DROPLET VAPORIZATION OF N-HEPTANE USING MOLECULAR DYNAMICS

A Thesis in
Aerospace Engineering

by

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ABSTRACT

The vaporization of an n-Heptane (C₇H₁₆) droplet is investigated using Molecular Dynamics (MD). This work is one of the first MD droplet vaporization studies done on a polyatomic molecule. Inter-molecular and intra-molecular forces are incorporated using the Lennard-Jones 12-6 potential. Due to the polyatomic nature of C₇H₁₆, a torsional potential, which is a function of an internal dihedral angle, is also included in intramolecular force calculations. During each integration step the structure of the molecule is maintained by constraining bond lengths and bond angles iteratively. The RATTLE method, a variation of the Velocity Verlet algorithm is implemented to maintain the constraints and advance the system through time. The system is initialized in a BCC lattice with each molecule in a helical structure and is allowed to evolve into a random arrangement, using velocity rescaling to ensure that the kinetic and internal temperature is maintained in this initial period. This rescaling is continued until the simulation has reached thermal equilibrium. Due to the high computational costs of vaporization a polyatomic molecule using MD, a parallel implementation of the system has been developed. Four simulations were done on systems of 1500 and 3000 molecules under pressures of one and two atmospheres. In all cases the droplet was initialized at a temperature of 293 K and the vapor initialized at 471 K. Results of the thermal relaxation and droplet vaporization of these systems are presented. Cross-sectional contour plots were created for each case, looking at the translational and internal kinetic energy as well as the average forces acting within the droplets. The evaporation rates were analyzed based on the Amsterdam method to determine the size of the droplets. All
four simulations adhered to $D^2$ law behavior with the higher pressure cases vaporizing at a rate nearly twice as fast as the lower pressure cases. This work provides a foundation on which future polyatomic, in particular hydrocarbon, droplet vaporization studies can be done.
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Chapter 1
INTRODUCTION

Droplet vaporization is a topic of significant interest in the development of chemical propulsion systems, such as rockets, jet engines, and internal combustion engines. To maximize the efficiency of a combustion process one wants to maximize the mixing of the constituents through atomization [13]. To maximize this mixing it is necessary to know the properties of the two phase system. For this reason droplet vaporization is of interest. In particular knowledge of the vaporization process in an environment where the temperature and pressure conditions exceed the critical values of the individual chemical species forming the mixture has been under extensive investigation [4,10,37,51]. However, the attainment of the critical condition at the gas-liquid interface and the progression of the equilibration process beyond this point are not completely understood. Difficulties arise from the appearance of cross terms in both the mass diffusion and heat fluxes, known as the Soret and Dufour terms [12,46]. Additional problems arise due to the anomalous behavior of the thermal-physical properties near the critical regime [22].

One way to avoid the difficulties mentioned previously is to employ Molecular Dynamics (MD) to simulate the phase-change process in the thermodynamic critical regime. This approach can also provide a means to calculate the anomalous behavior of the thermal-physical properties and hence can supplement the traditional continuum approach. Under MD, the vaporization process is calculated directly by solving the equation of motion for a suitable set of molecules representing the liquid droplet and the
surrounding gas. All that is needed to perform a MD simulation are the interaction potentials acting between the molecules [1], and any polyatomic constraints due to chemical bonds. This allows one to bypass the problematic transport coefficient predictions and thermodynamic behavior in the critical regime.

This work seeks to use MD to simulate an n-heptane droplet vaporizing. N-heptane was chosen as it is typically used as a model for diesel fuel. Simulating this molecule is unique in the fact that droplet vaporization of a polyatomic molecule has yet to be looked at using molecular dynamics. It is beyond the scope of this work to vaporize a droplet of n-heptane in a critical environment. Instead a model is put forth for simulating droplet vaporization in a subcritical environment. This first step presents a foundation on which further studies of hydrocarbon droplet vaporization can draw.

1.1 Literature Review

Droplet vaporization in an environment where the temperature and pressure conditions exceed the critical values of the individual chemical species forming a multicomponent mixture has been a subject of extensive investigation over the past two decades. Some of this work is documented in the review articles of Givler and Abraham [10], Bellan [4], Yang [51] and in the text by Sirignano [37]. In addition, the vaporization process in the sub-critical environment is understood quite well as the result of numerous studies. Rather than presenting this extensive body of work in detail, a more limited review of droplet vaporization consisting of molecular dynamic studies will be presented. Additionally, relevant MD studies of hydrocarbon systems will be mentioned.
1.1.1 Droplet Vaporization

Before vaporization studies, an MD study was done by Thompson et al. to look at the effects of surface curvature on small droplet properties [45]. This work showed that liquids drops could be simulated with the Lennard Jones (LJ) potential [19]. The LJ potential was cutoff and shifted at a distance of $2.5\sigma$, where $\sigma$ is the hard sphere diameter of the molecule in question. The size of the droplet systems ranged from 54 to 2048 molecules consisting of both liquid and vapor. Density profiles as well as the normal and tangential pressure tensors were calculated as a function of the distance from the droplet center. From these quantities the surface thickness was also calculated. These results were compared to theoretical calculations to check their applicability. Two methods the Cornell and Oxford definitions were used to calculate whether or not a molecule was part of the droplet. With these simulations the results of the pressure calculations were uncertain near the center of the droplets as a result of their small size.

The results of this early droplet study along with others [28, 31, 45] were a stepping stone to the vaporization studies done later. The first MD study of droplet vaporization was done by Long et al [21] in 1996. This vaporization study looked at argon vaporizing under sub-critical conditions. This study also used the LJ12-6 potential for the calculation of interatomic forces. The two phase system studied consisted of 2048 argon atoms at 78 K in a single drop surrounded by vapor. In this simulation the time step chosen was small to avoid errors and maintain stability based on (1).

$$\Delta t = 0.005 \sqrt{\frac{m\sigma^2}{\epsilon}}.$$  (1)
For argon this value was roughly 10 femtoseconds. This system was vaporized by raising the temperature of the vapor near the boundaries until only argon gas remained. The computed evaporation rate agrees with those predicted by the Knudsen theory. The Knudsen number is the mean free path divided by the droplet radius. The density profile of the droplet matched well with known results [45].

The study by Long et al in 1996 was followed by a simulation of liquid oxygen vaporizing under super critical conditions. This study was done in 1998 by Kaltz et al [14]. This simulation took MD studies of droplet vaporization a step further by looking at a diatomic molecule instead of just a monatomic system. In addition to this the droplet was put into a vapor environment of either hydrogen or helium. Calculations were performed for pressures ranging from 2 to 20 MPA and temperatures ranging from 200 K to 300 K. Eight simulations were performed with three vaporizing in a hydrogen environment and the rest in the helium environment. Calculation of the Knudsen number was done to determine whether it was a continuum or aerosol regime. For this simulation a time step of 2.5 femtoseconds was used. The size of these simulations ranged from 4900 to 9300 oxygen molecules in gas environments ranging from 16,000 to 35,000 molecules.

The results showed that there were significant differences depending on the pressure of the environment. At low and moderate pressures the droplet remained spherical until the droplet had vaporized. A distinct density profile was also observed for these pressures. In the case of higher pressure the droplet had similar characteristics to the low and medium pressure cases initially. However, there was a transition point where the surface tension disappeared resulting in a non-spherical shape to the droplet.
These results showed that because of the extremely high pressures required to cause this transition, the approximations often taken from sub-critical phase behavior and used in supercritical models might be valid predictions if the pressures are moderate enough. Additionally, support for this argument was provided by temperature histories which showed that above critical pressure the droplet temperature attained a constant value and remained there during vaporization. It was noted that hydrogen or helium molecules mixed into the droplet even at moderate pressures.

