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# Investigation of the growth of methane clathrate hydrates using molecular simulations

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Methane clathrate block embedded in the sediment of hydrate ridge, off Oregon, USA - *Wikipedia*

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## Abstract

There are a lot of industrial pipelines under the sea, these installations are under extreme levels of pressure and temperature, these conditions are favorable for the formation of clathrate hydrates, which could damage the pipelines. The study of this phenomenon will help avoid accidents as the precise conditions for the growth and melt of clathrates become more known. As the pressure rises, the temperature needed to melt the clathrates increases as well, therefore the need for precise information on different case studies is essential.

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# 1 Introduction

Discovered in 1810 by Humphry Davy, clathrate hydrates are crystalline inclusion compounds in which water molecules form, via hydrogen bonding, a network of polyhedral cages trapping guest molecules. Put simply, clathrates can be seen as another form of solid water. At first, they were considered only as laboratory curiosities. But then, Hammerschmidt discovered in 1934 that clathrate hydrates can form inside oil and gas pipelines, creating a plug that could damage the equipment, or at least reduce the flow. That is the reason why researches about them were getting more and more active since the 1950's.

We have yet to discover all the properties of the clathrates and that explains why they are still an active field of research.

This study will focus on the analysis of the growth and melt of the clathrates under different conditions of pressure and temperature, and the protocol is based on a paper written in 2010 by *Tung et al.*[1].

## 2 Clathrates, nucleation and growth

An “empty” clathrate cannot exist, the stability of a clathrate is guaranteed by the presence of the guest molecule. Among the multiple applications of clathrates one can note:

- Storage and transport of natural gases or dihydrogen. The latter option is very interesting since the storage of dihydrogen is hard at the moment
- A way of reducing cooling systems energy consumption and environmental impact

There are signs of great natural reserves of methane in clathrates, formed without human action. These kind of reserve can be found in the permafrost and the ocean floor. These estimated reserves are way beyond every other fossile energy combined, and are related to the formation and dissociation of these structures.

My work is about methane hydrates, mainly their formation, growth and melt.

Some information about nucleation:

1. The nucleation of clathrates is a stochastic process and is really hard to predict. This aspect gets in the way of the comprehension of the mechanisms behind nucleation. This aspect comes from the fact that the formation of the structure requires a very precise molecular configuration
2. The nucleation can be homogenous or heterogenous and happens usually at an interface (fluid + solid, gas + liquid, liquid + liquid). In case of a heterogenous nucleation, the energy needed to move from a state to clathrate is lessened.
3. Hydrate seem to have a “memory effect” which causes a quick re-formation of the hydrate if it is not given the time to completely melt or if heated close to the dissociation temperature

After the nucleation comes the growth, where mass and heat transfer become of major importance. However, the nucleation parameters are still important during the growth.

The question of growth and nucleation at a molecular level is a scientific challenge for mainly 2 reasons:

1. The stochastic nature of this phenomenon

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2. It is hard to perform an experimental study at small time and space scales, at which hydrates form

That is where computer simulations arrive, and more specifically molecular dynamics, even if they tend to stray away from the experimental conditions of clathrates formation, they are still a powerful tool to learn more about clathrates.

## 3 Algorithms

### 3.1 About Molecular Dynamics

Molecular Dynamics Simulation can be compared to a real experiment:

Experiment	Simulation
<ol style="list-style-type: none"> <li>1. We prepare a sample of the material that we wish to study</li> <li>2. We connect this sample to a measuring instrument and we measure the property of interest during a certain time interval The longer we average, the more accurate our measurement becomes</li> </ol>	<ol style="list-style-type: none"> <li>1. We select a model system consisting of <math>N</math> particles and we solve NEWTON's equations of motion for this system until the properties of the system no longer change with time (we equilibrate the system)</li> <li>2. After equilibration, we perform the actual measurement</li> </ol>

In order to make a simulation in molecular dynamics, we have to express the observable quantity as a function of the position and momentum.

