Northeastern University
Michael B. Silevitch and Claire J. Duggan Center for STEM Education

Northeastern University
College of Engineering

Molecular Computations for Understanding Crystallization Pathways for Amorphous Calcium Carbonate

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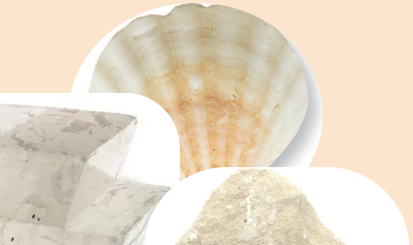
Context & Goals

Purpose for Research: To understand the mechanisms behind the crystallization and stabilization of Amorphous Calcium Carbonate (ACC) that prevents its immediate crystallization into Calcium Carbonate ($CaCO_3$) polymorphs; to use frameworks presented in literature to perform to digitally model the crystallization pathways of $CaCO_3$

Areas of Study: Chemistry, Physics, Materials Science, Computational Modeling

Real-World Applications:

- Mechanism used by marine life to produce shells, bones, skeletons, and other parts
  - Switching between crystalline and amorphous forms allows for easier transport of materials before production
- Used in 3D printing (amorphous filament → crystalline product)
- Means of carbon sequestration → combating climate change



Greenhouse gas → Carbonic Acid: $CO_2 + H_2O \rightarrow H_2CO_3$

Dissociation of Carbonic Acid: $H_2CO_3 \rightarrow H^+ + HCO_3^-$

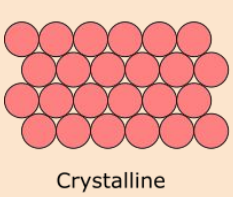
Dissociation of Ion: $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

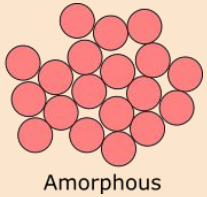
Crystallization of Calcium Carbonate: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

Relevant Background Information

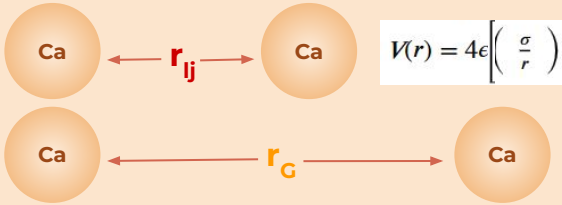
Vocabulary

Polymorphs: various forms of a substance
Amorphous: lacking shape or form
Crystalline: being packed in a well-defined, repeating pattern
Crystallization: the process of atoms arranging themselves into a stable form, typically into a well-defined, repeating pattern
Computations: a series of well-defined arithmetic procedures to accomplish a goal
Energy Curve (Pair Potential): graph showing potential energy within a pair as a function of distance between two particles

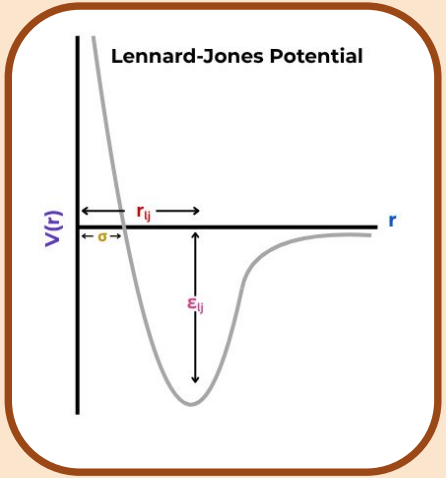


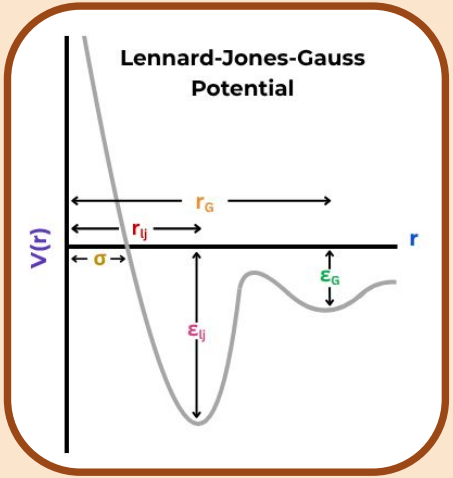


Energy Curves



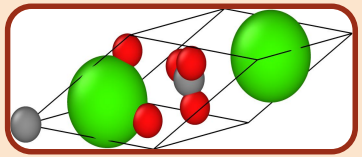
$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - C\exp\left(-\frac{(r-r_0)^2}{2w^2}\right)$$