Also in 1998 another study was done on the evaporation of a sodium droplet by Bhansali et al. [6]. This simulation used the LJ12-6 potential used in the previous studies. A system of 864 sodium molecules was used with a 5th order Gear predictor corrector method used for the advancement of the equations of motion each time step. The study first validated the model used by comparing data for the reduced potential energy and the reduced viral pressure to published data. It was also compared to a simulation performed by Haile [11] for a reduced density of 0.6 and reduced temperature of 1.54. The thermal characteristics of the sodium droplet were looked at as it evaporated. The bulk liquid density, vapor density, vapor pressure, surface tension, and interfacial surface thickness were calculated with respect to the temperature. The results showed similarities to previous studies however the surface tension of this liquid metal did not reveal a comparison to macroscopic limits as found for argon, an insulator. This lack of a comparison was attributed to the lack of ion screening effects being accounted for in the LJ12-6 potential.

After this study there were several more studies that were done on argon. The first of which was done by Walther and Koumoutsakos in 2001 [49]. This particular
argon simulation looked at sub-critical evaporation of a droplet at 300 K and 3 MPa. In this simulation tens of thousands of molecules were simulated. A study was done to determine the influence of the different parameters imposed by the numerical method. The size of the domain, the cutoff radius for the LJ potential, the droplet diameter, the frequency of heating, the size of the heating region, time step size and the initialization period. Using this large simulation size it was shown that the $D^2$ law for the vaporization of the droplet was obeyed. Additionally, instantaneous density and temperature profiles were presented.

In 2003 another study was done by Consolini et al. [8] on the vaporization involving Xenon droplets vaporizing in a nitrogen environment. This simulation looks at both spherical and non-spherical droplets under both sub-critical and supercritical conditions. An LJ potential is used for the Xe-Xe interactions as well as the N$_2$-N$_2$ and the N$_2$-Xe interactions. Like other simulations there was a heating stage in which vaporization was slow. After this there was a fairly constant liquid evaporation phase. For the sub-critical cases it was shown that the spherical droplets maintained their sphericity where as for the non-spherical droplets, they become spherical after vaporizing 10%. In the case of supercritical vaporization the droplets never returned to spherical symmetry. Instead rapid deterioration was observed as the temperature increased during vaporization. The study also concluded that the vaporization process associated with these submicron simulations is analogous to the vaporization of macro size droplets.

A further study on droplet vaporization using the Lennard Jones potential for argon was published by Sumardiono and Fisher in 2006 [41]. This study looked at the vaporization of a droplet under transient conditions first within a vapor composed of the
same particles and then vaporization was looked at in a vacuum. Three methods for calculating the number of particles in the droplet were discussed. The Cornell and Oxford methods previously mentioned followed by the Amsterdam method which was similar to the Oxford method. The calculations of hydrodynamic quantities was explained. The density profiles, drift velocity, the radial, tangential and total temperature and the mean kinetic energy per particle are presented as a function of radial distance from the center of the droplet and the evaporation time. In addition to the transient cases several simulations were done with adiabatic pressure jumps. It was shown that the final temperatures of each system were reasonably estimated based on the first law of thermodynamics. It is suggested that this study gives new insight into the evaporation of a droplet under a transient pressure jump. It was stated that larger simulations should be looked at in the future along with mixture droplets to better understand steady state evaporation into a vacuum.

The most recently published work was that of Landry et al in 2007 [16] which also looked at argon evaporation. Simulations were done for a wide range of temperatures with transitions from sub-critical to supercritical for varying Knudsen numbers. A technique was introduced for maintaining a constant ambient pressure. This was done to allow the investigation of the effects of different ambient conditions on the behavior of the droplet vaporization process. While the ambient pressure was less than the critical pressure the system was sub-critical and a pseudo bulk temperature was reached on the droplet surface. At supercritical conditions above this pressure the surface temperature remained transient for the entire vaporization process. It was found that the droplet diameter decreased linearly with time for an initial Knudsen number of 1 and a
low ambient pressure. At moderate pressure the square of the droplet diameter decreases linearly with time for a Knudsen number of 0.1. However, the $D^2$ law behavior of the evaporation constant is not observed due to too high of a Knudsen number to consider it a continuum vapor. Finally, it was observed that the rate of atoms leaving the droplet was constant over almost the entire droplet lifetime at high ambient pressure.

1.1.2 Polyatomic Hydrocarbon Systems

There were several polyatomic studies done using MD that were relevant to this study of n-heptane, which is a hydrocarbon and is part of the alkane family. The first group of alkane studies that will be discussed are all put forth by Ryckaert et al. The first one was published in 1977 [33]. This simulation involves the numerical integration of the equations of motion for alkanes, in particular n-Butane. This simulation looked at 64 n-Butane molecules. Its major contribution is the development of what is known as the SHAKE algorithm. This algorithm was developed to allow one to deal with the bond angle and bond length constraints present in alkane molecules. It uses the Verlet algorithm [48] for advancing the positions and velocities to the next time step. It then adds in LaGrange multipliers to deal with the Geometric constraints. A similar method will be discussed in the following chapter. This integration method is then used to model n-butane molecules with Cartesian coordinates. For this study C-C bonds were simulated using a bond length of 1.53Å and the C-C-C bond angles were set to 109.28°. This was done to compare the effectiveness of the SHAKE algorithm with integration using generalized coordinates and a Gear algorithm [30].
In 1978 Ryckaert and Bellemans [32] extended the study of alkanes using this SHAKE method. This paper looks at both n-butane and n-decane. The same bond length and angle parameters are used from the previous simulations. Lennard Jones parameters $\sigma$ and $\varepsilon/k_B$ are given as 3.923 Å and 72 K respectively. Something known as the united atom model, which groups each CH$_2$ and CH$_3$ monomer into single point mass systems rather than treat each carbon and hydrogen separately, was used in these simulations. A torsion potential is also presented similar to the one that will be discussed in the next chapter. The simulations were done to look at the internal relaxation of the chain molecules and to show that the simulation of dense systems of chain molecules is feasible. Trans and gauche conformations were looked at with the torsion potential presented. In 1985 Ryckaert [34] presented another iterative procedure based on SHAKE to look at a ring alkane, cyclo-tetradecane(C$_{14}$H$_{28}$).

Many additional studies have been done on n-Butane. One of these by Weber in 1978 [50] looked at simulating this alkane from fluid densities ranging from 288.80 to 721.99 kg/m$^3$. Similar to the work done Ryckaert, Weber used the united atom concept for each CH$_2$ and CH$_3$ group. However, instead of having rigid bond length and bond angle constraints, bond stretching and angle bending vibration was allowed. It was suggested that this increased the linear self diffusion of fluid. Trans and gauche torsional relaxation was also looked at. It was noted that results agreed well with experimental and simulation data. The torsion potential was again investigated by Steele [40] in 1985 for n-Butane. This simulation treated every bond including the C-H bonds rather than group them into “united atoms” as was done in previous studies.
Edberg et al [9] did a study looking at the differences between the SHAKE method and the matrix method for solving constraints in alkanes. The results are compared for simulations of butane with earlier work done on alkanes by Ryckaert et al. and Wielopolski et al. An algorithm was developed similar to SHAKE and the matrix method of Ryckaert et al. using holonomically constrained equations of motion. A bond length of 1.53 Å and bond angles of 109.47 degrees were used along with the 12-6 Lennard Jones potential truncated at 2.5σ with σ =3.923 Å and ε/κ_B =72 K. The vibrational degrees of freedom are considered frozen for this simulations. The holonomic bonding constraints look very similar to the constraints in SHAKE. They use a matrix method to solve for Gaussian multipliers. The simulation is started in a face centered cubic (fcc) lattice with all dihedral angles trans. Runs of at least 50ps, which is long enough to approach trans-gauche equilibrium were done, where the pressures and intermolecular and total energies relax after about 20 ps. The results discussed trans gauche conformational equilibrium

It is worth mentioning studies done by Lee et al. in 1996 [17] and 1997 [18] on a variety of thermodynamic and structural properties of liquid alkanes including viscosity, thermal conductivity, and self-diffusion coefficients. While there are many other alkane simulations that have been done, the ones mention above were the most useful for our simulations of n-heptane. In the following chapter some of the methods mentioned above will be discussed in more detail for our model of n-heptane.
1.2 Problem Definition

In order to better understand the vaporization process of droplets, MD methods are being employed to look at the process on the molecular level. As was documented in the previous section there has been some work in droplet vaporization using MD over the past decade. These studies have laid down the foundations of droplet vaporization research using the MD method. The next step is to start looking at more complex molecules than the monatomic and diatomic cases investigated so far. It is for this reason that this work focuses on the vaporization of a hydrocarbon droplet. Hydrocarbon fuels are used in a wide variety of applications and understanding the vaporization process of these kinds of droplets, particularly in the supercritical environment is of interest.