We will consider a simple program:

1. Initialize the system (initial position and velocities) in function of the thermodynamic conditions wanted
2. Compute the force on all particles, that means taking into account all the neighboring particles (longest part)
3. Integrate NEWTON's equations of motion
4. Increase the time by the timestep  $\Delta t$
5. Compute and print the average of measured quantities and stop

This algorithm applies for a simple atomic system. In this algorithm, the longest part is the calculation of the force acting on the particles. However, time is not an issue, it must indeed be taken into account, but there is more. Computations in molecular dynamics take a really long time, and need a lot of integration steps to reach thermodynamic equilibrium, especially when dealing with growth processes. Therefore it is better to have an algorithm as accurate as possible than a fast one in order to minimize the error on the molecular interaction energy computation.

When talking about simulation, one can think of the Monte Carlo method, which is a non-time dependant simulation consisting of a random sample taken from a population and statistical analysis of the results. However, this method will not work in this kind of study. We are interested in the trajectory of the particles throughout the simulation, the growth process is dynamic and is function of the time, therefore molecular dynamics simulations are more appropriate.

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## 3.2 Numerical methodology

All the molecular dynamics simulations done in this project are made with the program GRO-MACS<sup>1</sup>

This study will use a system composed of 3 phases enclosed in a periodic box of initial dimensions  $x = 12.8$  nm,  $y = 2.45$  nm,  $z = 2.45$  nm. The methane gas phase, the hydrate phase and the liquid phase, with the following compositions:

- methane gas phase: 160 methane molecules
- hydrate phase: 184 water molecules and 44 methane molecules
- liquid phase:
  - one slab of 736 water molecules
  - one slab of 736 water molecules and 128 methane molecules (supersaturated water slab)

Periodic box means that we consider a box without boundaries where the upper-side of the box is connected to its lower-side. Same goes for the lateral sides.

The dynamic simulation of the system is done in multiple steps:

The first step is a minimization of the energy of the system. After that, an equilibration (relaxation) is done at a temperature of 200 K and a pressure of 30 MPa for 20 ps. Once the system is equilibrated, we heat it (annealing) at a rate of  $0.5 \text{ K ps}^{-1}$ . After the annealing, the system is in good conditions to observe clathrate growth. The next step is then an NPT simulation for 40 ns at 30 MPa and 260 K to obtain the growth of clathrates.

Once this simulation is done, we can start the study on the melt of the clathrates. For that we start another batch of simulations. For all the following simulations, the starting system will be taken just after the NPT simulation at 260 K. The melt is done in two steps: firstly we heat the system to the desired temperature, then we once again do an NPT simulation at the desired temperature, this time for 20 ns. These melt simulations will be done for several barostats: 10, 30, 60 and 100 MPa. For each barostat, the system will be heated to 270, 280, 290 and 300 K. For 60 and 100 MPa, the system will also be heated at 310 K.

The main objectives here are to find the equilibrium point of the clathrate at different pressures, the temperature at which this equilibrium is broken (called melting point), find the distribution of cages (small, large, interface and irregular) at different point of the simulation.

## 3.3 Analysis algorithm

There are 3 methods that we will use to sort and identify the different structures. The number of water molecule in the neighbourhood of a methane molecule, the AOP of each water molecule in this neighbourhood and the hydrogen bonds between these molecules.

The first step in the analysis is to search for neighbouring water molecules for every methane molecule. In practice, the search is made between the carbon atom of the considered molecule and the neighbouring oxygen atoms. Any oxygen atom located in a radius of  $5.5 \text{ \AA}$  of the atom of interest is considered a neighbour. The number of neighbours for each methane molecule is noted  $n_w$ .

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<sup>1</sup>GROningen MAchine for Chemical Simulations

Among these molecules, we once again search for neighbours, this time the center molecule is a water molecule and we search for neighbouring water molecules in a radius of 3.5 Å. These neighbours are used to compute an index called the Angular Order Parameter (AOP). This index gives us information concerning the structure of a water molecule.

$$\text{AOP} = \sum \left( (|\cos \theta| \cos \theta) + \cos^2(109.47) \right)^2$$

where  $\theta$  is the angle between any pair of oxygen atoms in the neighbouring of the atom of interest (taken as the elbow of the angle). For example if an oxygen has 4 atoms in its neighbourhood, there are 6 angles to consider. The value of the AOP indicates the structure the considered water molecule belongs to:

- AOP = 0: ice
- AOP = 0.1: hydrate cristaline structure
- AOP = 0.8: liquid water (amorphous)

These values are averages, and for this study we will only consider molecules with an AOP < 0.4, considered hydrate-like molecules. The number of hydrate-like molecules among the neighbours is noted  $n_b$ .

