DROPLET VAPORIZATION OF N-HEPTANE IN SUBCRITICAL CONDITIONS USING MOLECULAR DYNAMICS

A Thesis in
Aerospace Engineering

by
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ABSTRACT

The vaporization of a n-Heptane (C\textsubscript{7}H\textsubscript{16}) droplet is investigated using Molecular Dynamics (MD). Inter-molecular and intra-molecular forces are incorporated in these simulations using the Lennard-Jones 12-6 and a torsional potential. 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 temperatures are maintained in this initial period. This rescaling is continued until the simulation has reached thermal equilibrium, then it is free to evolve. Due to the high computational costs of simulating the vaporization a polyatomic molecule using MD, a parallel implementation of the system has been developed. Ten simulations were performed on systems of approximately 1500 molecules under pressures ranging from one to twenty-five atmospheres. The droplet was evaporated for a time ranging from one to two nanoseconds depending on the pressure. In all cases the droplet was initialized at 293.15 K and the vapor was initialized at either 471 K or 550 K. The latter case is above the supercritical temperature of n-Heptane, a commonly used model for diesel fuel. Cross-sectional contour plots looking at the kinetic and internal energies as well as the average force acting within the droplets are presented. Results show that the droplet loses its spherical shape very fast, especially when the pressure is increased. The Amsterdam method was used to analyze the evaporation rate
for each case. It was found out that all cases adhere to the $D^2$ law fairly well and that increasing the pressure accelerates the droplet vaporization. Finally, the evaporation constant was calculated and this study shows that it increases linearly with the reduced pressure. This work provides a foundation on which future polyatomic, in particular hydrocarbon, droplet vaporization studies can be performed. The next step is also to increase the pressure above its critical value for n-Heptane, as well as increasing the size of the system.
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Chapter 1

INTRODUCTION

Droplet vaporization and combustion have been a critical research topic in an attempt to improve chemical propulsion systems for rockets and jet engines. Droplet vaporization is of particular interest because to maximize the efficiency of the combustion, it is necessary to maximize the mixing of the constituents through atomization [1]. It is therefore in addition necessary to know the properties of a biphasic system. The studies of droplet vaporization in an environment where the temperature and the pressure are above the critical value have been particularly investigated in the past two decades; some of this work is documented in the review articles of Givler and Abraham [2], Bellan [3], Yang [4] and in the text book by Sirignano [5]. However, the critical transition as well at the how the equilibration behaves is still to be fully understood. The calculation of the Soret and Dufour terms [6] [7], which are cross terms in the mass diffusion and heat fluxes, are an example of some of the difficulties encountered. Also, the thermal and physical properties behave differently near the critical regime.

An alternative approach to the problem is the use of Molecular Dynamics (MD) simulations. In this case, the equations of motion are solved for a liquid droplet surrounded by a gas environment. All that is needed are the interaction potentials among the molecules [8] and the polyatomic constraints due to chemical bonds.
This work is using MD to simulate a n-heptane (that is typically used as a model for diesel fuel) droplet vaporizing. Petrilla simulated the droplet vaporization of a polyatomic molecule using molecular dynamics at low pressures [9] [10]. The purpose of this work is to extend this study to higher pressures and to explore the transcritical and supercritical regimes.

1.1 Literature Review

A limited review of droplet vaporization consisting of molecular dynamics will first be presented, then additionally relevant MD studies will be mentioned and finally some results from n-heptane vaporization experiments will be summarized.

1.1.1 Droplet Vaporization

In 1996, Long et al [11] conducted the first MD study of droplet vaporization. A three-dimensional submicron argon droplet was evaporated under subcritical conditions. The two-phase system studied consisted of 2048 argon atoms modeled using a 12-6 Lennard-Jones potential for the interatomic forces. The argon droplet initial temperature was 78K and it was then surrounded by vapor and heated to 120K. The time step was chosen very small to avoid errors and ensure the stability of the system. The equation used was (1)

$$\Delta t = 0.005 \sqrt{\frac{m\sigma^2}{\epsilon}}.$$  \hspace{1cm} (1)
which is roughly 10 femtoseconds for argon. The computed evaporation rate agreed with that predicted by the Knudsen aerosol theory. The Knudsen number is defined as the mean free path divided by the droplet radius.

In 1998 another study was conducted at Penn State University by Kaltz et al [12]. In this case, instead of just looking at a monoatomic system, the vaporized droplet was diatomic (liquid oxygen). This three-dimensional droplet was put into quiescent environments comprised of either hydrogen or helium. The environment pressures and temperatures ranged from 2 to 20 MPa and 200 to 300 K respectively. Eight different simulations were performed, three vaporizing in a hydrogen environment, the remaining five in a helium environment. The Knudsen number was calculated to determine whether it was a continuum or aerosol regime. The timestep used was 2.5 femtoseconds. The size of the system ranged from 21,000 to 44,000 molecules with the size of the droplet ranging from 4,900 to 9,300 molecules. The results proved to be very different depending on the environment pressure. At low to moderate pressure the droplet remained spherical and retained a distinct temperature profile. On the other hand, at higher pressure, the droplet first had the characteristics of the low pressures cases, but then at some point the surface tension disappeared resulting in a non-spherical droplet shape. The results showed that the assumptions used in subcritical droplet vaporization analyses may be valid at pressures much higher than the critical pressure of oxygen, on the condition that the pressures are moderate enough. It was also noted that hydrogen or helium molecules mixed into the droplet even at moderate pressures.
Also in 1998, Bhansali et al. [13] studied the evaporation of a sodium droplet. Again, a LJ12-6 potential was used and the system consisted of 864 sodium molecules. Various thermal properties were obtained from the simulation and compared to the limiting macroscopic values. While the surface tension obtained by Maruyama et al. [14] accurately predicted the macroscopic limit for argon, which is an insulator, the surface tension data obtained for sodium, a liquid metal conductor, do not reveal such a comparison. This was attributed to the lack of ion screening being accounted for in the LJ 12-6 potential.

