PRESSURE EFFECT ON METHANE WATER MIXTURES

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in
Condensed Matter Physics

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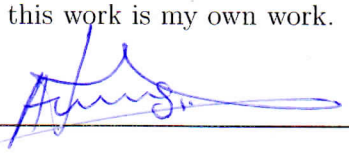
DECLARATION

I, AYIRWANDA Abraham, declare that the work presented in this thesis is my own and has not been presented to this institution or any other institution for any award. I confirm that where I have quoted from the works of other authors, the source is always provided. With the exception of such quotations, this work is my own work.

Signed: 

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DEDICATION

This work is dedicated to my family.

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Abstract

Molecular dynamics simulations on methane-water mixtures were performed to study the hydrophobicity of methane under different pressure and temperature conditions. Radial distribution functions (RDFs) and number of moleculars in first solvation shells were extracted from these simulations for analysis. These studies showed that methane aggregation is more dominant at high pressures and leads to phase separation. Thus, our results failed to conform experimental observations of increase in methane solubility with pressure. We recommend the development of more accurate force field to explain the molecular origin of methane solubility increase with pressure.

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Abbreviations

EFF: Empirical Force Field

HI: Hydrophobic Interaction

MD: Molecular Dynamics

OPLSUA: Optimized Potential for Liquid Simulation in the United Atoms

RDF: Radial Distribution Function

SPCE: Extended Simple Point Charge

vmd: Virtual Molecular Dynamics

1 Introduction

1.1 Methane

Methane is an organic compound; a colorless and odorless combustible alkane. It is a gas at room temperature and it has very low melting and boiling points of 90.15 K and 111.65 K, respectively. It is also insoluble in water at room temperature. Methane has 1.8ppm (mole fraction in dry air) of concentration in the troposphere and it constitutes the third[4] most important greenhouse gases after water vapor and carbon dioxide. With a chemical formula of CH_4, methane contains two types of atoms. Carbon in the centre surrounded by four hydrogen atoms as in Fig 1. This compound is typically nonreactive. It does not react with water, acids, bases or metals. However, its combustion produces heat, making it very useful as fuels[5].

In nature, methane can be typically produced as a result of anaerobic bacterial decomposition of organic matter under water[6]. Fig 2 shows the methane cycle at the surface of the earth, its production and its consumption where the cycle starts from the creation of methane in the soil by microbes (methanogens) and consumed by methanotrophs. Methanogens make more methane than that consumed by methanotrophs[6, 5]. Methanogegens also occur at the bottom of oceans and other water bodies where their production leads to the formation of hydrates of methane, also known as methane clathrates. It is interesting that methane forms a structure with water despite the fact that methane is hydrophobic (as evidenced by its law solub)

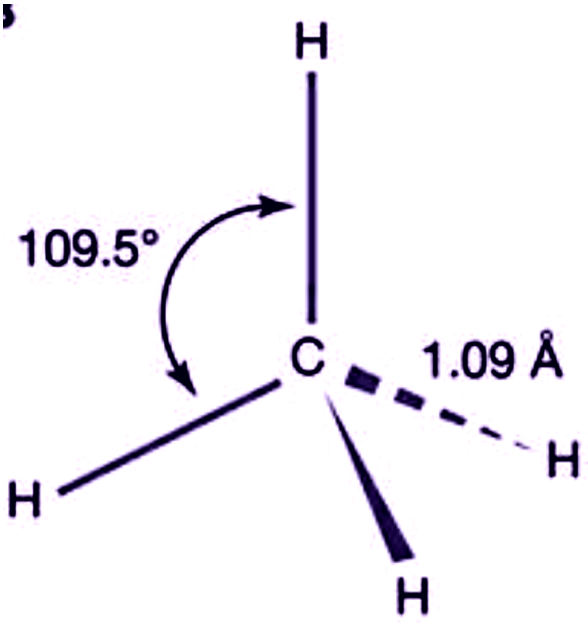

Figure 1: Methane structure. In equilibrium all the CH bond lengths are equal as well bond angles

1.2 Methane-water as a model for hydrophobicity studies

It is commonly experienced that oils and fats do not mix with water [7]. The aggregation of non-polar substances in aqueous solution to exclude water molecules is the essence of the hydrophobic effect [8]. Hydrophobic interaction (HI) plays a significance place in many biological phenomena. It is found to have a fundamental role in proteins folding and cell membrane formation[7, 8]. Its importance compared to other interactions (e.g: the hydrogen bonding interaction) in these biological systems may not be easy to quantify. Thus, it may be helpful to study simple systems in order to better understand the hydrophobic effect. Methane in water is arguable the sim-

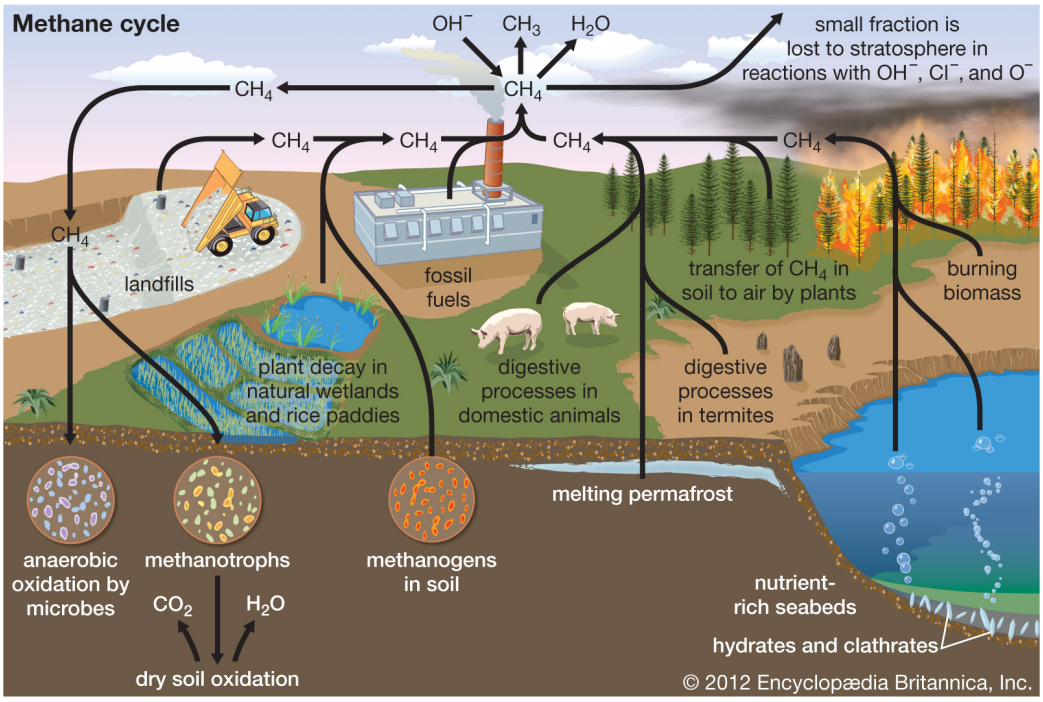

Figure 2: Methane cycle diagram which illustrates the flow of methane into the atmosphere and its consumption [1]

plest model systems for this purpose. Other small hydrocarbons in water can also be examined. HI can be investigated by considering the solubility of these simple molecules in water.

1.2.1 Solubility of methane

The solubility of gases in liquids at standard temperature and pressure is governed by Henry's law which states that "the saturated solubility of a gas in a liquid is proportional to the partial pressure of the gas". This is commonly experienced for polar and non polar material[9]. Practically, at ambient temperature and pressure, methane is insoluble in water.

Methane gas follows Henry's law at nearly ambient condition and low pressures. It shows a weak solubility (up to $8 \times 10^{-3} mol\%$) at 373 K and 0.2 Gpa[10, 9] and exhibits a sub-linear increase to about 1 mol% up to a pressure of 1Gpa[8]. However, it shows a dramatic increase of solubility at a temperatures of 373 K when the pressure is increased and saturates with a maximum of 44(3) mol% at 2 GPa[8, 10].