The last point to consider is the hydrogen bonding between the water molecules. Since the oxygen has a high electronegativity, there is a high chance of hydrogen bonding with other water molecules if certain conditions are met. These conditions are the following:

- $2.5 \text{ Å} < d_{\text{O}^1\text{O}^2} < 3.5 \text{ Å}$  with  $d_{\text{O}^1\text{O}^2}$  the distance between the 2 oxygen atoms
- looking at the molecule with the potential donor hydrogens, we take the hydrogen the closer to both oxygen atoms (distance  $\text{O}^1 - \text{H} - \text{O}^2$ ), the angle  $\widehat{\text{O}^1\text{H}\text{O}^2}$  must be between  $90^\circ$  and  $180^\circ$

If these 2 conditions are met, the hydrogen is considered a donor atom and a hydrogen bond is counted between the 2 molecules. The number of hydrogen bonds among the hydrate-like molecules in the neighbourhood of a methane molecule is noted  $n_b$ .

After the computation of these 3 numbers, we can identify clathrates. If  $n_w = n_b = 24$  and  $n_b = 36$ , the methane is imprisoned in a large cage; if  $n_w = n_b = 20$  and  $n_b = 30$ , the methane is imprisoned in a small cage; if  $10 < n_b < 13$ , the methane is in a half-complete cage (interface cage); if  $n_b \leq 14$  and  $n_b \neq 20, 24$ , the methane is in an irregular cage; if anything else, the methane is not considered in a cage.

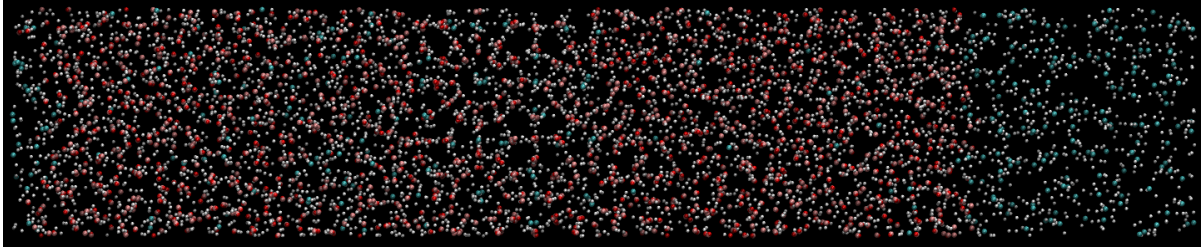
A point of interest is the width of the clathrate phase throughout the melt simulation. Once we know which molecule is/is not in a cage, it is rather easy to find the width of the clathrate phase. We take the carbon atoms in large and small cages and compute the difference between the lowest and the highest values of  $x$ . That gives us a rough idea of the width of the clathrate phase for the frame. Doing this for several frames of the same simulation shows us if the phase size is reducing or not and therefore, if the clathrates are melting.

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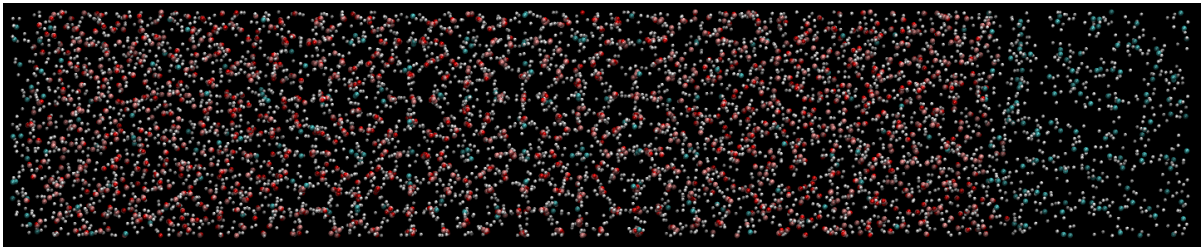
## 4 Results and discussion

