

Molecular Dynamics Study of Seed Crystallization using LAMMPS

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Introduction

Even though crystallization is ubiquitous and has a potential field of applications, its fundamental mechanisms remain concealed.

- A superior understanding is needed for satisfying possible applications like Material science, pharmaceuticals, geology, etc.
- Crystallization becomes challenging to simulate using Molecular Dynamics from liquids.
- We proposed to perform MD simulations around an artificial crystal seed.
- Identify effects of crystal lattice spacing, crystal size, and density for the crystallization process in colloids.

Methods

Essentially, we have used two methods: **Radial distribution function** (RDF) and **bond-orientational order parameters** (q_6) to recognize whether crystallization is occurring in our systems.

Methods

Radial Distribution Function (RDF)

RDF denoted by $g(r)$ represents the probability to find an atom at the distance r of another atom chosen as a reference point.

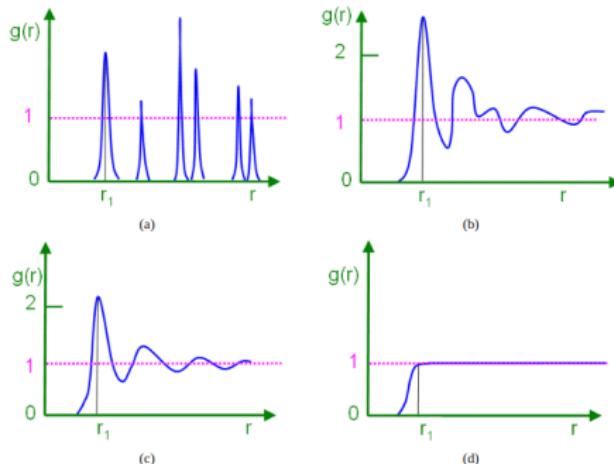


Figure 3097b. Schematic illustration of pair distribution functions of (a) crystal, (b) amorphous, (c) liquid, and (d) gas states.

Image taken from J. Lu and J. A. Szpunar, Phil. Mag. A 75, 1057-1066 (1997).

Methods

Bond-orientational order

Bond-orientational order can be used to identify hexagonal lattice in two-dimensional systems:

$$q_n = \frac{1}{nnn} \sum_{j=1}^{nnn} e^{ni\theta(r_{ij})}$$

where nnn is the number of the nearest neighbors of the selected atom, n is the degree of the order parameter, and $\theta(r_{ij})$ is the angle formed by the bond vector r_{ij} and the x-axis.

Note that for a perfect hexagonal lattice with $nnn = n = 6$, for all atoms, getting:

$$q_6 = \frac{1}{6} \sum_{j=1}^6 e^{6i\frac{j\pi}{3}} = 1$$

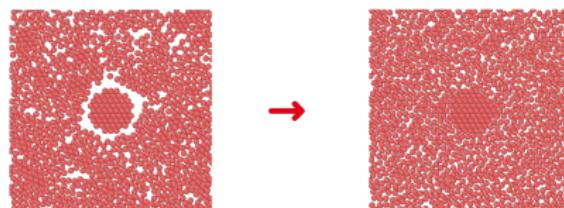
Nelson, Halperin, Phys Rev B, 19, 2457 (1979).

Simulation details

The main parameters used for MD simulations are:

- 2D hard-sphere model; Lennard-Jones units.
- Box length: 20×20 , time: 10^7 , temperature: 0.025.
- LJ cutoff = $2^{1/6} = 1.122$.
- Canonical ensemble (nvt).
- Systems with different densities of colloidal: 0.734, 0.687.
- Crystal seeds are composed of 37, 55, and 109 atoms.
- Crystals seeds with different lattice spacings: 1.29, 1.38, 1.52, 1.70, 1.96.