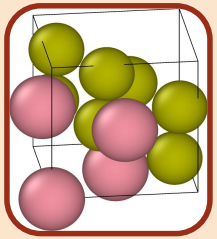


Methods - OVITO

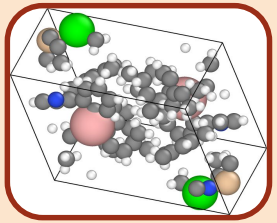
$CaCO_3$ Polymorphs via OVITO Software



Calcite



Aragonite



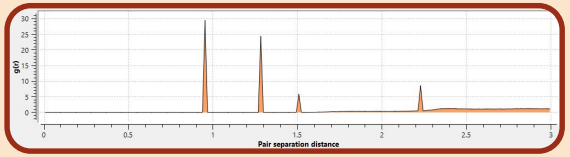
Vaterite

Radial Distribution Function Analysis (RDF)

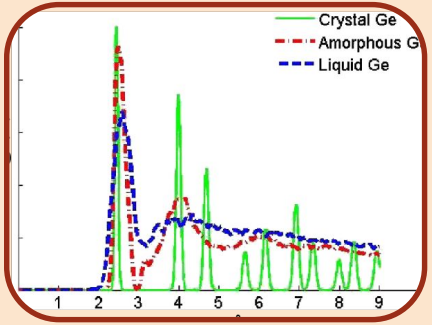
RDF Measure:
Density of a sample as a function of its radius from a reference point

RDF Significance:
Determine whether a substance is <u>crystalline</u> (ordered; indicated by sharp, isolated, and defined peaks) or <u>amorphous</u> (lacking shape; indicated by weakly defined peaks and a smoother curve)

Crystalline $CaCO_3$ Sample via OVITO



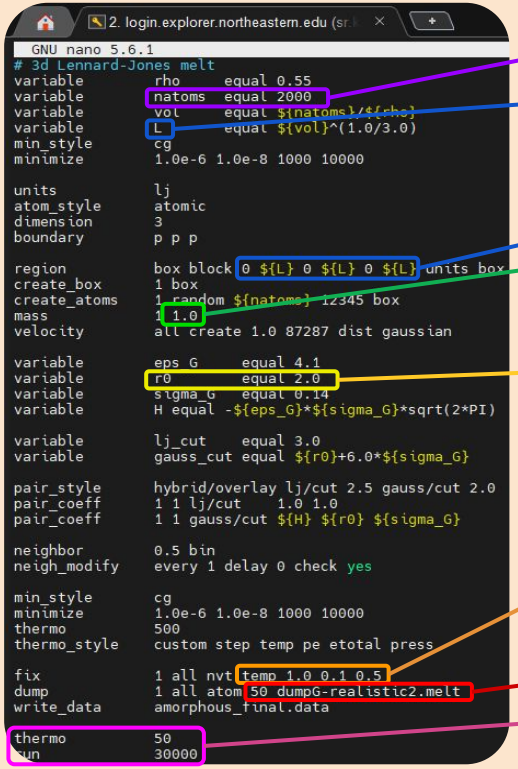
Germanium Sample w/ Varying Forms and their RDFs