### 4.1 Growth

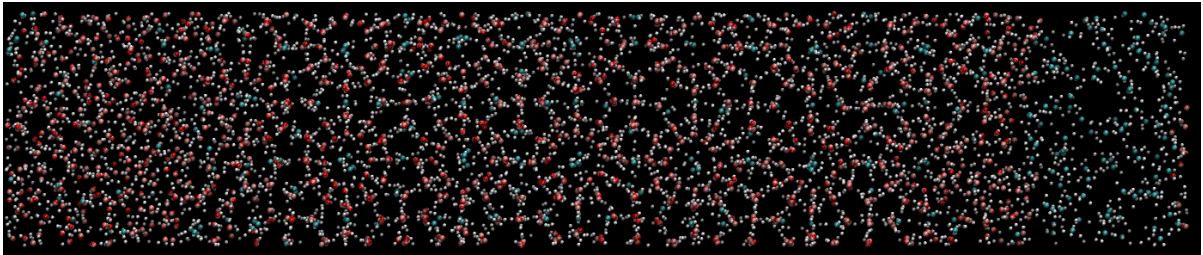
The first part of this study is about the growth of clathrates at 30 MPa and 260 K. What follows are 3 snapshots taken at the beginning, halfway through and at the end of the simulation.



(a) Snapshot at  $t = 0$  ns



(b) Snapshot at  $t = 20$  ns



(c) Snapshot at  $t = 40$  ns

Figure 1: Snapshots at different times of the simulation

On the [Figure 1a](#), we can see a bit of a clathrate shape in the middle, it is because when the heating was approaching 260 K, the system was almost at the conditions required for the formation of clathrate and methane molecules were moving to the liquid phase, therefore cages already started forming at that point.

On [Figure 1b](#) and [Figure 1c](#), we notice that as the clathrate phase widens, the gas of methane to the right of the figures is slowly thinning down.

The [Figure 2](#) shows the width of the clathrate phase during the growth process. The growth rate of clathrates is somewhat linear, with variations along the simulation. In this simulation the rate was about  $0.129 \text{ nm ns}^{-1}$ , which is close to the experimental and computational results mentioned in *Tung et al.*'s paper. The clathrate phase constantly switches between increasing and decreasing its size, but looking at the big picture, the phase width is expanding. I think that this pulse is due to the precision of the program to detect the boundaries of the clathrate phase. The program only looks for the highest and lowest values of the  $x$  position for the carbon atom among the small and large cages, but it does not take into account the size of the cage. In practice, the width of the phase will always be a bit higher than the computed width since the last small and large cages (just before

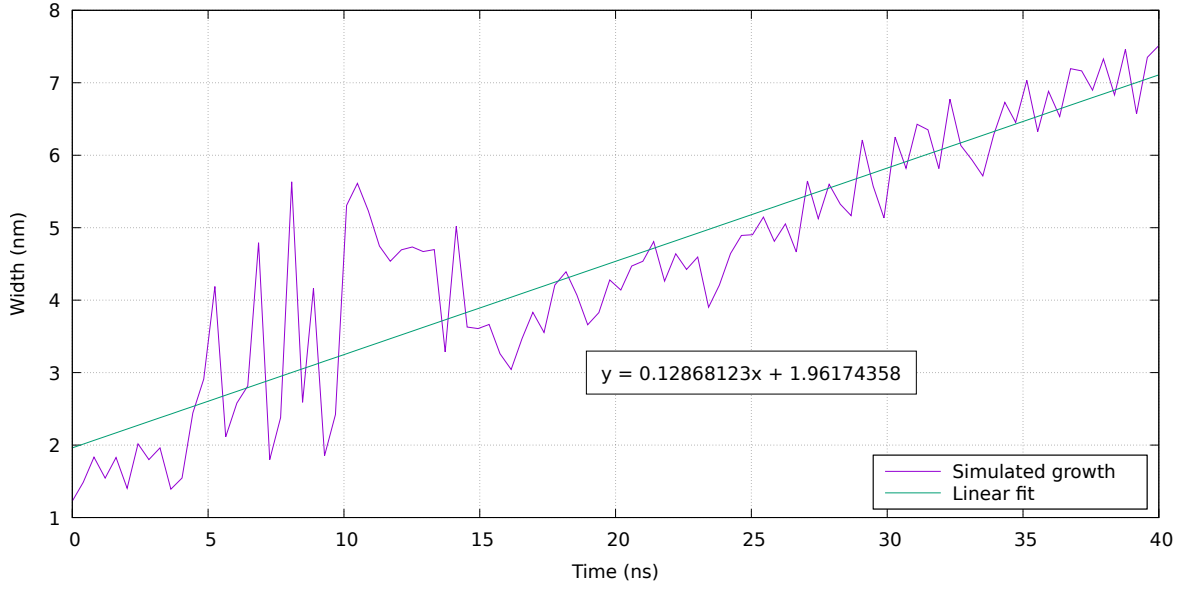


Figure 2: Width of the clathrate phase during growth process

the interface cages) are “cut” in half (because the program only looks at the  $x$  position of the carbon atom, supposed to be at the center of the cage). Concerning the high peaks between 5 and 15 ns, it could be explained if at some point, the system gets carried away and speeds up the simulation, along with cases of false positive (typically cages forming inside the liquid phase).