One of the contributions to solubility is the solvation free energy (ΔG_{solv}). The solvation free energy is the energy involved in the dissolving of solutes in solvent s and is believed to be comprised of four main components that are related by Eq(1): (a) the necessary work to create a cavity in the solvent around solute (ΔG_{cav}), (b) the free energy of electrostatic interaction (ΔG_{el}), (c) short-range van der Waals interactions (ΔG_{vw}) and (d) the free energy of hydrogen-bond formation(ΔG_{HB})[11, 12].

$$\Delta G_{solv} = \Delta G_{cav} + \Delta G_{el} + \Delta G_{vw} + \Delta G_{HB} \tag{1}$$

The solvation free energy is related to the Ostwald solubility coefficient by [11, 12] Eq(2)

$$\Delta G_{solv} = -2.3RTlogL \tag{2}$$

where L is the ratio of the liquid-gas phase molar concentration of the solute Eq(3):

$$L = \frac{C_l}{C_g} \tag{3}$$

At ordinary temperature ($\leq 373K$) methane shows a very low solubility at near ambient condition. At $373K$ and 0.0001 GPa (1 atm) the solubility of methane in water is 6×10^{-3} mol% which can be raised to 8×10^{-3} mol% at 0.2 GPa [10]. Thus, an increase in pressure induces the mixing of methane in water. Methane-water mixtures are widespread throughout the natural world since methane is present naturally at the bottom of oceans as a biogenic output. Its compression forms solid methane hydrates [13] which are stoichiometric mixtures of methane and water (ice). It is believed that methane and water are the major constituents of planets Uranus and Neptune as a fluid mixture[14]. The interior temperature of the two planets is estimated to be 8000 K [13, 14]. Studies predict that under high pressures and temperatures in the interior of Uranus, there is a breaking down of methane to form different compounds and pure elements like carbon and diamond which fall inward and warm up its interior [14]

On Earth, natural gas which is mainly methane gas is useful as source of energy for power generation [15, 16], heat sources in industries [15] and vehicle fuel [17] for environmental benefit since the combustion of natural gas reduces the amount of SO_2, CO and CO_2 in the atmosphere by 90, 97, and 24% [17] respectively. The combustion of natural gas releases mainly carbon dioxide and water vapor. Compared to coal and fuel oils, natural gas releases low levels of sulfur dioxide, nitrogen oxides, carbon dioxide, carbon monoxide and some reactive hydrocarbons [18]. Thus, natural gas is a good substitute for these oils. However, current methods of the compression required to make compressed natural gas(CNG) or liquefied natural gas(LNG)

for storage are very expensive [17]. It is economical to pay attention to the storage of natural gases in hydrates because one volume of methane hydrate contains more than 164 volume of methane gas at STP [19, 20] (Standard Temperature and Pressure) and it requires only 15% of the total energy to dissociate [20]. Thus, it is useful to understand how methane-water mixtures behave under pressure.

1.2.2 Methane clathrates

In nature, methane-water crystals called, methane clathrates, form at low temperatures, oxygen poor regions in the seabeds. An example of these "crystals", also called methane hydrates is shown in Fig 3. They are formed when large amounts of methane gas are trapped within a crystal structure of water and form solid crystal-like ice.

These hydrates of natural gas which is mainly methane gas dissolved in water plays an important role in energy development as a potential energy source or stores [20]. At STP, one volume of gas hydrate can generate 180 volumes of gas by dissociation and only 15% of the recovered energy is spent on dissociation[20].

Methane hydrates come to stability at low temperatures and high pressures. They form naturally at the bottom of seas at temperatures ranging from 273-288K and pressures of 2-35 MPa [21]. The detailed effects of pressure and that of temperature on the behavior of methane-water mixtures is the

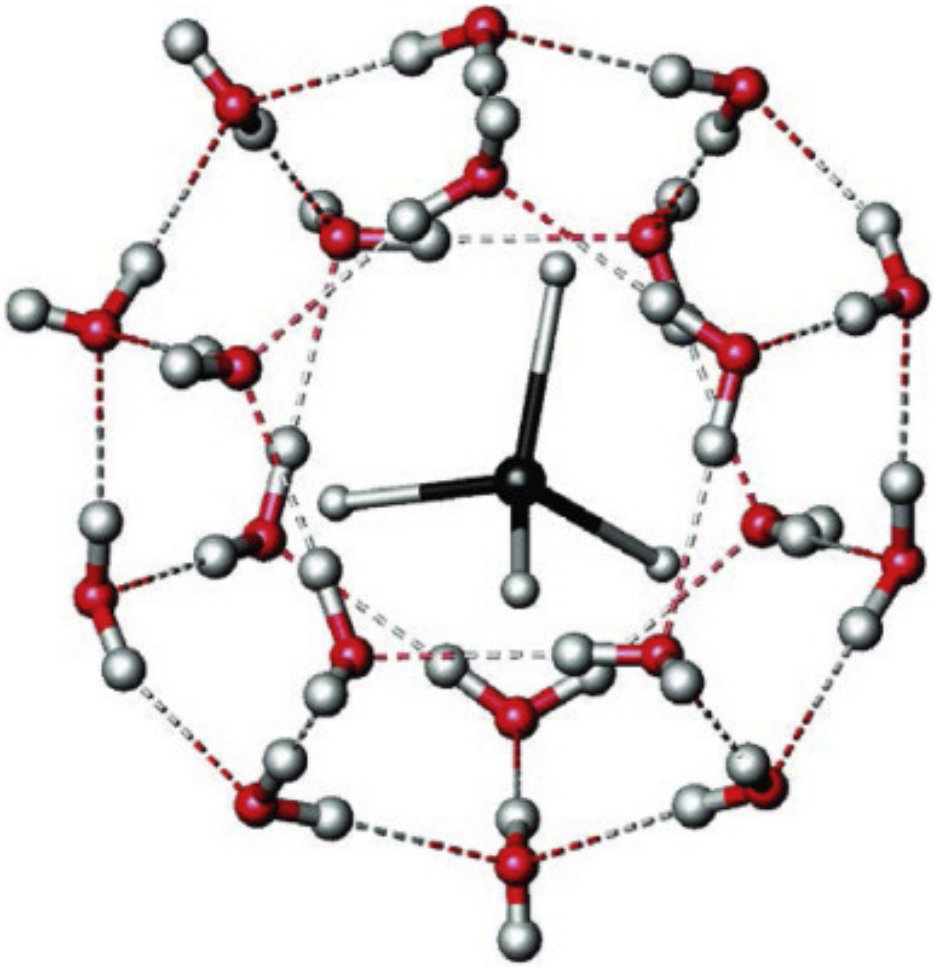

Figure 3: Methane claterate structure. The methane molecules are shown at the center and the dashed lines denote hydrogen bonds [2]

subject of this thesis.

Atomistic knowledge of how methane-water solubility increases with pressure at low temperature and the temperature range of such solubility is a key to studying how extreme pressures modulate the solubility of methane in water. This can help in developing realistic models of the interior of planets. The studies of temperature effects on methane-water solubility at the atomic level are useful for exploiting natural gas storage where methane reacts with water at different pressures and temperatures to produce methane gas hydrate [22]. An effective and inexpensive way to study methane under different pressure and temperature conditions is by molecular simulations.

1.3 Molecular simulations

Computer modeling bridges theory and experiment by solving equations numerically. It models the system and is a tool to verify or predict experimental observations and make predictions. Molecular simulations which fall under computer modeling has statistical mechanics as the basis for studying bulk properties of materials from atomistic defects.

In our study we engaged classical molecular dynamic (MD) simulation to investigate the effect of pressure on the solubility of methane. The used potential was based on an empirical force field (EFF) presented in Ref [23]. The potential used for methane-methane interactions was the optimized potential for liquid simulation in the united atom [24] (OPLSUA) model, the one for water water interactions by the extended simple point charge [25] (SPCE) and methane water interaction by combination rules [23, 26]. The

simulation performed in the pressure ranging from 0.0006 Gpa to 3 Gpa at 215K and 300 K disagree with the experimental observations [10] but shown the methane aggregate under pressure, the same as results from simulation with classical force fields [9].