Methods - LAMMPS

MobaXterm

Input File Interface



Number of Atoms

Cell Size

Mass

Interatomic Bonding/Separation Distance

Temperature Control

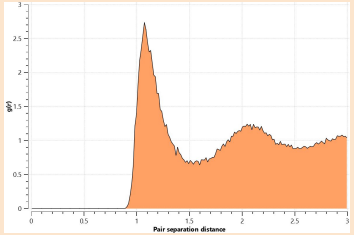
File Naming

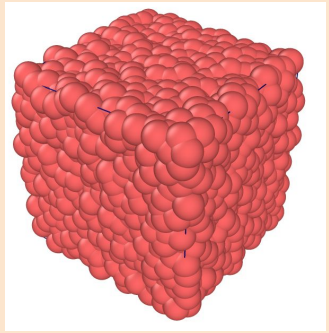
Time Interval Control

Results - Simulation Files

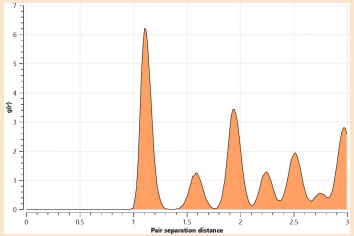
Adjusting Temperature

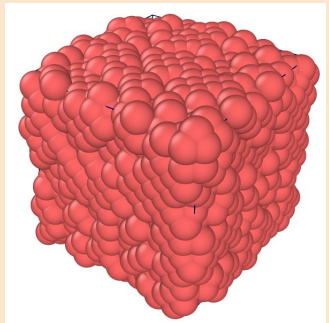
Temperature = 0.8 (Dimensionless Units)





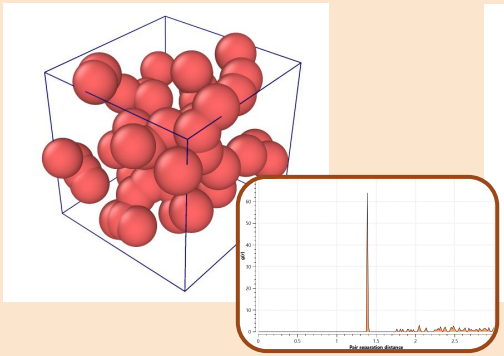
Temperature = 0.2



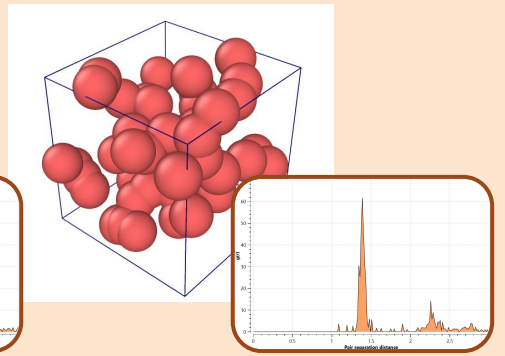


Adjusting Mass

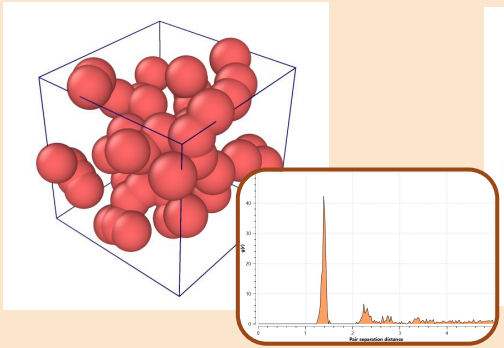
Mass = 2.0 (D.U.)