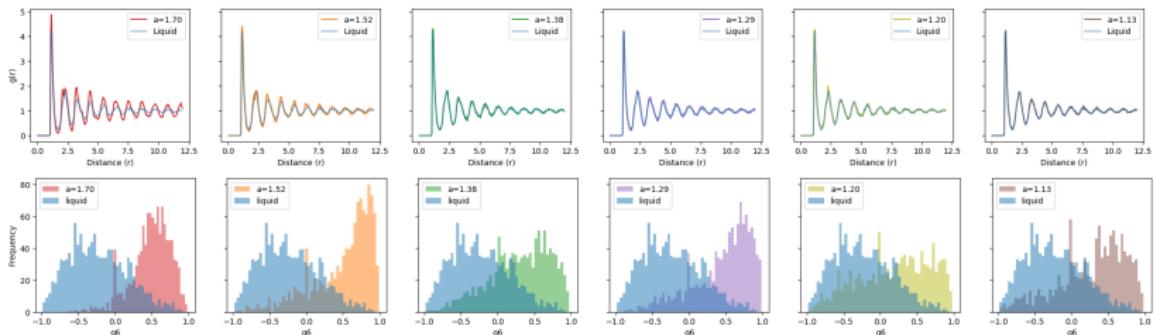
Before and after MD simulation



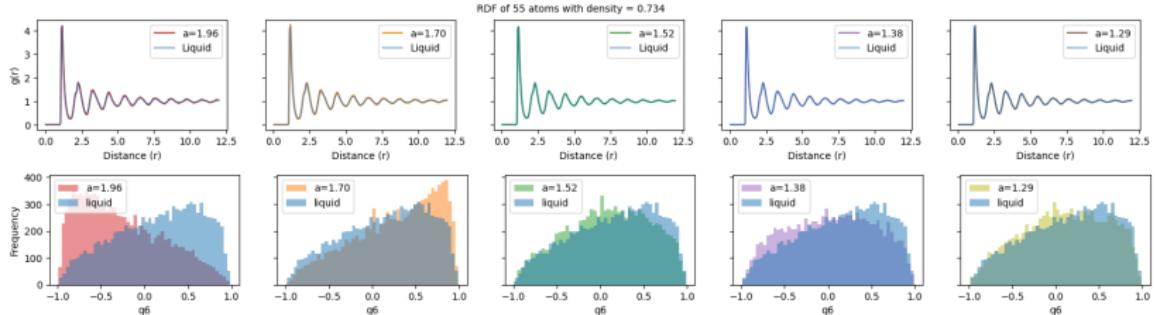
Results for $\rho = 0.734$

Seed of 55 particles

RDF analysis & Bond order analysis for a system with 1175 particles



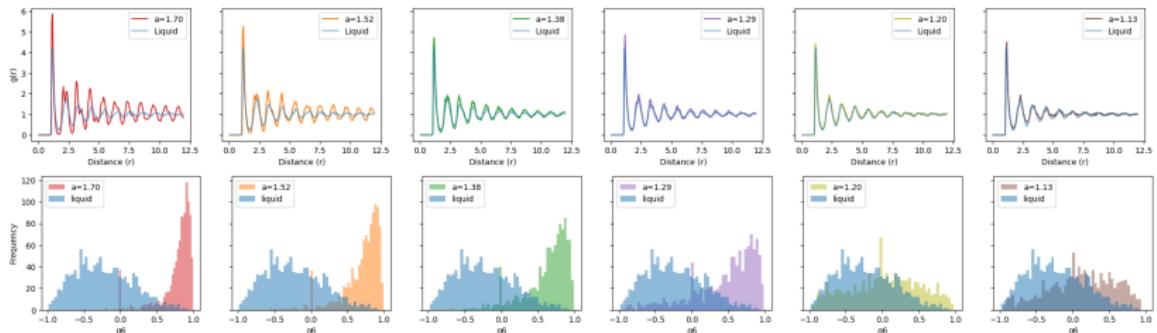
RDF analysis & Bond order analysis for a system with 10000 particles