1.3.1 Molecular dynamics

There are a number of steps to follow in running molecular dynamic simulations. First, the system is set to an initial configuration, for example, by using the gradients of the potential energy with respect to the atomic positions to minimize the potential energy of the system. This gradient of the energy gives the (negative of the) force[27]. There are algorithms which are able to search for the atomic coordinates which gives zero forces. Null forces occur at stationary points (saddle, local maximum, local minimum) of the potential energy surface. The molecular interactions and chemical bonding in a system of molecules are keys to studying the dynamics. The sum of such interactions is potential energy. It depends on all the coordinates in the system. As mentioned above, the force (an atom i) $\vec{f}_i$ is obtained from U by

$$\vec{f}_i = -\nabla_i U \tag{4}$$

In addition to initial coordinates, initial velocities also need to be set. These are drown from a Boltzmann distribution breed upon the derived initial temperature of the system.

1.3.2 The equations of motion

Newton's equation of motion is:

$$\vec{f_i} = m_i \vec{a}_i \tag{5}$$

where $\vec{a}_i$ is the acceleration of particle i with mass m_i. Newton's equation can be re-expressed as:

$$\frac{d\vec{v}_i}{dt} = \frac{\vec{f}_i}{m} \tag{6}$$

where $\vec{v}_i = \frac{d\vec{r}_i}{dt}$

If a particle has an initial velocity, $v_i(0)$, and moves under the action of this force for a time , τ, its new velocity afterwards will be given by:

$$v_i(\tau) = v_i(0) + \int_0^\tau \frac{\vec{f}_i}{m_i}\, dt \tag{7}$$

$$r_i(\tau) = r_i(0) + \int_0^\tau \vec{v}_i(t)\, dt \tag{8}$$

Molecular dynamics is about integrating these equations of motion such that continuous trajectories are obtained numerically. Trajectories for $O(10^{23})$ atoms are hard to track. For this reason, we use periodic boundary conditions to reduce the number of particles to $O(10^2 - 10^5)$ while still mimicking large $O(10^{23})$ system.

1.3.3 Periodic boundary conditions (PBC)

We use periodic boundary conditions, such that a system with a finite size is virtually multiplied infinitely into all directions. From Fig 4, this assumes that a particle on the bottom boundary of the system interacts with the par-

ticle on the top boundary of the system. The same ideal applies for a particle that leaves the system to the top will turn up at the bottom [27, 3]. There are no walls at the boundary of the central box. This type of PBC in which there is no surface effects, use a small number of particles $O(10^2 - 10^5)$ to approximate the conditions of a large system, $O(10^{23})$.

The Eq (9) compute the total energy of the system where N is the number of molecules at any periodic box, L is the lateral dimension of the periodic box and $\vec{n}$ stands for an arbitrary vector of 3 integer numbers, among which the prime over the sum indicates that the term with i = j is to be excluded when $\vec{n} = 0$.

$$U = \frac{1}{2} \sum_{i,j,n}^{N}{}' (|\vec{r}_{ij} + \vec{n}L|) \tag{9}$$

It is important to mention that the boundary of a periodic box has no special significance: the origin of the periodic lattice may be chosen anywhere and it will not affect the properties of the system. Once the equations of motion are integrated and the trajectories are obtained, different system observables can then be computed. One of such is the radial distribution function, RDF, which will be used often in this work.

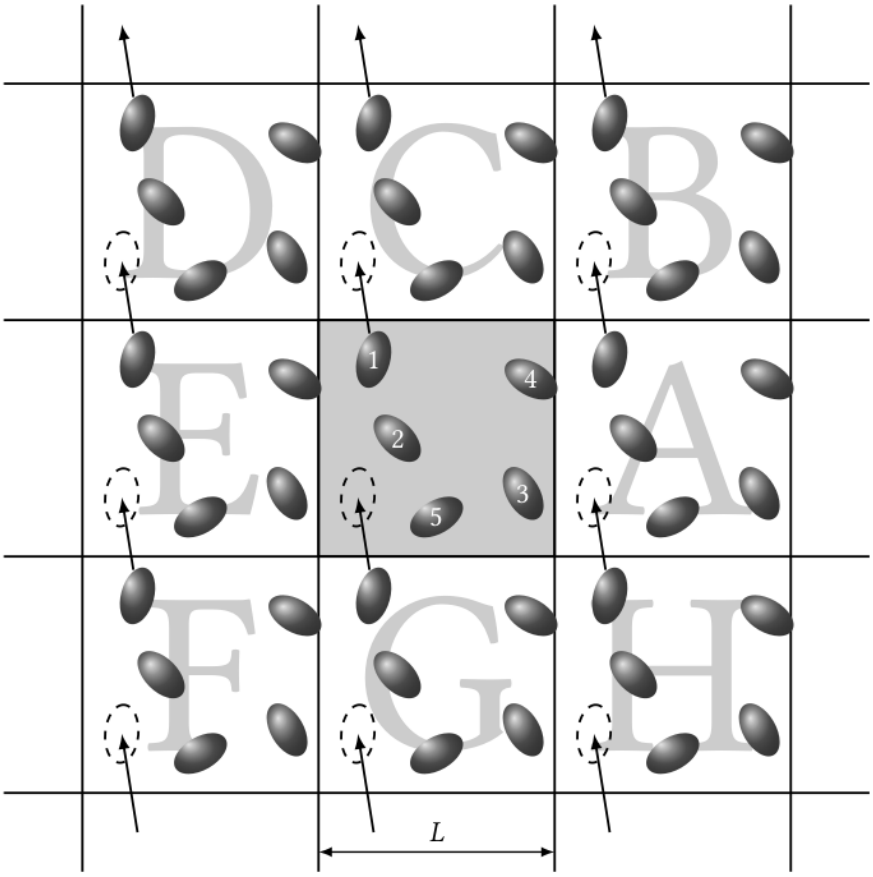

Figure 4: A two-dimensional periodic system. Molecules can enter and leave each box across each of the four edges. In a three-dimensional example, molecules would be free to cross any of the six cube faces [3].

1.3.4 Radial distribution function(RDF)

RDFs plays very important in this study, to analyse our data output. It defined as a probability of finding a particle at a distance apart from a radial particle taken as reference. It is more useful in molecular simulations to show

the peak variations with as the particles goes apart from a targeted one. The RDF is well linked to the function quantifies the average structure of the system; it assumes the pair interactions and, dynamic quantities of the system (diffusion coefficient) [28]. A peak indicates a especially favored separation distance for the neighbors to a given particle. Thus, RDF show detailed information about the atomic structure of the system being simulated [29].

1.4 Aim and objectives of the study

The aim of this work is to determine the change in methane solubility with pressure for different temperature ranges.

Objectives:
To perform molecular dynamics simulations based on available forces field presented by [23].
To compare results with those from ab initio molecular dynamic simulation of Ref [8].
To compare results with those from classical potentials by Pruteanu et al [9].

1.5 Structure of the study

This work is composed of five sections: the first contains the general introduction. The second is a literature review. The third part describes the used methodology for this work. In the fourth, we discuss and analyse the results, and finally, we conclude.

2 Literature review

2.1 Methane water mixture under extreme conditions

Common experience tells us that like dissolves like [8, 30]. It means that polar substances can mix and non polar substances do also, but those of opposite polarity would separate. This is the result of the hydrophobic effect which have been a challenge and later on a topic for many researchers. Thus methane-water mixtures seem impossible yet there exist stable natural gas-water mixtures as clathrate at certain thermodynamic conditions. Several different experiments have been done to prove pressure induced methane-water mixing. These studies are not only for responding to world energy demand (from methane clathrates) but also they are fundamental for understanding different biochemical process such as protein folding, cell membrane formation [8] and other chemical reactions.

To date, it is confirmed that at high pressure and law temperature, methane mingles with water. This follows from the experimental observations by Pruteanu et al [10]. There is a continuous reduction of methane cluster size that favors the decrease of carbon-carbon distance. As pressure increases there is a continuous compression of methane clusters and this combines with water network which is incompressible [10, 30]. However, above a pressure of 1.3 GPa, the methane cluster diameter falls below its critical value and it dissolves into a well connected hydrogen bond network. Physically, there is a balance between the creation of free energy of the system, the free

energy from the increase entropy of dissolution and $P\Delta V$ component from mixed phase. But since all are near pressure independent, this implies that at certain value of pressure, $P\Delta V$ will bring a negative free energy. Thus spontaneous process in the forward direction to form more mixtures.