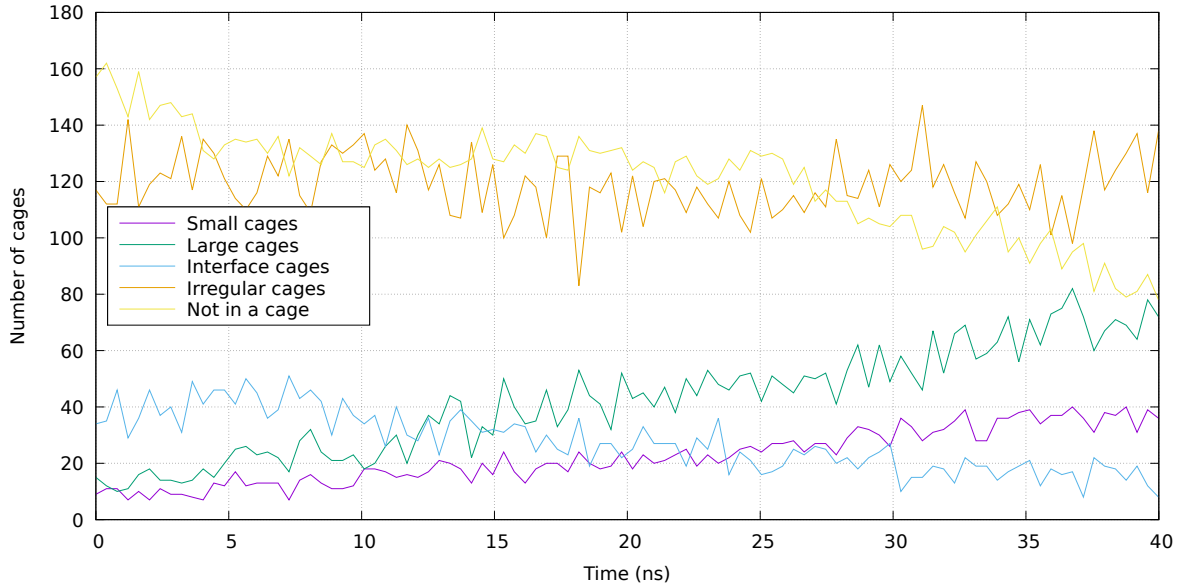


Figure 3: Distribution of cages during the growth

The [Figure 3](#) show the distributions of the different detected cages during the growth of the clathrates. We see that at the beginning of the simulation, there is a small number of small and large cages, a bit more of interface cages and a lot of irregular cages. As the simulation goes on, the number of small and large cages increases and the one of interface cages decreases. Since the interface cages are considered as incomplete cages, the decreasing number over time indicates that the cages are most likely forming themselves completely, which would also explain the rise of small and large cages. Everything called irregular cages correspond to methane molecules close to 14 or more water cages,



but with a symmetry that does not resemble the one of a clathrate. Finally, the “not in a cage” category corresponds to every other methane molecule. Since most of the methane molecules in liquid and clathrate phases are surrounded with water molecules, most of the methane in this category are in the methane gas phase. Its number decreases, confirming that the methane molecules are indeed caught by the forming clathrates.

## 4.2 Melt

The second part of this study concerns the melt of the clathrates. Unlike the growth of the clathrates, the melting simulation was done at different pressures: 10, 30, 60 and 100 MPa. The following table shows the results for the melting simulations.

