Low-Dimensional Perturbation Self-Assembly in Free Lenard-Jones Chain Relaxations

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## Abstract

In order to study the structural behavior of free, single Lenard-Jones chains under n-dimensional perturbations, a molecular dynamics (MD) simulation based relaxation is performed. A “rule of thumb” is inductively discovered that a disordered initial structure of a single Lenard-Jones particle chain of a certain dimension m acted on with an orthogonal perturbation of dimension n results in a highly ordered structure with a dimension m + n, but only for m + n less than the full spatial dimensions. This is investigated for systems of (m,n) = (0,1), (0,2), (1,1), and (1,2). While a low-dimensional perturbation is a non-physical construct, these results suggest that self-assembly can occur as a result of very simply models and constraints.

## Background

The phenomenon of self-assembly is essential to many chemical processes, especially crystallization [1]. Physically, the phenomenon of a lower-dimensional disorderly structure to an orderly higher dimensional structure has been observed in two-dimensional (2D) materials such as nickel hydroxide [2].

## Simulation Methods

The initial positions are prepared in a disordered state in m dimensions. For example, an initial state of m = 1 is a line of randomly positioned particles which is uniformly distributed along the length of a cubic periodic cell. The length of this cell is chosen to enforce a density 0.08 particles per dimensionless volume. Each system is composed of a single chain of 50 particles.

In the simulation a perturbation is defined as a small uniform random displacement (maximum $10^{-4}$) to the initial position in a defined dimension orthogonal to the m dimension(s).

Each particle is identical and defined by a Lenard-Jones potential with a cut and shift at $r_c = 2.5$. The system is composed of a single chain with bonds enforced prior to the simulation by the index of the particle. The dimensionless energy is defined by

$$U^* = \sum_{i<j,\ ij\ not\ bonded} 4(r_{ij}^{-12} - r_{ij}^{-6}) + \sum_{i<j,\ ij\ bonded} (k/2)(r_{ij} - r_0)^2.$$

Neither $r_0$ nor $r_c$ change the qualitative behavior of the self-assembly. The harmonic oscillator which is used to represent bonded particles uses parameters $r_0 = 1.0$ and $k = 3000$.

The energy minimization with respect to structure is performed with the conjugate gradient method with line searches that efficiently estimate the minima with a parabola. Since the final systems are constrained in at least one dimensional degree of freedom, the final states do not represent the global energy minimum for these particles in the overall simulation cell. However, the qualitative regularity of the structured final states will suggest that the system is at or near the global minimum for its lower dimensional subspace (see next section).

**Results and Analysis**

Four trials were performed (Table 1). Cases A and B represent 0 dimensional input states (all particles at the same point) perturbed in 1 or 2 orthogonal directions respectively. It is found for both cases that the resulting structure exists only in 1 and 2 dimensions respectively. This suggests a simple summation rule, in which the final dimensions of the relaxed structure form a regular structure in dimensions m + n.

Table 1. Qualitative results of the three cases. Each case has an input m and n and results in a highly-ordered end structure with the dimensions m + n.

| Case | Inital dimensions (m) | Perturbation dimensions (n) | End structure dimensions (D) | Ordered structure type |
|---|---|---|---|---|
| A | 0 | 1 | 1 | Line |
| B | 0 | 2 | 2 | Hexagonal Plane |
| C | 1 | 1 | 2 | Hexagonal Plane |
| D | 1 | 2 | 3 | (Unstructured) |

Case C supports this conclusion as well, self-assembling from an unstructured line into a regular hexagonal plane from a uniform randomly distributed perturbation in one direction. Case D, however, suggests a qualification to the rule. When the line of randomly distributed particles is perturbed in two orthogonal directions, it no longer forms a structured state in m + n dimensions, but rather an unstructured one. Although this suggests a ‘rule of thumb’ for low-dimensional perturbations,

