

AT THE UNIVERSITY OF FREIBURG

Master Thesis

February 18, 2021

Author:

Wilkin Wöhler

Supervision:

Tanja Schilling

Abstract

A raw writing of hard sphere nucleation, a simulation to measure quantiteis, and a analysis of data generate by means of the simulation. A test citation: [1]

Contents

1	Theory	1
1.1	Hard sphere system	1
1.2	metastable fluid/ phase diagram	1
1.3	Classical nucleation theory :/	1
1.4	Computer Precision	1
1.5	Comparsion to Real world experiments	1
2	Simulation details	2
2.1	Algorithm and Simulation details	2
2.1.1	Event driven molecular dynamics (EDMD)	2
2.1.2	Details of the Implementation	2
2.2	Probe of simulation code	2
2.2.1	Diffusive behaviour	2
2.2.2	Radial distribution function	2
2.3	Estimate of required resources	2
2.3.1	Calculation time estimates	2
2.3.2	File sizes estimates	2
2.4	Produced Data	3
2.4.1	Equilibration steps	3
2.4.2	Initial density	3
3	Data Analysis	4
3.1	Diffusion of the lquid	4
3.2	Diffusion of the metastable liquid	4
3.3	Cluster growth	4
3.4	Tensor of Gyration properties	4
3.5	ACF largest cluster?	4
3.6	Nuclection time dilemma	4
3.7	Induction time by exponential distribution	4
3.8	Nucleation rate comparison	5
3.9	Memory Kernels	5

4	Conclusion - Summary	6
4.1	Conclusion	6
5	Appendix	7
.1	A	7

List of Figures

List of Tables

1 Theory

1.1 Hard sphere system

The Hard Sphere system is the simplest model of a fluid including interactions between the single particles. Its well known potential between particles i and j reads:

$$V(r_{ij}) = \infty \cdot \Theta(\sigma - r_{ij}) \quad (1.1.1)$$

In this equation r_{ij} indicates the distance between the two particles, σ is the diameter of the Hard Spheres and Θ is the Heavyside function.

While the ideal gas model without pair interactions already makes it possible to derive famous equations as $pV = NkT$, it does not include phase transitions yet. But these can be observed when granting the particles to take up space. Because it is the simplest model and it is well feasible for computer simulations the Hard Sphere system is very well suited to study basic properties of phase transitions.

Compared to experiments where similar systems can also be realized, general properties of the system at hand can be varied very precisely without much effort and position data of the single particles can be extracted easily as well, because they naturally are required for the simulation.

On the downside computer simulations are much more constraint in their size, but with todays computational possibilities system of the order of 1 million particles become tractable, and such computer simulations become a powerful tool to study also phase transitions in simple systems.

The beginning of such simulations actually dates back to the beginning of electronic computer technology (cite Alder and Wainwright 1959). Since then more algorithms to increase efficiency have been elaborated, and technology advanced giving today the possibility of studying large systems.

1.2 metastable fluid/ phase diagram

The equation of state for the simple Hard Sphere system has various approximations, (cite an overview paper), The probably most common approximation due to its simplicity is the Caranhan-Sterling ap-

proximation:

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (1.2.1)$$

(cite <https://aip.scitation.org/doi/10.1063/1.1672048>) It approximates the compressibility factor Z depending on the packing fraction η for the Hard Sphere fluid.

For the stable brach after nucleation a common approximation is given by the Almrza equation of state(cite <https://aip.scitation.org/doi/full/10.1063/1.3133328>).

$$\frac{p(v - v_0)}{k_B T} = 3 - 1.807846y + 11.56350y^2 + 141.6y^3 - 2609.26y^4 + 19328.09y^5 \quad (1.2.2)$$

where p is the pressure, v is the volume per particle $v_0 = \sigma^3/\sqrt{2}$ is the volume per particle at close packing, including the diameter of the spheres σ , and $y = p\sigma^3/(k_B T)$, where k_B is the Boltzman constant and T is the temperature of the crystal.

From these two equations of state we can draw the phase diagram: (include grapic of phase diagram.)

The chemical potential difference between the two equations of state can be calculate from the difference between the two equations of state.

Eventhough not further discussed in this thesis it might be said that for polydisperse radii the phase diagram becomes even richer as show for example in (<https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.91.068301>)

1.3 Classical nucleation theory :/

Estimate of r_{crit} by Δ_μ

SOMehow this wshould be doable ;)

1.4 Computer Precision

Explain a little about what numerics does, compared to the real world.

Maybe include the time evolution of minimal changes

1.5 Comparsion to Real world experiments

Compare, regadring the solvent. Esspeically with Hajos finding.// Maybe connect it with the Computer precision part, to talk about what the s<ytem is and what the system is not

2 Simulation details

2.1 Algorithm and Simulation details

EDMD and Simulation details

2.1.1 Event driven molecular dynamics (EDMD)

Explain the EDMD algorithm

2.1.2 Details of the Implementation

Add Details of for example FEL, and backupevent handling, double time precision, reset sim

2.2 Probe of simulation code

To probe we have to measure known quantities

2.2.1 Diffusive behaviour

Show the diffusive behavior of at least the fluid

2.2.2 Radial distribution function

Show a RDF of the fluid , if possible with the theoretical cervus-pevick approximation

2.3 Estimate of required resources

2.3.1 Calculation time estimates

Give some profiling numbers of the simulation Also conclude that missing q6q6 $O(N^2)$, broke the walltime.

2.3.2 File sizes estimates

Show the estimate on the file size

2.4 Produced Data

Overview of produced data with visualized snapshot?

2.4.1 Equilibration steps

Show dependence of equilibration steps on simulation

2.4.2 Initial density

Show dependence of initial density on simulation

3 Data Analysis

This is the analysis part

3.1 Diffusion of the liquid

This contains analysis of diffusion in the liquid to prove the simulations accurate

3.2 Diffusion of the metastable liquid

This contains Diffusion constants to normalize the rates

3.3 Cluster growth

Cluster growth depending on density

3.4 Tensor of Gyration properties

Well only swamp here, but it can be shown to conclude the swamp.

3.5 ACF largest cluster?

Just in case anything can be seen here

3.6 Nucleation time dilemma

Evaluation of induction time. Problem with accuracy and precision. Compare methods.

3.7 Induction time by exponential distribution

Obtain exp assumption and best estimator

3.8 Nucleation rate comparison

All Nucleation rates that can be found.-> mayhap ask Hajo.

3.9 Memory Kernels

Memory kernels of systems at various densities. Depends strongly on what is found here

4 Conclusion - Summary

4.1 Conclusion

5 Appendix

.1 A

Bibliography

- ¹D. M. Heyes, M. J. Cass, J. G. Powles, and W. A. Evans, “Self-diffusion coefficient of the hard-sphere fluid: System size dependence and empirical correlations”, *Journal of Physical Chemistry B* **111**, 1455–1464 (2007).