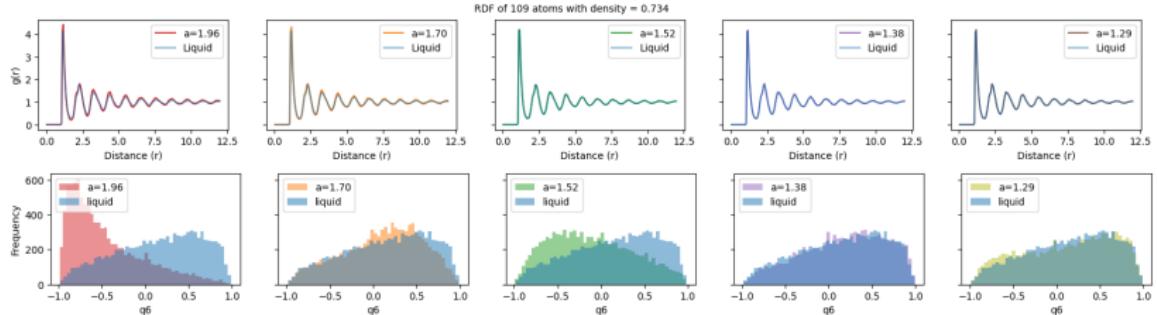
Results for $\rho = 0.734$

Seed of 109 atoms

RDF analysis & Bond order analysis for a system with 1175 particles



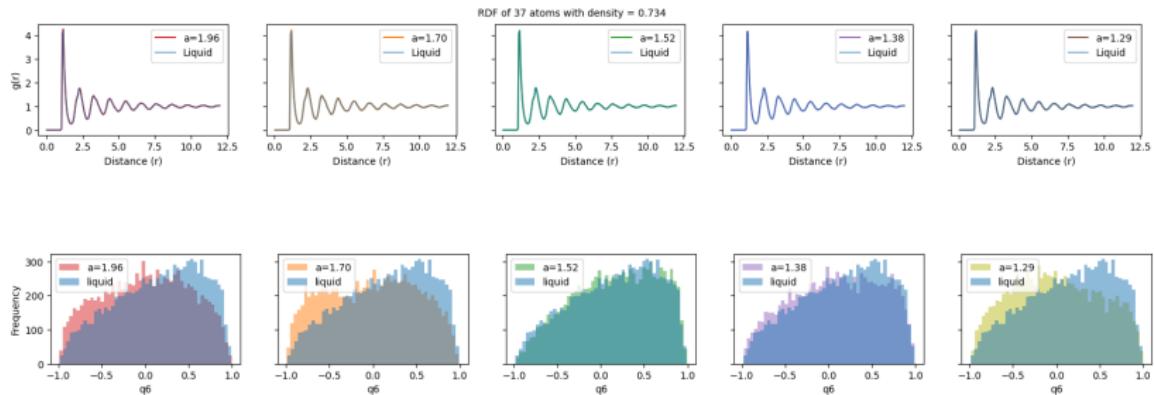
RDF analysis & Bond order analysis for a system with 10000 particles



Results for $\rho = 0.734$

Seed of 37 atoms

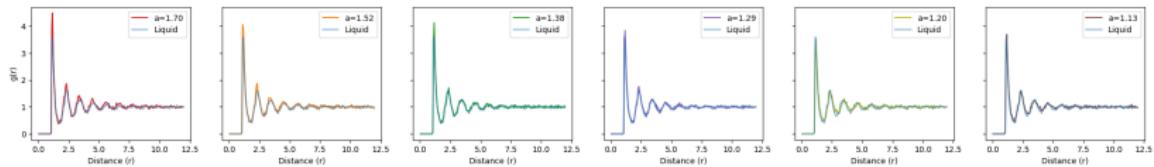
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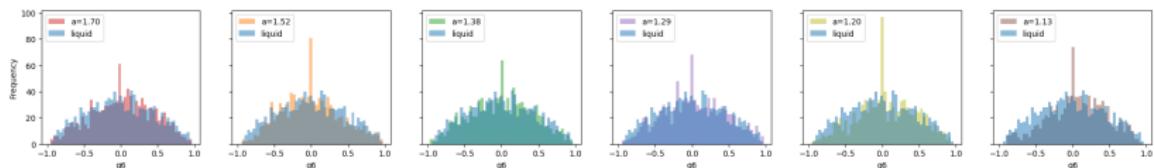
Results for $\rho = 0.687$

