, and 4500 ts observation times. However, the effect size was much larger for shorter observation times than for longer observation times.

Conclusions

This project investigated the influence of defect geometry on the melting behavior of crystal lattices. Analysis of the calculated slope coefficients showed that defect shape has a measurable effect on melting behavior, with statistically significant differences observed between defect types at shorter simulation runtimes.

However, as simulation runtime increased, these differences diminished substantially. This trend suggests that defect geometry does not significantly alter the equilibrium thermodynamic properties of the lattice, but instead primarily affects the kinetics of the melting process.

In most MD studies of materials, simulations are conducted over significantly longer timescales than those used in this work, often on the order of 10^5 timesteps. As a result, the effects of defect shape on melting are likely negligible in conventional studies and may often be reasonably ignored.

Despite this, the findings indicate that defect geometry plays a meaningful role during the early stages of phase transitions. Future research should further quantify the impact of defect structures on melting kinetics. Additional work could also explore a broader range of defect geometries and extend the analysis to other crystal structures, including body-centered cubic and hexagonal close-packed lattices.

References

Agrawal, P. M., Rice, B. M., & Thompson, D. L. (2003) Molecular dynamics study of the effects of voids and pressure in defect-nucleated melting simulations. *Journal of Chemical Physics*, *118*(21), 9680–9688. https://doi.org/10.1063/1.1570815

Karavaev, A. V., Dremov, V. V., & Pravishkina, T. A. (2016). Precise calculation of melting curves by molecular dynamics. *Computational Materials Science*, *124*, 335–343. https://doi.org/10.1016/j.commatsci.2016.08.014