The experiments carried out by Pruteanu et al [10] using Raman spectroscopy, on methane-water mixtures at 1.3 Gpa and 330 K, showed two distinct fluids but this mixture became homogeneous fluid when the pressure was 2 Gpa and beyond.

Molecular simulations by Hummer et al [31] showed that high pressures remove solutes contact and allow water to mix into the hydrophobic system and attain its stability at minimum volume. These anther formed that, for solvent-separated pair configuration [23] the potential of mean forces between two methane-sized cavities, increasing the pressure provoked solvation of methane.

The simulation of mixture of methane and water with classical force field predict demixing even under high pressure. Thus Ref [9] did not reproduce the experimental observations because the classical intermolecular potential with large molecular dimension does not predict mixing [9].

Abi-initio molecular dynamic simulation [8] showed that at reasonably higher pressure, after 1.3 GPa, the solubility of methane increase to 41(3) mol%. In this simulation, the electronic degree of freedom built in to be fundamental

of computation and it provides for user the choice of system size and simulation times [8]. Thus, ab initio simulations are in qualitative agreement with experiments.

3 Methodology

3.1 Initial configuration

In order to start DL_POLY Classic MD simulations it is necessary to have initial coordinates of all atoms in the system. PACKMOL [32] is such package for constructing initial configurations for further simulations. This consists of providing the geometry and structure of one of each type of molecules in the system.

In this simulation, we chose the ratio of number of water molecules to the number of methane molecules, $\frac{n_{H_2O}}{n_{CH_4}} = 9$. We took 360 water molecules and 40 methane molecules. To calculate the size of the box, knowing the molar mass (M) and the density (ρ) of substance, the volume (V) of one molecule of such substance is given by $V = \frac{M}{N_A \rho}$ and N_A, is the Avogadro's number and is $N_A = 6.02214076 \times 10^{23} mol^{-1}$.

For our system, we have $18 g/mol$ of molar mass and $1 g/cm^3$ of density, the volume of one molecule of water is $3 \times 10^{-23} cm^3$. And methane of $16 g/mol$ and density of $0.4256 g/cm^3$, the volume of one molecule is $6.24 \times 10^{-23} cm^3$. With PACKMOL, we constructed an orthorhombic crystal with two equal sides of 18 Å each and the third of 40 Å. Within this crystal, we have a sphere of 8.4 Å of radius containing 40 CH_4 molecules surrounded by 360 H_2O molecules. The XYZ file obtained from PACKMOL is later transformed into a CONFIG file format to be one of the input files of the DL_POLY simulation program.

3.2 Choice of force fields

There are several force fields available in different documentations. For the simulation done in this work, we used the following available force fields: for methane-methane interaction, the optimized potentials for liquid simulation (OPLS) in the united atom (UA) form developed in Ref [24]. Its Lennard-Jones (LJ) parameters are $\epsilon_{CC} = 0.294 kcal/mol$ and $\sigma_{CC} = 3.73$ Å. The force field for water-water interactions is the SPCE model. This is a three point model with charges on the hydrogen and oxygen of $+0.4238e$ and $-8476e$ respectively. The OH bond length is 1 Å and the HOH angle is 109.47^0 [25]. The Lennard-Jones parameters for this model are obtained from the relation of Lennard-Jones potential expression $V_{LJ} = -(\frac{A}{r})^6 + (\frac{B}{r})^{12}$, given the values of $A = 3.7122(KJ/mol)^{(1/6)}$ Å and $B = 3.428(KJ/mol)^{(1/12)}$ Å [25], and related to the known formula of LJ-potential,

$$V_{LJ} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] \tag{10}$$

thus $\epsilon_{OO} = 0.1553943 kcal/mol$ and $\sigma_{OO} = 3.16555789$ Å. The LJ parameters for carbon-oxygen interaction we obtained by combination rules [23, 26] $\epsilon_{CO} = \sqrt{\epsilon_{CC}\epsilon_{OO}}$ and $\sigma_{CO} = (\sigma_{CC} + \sigma_{OO})/2$ giving $\epsilon_{CO} = 0.2134 kcal/mol$ and $\sigma_{CO} = 3.4478$ Å.

3.3 Detail of simulation procedures

The DL_POLY simulation require mainly three input files: CONFIG, CONTROL and FIELD file to start its running procedure. We performed simulations with detailed different inputs shown in Table 1.

The simulations were carried out in the isothermal-isobaric ensemble at a temperature of 298.15 K and pressure of 1.0000E-04 GPa by applying thermostat and barostat relaxation times of 0.5 ps. The equations of motion were integrated in DL_POLY using the Velocity Verlet algorithm. The system of 40 methane and 360 water molecules were placed in an orthorhombic box of $18\mathring{A}\times18\mathring{A}\times40\mathring{A}$. Periodic boundary conditions and minimum image convention were imposed with the interaction cutoff distance of 7.5 Å. The charges of -0.82e of oxygen and +0.41e of hydrogen were used for water molecule and on the side of methane, -0.00e of carbon and +0.00e of hydrogen were used. The Leonard-Jones potential parameter used are the one calculated in section 3.2. Coordinates, velocities and forces on the interacting sites were saved in REVICON every 0.001 ps in 5000steps.

Finally, the simulations were repeated but with some modifications. The final REVICON file produced used as input CONFIG file for this final simulation carried out in the isothermal-isobaric ensemble at temperature of 215 K, melting temperature of SPCE water model [33] and 300 K and different pressure values ranging in 0.0006 to 3 GPa. The results were saved every 0.002 ps in 275000. The output files are also produced, the most important in our analysis are HISTORY and OUTPUT. The HISTORY file is the record of coordinates, velocities and forces as a dump file. This is used as input file in virtual molecular dynamics (vmd) to visualize the motion of particles. The OUTPUT file contains different sections including simulation control specification and radial distribution functions (RDF) which we plot and use in analysis.

3.4 Quantification of solubility

We calculated the radial distribution function (RDF) to help guide in quantifying solubility specifically. We used RDF data to determine methane-methane and methane-water interaction behavior under pressure increase. The RDF provides the probability of finding a particle at distance, r, away from a reference particle.

Additionally we calculated the running coordination numbers of methane around methane and methane around water up to the first solvation shells. They gives the number of atoms bonded to the central one and are also useful metrics to quantitatively understand whether there is an agglomeration of methane or not.

4 Results

4.1 Pressure effect observations

The objective of this work was to study the effect of pressure on a system of mixed water and methane at different temperature ranges. Our main tool for quantifying the effects of pressure on methane solubility in water is RDF.

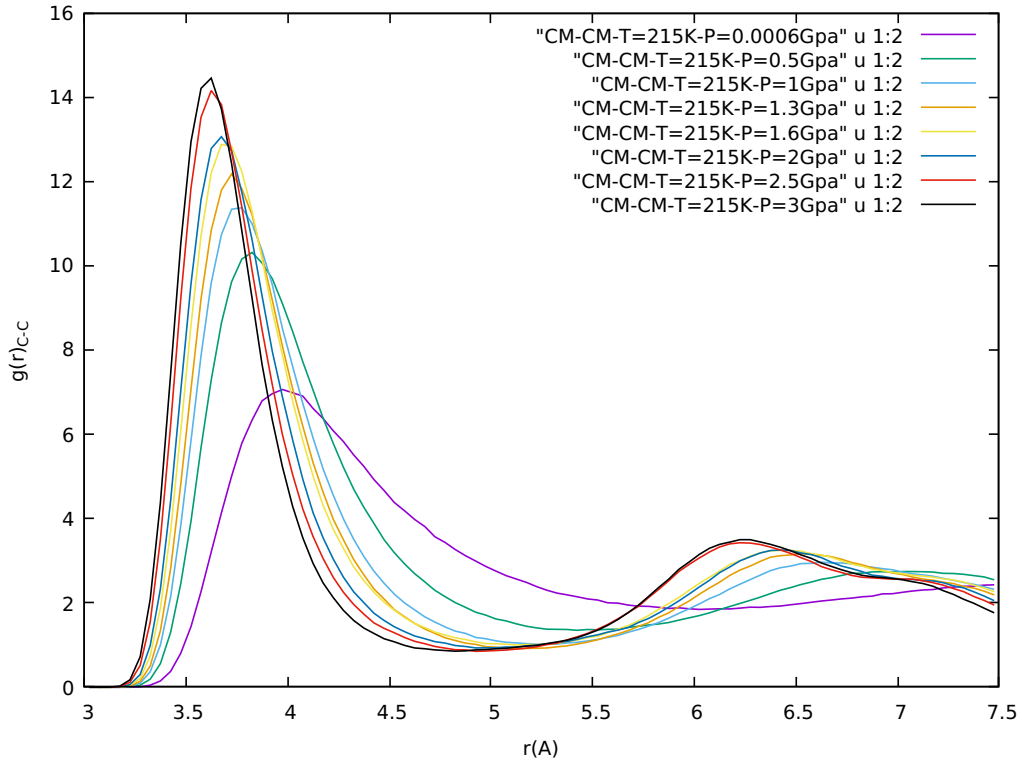

Figure 5: Methane-methane RDF at 215 K for different pressures $\mathbb{P}$

From the MD simulations, we have extracted the radial distribution functions (RDFs), $g(r)_{CC}$ for the correlation of one methane with another methane molecules. This function, $g(r)_{CC}$ is a measure of the probability that an-