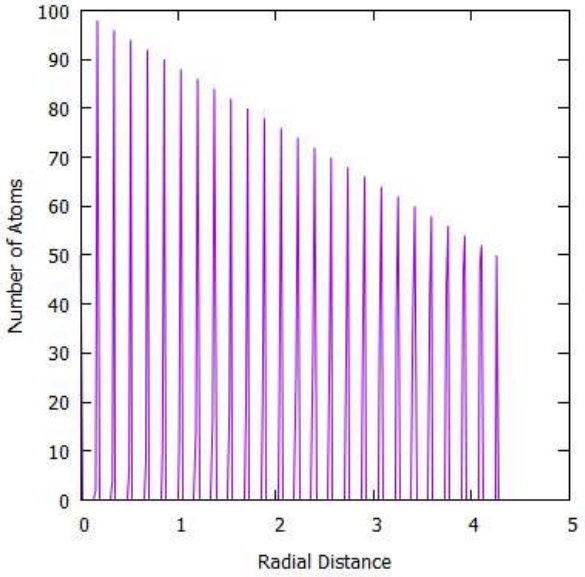
$$P = m + n \text{ ;} \qquad (1)$$

P is a structured state for P < R,

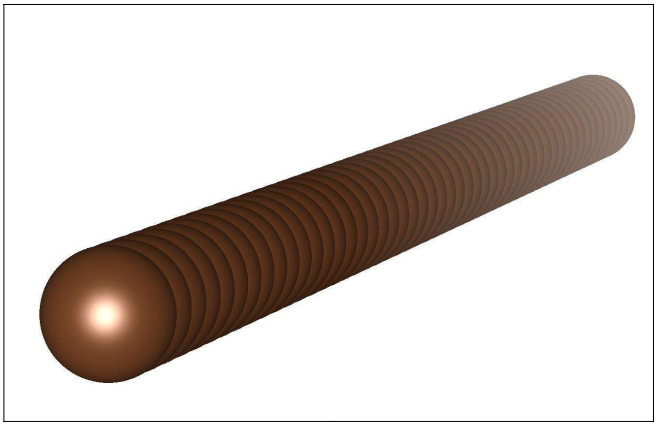
where R is the full number of dimensions of the system and “structured state” refers to a regular packing of the subspace of P dimensions.

The radial distribution function (RDF) can quantitatively indicate the regularity or irregularity of each case that is qualitatively observed (Fig. 1). A smooth RDF is a quantitative indicator of an unstructured state because the radial perspective of one atom looking at the others will be different for each atom. In a highly structured state the RDF should have sharp peaks and low valleys because of the similarity of the radial perspective of each atom. Therefore, the RDF should show sharp peaks for highly regular structures (Fig. 1A-1C) and show a smoother curve in unstructured states (Fig. 1D).