Common hydrocarbon fuels such as diesel or gasoline do not consist of just species of hydrocarbon. However, as this is a first step into the study of hydrocarbon droplet vaporization, a single species hydrocarbon droplet was chosen. For these simulations n-heptane was used as it is a major component of diesel fuel in particular and is often used as a simplified version of the fuel in continuum studies. While the ultimate goal or motivation of this work is to study hydrocarbon droplets in the supercritical regime, the objectives of this work were to develop a working MD model of n-heptane and to then vaporize this droplet in a sub-critical environment with n-heptane vapor. The goal is to present a working model of hydrocarbon vaporization that can be used in the future for supercritical vaporization studies.
The proceeding chapters will present the model, as well as the process by which the droplets were vaporized, and the results of the vaporization process. The n-heptane molecule will be presented along with the algorithm used to apply the equations of motion. Following this, a method for controlling the temperature and ways of improving the efficiency of the simulation are documented. Then results are presented on first single phase systems followed by the multiphase vaporization simulations. Finally, some conclusions and future work are discussed.
Chapter 2

N-HEPTANE MODEL

The modeling of a system of n-heptane molecules requires first and most importantly an adequate model of the molecular structure along with the associated bonds. Secondly, the forces that act within each molecule as well as between different molecules must be defined. And finally, a systematic way of applying these forces while still maintaining any molecular constraints must be used.

2.1 Molecular Representation

The most accurate model of an individual molecule would model every single atom present in each molecule along with all of the bonds associated with each atom present. To have the most accurate model it would be required that one use a quantum mechanical formulation of the bonds to account for the vibrational modes present. While this would be the most ideal way of representing the molecules it is not practical from a numerical simulation standpoint. If one were to use no simplifications the computation time would be so large that simulating any significant system would become impractical. In order to simulate a meaningful system several simplifications are used that still allow a fairly accurate description of the molecular properties important to this simulation. For this simulation of n-heptane a “united atom model is used along with classical
formulations for the bonds associated with each atom in the molecule, due to the relatively low energy present in the system at the temperatures considered. There is not enough energy to excite the vibrational modes out of the quantum ground state allowing one to treat them in a classical fashion [29].

2.1.1 United Atom

The model of n-Heptane used in this work is based on the “united atom” concept, which groups each CH$_2$ and CH$_3$ monomer into single point mass systems as shown in Fig. 1

![Fig. 1: A CH$_3$ group treated as a point mass](image)

The primary reason for doing this is to simplify the simulation by reducing the number of computations and interactions that are necessary. In order to insure that these united atoms behave similar to the monomers they represent, their bond lengths, bond angles, torsion forces, as well as the $\sigma$ and $\varepsilon$ parameters of the intermolecular potential must be properly determined based off of empirical data. While this model doesn’t allow one to study some of the internal properties of the molecules, it does allow for much faster
simulation times and is therefore widely used in MD simulations. It is assumed that this approximation is accurate enough as the site-site interactions between each methyl or methylene group should be the same [27]. Also it has been shown in several studies that accurate results are still obtained for thermodynamic properties and some internal structural properties using this approximation [9,17,18,24,27,32,50].

2.1.2 Geometrical Constraints

In molecules individual atoms are bonded to each other through chemical bonds, which are simply inter-atomic potential energy terms. Ideally, it would be best to treat all aspect of chemical bonding using quantum mechanics; however this has been too difficult to accomplish so far[1]. Instead molecules are often treated as rigid or semi-rigid systems. This is done by constraining the bond lengths and in some cases the bond and torsion angles between monomers. The model we used constraints both bond lengths and bond angles, while leaving torsion angles free to evolve based on a torsion potential. The torsion potential will be presented in detail in the following section. For the case of n-heptane with a united atom model the bond lengths used were 1.53 Å and the bond angles were set at 109.47° [9]. All of the parameters associated with n-heptane that were used are presented in Table. 1.

Table. 1: LJ interaction parameters and molecular constrainst for the n-Heptane molecule.

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Bond Angle</th>
<th>σ</th>
<th>ε/kB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.53 Å</td>
<td>109.47°</td>
<td>3.932 Å</td>
<td>72.0 K</td>
</tr>
</tbody>
</table>
The bond angles were constrained similar to the bond lengths, but instead of constraining the distance between two adjacent monomers, the length between every other monomer (for example: monomers 1 and 3) is constrained to the proper bond angle distance. A skeletal model of n-heptane is formed by applying these bond lengths and bond angles to each monomer, which can be seen in Fig. 2.

![Fig. 2: Constraints applied to n-heptane. Bond angles $\phi$ are maintained by constraining the distance between next nearest monomers.](image)

### 2.2 Force Calculations

Molecular dynamics is based on Newton’s Second Law, $F=ma$. By calculating the force exerted on an individual atom or monomer, one can track the motion of that particle. In this particular simulation of n-heptane there are both intermolecular and intra-molecular forces acting. These forces are calculated through two potentials, the Lennard Jones (LJ) potential and a torsional potential.

The LJ potential is applied to all intermolecular interactions. Within a given molecule the LJ intra-molecular interaction is limited to pairs of monomers that are not constrained to each other by either bond length, bond angle, or through torsion forces. By
contrast the torsion potential and its resulting force is only an intra-molecular event applied internally in each n-heptane molecule.

2.2.1 Lennard Jones Potential

The inter-atomic forces acting on a particle can be modeled in a variety of ways. These inter-atomic forces are based on the potential energy of the interacting particles. In general the potential energy can be calculated as follows in (2).

\[ E_{pot} = \sum_i u_1(r_i) + \sum_{i \neq j} u_2(r_i, r_j) + \sum_{i \neq j} \sum_{k > j > i} u_3(r_i, r_j, r_k) + \ldots \] (2)

The first term represents the effect of an external field, while the remaining terms represent particle interactions [35]. In most MD simulations only two body interactions are calculated. This is primarily due to the fact that 3-body interactions and above require extensive computation time and the two-body interactions account for nearly all of the energy in most cases. In the case of solid argon it has been found that 3-body interactions account for nearly 10 percent of the potential energy. It can be assumed that in the liquid and gas phases those 3-body interactions could conceivably account for almost as much of the potential energy. For this reason 2-body interactions are often referred to as effective pair potentials because they are often based off experimental data and fitted to include much of the 3-body interaction energy [1].

To calculate the potential energy from two body interactions there are several different potentials that have been developed. The one used is the simplest and most commonly used potential that simulates both the repulsive short range contributions and
long range attractive parts necessary to simulate a liquid or gas phase, the Lennard Jones (LJ) 12-6 Potential [1] shown in (3). It has been shown in numerous studies to produce fairly accurate thermodynamic and structural properties for alkanes [9,17,18,24,27,32].

\[ \Phi_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  

(3)

This potential is based solely on the distance between the interacting particles and on the parameters \( \sigma \) and \( \varepsilon \) which are determined by comparison to experimental results. The \( r^{-6} \) dependence of the attractive part of the potential is based on the first term in the expansion of dispersion energy, however \( 4\varepsilon \sigma^6 \) is typically an overestimate by a factor of two compared with experimental data. This can be partly justified by the fact that there are no \( r^{-8} \) or \( r^{-10} \) terms. The \( r^{-12} \) term that is in the LJ potential has no theoretical justification [35]. This potential can be seen in Fig. 3.