Seed of 55 atoms

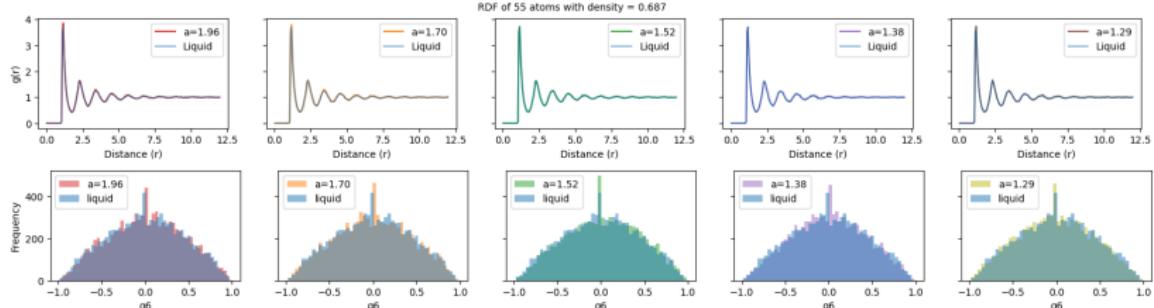
RDF analysis & Bond order analysis for a system with 1175 particles



Bond order analysis



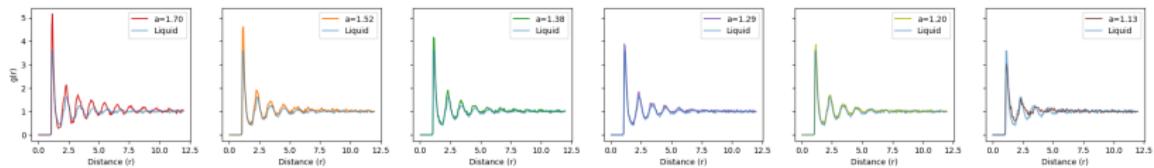
RDF analysis & Bond order analysis for a system with 10000 particles



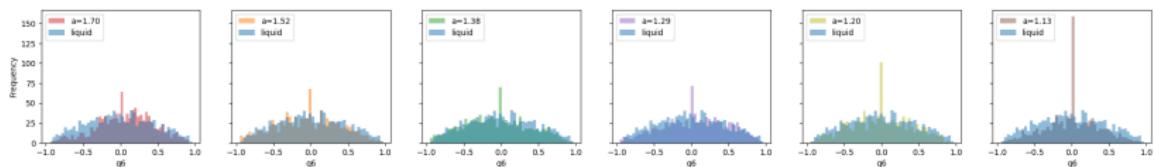
Results for $\rho = 0.687$

Seed of 109 atoms

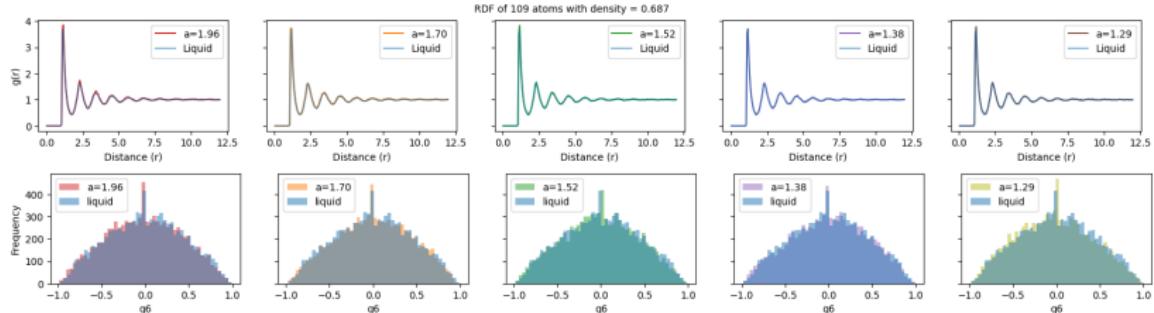
RDF analysis & Bond order analysis for a system with 1175 particles