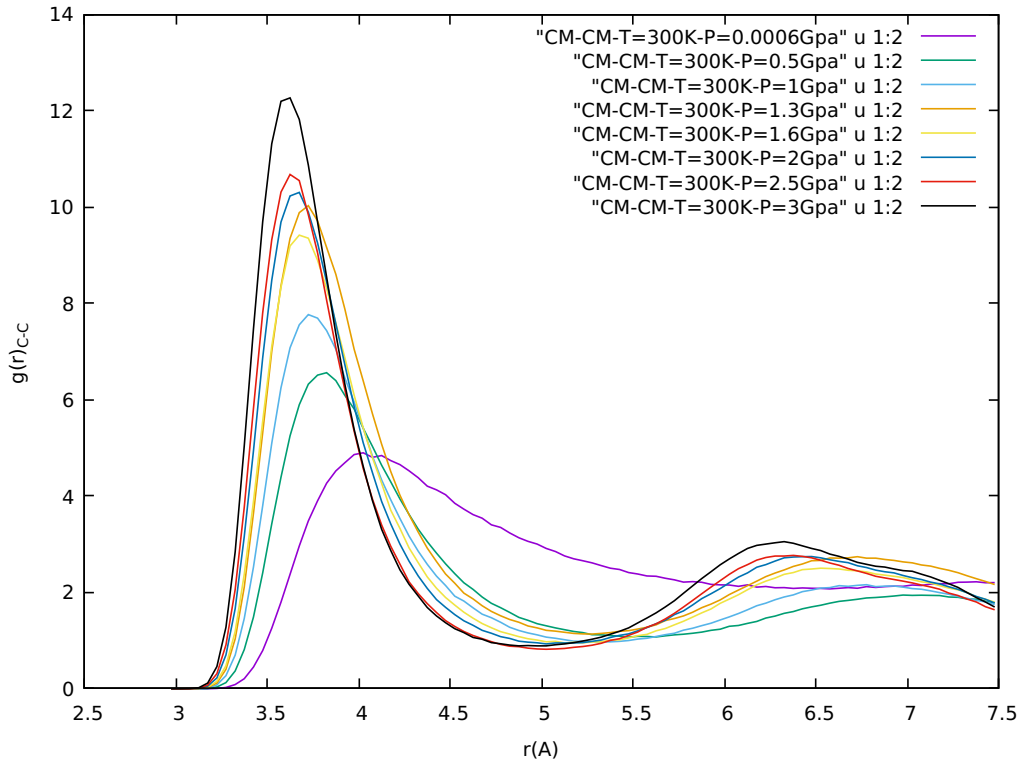

Figure 6: Methane-methane RDF at 300 K for different pressures $\mathbb{P}$

other methane molecule can be found at a distance, r from a given methane molecule. In Fig 5, $g(r)_{CC}$ at the melting temperature (215 K) of SPCE water is shown for different pressures, $\mathbb{P}$=[6×10^{-4}, 0.5, 1.0, 1.3, 1.6, 2.0, 2.5, 3.0] GPa. We observe that the height of the peak of $g(r)_{CC}$ is smallest for the lowest pressure of 6×10^{-4} GPa and increases with increasing pressure. This suggests that methane molecules increasingly "come together" (i.e aggregate) at this temperature as pressure increases. We have also extracted $g(r)_{CC}$ for the same pressures set $\mathbb{P}$ at 300K, Fig 6 which is 85 K above the melting temperature of SPCE water. Again, here, we observed an increase in the height of first peak of $g(r)_{CC}$ as pressure increases.

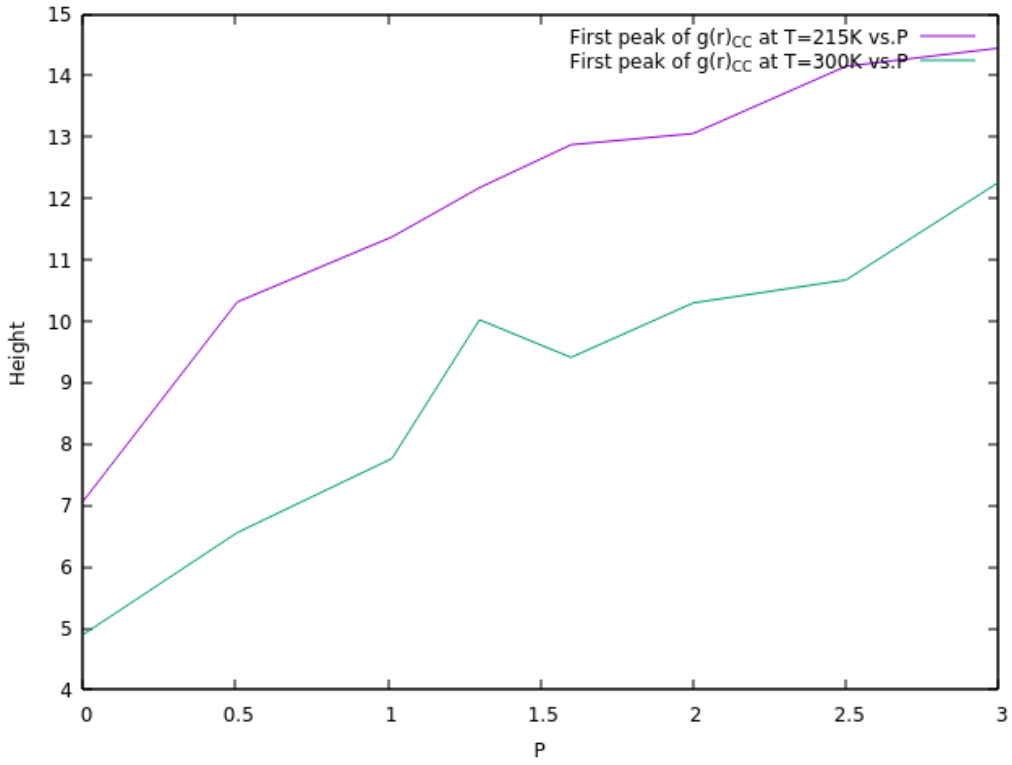

Figure 7: Height of first peak of $g(r)_{CC}$ vs. pressure at 215 and 300 K

In Fig 7, we have made an observation clear by plotting the heights of the first peak of $g(r)_{CC}$ as a function of pressure for both temperatures. We note that this behavior (increasing peak height with pressure) could simply be a result of reduction in system volume as the pressure increases all the molecules come closer together as pressure increase. In order to check this, we have also extracted the RDF for methane-water correlation $g(r)_{OC}$ for different pressures $\mathbb{P}$ at 215 K (Fig 9)and 300 K (Fig 10) and in Fig 8 we show a plot of the corresponding first peak height against pressure. While at 215 K, the heights increases with pressure, this is not the case for 300 K. In order to further investigate, we calculated also the coordination number