The calculation of forces based of the Lennard Jones potential is one of the longest sets of calculations performed during each step of the simulation. In order to reduce this computation time the LJ potential is often truncated by cutting off the end of the tail at a value of 2.5\( \sigma \). At this distance nearly all of the potential energy due to the potential has been accounted for, making it inefficient to calculate the interaction between particles beyond this distance. However, cutting the tail off at this point means that there is a discontinuity in potential energy. One can choose to just ignore this fact and accept that there will be a slight drift in the energy of the system. In most cases however, this is not desirable. There are two ways this discontinuity is typically accounted for. The first way is to add a long distance correction term. The other way is to shift the potential so that it equals zero at the cutoff distance.
If using the method of adding a long range correction for the tail, the influence of the tail is estimated analytically by assuming that for distances greater than the cutoff radius $g(r)=1$. However, if one is interested in interfacial properties between liquid and gas phase, then this long range tail correction cannot be added straightforwardly [38]. In fact the way to calculate the long range correction for this case is disputed.

Both methods of truncation have little effect on most of the bulk properties up to about 90 percent of the critical temperature. In the case of the liquid vapor coexistence curves there is a significant difference. For the shifted potential it is found that the critical temperature is significantly underestimated [35].

Fig. 3: Lennard-Jones Potential for n-Heptane
2.2.2 Torsion Potential

Bond torsion forces are added to the simulation to account for twisting around a bond or perhaps even two bonds at the same time. This torsion force is calculated in terms of the relative locations of four consecutive monomers in a chain, as seen in Fig. 4.

![Diagram of dihedral angle for bond torsion forces](image)

Fig. 4: Dihedral angle for bond torsion forces

Since bond lengths and angles are fixed this force depends on rotation around the bond between atoms 2 and 3 in the group being looked at. This is called the dihedral angle. To begin calculating the torsion force associated with the four monomers being looked at, one must start by determining the vectors between each pair of monomers in the group. Monomer (i-2), (i-1), (i) define a plane with normal vector \((\mathbf{d}_{i-1} \times \mathbf{d}_i)\), while monomers (i-1), (i), and (i+1) define another plane with normal vector\((\mathbf{d}_i \times \mathbf{d}_{i+1})\), where \(\mathbf{d}_i = \mathbf{r}_i - \mathbf{r}_{i-1}\). The angle between these normal vectors is called the dihedral angle \(\theta\) and is given by (4).

\[
\cos \theta_i = \frac{\left(\mathbf{d}_{i-1} \times \mathbf{d}_i\right) \cdot \left(\mathbf{d}_i \times \mathbf{d}_{i+1}\right)}{|\mathbf{d}_{i-1} \times \mathbf{d}_i||\mathbf{d}_i \times \mathbf{d}_{i+1}|}
\]

(4)

Additionally, the angle between bonds \(\mathbf{d}_{i-1}\) and \(\mathbf{d}_i\) is expressed by (5).
The torsion force on all four monomers, (i-2) through (i+1) above is calculated from the relation in (6).

\[
\cos \alpha_i = \frac{d_{i-1} \cdot d_i}{|d_{i-1}| |d_i|} \tag{5}
\]

The torsion force on all four monomers, (i-2) through (i+1) above is calculated from the relation in (6).

\[
-\nabla r_j u(\theta) = -\left. \frac{du(\theta)}{d(\cos \theta)} \right|_{\theta = \theta_i} \nabla r_j \cos \theta_i , \tag{6}
\]

where \( u(\theta) \) is the torsion potential given by (7).

\[
u(\theta)/k_B = \left[ 1.000 + 1.310 \cos \theta - 1.414 \cos^2 \theta - 0.330 \cos^3 \theta \\
+ 2.828 \cos^4 \theta - 3.394 \cos^5 \theta \right] 10^3 K \tag{7} \]

Here \( k_B \) is the Boltzmann constant. After calculating those torsion forces and the forces associated with monomer groupings 3,4,5,6 and, 4,5,6,7 the total torsion force acting on each monomer can be summed and added to the total force exerted on that monomer by all interactions.

### 2.3 Maintaining Constraints

During each time step of the simulation bond lengths and bond angles have to be readjusted to make up for errors in the numerical integration of the equations of motion; if not the molecules would eventually be torn apart. Several algorithms have been developed to handle these constraints while advancing the simulation to the next time step. The first method which is the most widely used method for constraining molecules is called the SHAKE method. A second method called the RATTLE method is also used to constrain molecules and is the one chosen for our simulations. The reason that
RATTLE was chosen over the SHAKE method is that SHAKE suffers from some
limitations due to the fact that the atomic velocities are not used in the integration of the
equations of motion. Approximate values are calculated following each integrations step,
which makes it difficult to start with previously chosen values of coordinates and
velocities. Additionally, it also has a greater loss of precision because it adds quantities of
vary different magnitudes [35].

The RATTLE method was developed by Andersen in the 1983 [2]. Given the
following differential equation, (8).

\[ \ddot{r}(t) = f(r) \]  \hspace{1cm} (8)

where \( r \) is the set of Cartesian coordinates that specify the configuration of the system,
one can solve it in terms of the Verlet Algorithm [48] in (9).

\[ r(t + h) = 2r(t) - r(t - h) + h^2 f \left[ r(t) \right] \]  \hspace{1cm} (9)

To determine the velocity using this algorithm the approximation below is made.

\[ \dot{r}(t) = \frac{[r(t+h) - r(t-h)]}{2h} \]  \hspace{1cm} (10)

However, the velocity at time \( t \) can only be obtained after the position at time \( t+h \) has
been calculated. The Velocity Verlet algorithm that is derived from the Verlet algorithm
takes care of this problem [43]. The Velocity Verlet algorithm is shown in (11) and (12)
below.

\[ r(t+h) = r(t) + h \dot{r}(t) + \frac{h^2 f \left[ r(t) \right]}{2} \]  \hspace{1cm} (11)
This reformulation of Verlet allows the incorporation of the velocity directly into the equations of motion thus making it more accurate. In this form however, the algorithm was not designed to be used with molecules that are subject to constraints. As a result Andersen developed the RATTLE method shown in (13) and (14). These equations are similar to the equations from the SHAKE Algorithm, however, SHAKE was based of the original Verlet method and thus velocities were not used in the integration of the equations of motion.

\[
\dot{r}_i(t+h) = \dot{r}_i(t) + \frac{h}{2m_i} \left[ F_i(t) + \sum_j^N \lambda_{Rij} (t) r_j (t) \right]
\]

\[
\dot{r}_i(t+h) = \dot{r}_i(t) + \frac{h}{2m_i} \left[ F_i(t) + \sum_j^N \lambda_{Rij} (t) r_j (t) + \sum_j^N \lambda_{Rij} (t+h) r_j (t+h) \right]
\]

During the first part of RATTLE the new positions and velocities are calculated based on the forces acting on the molecules at time \( t \) as shown in (15) and (16) respectively.

\[
r_i(t+h) = r_i(t) + h \dot{r}_i(t) + \frac{h^2}{2m_i} F_i(t)
\]

\[
\dot{r}_i(t+h) = \dot{r}_i(t) + \frac{h}{2m_i} F_i(t)
\]
These positions and velocities are subsequently checked to ensure that they satisfy bond length and angles constraints, as given in Table 1. If violations of these constraints are detected, (17) and (18) shown below are iteratively solved to ensure the constraints are maintained, within a given tolerance.

\[
\mathbf{r}_i(t+h) = \mathbf{r}_i(t+h) - \frac{2h^2 \sum_j \lambda_{RRij}(t) \mathbf{r}_j(t)}{2m_i}
\]  \hfill (17)

\[
\mathbf{\dot{r}}_i(t+h) = \mathbf{\dot{r}}_i(t+h) - \frac{2h \sum_j \lambda_{RRij}(t) \mathbf{r}_j(t)}{2m_i}
\]  \hfill (18)

where \( \lambda_{RR} \) is calculated in (19).

\[
\lambda_{RRij} = \frac{\left| \mathbf{r}_j(t+h) \right|^2 - b_{ij}^2}{2\left[ \mathbf{r}_j(t+h) \cdot \mathbf{r}_j(t) \right](m_i^{-1} + m_j^{-1})}
\]  \hfill (19)

After all bond lengths and bond angles in all the molecules are constrained, the velocity is then advanced over the second half step of RATTLE in (20) by recalculating the forces based on the new positions and velocities.