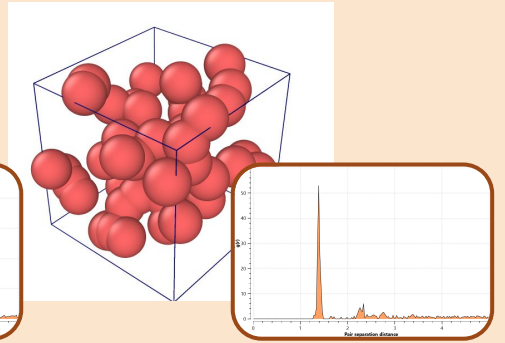
Mass = 5.0



Mass = 6.0



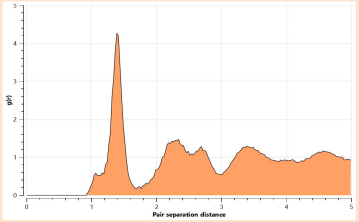
Mass = 7.0

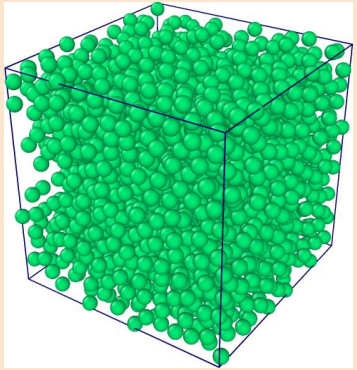


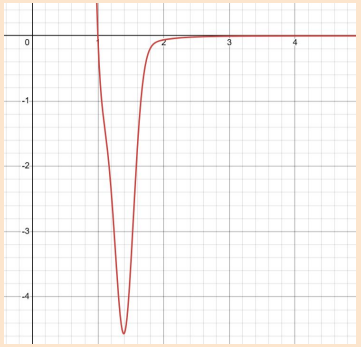
Results - Most Realistic Simulations

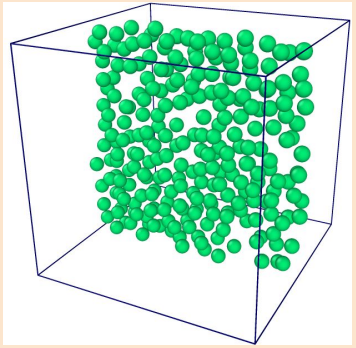
Single-Well (Lennard-Jones) Simulation

ε = 4.1
r_0 = 1.4
σ = 0.14
Thermo = 50
Run = 15000



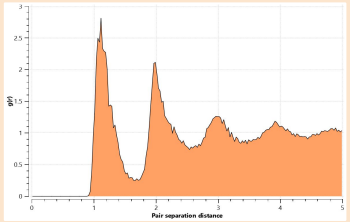


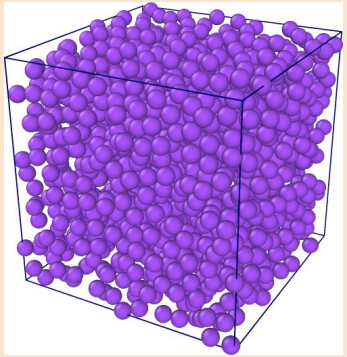


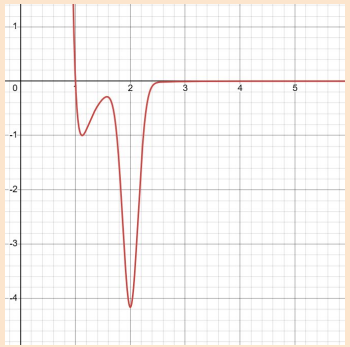


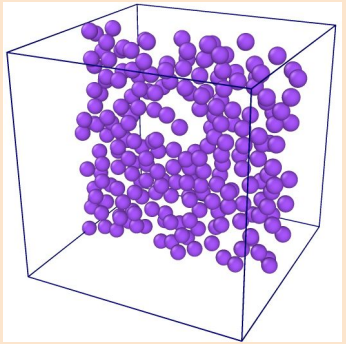
Double-Well (Lennard-Jones-Gauss) Simulation

ε = 4.1
r_0 = 2.0
σ = 0.14
Thermo = 50
Run = 15000









Conclusions

- Coarse-grained Ca–Ca simulations show ACC's amorphous structure arises from multiple wells in the Lennard-Jones-Gauss binding energy curve. These interactions, influenced by carbonate ions and water, are geometrically frustrated, allowing stable structures to form despite conflicting interactions.
- Lower temperatures allow for structures to crystallize more easily
- The locations of energy minima correlate directly with RDF peak positions. By adjusting r_o, we can shift these minima to create separate or merged wells, thereby tuning Ca–Ca interaction behavior.
- **Key result:** ACC can exist as a stable, metastable structure under the right parameters, rather than immediately crystallizing. Computations allowed us to identify mechanisms for stabilizing the amorphous structure.