Pressure (MPa)	Simulation time (ns)	Melting temperature (K)	Melting rate (nm ns <sup>-1</sup> )
10	20	295(10)	0.130
30	20	295(10)	0.081
60	20	305(10)	0.265
100	20	305(10)	0.159

Table 1: Conditions and results for the melt of clathrates

This first thing we notice is that for a higher pressure, the temperature needed for the clathrate to melt is higher aswell. It was expected since as predicted by thermodynamics, an increase in pressure without volume change induces a higher temperature required to reach melting point. These results, although a lot less precise than those of *Tung et al.*, are in the same range

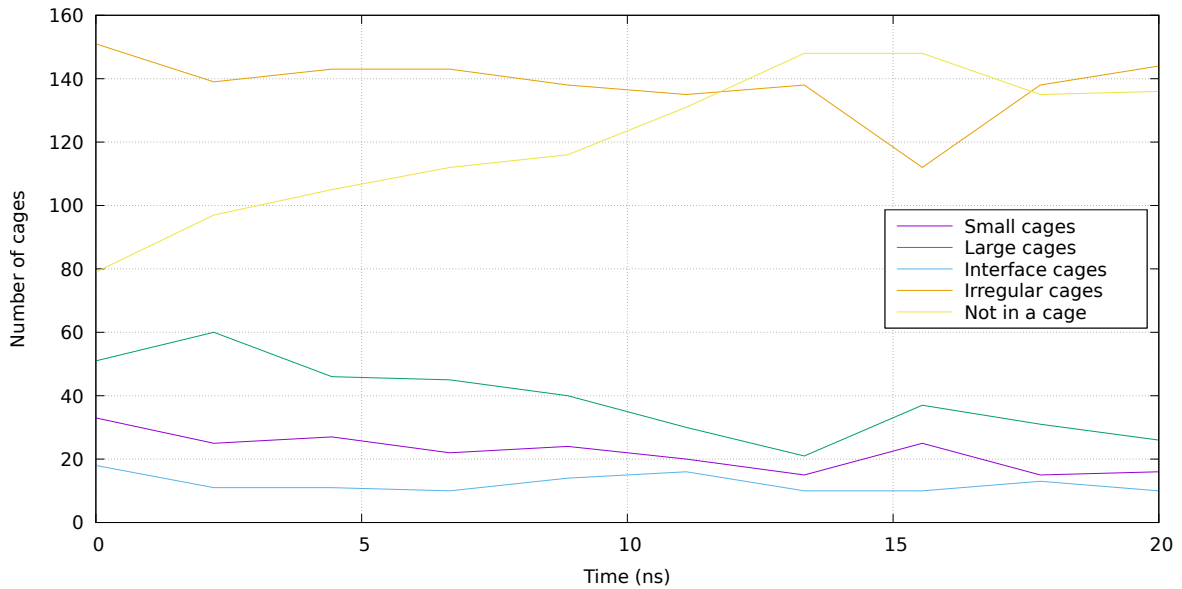


Figure 4: Cages for a melting simulation at 100 MPa and 310 K

The [Figure 4](#) shows the distribution of cages for the simulation at 100 MPa at a temperature higher than the melting point. Not only the small and large cages, but the interface cages number decrease aswell after the melting temperature is crossed. Naturally, as cages melt, they release the enclosed methane molecule, therefore the number of methane that are not in a cage increases.