\[
\mathbf{\dot{r}}_i(t+h) = \mathbf{\dot{r}}_i(t+h) + \frac{\hbar}{2m_i} \mathbf{F}_i(t+h)
\]  \hfill (20)

The velocities are then checked against rate of displacement constraints to ensure that they fall within a given tolerance. If this fails the new velocities are recalculated by imposing the constraint in (21).

\[
\mathbf{\dot{r}}_i(t+h) = \mathbf{\dot{r}}_i(t+h) - \frac{-2h \sum_j \lambda_{Rij}(t+h) \mathbf{r}_j(t+h)}{2m_i}
\]  \hfill (21)
where $\lambda_{RV}$ is shown in (22).

$$
\lambda_{RV_{ij}} = \frac{|r_{ij}(t+h)||\mathbf{r}_i(t+h) - \mathbf{r}_j(t+h)|}{b_{ij}^2(m_i^{-1} + m_j^{-1})}
$$

(22)

The Lagrange multiplier calculations for $\lambda_{RR_{ij}}$ and $\lambda_{RV_{ij}}$ are performed for each molecule through an iterative procedure until $|r_{ij}(t+h)| - b_{ij}^2$ is within a specified tolerance of zero for all bonds as follows; where $b_{ij}$ is the fixed bond distance between monomers (i) and (j).

After updating the velocities of all of the monomers in all of the molecules to satisfy the constraints, the system moves to the next time step using RATTLE again to update the positions and velocities. This method is more attractive for our simulations because it is more accurate and the time step can be altered in the middle of the calculation if necessary.
Chapter 3

TEMPERATURE REGULATION AND EFFICIENCY OF NUMERICAL SIMULATIONS

Simulating an n-heptane system using molecular dynamics first requires regulating the system. One could choose to use a constant energy system or a constant temperature system. For these simulations a constant temperature was maintained via velocity rescaling. In addition to this one must also consider ways to reduce the simulation time. This is done through the use of periodic boundary conditions, the use of neighbor lists while calculating the LJ forces acting on each molecule, and the parallelization of the code. Additionally, one must consider how to initialize the simulation.

3.1 Velocity Rescaling

Velocity rescaling is used to maintain a constant temperature in the simulation. For monatomic systems this is straightforward. One simply applies a scaling factor to the velocity of the particle. For a polyatomic system it is not as straightforward, both translational as well as rotational energy must be considered. While the temperature of any bulk system is directly proportional to the translational motion of its molecules, known also as kinetic temperature [44], something known as the internal temperature can...
also be defined. The Equipartition theorem [36] states that the kinetic energy is distributed, on average, evenly over all degrees of freedom. For an alkane constrained by both bond lengths and bond angles the, number of degrees of freedom are $n_s + 3$ degrees of freedom [32]. For our system of n-heptane there are 10 degrees of freedom, 3 associated with translation and 7 with internal motion. Comparison of the internal temperature calculated from these 7 internal degrees of freedom to the kinetic temperature provides a convincing way of showing that the system has reached equilibrium, as the Equipartition theorem should hold if equilibrium has been achieved.

To calculate the kinetic and internal temperatures of the system we must separate the velocity of each monomer, $v_i$, into the molecular center of mass velocity, $v_{cm}$, and a fluctuating component, $v'_i$. The derivation that follows shows how this is accomplished.

The energy of a given molecule can be expressed as shown in (23).

$$E_{k,\text{mol}} = \sum_i \left[ \frac{1}{2} m_i v_i^2 \right] = \sum_i \left[ \frac{1}{2} m_i v_i \cdot v_i \right]$$

where,

$$v_i = v_{cm} + v'_i; \quad v_{cm} = \frac{1}{m_{\text{mol}}} \sum_{i=1}^{7} m_i v_i; \quad m_{\text{mol}} = \sum_{i=1}^{7} m_i$$

Here $v_i$ is a velocity in a fixed reference frame, $m_i$ is the mass of a monomer, and $m_{\text{mol}}$ is the molecular mass. The summation is over all monomers within a given molecule. Equation (23) can be rewritten as shown below.
From (24) it can be shown that \( \sum_i m_i \left( \mathbf{v}_{cm} \cdot \mathbf{v}'_i \right) = 0 \)

\[
\sum_i m_i \left( \mathbf{v}_{cm} \cdot \mathbf{v}'_i \right) = \sum_i m_i \left( \mathbf{v}_{cm} \cdot [\mathbf{v}_i - \mathbf{v}_{cm}] \right)
= \sum_i m_i (\mathbf{v}_{cm} \cdot \mathbf{v}_i - \mathbf{v}_{cm} \cdot \mathbf{v}_{cm})
= \mathbf{v}_{cm} \sum_i m_i \mathbf{v}_i - (\mathbf{v}_{cm} \cdot \mathbf{v}_{cm}) \sum_i m_i
= \mathbf{v}_{cm} \mathbf{v}_{cm} m_{sys} - (\mathbf{v}_{cm} \cdot \mathbf{v}_{cm}) m_{sys} = 0
\]

This eliminates the term \( \sum_i m_i \left( \mathbf{v}_{cm} \cdot \mathbf{v}'_i \right) \) from the result of (24) giving the form shown in (26).

\[
E_{k,mol} = \sum_i \left[ \frac{1}{2} m_i \left( \mathbf{v}_{cm} + \mathbf{v}'_i \right) \left( \mathbf{v}_{cm} + \mathbf{v}'_i \right) \right]
= \sum_i \left[ \frac{1}{2} m_i \left( \mathbf{v}_{cm} \cdot \mathbf{v}_{cm} \right) + \frac{1}{2} m_i \left( \mathbf{v}'_i + \mathbf{v}'_i \right) \right]
= \sum_i \left[ \frac{1}{2} m_i \mathbf{v}_{cm}^2 + \frac{1}{2} m_i \mathbf{v}'_i^2 \right]
\]

\[
E_{k,mol} = \sum_i \left[ \frac{1}{2} m_i \mathbf{v}_{cm}^2 + \frac{1}{2} m_i \mathbf{v}'_i^2 \right]
\]

Or written as shown in (27).

\[
E_{k,mol} = \sum_i \left[ \frac{1}{2} m_i \mathbf{v}_{cm}^2 \right] + \sum_i \left[ \frac{1}{2} m_i \mathbf{v}'_i^2 \right]
\]

The first term in (27) is the pure translational component and the second term corresponds to internal motions. If we perform a sum of the translational component over all the molecules in the system, we arrive at the global kinetic temperature in (28)

\[
T_{kin} = \frac{2}{3} \frac{1}{Nk_B} \sum_j \left( \sum_{i=1}^{7} \left[ \frac{1}{2} m_i \mathbf{v}_{cm}^2 \right] \right)
\]
Here $k_B$ is again the Boltzmann constant, the summation $(j)$ is over all molecules $N$ of the system. The factor 3 in the denominator corresponds to the three translational degrees of freedom. Similarly, the expression for the internal temperature is given in (29).

$$T_{\text{int}} = \frac{2}{7} \frac{1}{Nk_B} \sum_{j} \left[ \frac{1}{2} m_j \left( v_i' \right)^2 \right]$$

(29)

During the equilibration period a constant temperature is imposed in both the internal and kinetic temperature. (By the equipartition theorem these temperatures are equal.) Hence the center of mass and fluctuating velocities are respectively rescaled in (28) and (29). This process is continued for a large number of time steps until the system has reached thermal equilibrium and the rescaling is no longer required to maintain a constant energy state in the system. It should be noted that if the system is not in equilibrium the calculation for the kinetic temperature in (28) is not the true temperature as there will be drift velocity present for the system which must be accounted for.