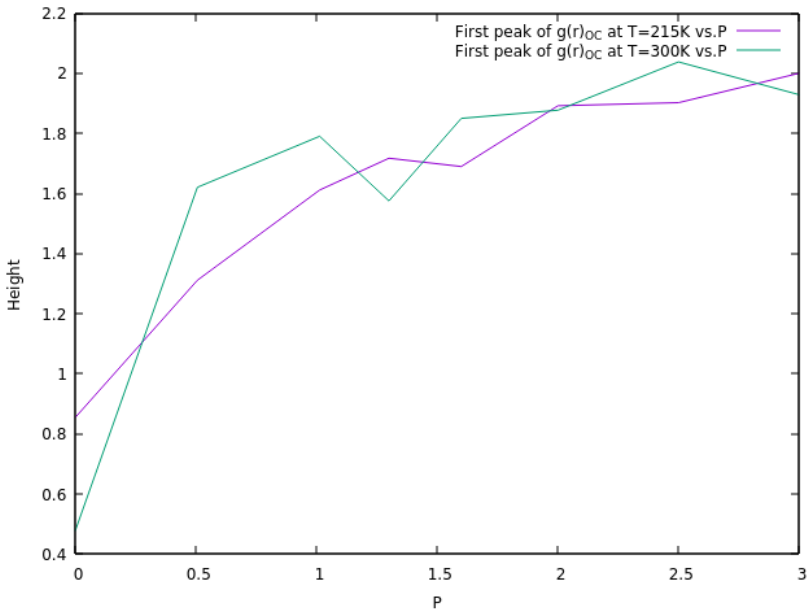

Figure 8: Height of first peak of $g(r)_{OC}$ vs. pressure at 215 and 300 K

$n(r)_{CC}$, is the number of methane molecules within a sphere of radius r centered at the position of a given methane molecules. Fig 11 and Fig 12 show $n(r)$ at 215 K and 300 K, respectively for different pressures. The particles scattering shows the increase of running coordination number of $CH_4 - CH_4$(Fig 11 and 12) and $CH_4 - H_2O$(Fig 14 and 15) with pressure. The number of methane as well number of water molecules surrounding one methane increases with pressure but come to equilibrium around the first solvation shell (Fig 13).

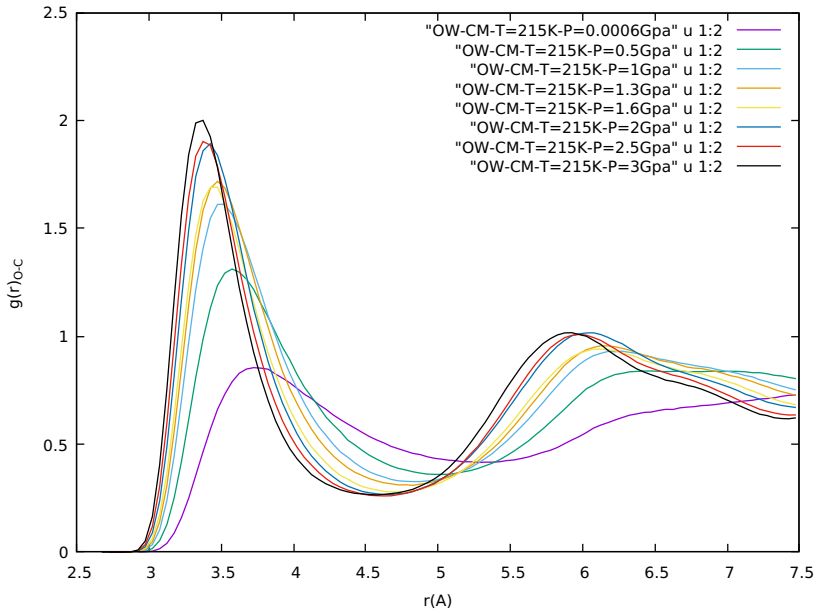

Figure 9: Methane-water RDF at 215 K for different pressure $\mathbb{P}$

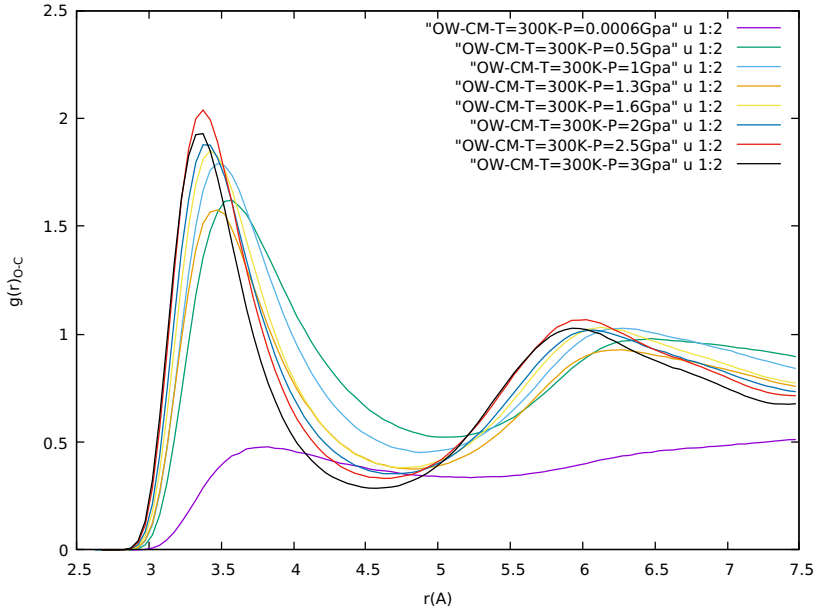

Figure 10: Methane-water RDF at 300 K for different pressure $\mathbb{P}$

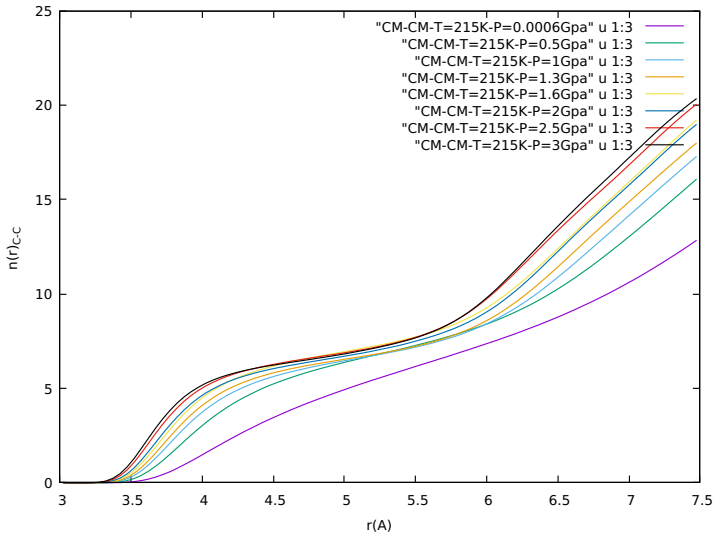

Figure 11: Methane-methane running coordination at 215 K for different pressures $\mathbb{P}$

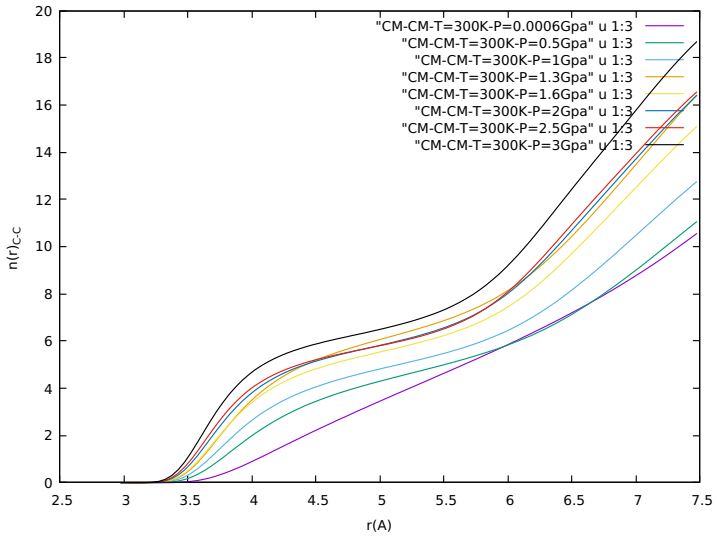

Figure 12: Methane-methane running coordination at 300 K for different pressures $\mathbb{P}$