Bond order analysis



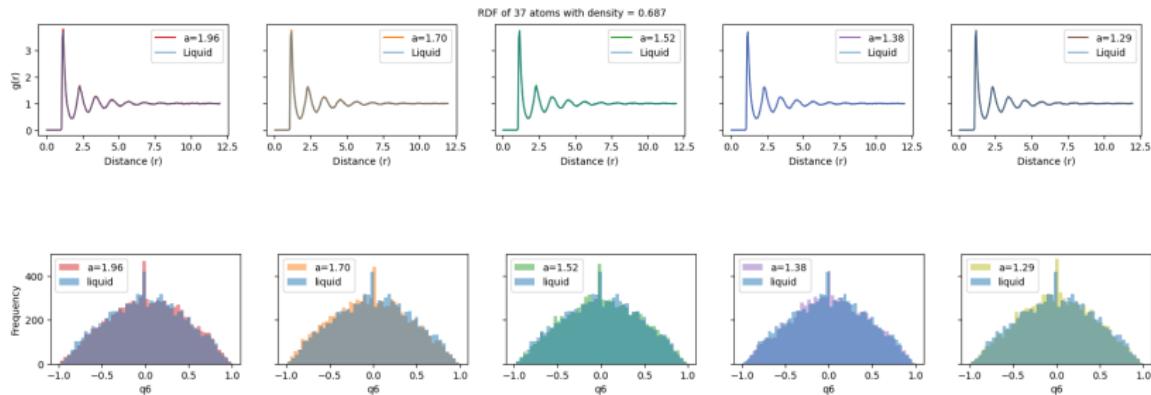
RDF analysis & Bond order analysis for a system with 10000 particles



Results for $\rho = 0.734$

Seed of 37 atoms

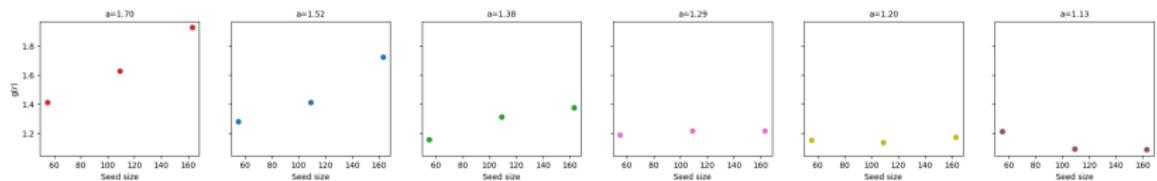
RDF analysis & Bond order analysis for a system with 10000 particles