### 3.2 Simulation Refinements

MD simulations require large amounts of computation time as well as memory. Over the years there have been algorithms and approaches developed to reduce computation time and memory requirements. The most widely used of these are to employ periodic boundary conditions, use a neighbor list, and implement parallel processing. These three methods allow one to greatly reduce the computation time.
3.2.1 Periodic Boundary Conditions

The use of periodic boundary conditions has multiple purposes. First of all, in a finite simulation molecules near the edge wall of the simulation will experience much different forces and motion than molecules in the bulk \cite{1}. This surface effect was overcome through the use of periodic boundaries by Born and von Karman in 1912 \cite{7}. In addition to overcoming surface effects, employing periodic boundaries allows one to simulate the effect of a much larger bulk system without increasing the actual size of the system, which would increase computation time significantly.

Periodic boundary conditions work by allowing a molecule that moves through the boundary on one edge to return to the system by moving it to the opposite edge of the domain. For example if one were to consider a two dimensional square domain, you would have mirror images of the domain surrounding it as shown in Fig. 5.
Each molecule in the domain may pass through one of the boundaries and enter a mirror domain. In turn the image of that molecule will reenter from the mirror domain on the opposite side. For a two dimensional square domain you have eight mirror domains surrounding the simulation domain. If one were to extend this to a three dimensional system there would be a total of 26 mirror domains surrounding the simulation. For the case of n-heptane the center of mass position for each molecule is used to determine whether or not the molecule has left the domain.

### 3.2.2 Neighbor Lists

Another method for significantly reducing computation time is through the use of neighbor lists for the calculation of LJ forces. This method was first proposed by Verlet in 1967 [48]. In the calculation of LJ forces a cutoff is used at a distance of 2.5σ. Rather than determine whether or not each pair of molecules have LJ interactions each timestep, a list can be created for each molecule that keeps track of which molecules fall within a distance of 2.5σ. Doing this significant reduces the number of calculations done during the force calculations.

Rather than updating these neighbor lists each timestep it would be better to update it less often. This is accomplished by expanding the cut off distance for each neighbor list to 3.1σ as shown in Fig. 6. The cutoff distance for the neighborlist was varied to improve the performance of the neighborlist calculation [1]. 3.1σ was found to be the optimal cut-off distance, as it gave the shortest simulation times for the 1000 to 3000 molecule systems being looked.
Several simulations were performed to confirm that increasing the time between updates could be increased as high as 80 timesteps before the neighbor lists need to be updated. The results are shown in Fig. 7. This study shows that there is no difference in the temperature calculations for update periods of 20, 60, and 80 timesteps. They all had the exact same average kinetic and internal temperatures, 483.1291 K and 482.6246 K respectively. For an update period of 100 timesteps, this was not the case and average value of the kinetic temperature was 447.5243 K and for the internal temperature the average was 479.2546 K. Additionally, in Fig. 7d one can see that there is a wide deviation in the kinetic and internal temperatures. This is convincing evidence that beyond an update period of 80 timesteps, one starts to lose track of interaction molecules for the neighborlist. Therefore these simulations were run with an update period of 80 timesteps.
3.2.3 Parallelization

One of the major ways to reduce the time required to run a simulation is to use parallel programming. Parallel programming decreases simulation time by using
multiple processors to split up the computations performed each time step. To do this the code must be altered to allow message passing between processors. The standard widely used in parallel programming is MPI and MPI2 (Message Passing Interface).

There are two ways in which the calculations can be split up. One can split up the calculations by “domain decomposition”, which splits up which molecules have their calculations performed on each processor based on their location within the computational domain. The other method used to split up the calculations is to use “atom or molecule decomposition” [25]. This method splits up the molecules evenly without regard to their location within the system. While the “domain decomposition can be more efficient as there is an increase in the number of molecules in the simulation, it was not used in this work. The reason for this is that this method has a very uneven distribution of molecules in the case of droplet vaporization. In this work on droplet vaporization large differences in molecular density are encountered. As a result “molecular decomposition” was chosen. The parallelization of the code using MPI functions is outlined in Appendix A along with how the molecular decomposition method was implemented.

### 3.3 Initialization

Before the droplet vaporization could be started it was necessary to initialize the system by first simulating the liquid and gas phases separately. The liquid phase and gas phase were given an initial temperature of 293 0K and 471 0K, respectively. They were
then allowed to evolve over time until thermal equilibrium was achieved. After this the liquid and gas phases were combined to form the initial droplet vaporization setup.

This process by which the liquid and gas phases were initialized was started by placing both phases (separately) in a cubic domain with periodic boundary conditions. The size of each domain was chosen so that the appropriate densities where achieved. Densities of 679.5 kg/m$^3$ and 2.586 kg/m$^3$ were used for the liquid and gas phases respectively. Both densities were chosen based on 1 atm of pressure at their specified temperatures with the gas density based off the ideal gas law. The molecules were initially arranged on a body centered cubic (BCC) lattice, suggested by Rapaport for alkanes in his book *The Art of Molecular Dynamics Simulation* [29]. This lattice can be seen in Fig. 8.

![3-D rendering of a BCC lattice](image)

**Fig. 8:** 3-D rendering of a BCC lattice Taken from[3]; molecules are placed at the center of the cube and at the corners.

For the liquid phase an additional modification is required, which consists of placing the monomers in a helical shape arrangement for each molecule. This is done to ensure the correct liquid density is achieved without having overlap issues. If a linear chain is used for each molecule it was found that the end monomers on each chain were
so close to the end monomers on other chains that extremely large repulsive forces made it impossible to maintain the bond constraints using Lagrange multipliers. Essentially the molecules were ripped apart. As a result, this helical structure was chosen to reduce the linear length of each molecule such that large repulsive forces were not experienced. This initial helical setup for the system is shown in Fig. 9.

Fig. 9: Initialization of 200 molecules in a cubic domain. A helical shape was used on each molecule to ensure the proper liquid density without introducing excessively large repulsive forces.

An initial random velocity based on a Gaussian distribution was then given to all monomers. This was achieved through the use of random number generators taken from reference [26].
After initializing the molecules on a BCC lattice and assigning initial velocities both the liquid and gas phase systems were allowed to evolve through the use of the RATTLE algorithm described previously. During the first half of these simulations it was necessary to use velocity rescaling to ensure that a constant system temperature was maintained. This scaling was applied to every molecule in the system. It was decided that after the system had relaxed to a random state (the artificial lattice structure had disappeared), velocity rescaling could be shut off. The systems were then allowed to run for a sufficiently long time to determine that the system had reached equilibrium through the comparison of the kinetic and internal temperatures.

Once the liquid and gas phases have reached equilibrium the droplet vaporization can begin. To initialize the droplet vaporization simulation a spherical droplet is cut from the liquid phase and placed at the center of the gas domain. Any gas molecules that occupy this space are removed so that no overlap will occur. This initial setup is shown in Fig. 10

For the droplet vaporization phase velocity rescaling is not applied to the entire volume to maintain a constant energy state. Instead it is used near the boundaries to simulate a far field temperature. This is achieved by only rescaling the velocities of molecules near the boundary to maintain a specified far field temperature. This system is run until the droplet vaporizes and thermal equilibrium is achieved.
Fig. 10: Initial setup for a 301 molecule droplet vaporization simulation
Chapter 4

Results

4.1 Equilibration of Gas and Liquid phases

The simulation of the n-heptane droplet first required the separate equilibration of a liquid phase and a gas phase before it could proceed. The initial setup up of the liquid and gas systems was discussed in the previous chapter. An example of this configuration can be seen in Fig. 11. A 200 molecule system is shown rather than the larger systems simulated as it is easier to see individual molecules.

Fig. 11: Initial configuration for the 200 molecule liquid phase.
During the equilibrium process both the liquid and gas phases used a timestep of 1.25 femtosecond (fs). Velocity rescale was applied for a period of 0.125 nanosecond (ns), at which point it was shut off and the system was allowed to evolve for a further 0.125 ns to confirm that equilibrium was achieved. This resulted in a total simulation time of 0.25 ns. The final positions of a 200 molecule liquid system can be seen in Fig. 12, which again is shown over the real cases because it is easier to distinguish between individual molecules.