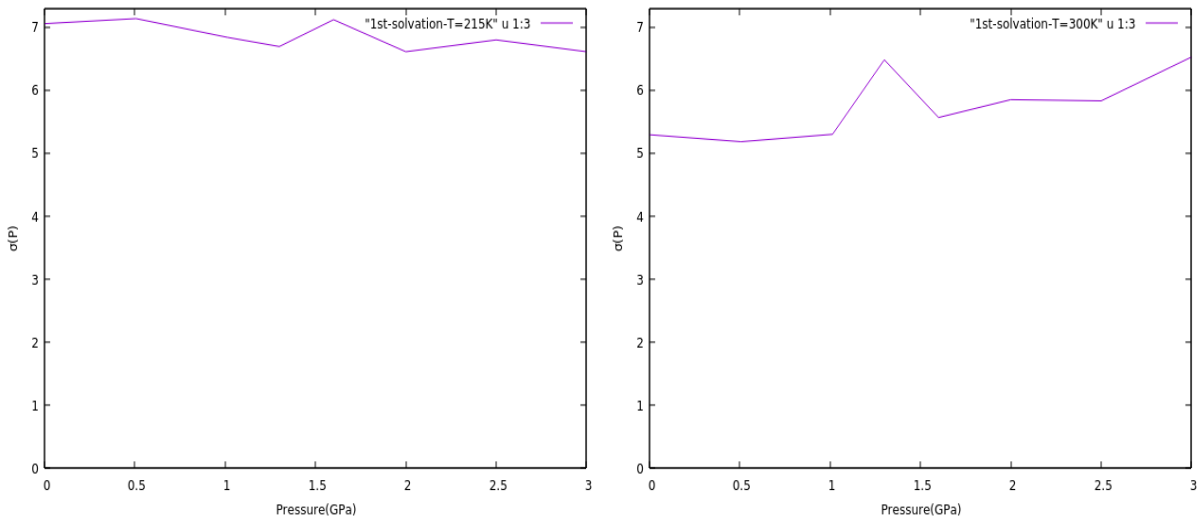

Figure 13: First solvation shell of σ with respect to the pressure

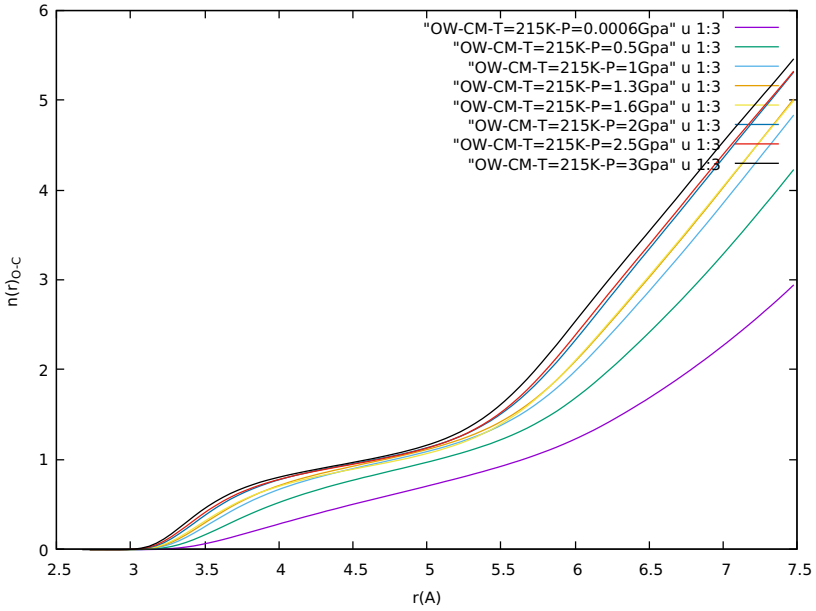

Figure 14: Methane-water running coordination at 215 K for different pressures $\mathbb{P}$

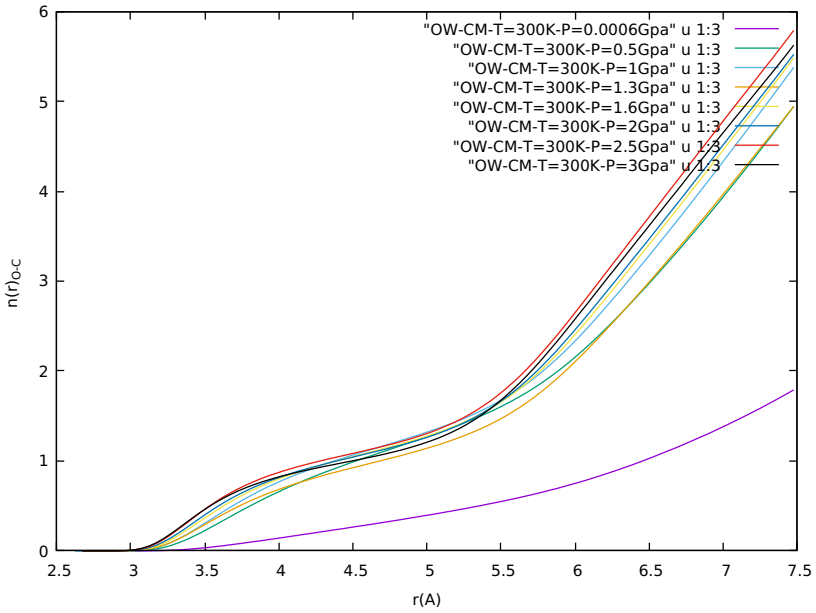

Figure 15: Methane-water running coordination at 300 K for different pressures $\mathbb{P}$

The number of methane molecules surrounding other methane look not to change much with pressure but there is valuation but they change with temperature. Fig 13 shows the difference of temperature effect in solvation with respect to pressure. At temperature of 215K, the number of methane molecules surrounding other methane molecule are valuing around 7molecules while for 300K they value around and much below 6molecules.

4.2 Temperature effect observations

The decrease of interactions between methane molecules and water, methane and water themselves with increasing temperature have shown in this simulation. The temperature increase weaken the particles interaction and induce the the increase of kinetic energy of particles in the system. For the temperature range considered, the effects of temperature on the RDFs/solubilities are not as drastic at the effect of pressure.

The peaks of RDFs calculated shows that methane-methane(Fig 16 top left), methane-water(Fig 16 top right) and also water-water (Fig 16 bottom left) interactions decrease with temperature increase. The running coordination numbers of methane around methane decrease with temperature(Fig 16 bottom right) whereas the number of water molecules surrounding methane molecules remain unaffected with temperature.