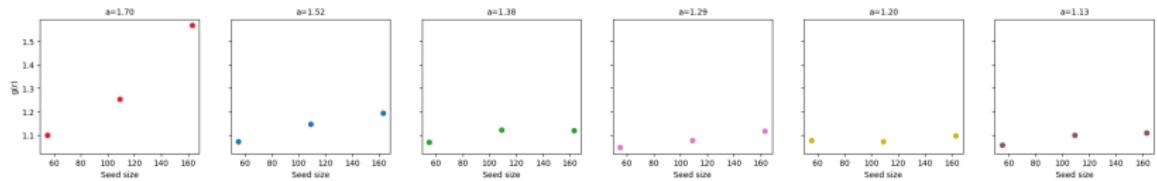
Final RDF Analysis

RDF vs Seed Size: Small systems

$$\rho = 1175/40 \times 40 = 0.734$$



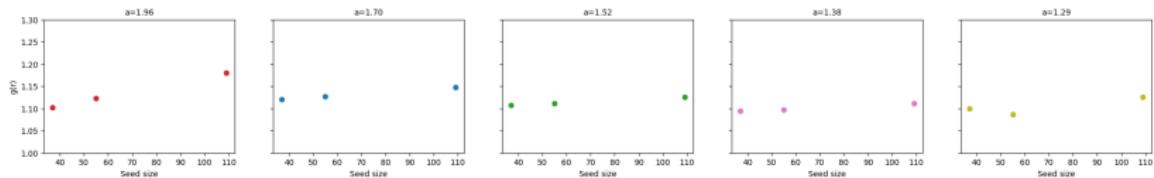
$$\rho = 1100/40 \times 40 = 0.687$$



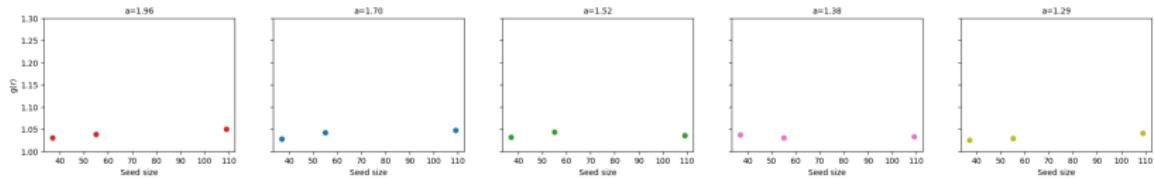
Final RDF Analysis

RDF vs Seed Size: Large systems

$$\rho = 10000/116.72 \times 116.72 = 0.734$$



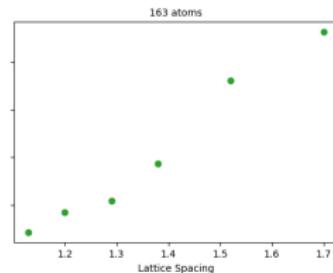
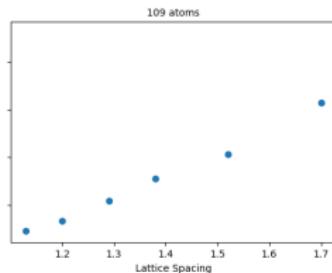
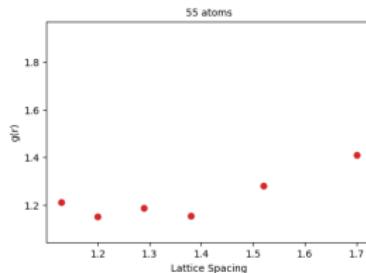
$$\rho = 10000/116.72 \times 116.72 = 0.687$$



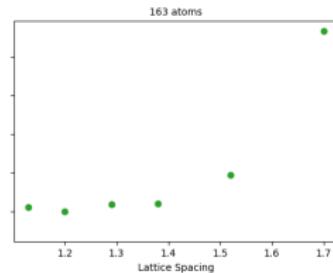
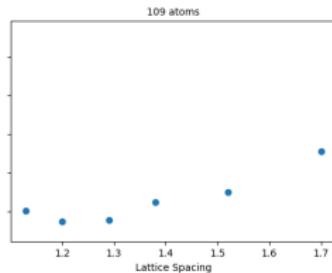
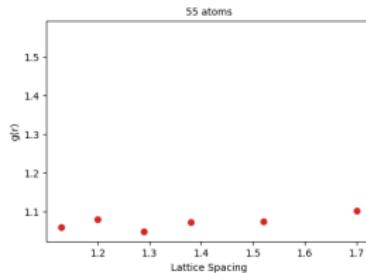
Final RDF Analysis

RDF vs Lattice Spacing: Small systems

$$\rho = 1175 / 40 \times 40 = 0.734$$



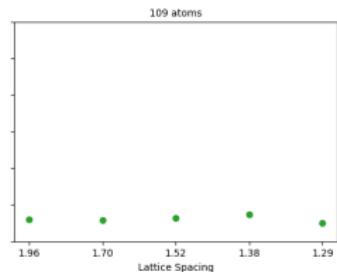
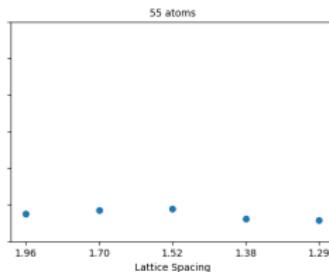
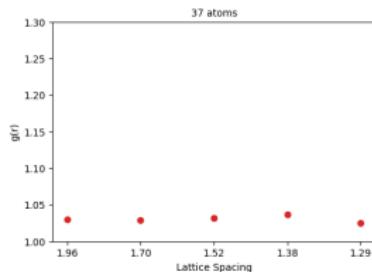
$$\rho = 1100 / 40 \times 40 = 0.687$$