![Random arrangement of the 200 molecule liquid system after equilibrium is achieved](image)

The primary way of confirming that the system had reached equilibrium was through comparison of the internal and the kinetic temperatures of the system. The equipartition theorem states that when a system is in equilibrium all degrees of freedom should contain $\frac{1}{2}k_BT$ kinetic energy. Therefore when the system is in equilibrium the kinetic and
internal temperatures of the system should be equivalent. The kinetic and internal temperatures for both a 1000 and 2000 molecule liquid system can be seen in Fig. 13.

Fig. 13: (a) Temperature plot for a 1000 molecule liquid system. (b) Temperature plot for the 2000 molecule liquid system.
In both systems one can see good agreement between the translational and internal modes. If a comparison between the 1000 molecule case in part (a) is done with the 2000 molecule case in part b of Fig. 13, it can be seen that although there are oscillations in both the kinetic and internal temperatures they decrease from the 1000 molecule to 2000 molecule case. By comparing the averages of the kinetic and internal temperatures over the entire run for the both system one can see there is good agreement. The difference between the two averages is only 0.30 K with the internal temperature at 286.42 K and the kinetic temperature at 286.72 K. Another indication that the system has indeed reached equilibrium is the lack of any observable drift of the temperatures after the initial rescaling period.

4.2 Droplet Vaporization

After equilibrating the gas and liquid phases the droplet vaporization could proceed. Four cases were run using systems of 1529 and 1526 molecules at pressures of 1 and 2 atmospheres respectively, as well as systems of 3031 and 3041 molecules at 1 and 2 atmospheres respectively. Table 2 lists each case and the conditions at which they were run.

<table>
<thead>
<tr>
<th>Case</th>
<th>Environment</th>
<th>Total Number of Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapor</td>
<td>Liquid</td>
</tr>
<tr>
<td></td>
<td>P(kPa)</td>
<td>ρ (kg/m³)</td>
</tr>
<tr>
<td>1</td>
<td>101.0</td>
<td>2.586</td>
</tr>
<tr>
<td>2</td>
<td>202.0</td>
<td>5.172</td>
</tr>
<tr>
<td>3</td>
<td>101.0</td>
<td>2.586</td>
</tr>
<tr>
<td>4</td>
<td>202.0</td>
<td>5.172</td>
</tr>
</tbody>
</table>
The vaporization of one of the larger 3000 molecule systems is shown at several instances in Fig. 14. Enough of the vaporization process occurred to analyze the thermodynamic properties and make an assessment of the vaporization rate.

Fig. 14: Snapshots of 1000 molecule droplet vaporizing in a gas
The first step in analyzing the data was to look at cross-sections of the droplet using contour plots of both the kinetic and internal temperatures as well as the net forces acting within the droplet. It should be noted that since these systems are not in equilibrium the kinetic temperature is more a measurement of the translational kinetic energy on the Kelvin scale than the true temperature of the system as the mean motion or drift velocities were not easy to account for due to the non-spherical shape of the droplets during vaporization and were therefore excluded. Fig. 15 through Fig. 18 show contour plots for the first through fourth cases respectively. Each plot has an overlay of the center of mass of each molecule in the system. Additionally, for conciseness only one collinear cross sectional plane is presented for each case as the cross sections for the other 2 collinear planes show similar thermodynamic results but do not provide significant additional insight into the behavior of the droplets during vaporization.

Unlike the contour plots shown by Little [20] on argon droplets and Kaltz [15] on oxygen droplets, these plots do not have as nicely shaped droplets or temperature distributions. This difference is due to the much smaller simulation size of the system as well as the presence of internal motions within each molecule. The small size of the system is much more comparable to the systems looked at by Sumardiono and Fisher [41] although their systems were monatomic. The average force calculations in Fig. 15 through Fig. 18 show that these droplets are too small to stay spherical for very long. This results in the absence of a distinct surface tension force acting on the surface of the droplet as was seen in the work done by both Little [20] and Kaltz et al. [14,15]. Instead a more random distribution of the forces is observed as the droplet shape evolves over time. The average forces shown were calculated by summing up the average forces
acting on each monomer about the center of mass of each molecule to determine the average force on each molecule.

A comparison of the results shown in Fig. 15 through Fig. 18 shows that in all cases the variation of temperature within and around the droplets increase as the droplet vaporizes, with a core still remaining near the initial liquid temperature. The somewhat large variations noticed are due in large part to the small size of the system. The larger systems shown in the work by Little [20] and Kaltz et al. [14,15] have a much larger sampling of molecules and therefore much less variation in their temperature plots than observed in these simulations. Additionally, the temperature contours of these polyatomic systems differ from the ones presented by Little and Kaltz because there is energy being transferred back and forth between the translational degrees of freedom and internal degrees of freedom in each molecule. By comparing the average force plots it can be seen that both of the higher pressure cases have a less spherical droplet shape than the lower pressure cases. Additionally, the smaller 1500 molecule systems have less spherical droplets than the 3000 molecule systems under the same conditions.
Fig. 15: Contour plots for 1529 molecule system at 101 kPa. vs time
Fig. 16: Contour plots for 1526 molecule system at 202 kPa. vs time
Fig. 17: Contour plots for 3031 molecule system at 101 kPa. vs time

<table>
<thead>
<tr>
<th>Time</th>
<th>Translational Kinetic Energy</th>
<th>Internal Temperature</th>
<th>Average Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 ns</td>
<td>0.98D²/D₀²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.500 ns</td>
<td>0.88D²/D₀²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.125 ns</td>
<td>0.79D²/D₀²</td>
<td></td>
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</tr>
</tbody>
</table>
Fig. 18: Contour plots for 3041 molecule system at 202 kPa. vs time

Translational Kinetic Energy

Internal Temperature

Average Force
Further analysis of the system was done by using the Amsterdam method to
determine the number of molecules in the droplet. In the work by Sumardiono and Fisher
[41] a value of 1.5σ was used in the Amsterdam method for determining which molecules
belonged to the droplet. The Amsterdam method requires that a minimum of 4 molecules
be present within this distance for the molecule to be considered part of the droplet. Since
this system used a polyatomic molecule, n-heptane, a value of 1.5σ was not sufficient to
determine the number of molecules in the droplet. The hard sphere diameter σ used in
monatomic systems is representative of the entire molecule. In this polyatomic
simulation σ is not representative of an entire n-heptane molecule but rather it is based on
the CH₃ and CH₂ monomers in each molecule. As a result a larger radius needs to be
used to accurately determine the droplet size. Several values, 1.7σ, 1.9σ and 2.1σ were
compared for evaporation rates to determine which was most suitable for an n-heptane
droplet. The results of that comparison can be seen in Fig. 19.
In Fig. 19 it is shown that a value of 1.7\(\sigma\) was too low to be considered because a significantly lower number of molecules were considered part of the droplet compared to the reference estimate. However, both the 1.9\(\sigma\) and 2.1\(\sigma\) cases showed much better agreement with a reference estimate for the number of molecules in the droplet with the 2.1\(\sigma\) case being closer to the estimate. The reference estimate was based off of a density between the liquid density and gas density for the system. This value of 1.6\(\sigma\) was used to determine the number of molecules in the droplet by seeing if each molecule had a neighbor within this distance. While this estimate isn’t as reliable as the Amsterdam method it did give the correct number of molecules initially in the droplet, and thus was used as a reference estimate for comparing different Amsterdam cutoffs. Using these
cutoff values for the Amsterdam method each case was compared to the $D^2$ law for sub-critical droplet vaporization. The $D^2$ law says that the square of the droplet radius should decrease linearly over time. Although these droplets are not spherical a scaled estimate of the droplet diameter can be obtain by taking the number of droplet molecules present and raising them to the two-thirds power. If it was spherical this would be the exact measure of the droplet diameter. The results of this for run 3 can be seen in Fig. 20.

![Fig. 20: Comparision of 3031 molecule droplet evaporation run to the $D^2$ law.](image)

It should be noted that regardless of which Amsterdam cutoff radius was used similar behavior is noticed if all systems are scaled to 1, although the 1.7σ case had a lot of fluctuation. This is likely due to the fact that this cutoff value is too low to give an
accurate estimate of the number of molecules in the droplet. Additionally, on this scale the \( D^2 \) law seems to apply.