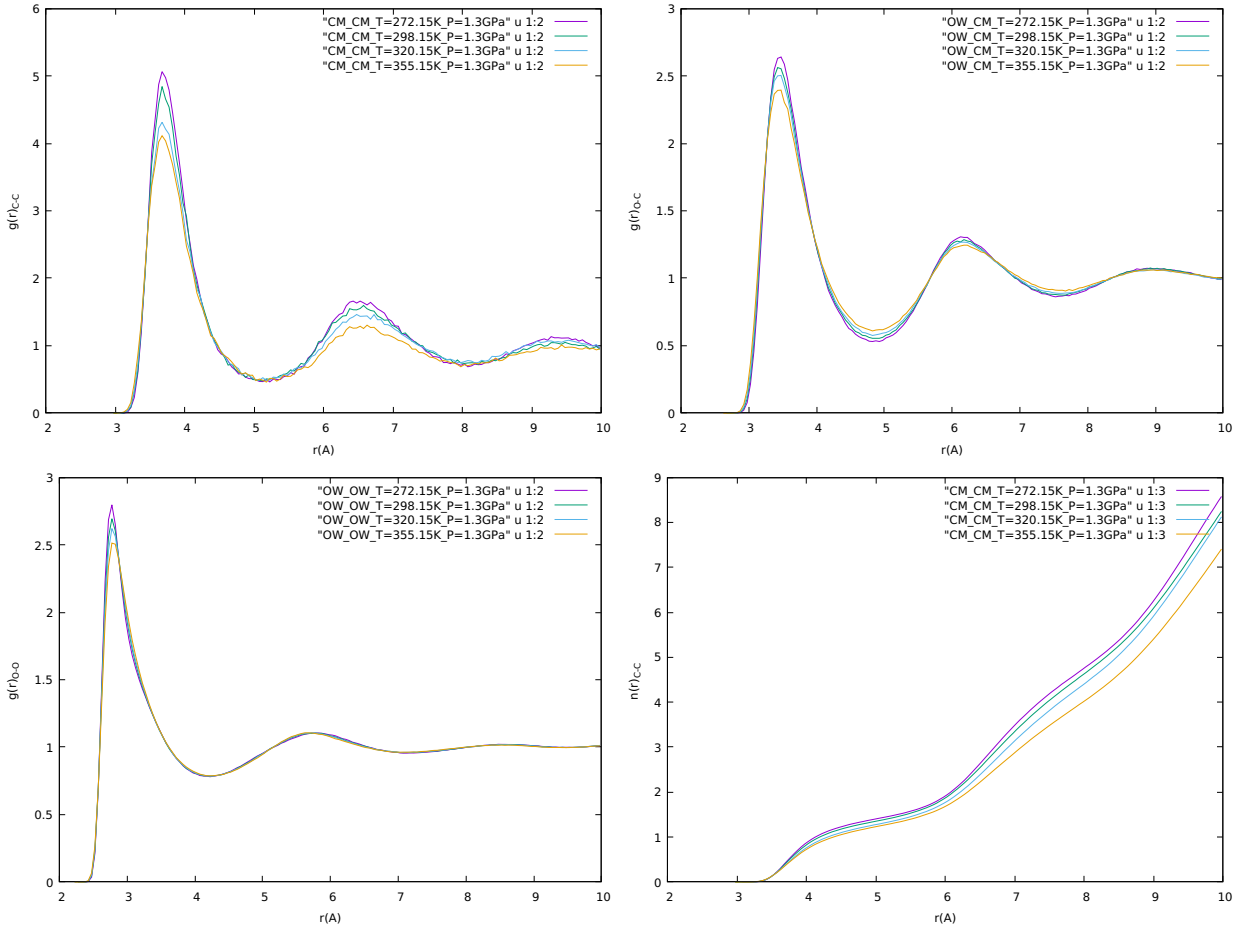

Figure 16: Temperature effect on methane-water mixture at fixed pressure of 1.3GPa

5 Discussion and Conclusion

5.1 Results discussion

The result of simulation using OPLS-UA model for methane and SPCE model for water show that pressure increase on this system induce methane aggregation with some reversal in the hydrophobicity effect. To be more specific on the effect, we simulated using a mixed slab and it end up giving almost the same result as the unmixed(initial configuration) results. Figure 17 (Top figure for methane-methane interaction and bottom figure for methane-water interaction) show the RDFs for mixed slab and in comparison to the results of Fig 5 and 6 for the methane-methane RDFs and Fig 9 and 10 for methane-water RDFs discussed in Chapter 4, the peaks of RDFs increase with pressure either for methane-methane or methane-water interaction.

We found a simply disturbed hydrophobic effect for forty methane molecules in water under pressure. However if we compare with the experimental result in [10] and the ab initio molecular dynamics simulation result [8] where the hydrophobicity of methane depart under pressure up to 44 mol %. Our results are consistant with some recent simulation in Ref [23] that found that methane in water tend to aggregate with the gain in energy. Our result shows that at extreme pressures at low temperature (nearly less than ambient) the methane cluster is surrounded by water.

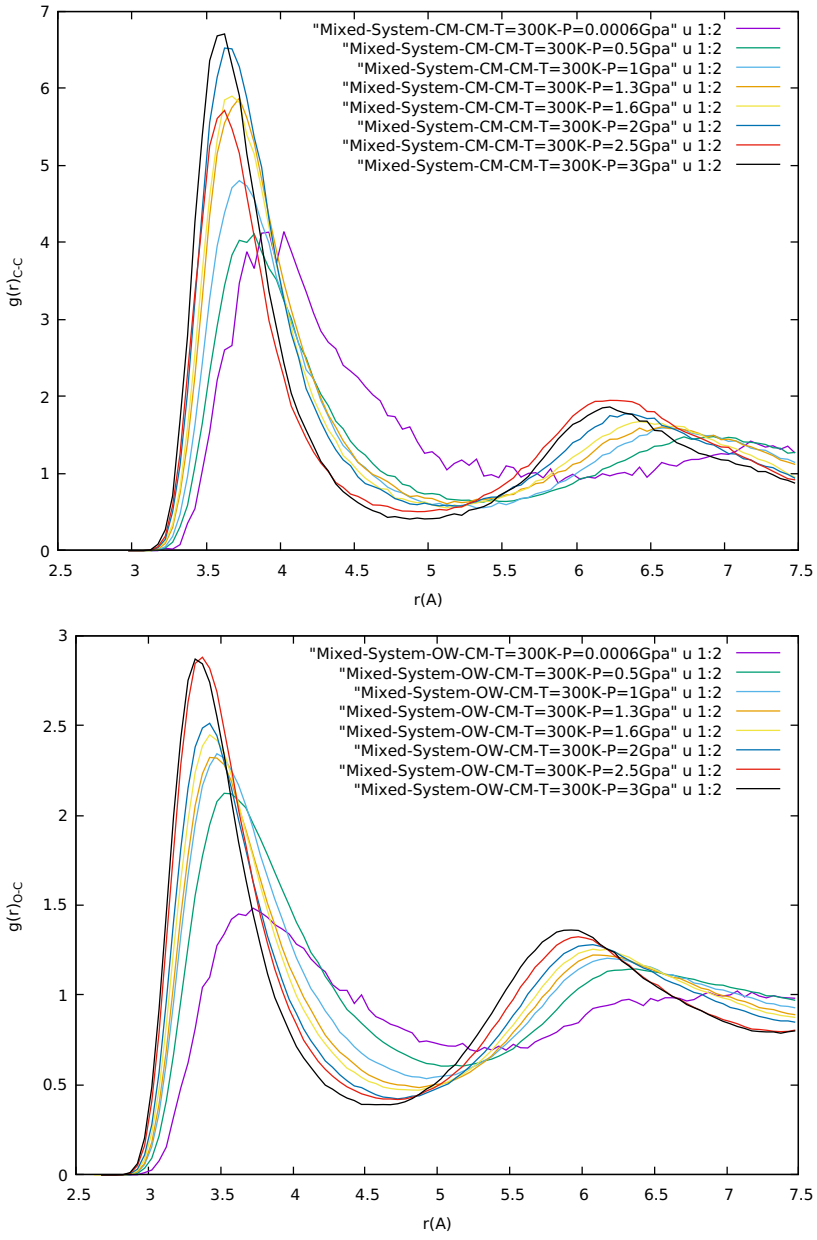

Figure 17: Methane-methane(top) and water-methane(bottom) RDFs increase with pressure. The calculations from initially mixed slab

5.2 Conclusion

We have performed DL_POLY Classic simulation using OPLS (United Atom) model for methane and SPCE for water model for a mixture of 40 methane in 360 water molecules. We presented different calculated radial distribution functions and the running coordination numbers. The results shown that H-bonding remain maintained with the increase of pressure. The increase of methane-methane coordination numbers indicate the agglomerations of methane in the system. And the phase separation of methane and water can be shown by the increase of methane coordination number.

The expected mixing would caused by the change of H-bonding and dipole moment under pressure where the squeeze may change the relative molecular volume of methane to compress it into stable water H-bond network. The local environment may also charged to have a significant effect on methane potential. Our results disagreed with the experimentally observed results, hence, disagreed also with those obtained by ab initio force fields. But, the results from our simulation agreed with those calculated by classical force fields where pressure induce methane aggregation. The compressibility of methane-water mixture at higher pressure does not induce polarizability effect in our modeling.

6 AppendixA

Number of CH_4 molecules	Number of H_2O molecules	Box shape	Box size (Å)	Kind of slab (Initial configuration)	Simulation time (Ps)
10	200	Cube	18	un mixed slab	500
20	400	Cube	24	un mixed slab	500
20	400	Cube	24	un mixed slab	500
40	360	orthorhombic	18, 18, 40	un mixed slab	550
40	360	orthorhombic	18, 18, 40	un mixed slab	550
40	360	orthorhombic	18, 18, 40	mixed slab	100

Table 1: A table with all simulations and details

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