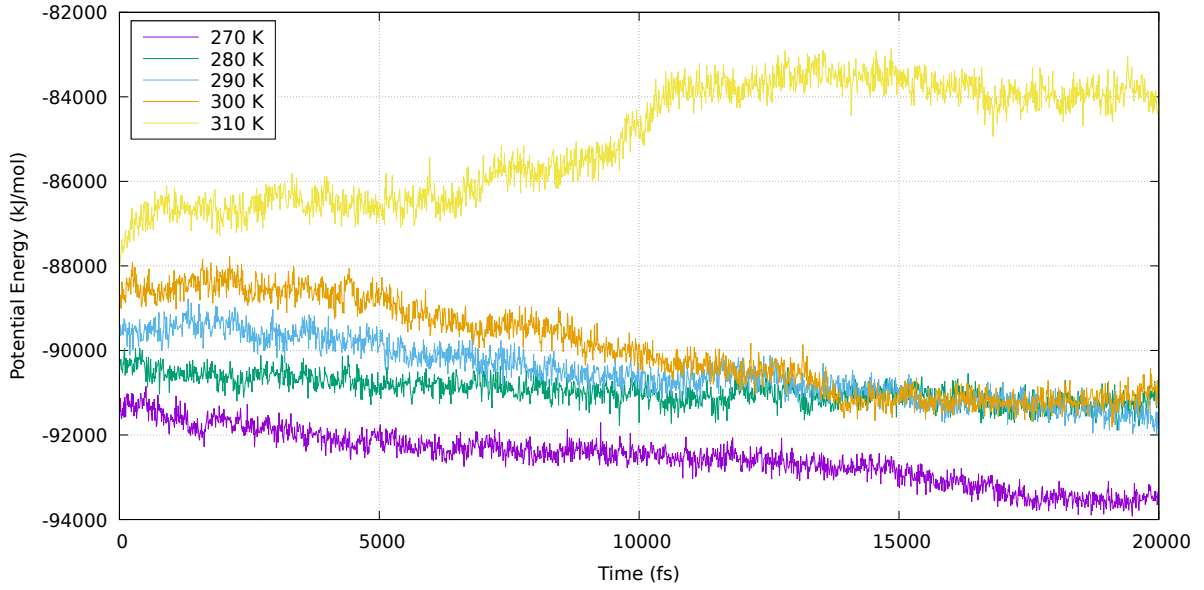


Figure 5: Potential energy for a melting simulation at 100 MPa

The state of the system can also be studied by looking at the potential energy. In [Figure 5](#), we see that before reaching the melting temperature, the potential energy decreases, but once the melting temperature is crossed, the potential energy increases. A rise of potential energy means that the system is melting, while a drop in potential energy indicates that the system crystalizes.

One more thing that we can consider to check our results is the AOP. The [Figure 6](#) show the AOP for the melting simulation at 100 MPa and 310 K. As stated earlier, the AOP of water molecules that are part of a clathrate cage is low. Here, we see that the AOP somewhat corresponds to the target value ( $< 0.4$ ) between around 2 and 6 nm. Comparing it with a snapshot from the same frame ([Figure 7](#)), we see that the positions of the clathrate phase correspond. We can also see that the AOP after 10 nm is rising a little, it is because the system is periodic, some molecules of water went to the other side of the box, in the gas phase, therefore we have a bit of computed AOP at the end of the box.