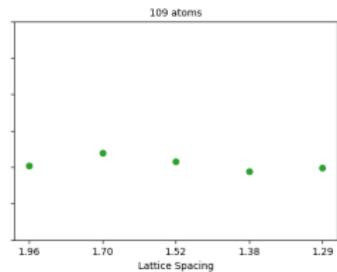
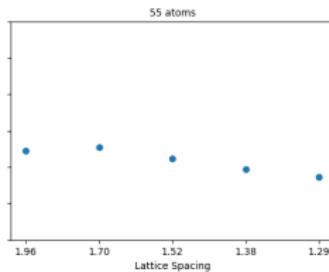
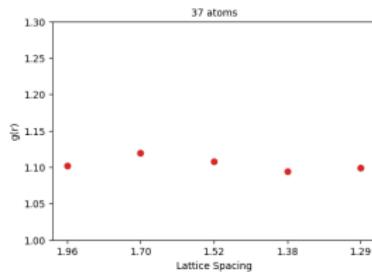
Final RDF Analysis

RDF vs Lattice Spacing: Large systems

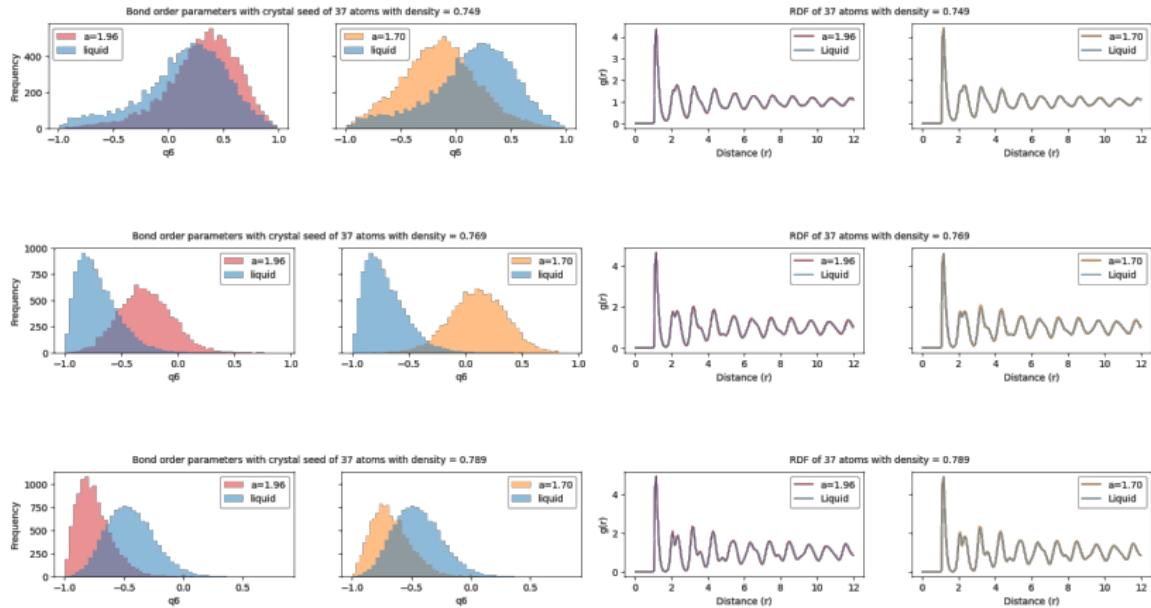
$$\rho = 10000/116.72 \times 116.32 = 0.734$$



$$\rho = 9359/116.72 \times 116.72 = 0.687$$



Looking for crystallization with a crystal seed of 37 atoms



Conclusions

- Small systems tend to overestimate crystallization.
- Large systems gave us more realistic results; realizing that crystallization is difficult to achieve with the proposed parameters.
- A crystal seed of 37 atoms is not large enough to enhance crystallization in a large system for example, 10000 particles.
- Densities larger than 0.8 were inappropriate since outside particles got stuck with to without a crystal seed.
- In the same way, larger lattice distances than 1.96 were proved, but there were no good choices because particles of the liquid started to come through the seed.
- Increasing time to 10^9 did not show an improvement in crystallization.
- The most promising system configuration we find is a density of 0.734, with a lattice spacing of 1.96. We are sure it will improve by increasing the crystal seed size, but this could be hard to achieve experimentally.

Thank you for listening!

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