Using just the cutoff value of \( 2.1\sigma \) for the Amsterdam method all four cases are compared to the \( D^2 \) law without scaling the system to 1. All cases adhere to the \( D^2 \) law fairly well, with some variations between runs. This comparison is shown in Fig. 21

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**Fig. 21:** Comparison to the \( D^2 \) law for four different cases: a.) 1529 molecule system at 101 kPa, b.) 1526 molecule system at 202 kPa, c) 3031 molecule system at 101 kPa, and d.) 3041 molecule system at 202 kPa.
All four of the cases follow the D\(^2\) law well, however it is noticed that for the higher pressure cases there is an increase in the vaporization rate. For the 1500 molecule system the increase in vaporization rate is approximately 1.9 times as fast for the 202 kPa run compared to the 101 kPa run. For the 3000 molecule system you also see an increase in the vaporization rate by, approximately 1.7 times for the 202 kPa case compared to the 101 kPa case. These differences between the vaporization rates for the two different pressures are the result of more heat flux into the droplet from the gas region for the higher pressure cases. The differences between the smaller system and the larger system is most likely due to the smaller system size and the less spherical droplet shape for the 1500 molecule systems.

The results of these simulations show that even a nanometer sized droplet of n-heptane follows the D\(^2\) law. Additionally, it shows that molecular dynamics can be used to simulate the vaporization of n-heptane molecules. This first step in simulating droplet vaporization of polyatomic molecules using MD can be extended in the future to simulating larger systems and scaling the results to macroscopic sizes using the Long-Micci [21] method for comparison of vaporization rates and thermodynamic properties to experimental data for validity.
Chapter 5

Conclusions

Understanding the vaporization process is very important for improving the efficiency of combustion processes. These processes are already well understood; as a result improving the efficiencies of these systems requires a better understanding of the atomization of the fuel. With this aim vaporization in the critical and supercritical regime has been under intensive study. In the past decade molecular dynamics has been employed to explore these topics. In particular droplet vaporization has been investigated to better understand the properties in a critical environment. Up to this point however MD has only been used to simulate the vaporization of monatomic and diatomic systems. Several studies have been done on argon vaporizing under various conditions as well as sodium and oxygen. This work sought to take the next step and look at the vaporization of a more complex molecule. Many combustion processes involve the use of hydrocarbon fuels; for this reason n-heptane was simulated, as it is typically used in diesel fuel simulations.

To simulate droplet vaporization using molecular dynamics, knowledge of the molecular structure of n-heptane was necessary. The united atom concept was used to condense each CH₂ and CH₃ into single point mass systems to reduce computation time. Bond lengths and angles were constrained to maintain the proper geometrical structure in each molecule. The Lennard-Jones 12-6 potential was used to simulate the forces acting between each molecule. The Lennard-Jones potential along with a torsion potential were
also used to simulate the forces acting between unconstrained monomers within each molecule. Maintaining these constraints was achieved through the use of the RATTLE algorithm developed by Andersen. This allowed the molecular shape to evolve over time without compromising the constraints through the equations of motion.

To improve the efficiency of the simulations beyond the structural simplification employed, several things were used. Periodic boundary conditions were used to allow the system to be simulated as if it were in a much larger environment. Additionally, a neighbor list was employed for each monomer to keep track of which particles interacted with it through the LJ potential. This reduced the $N^2$ force calculations to a much smaller amount. Another major refinement was to parallelize the code to allow the use of multiple processors, thus increasing the size of the systems that could be simulated in a practical amount of time.

The simulation of a droplet vaporizing first required the equilibration of a liquid and gas phase separately. The molecules were put on an artificial BCC lattice with random velocities and then allowed to evolve into a random arrangement. The average kinetic and internal temperatures of the systems were monitored to determine if thermal equilibrium had been achieved. Once thermal equilibrium was achieved a spherical droplet was cut from the liquid phase and placed in the center of the gas domain. At this point the vaporization process could begin. Four cases were looked at including a 1500 molecule system at 1 and 2 atmospheres of pressure as well as a 3000 molecules system at 1 and 2 atmospheres.

The results of these simulations showed that the droplets were not truly spherical in shape. Despite the lack of sphericity, a droplet diameter was still determined based on
the number of molecules present in the droplet. The size of the droplet was determined based on the Amsterdam method with a cutoff radius of 2.1σ. Through calculation of the vaporization rate of these subcritical systems, D² behavior was observed for all four cases. For the 202 kPa pressure cases higher vaporization rates were observed of about 1.7 and 2.0 times the 101 kPa cases for the 1500 and 3000 molecule systems respectively.

This important first step showed that using MD to simulate droplet vaporization is possible. Additionally, it confirmed that even in very small droplets, D² law behavior was observed for subcritical vaporization. As a next step one should look at ways to further increase the size of the systems being simulated while still maintaining reasonable simulation times. Validation of the Long-Micci method of extrapolation to larger systems would be an appropriate extension of this work. The ultimate goal of this work was to provide a means for further exploration of hydrocarbon vaporization in critical and supercritical environments, as theses environments for droplet vaporization are still the focus of study using methods ranging from experimentation, to computational fluid dynamics to molecular dynamics. With respect to this goal the current work provides a foundation for continuing vaporization studies of n-heptane into these regimes.
Bibliography


Appendix A

MPI Code

For these simulations several important MPI commands were used. First three commands were required to initialize the MPI process.

call MPI_INIT(ierr)
call MPI_COMM_RANK(MPI_COMM_WORLD,myid(ierr)
call MPI_COMM_SIZE(MPI_COMM_WORLD,numprocs(ierr)

After initializing the system it was necessary to set up the data structure used to sent the heptane data between processors. To accomplish this, the MPI_ADDRESS, MPI_TYPE_CREATE_STRUCT, and MPI_COMMIT commands were used.

!*** Setup MPI Datatype for Sending Particle Data ***
call MPI_Get_Address(heptane(1)%monomer(1)%mass,offsets(1),ierr)
call MPI_Get_Address(heptane(1)%monomer(1)%nlmol(1),offsets(2),ierr)

!***Set up description of 10 MPI_REAL8***
oldtypes(1)=MPI_REAL8
blockcounts(1)=10
base=offsets(1)
offsets(1)=offsets(1)-base

!***Set up description of 2 MPI_Integer arrays***
oldtypes(2)=MPI_INTEGER
blockcounts(2)=2*NA*nls
offsets(2)=offsets(2)-base

call MPI_TYPE_CREATE_STRUCT(2,blockcounts,offsets,oldtypes,particletype,ierr)
call MPI_TYPE_COMMIT(particletype,ierr)

!***Setup description of molecule array***
call MPI_Get_Address(heptane(1)%cmx,offsets2(1),ierr)
call MPI_GET_Address(heptane(1)%monomer(1),offsets2(2),ierr)

!***setup MPI Heptane description***
!*** Set up center of mass description ***
oldtypes2(1)=MPI_REAL8
blockcounts2(1)=9
base2=offsets2(1)
offsets2(1)=offsets2(1)-base2

!*** Set up particle description ***
oldtypes2(2)=particletype
blockcounts2(2)=NA
offsets2(2)=offsets2(2)-base2

call MPI_TYPE_CREATE_STRUCT(2, blockcounts2, offsets2, oldtypes2, heptanetype, ierr)
call MPI_TYPE_COMMIT(heptanetype, ierr)

Two other commands were then used to actually send the data to each processor and then collect the new updated data back to the root processor. These commands are **MPI_BCAST** and **MPI_GATHER** respectively.

call MPI_BCAST(heptane, N, heptanetype, 0, MPI_COMM_WORLD, ierr)

---

! *** Collect the updated molecule data on master ***
do cc=1, counter
! write(1,*') cc=', cc
localhep(cc)=heptane(molbegin(myid+1)+cc-1)
end do

call MPI_Gatherv(localhep, counter, heptanetype, heptane, counts, displacements, heptanetype, 0, MPI_COMM_WORLD, ierr)

Finally to end the MPI process when the simulation is finished the following command could be used **call MPI_Finalize(ierr)**

! *** Close down MPI connections ***
Call MPI_Finalize(ierr)