Future work: Explore parameters that drive full crystallization (as opposed to stable ACC); incorporate carbonate ions and water molecules directly into simulations for more realistic modeling.

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Molecular Computations for Understanding Crystallization Pathways for Amorphous Calcium Carbonate

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Abstract

The focus of this study is on amorphous calcium carbonate (ACC). The overarching goal for this project is to study the structure and stability of ACC, and the mechanisms associated with its crystallization. We used computational modeling based on calcium-ion interactions to stabilize ACC and explored a combination of pair-wise intermolecular interactions to understand the origin of the amorphous structure. Our goal was to understand more about this mechanism: What conditions cause it? Can ACC exist as a metastable structure, and not just as an ephemeral prerequisite for crystalline Calcium Carbonate ($CaCO_3$)? How can we replicate this mechanism using molecular dynamic (MD) simulations?

Background

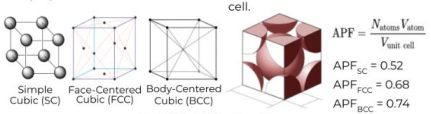
Unit Cells

Unit cells are the smallest repeating unit of a crystalline structure. Its atomic arrangement can determine the properties of a material.

Atomic Packing Factor

Atomic Packing Factor is a measure of how efficiently atoms condense and arrange themselves within a given unit cell.

$$APF = \frac{N_{atoms} V_{atom}}{V_{unit\ cell}}$$



$APF_{SC} = 0.52$
$APF_{FCC} = 0.68$
$APF_{BCC} = 0.74$

Real-World Applications

The focus of this study is on amorphous calcium carbonate (ACC). It is the intermediate for crystallization - the arrangement of atoms into an organized formation - and also important for:

- **Carbon sequestration:** A series of methods combating harmful greenhouse gas emissions that exacerbate climate change.
- **Biomineralization:** One of many such methods include a mechanism adopted by marine life to form shells, bones, exoskeletons, and beyond. See these chemical mechanisms to understand:
  - *Greenhouse gas → Carbonic Acid:* $CO_2 + H_2O \rightarrow H_2CO_3$
  - *Dissociation of Carbonic Acid:* $H_2CO_3 \rightarrow H^+ + HCO_3^-$
  - *Dissociation of Ion:* $HCO_3^- \rightarrow H^+ + CO_3^{2-}$
  - *Crystallization of Calcium Carbonate:* $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
- **Sustainable materials:** Can be used to develop next generation technologies such as cements and more.
  Examples: Eggshells, seashells, limestone, marble, pearls, coral

Figure 1: Samples of $CaCO_3$ in the forms of (from left to right) crystal, pearl, powder, shell, and limestone

Methods

Simulation tools: Used LAMMPS, a classical MD simulation engine, run on Northeastern University's Explorer supercomputing cluster in MobaXterm, in tandem with OVITO, a 3D molecular visualization tool, for visual feedback and analysis.

Simulation method: Performed molecular computations using Newton's classical equations of motion, with time integration via time discretization.

Crystalline vs. amorphous identification: Used the radial distribution function (RDF) tool in OVITO to analyze density-versus-radius curves.

- Well-defined spikes indicate a crystalline structure.
- A flatter curve indicates an amorphous structure.

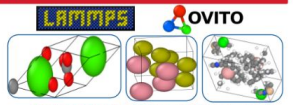


Figure 2: Unit cells of $CaCO_3$ variations (in order) Calcite, Aragonite, and Vaterite in OVITO

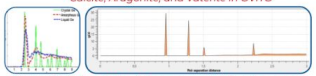


Figure 3: left (a) - RDF of Germanium in different states of matter; right (b) - sample RDF curve in OVITO

Interaction potentials: Studied Lennard-Jones (LJ) and Lennard-Jones-Gauss (LJG) energy curves.

- For LJ-Gauss, calculated the resulting double wells and varied input values in the Gaussian term (circled) to observe changes in the curve.