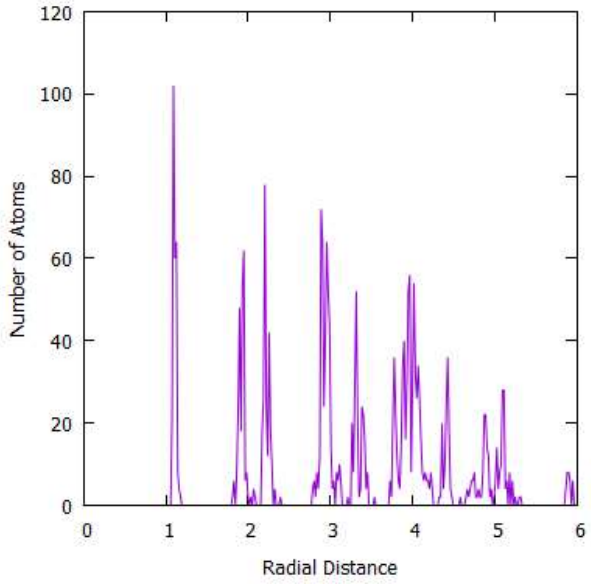
**Aa)**



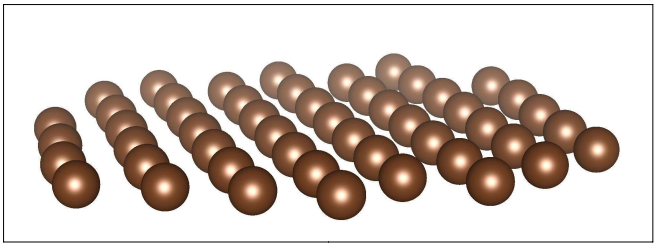

**Ab)**



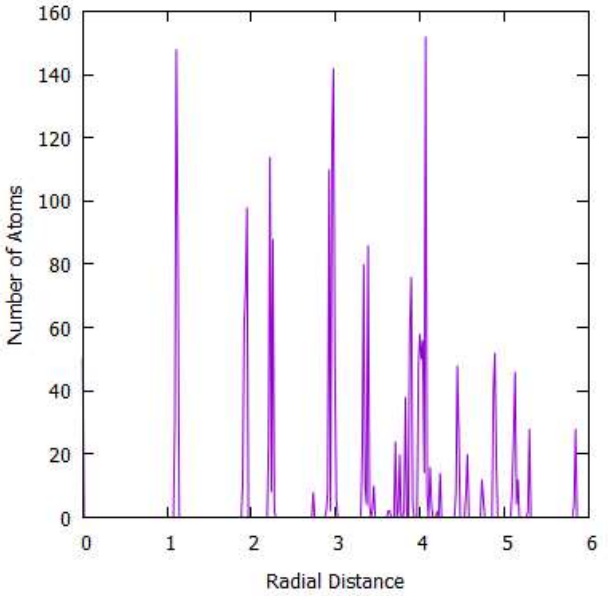
**Ba)**



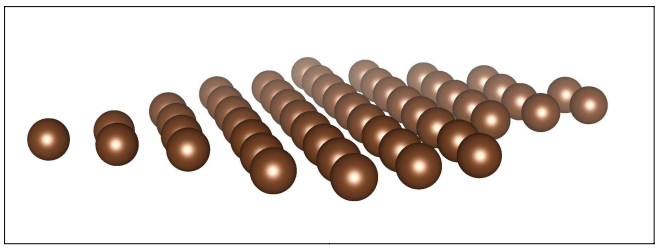

**Bb)**



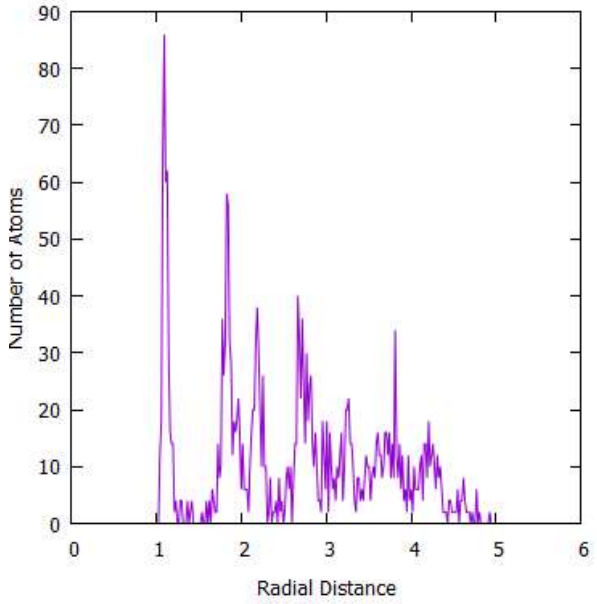
**Ca)**




**Cb)**



**Da)**




**Db)**

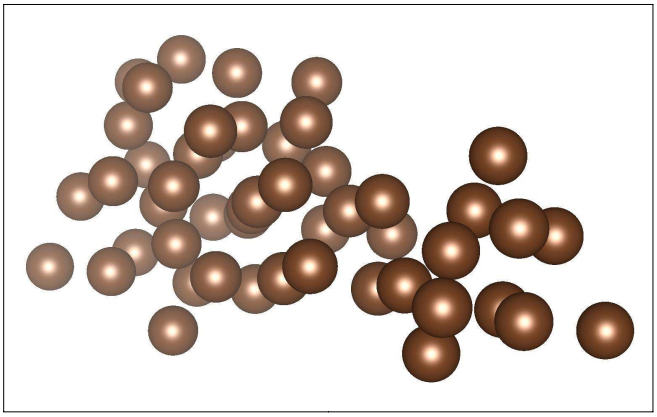


**Fig. 1:** Letters in this figure correspond to case letters in column 1 of Table 1. Aa, Ba, Ca, and Da are sums of radial distributions for each atoms as a function of radial distance. The values for each distance represent the counts of atoms that fall within a radial bin size of $L/(10 * N)$ where N is the number of atoms. Ab, Bb, Cb, and Db are the final structures for each case considered (A-D), where the initial structures are described by Table 1. The radial distribution functions are non-normalized for comparative clarity (see continued analysis).

The RDFs confirm qualitative observations of structured versus unstructured states. It also suggests that the qualitatively structured state of Case B (Fig. 1Ba) is less structured than Case C (Fig. 1Ca), although qualitatively they appear to be nearly identical hexagonal planes.

The unstructured state D shows large peaks near distance r = 1 and r = 2, but this does not indicate structure, since the relaxed states of an unstructured system will still be bonded to atoms close to the $r_0 = 1$ value. The rapidly fading magnitude of peaks and smooth distribution relative to cases A-C (Fig. 1Aa-Ca) demonstrates the unstructured state.

The radial distribution functions are non-normalized for comparative structural clarity. The linear structure has 100 bonds at its closes pair distance around $r_0 = 1$, while the hexagonal planar structures are capable of more than 100 pairs at this distance.

In conclusion, both through qualitative appearance and an analysis of the RDFs for four cases, the hypothesized rule described by equation 1 is inductively suggested.

## Movie

Self-assembly of an ordered plane of P = 2 dimensions from a single Lenard-Jones chain given initial dimension m = 1 and an orthogonal perturbation n = 1.

## References

[1] Guanglu Ge and Louis Brus *The Journal of Physical Chemistry B* **2000** *104* (41), 9573-9575

[2] Shintaro Ida, Akihide Takashiba, and Tatsumi Ishihara *The Journal of Physical Chemistry C* **2013** *117* (44), 23357-23363