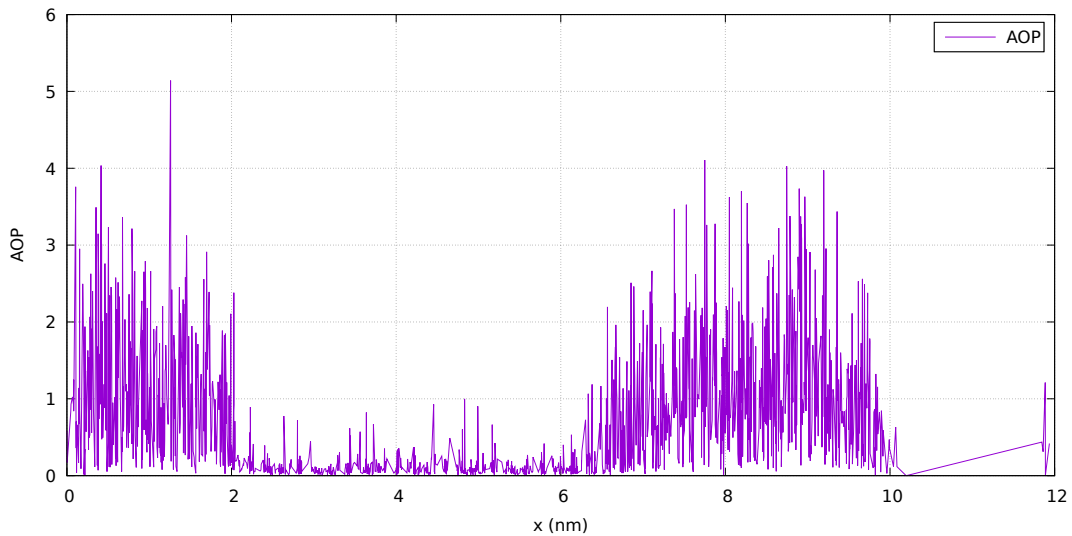


Figure 6: AOP at the end of the melting simulation for 100 MPa and 310 K

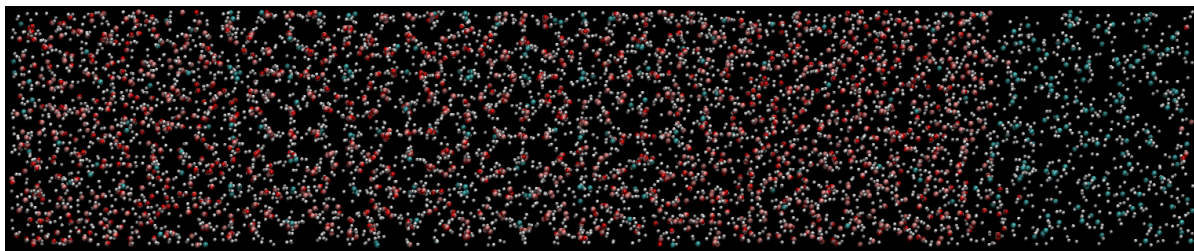


Figure 7: Snapshot of the melting at 100 MPa, 310 K and 20 ns

## 5 Conclusion

As stated earlier, the simulation of growth and melt of clathrates via molecular dynamics requires a great computational power due to the complexity of the system, the analysis was also a rather long task. The calculations may be simple, but with the number of atoms in the systems, even the simplest calculation can take some time. The study was carried out for different thermodynamic conditions in order to analyse the behavior of such a system and the analysis was conducted following the guidelines stated by *Tung et al.*

Since there are a lot of underwater pipelines, the simulations at different pressures give an idea of the temperature conditions for the growth and melt of clathrate at different depth levels (100 MPa corresponds roughly to the pressure at the bottom of the Mariana Trench). The further down we go, the higher the temperature must be for the clathrates to melt completely. Such a condition constitute a challenge as the deeper we go, the colder it gets.

## References

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| <p>[1] Tung Y. et al. "The Growth of Structure I Methane Hydrate from Molecular Dynamics Simulations." <i>The Journal of Physical Chemistry B</i> 114.33 (2010), pp. 10804–10813.</p> <p>[2] Patt A. "Simulation moléculaire d'hydrates de gaz mixtes en conditions astrophysique." PhD thesis. 2020.</p> | <p>[3] Dendy Sloan E. and Koh C. A. <i>Clathrate Hydrates of Natural Gases Third Edition</i>. CRC Press, 2007.</p> <p>[4] Frenkel D. and Smit B. <i>Understanding Molecular Simulation</i>. Academic Press, 1996.</p> <p>[5] Cui J. et al. "Fundamental mechanisms and phenomena of clathrate hydrate nucleation." <i>Chinese Journal of Chemical Engineering</i> 27.9 (2019), pp. 2014–2025.</p> |
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## 6 Appendices

### 6.1 About the code

The molecular dynamics simulations ran on the computing center, and the analysis on my computer (Intel i5-8365 vPro, 8 GB RAM, running on Arch Linux 5.10). The analysis for a single frame took about 1 min for my computer.

Initially, the code was written in Python. However, due to heavy computations, the code was too slow to get results on time. I rewrote most of the heavy functions in C, compiled them as shared objects (.so files) and used them in the Python code. This method allowed me to run the analysis way faster (more than a hundredfold faster). However this came with a cost, using the C integration “broke” the program and I could not make it run on Windows (apparently due to versions conflict for the module ctypes), it only works on my linux machine.

The code is provided with the report, but it requires heavy input files (200+ MB) that I cannot provide to work. These input files are the positions of each atom at each timestep (frame).

All the framework of the project was made in python, the file *main.py* pilots the program; the file *analysis.py* contains quality of life functions, basic functions, and the Python functions that have be replaced with C functions for speed purposes; the file *cintegration.py* contains the functions used to bridge between Python and C; the file *parameters.py* contains the input parameters (filename, number of frames and max time).

Each computation involving distances in the code must respect the periodic conditions as follows:

Let  $d_i = i_2 - i_1$  and  $i \in \{x, y, z\}$ , then the periodic conditions applied for the system are:

$$d_i = d_i - \text{int}\left(\frac{d_i}{box_i}\right) \times box_i$$

with  $box_i$  a dimension of the box.

As C functions could not return values for Python (the memory gets erased before Python gets the chance to retrieve the data), for each call of C inside Python, I had to provide a variable to store the result, this is the reason why there are a lot of pointers in the C code.