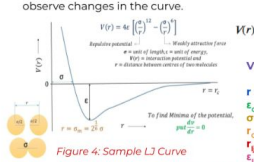


Figure 4: Sample LJ Curve

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - C\exp\left(-\frac{(r-r_0)^2}{2\sigma^2}\right)$$

$V(r)$ = Total potential between energy between two particles
r = Distance between the particles
ϵ_G = Depth of Gaussian minimum
σ = Distance at which potential energy is zero
r_G = Position of the Gaussian minimum
r_{ij} = Position of the Lennard-Jones minimum
ϵ_{ij} = Depth of Lennard-Jones potential well

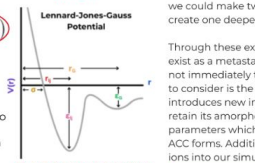


Figure 5: Sample LJG Curve

Force/motion calculations: F(x) = -dU/dx

- Used force and known mass to calculate acceleration to then determine final velocity and displacement.

Results

When we lowered the temperature, we noticed emerging crystalline clusters in figure 6b, suggesting that the sample crystallizes or stabilizes within this temperature range.

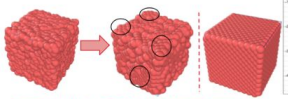


Figure 6: left (a) - Ca-Ca interactions of sample at temperature of 0.8 (arbitrary units); middle (b) - Ca-Ca interaction at temperature of 0.2, emerging FCC crystalline clusters circled; right (c) - reference crystalline sample, FCC

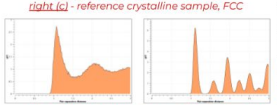


Figure 7: left (a) - RDF of sample from figure 6a; right (b) - RDF of sample from figure 6b

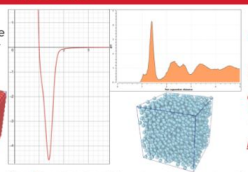


Figure 8: left (a) - Energy curve with parameters $\sigma = 0.14$, $\epsilon = 4.1$, $r_0 = 1.4$ (arbitrary units), showing single-well curve with absolute minimum at $x = 1.4$; upper right (b) - RDF of sample, peaking at a distance of 1.4; lower right (c) - sample of Ca-Ca interactions

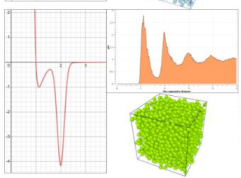


Figure 9: left (a) - Energy curve with parameters $\sigma = 0.14$, $\epsilon = 4.1$, $r_0 = 2.0$, showing a double-well curve with local minima at $x = 1.1$ and $x = 2.0$; upper right (b) - RDF of sample, peaking at a distance of around 1.1 and 2.0; lower right (c) - sample of Ca-Ca interactions

Conclusion and Future Steps

When performing our molecular simulations by focusing on coarse-grained Ca-Ca interactions, we showed that the amorphous structure arises from the multiple wells in the Lennard-Jones-Gauss binding energy curves. In other words, the stable crystalline structure was unable to form due to the geometric frustration created by the double wells.

In figure 6, we noticed that lower temperatures lead to emerging crystalline clusters. Figure 7 corroborates this further as 7a's continuous and undefined peaks indicate an amorphous structure while 7b's peaks are isolated and defined, indicating an emerging crystalline structure.

In figures 8 and 9, there is a correlation between the distance where local/absolute minima exist and the pair separation distances in the RDF functions where sharp peaks/maxima exist. For the energy curves, adjusting the σ value - and therefore the bond distance - moved the larger minima side-to-side. With this, we could make two separate minima or superpose the curves to create one deeper minima.

Through these experiments, we realized that ACC, in fact, *can* exist as a metastable structure with the correct parameters and not immediately transition into a crystalline form. Another factor to consider is the hydrated nature of ACC; the presence of water introduces new intermolecular interactions that allow ACC to retain its amorphous shape. In the future, we could explore parameters which lead to full crystallization as opposed to stable ACC forms. Additionally, we could visually incorporate carbonate ions into our simulations to imagine more realistic scenarios.

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