A further study on droplet vaporization using MD simulations was published by Walther and Koumoutsakos in 2001 [15]. A nanometer-size argon droplet was evaporated at sub-critical condition (300K and 3 MPa). The main conclusion was that the D² law (the droplet diameter squared varies linearly with the time) for the vaporization was obeyed for a large simulation size (thousands of molecules in the droplet).

Also, in 2003, Consolini et al. [16] studied the vaporization of xenon droplets in a nitrogen environment, in both sub- and supercritical conditions. Both spherical and non-spherical droplets were considered. For subcritical conditions, it was shown that a spherical droplet maintained its sphericity and a non-spherical one became spherical after vaporizing 10% of the droplet. For the supercritical case, the droplet did not return to the spherical configuration and it was also observed that the temperature increased continuously during the vaporization process.

The most recent study was published in 2007 by Landry et al. [17]. Molecular dynamics simulations were used to model the evaporation of a Lennard–Jones argon nanodroplet into its own vapor for a wide range of ambient temperatures and ambient
pressures. The transitions from (i) high to low Knudsen number evaporation and (ii) subcritical to supercritical evaporation were observed. At a low ambient pressure of 0.4 MPa, the initial droplet Knudsen number was 1 and the droplet diameter decreased linearly with time, consistent with kinetic theory predictions. For a moderate ambient pressure of 3.0 MPa, the initial droplet Knudsen number was 0.1 and the square of the droplet diameter decreased linearly with time. For a high ambient pressure of 6.1 MPa, the evaporation was supercritical and the number of atoms in the droplet decreased linearly for the majority of the droplet lifetime. A technique was introduced to maintain a constant ambient pressure over the droplet lifetime, allowing for the observation of the influence of the ambient conditions on the droplet surface temperature. When the ambient pressure was greater than or equal to 1.4 times the critical pressure, the droplet surface temperature reached the critical temperature and the evaporation was supercritical. Below this ambient pressure, the droplet surface temperature reached a pseudowet-bulb condition.

1.1.2 Polyatomic Hydrocarbon Systems

Ryckaert et al. were major contributors to the development of alkane MD studies. The first study was published in 1977 [18] and involves the numerical integration of the equations of motion for n-butane. Its major contribution is the development of the SHAKE algorithm. The method is applied to a MD simulation of a liquid of 64 n-butane molecules and compared to a simulation using generalized coordinates. SHAKE uses the Verlet algorithm [19] for advancing the position and the velocities to the next time step, and then adds Lagrange multipliers to deal with the geometric constraints.
In 1978, Ryckaert and Bellemans [20] used the SHAKE method to look at both n-butane and n-decane. They also used the united atom model to simplify each CH2 and CH3 group, and introduced a torsion potential. The configuration properties and the internal relaxation behavior of the alkane chain were studied.

Another study on n-butane was published by Weber in 1978 [21]. A simulation of a fluid n-butane system was carried out using a straight chain skeletal model. The calculations reported here involved fluid densities from 288.80 to 721.9 kg/m$^3$ at several distinct temperatures. The linear self-diffusion constant, the rate of torsional gauche/trans relaxation and rotational tumbling of the fluid were studied. The model showed a high degree of cooperativity between the molecular vibration and rotation, and the bulk fluid motion.

Finally, Lee et al. published two studies in 1996 [22] and 1997 [23] on a variety of thermodynamic properties of liquid alkanes including viscosity, thermal conductivity and self diffusion coefficients. These studies were particularly important for our study on n-heptane. Some of the methods mentioned above will be discussed in the following chapter.

### 1.1.3 Experimental Vaporization Results

A number of experimental studies have been conducted to look at the evaporation of alkanes (including n-heptane) in both sub- and supercritical conditions.

In 1993, Sato [24] studied the effects of temperature and pressure on the evaporation constant of a n-heptane droplet in ambient nitrogen for both normal and microgravity fields. The pressure was increased up to 15 MPa. It was found that when the
ambient temperature was low, the evaporation constant decreased, reached a minimum, and then increased with the ambient pressure. If the ambient temperature increased and approached the critical value (above $T/Tc=0.85$), the evaporation constant did not take a minimum and increased monotonously. When the ambient temperature was above the critical value, the evaporation constant increased rapidly with pressure.

In 1993, Chauveau et al. [25] conducted experiments on the vaporization of a n-heptane droplet in ambient air at 300 K. They found that the average vaporization constant (which is defined as the slope of the variation of the squared droplet diameter in the quasi-steady evaporation period) was strongly decreasing for $P/Pc<1$, reaching a minimum at $P=Pc=27.4$ bar and then slowly increasing for $P/Pc>1$. Those results confirm the trend found by Sato at low ambient temperatures. In 1994, the same team published another study [26]. In this one, they were vaporizing methanol droplets in dry nitrogen and humid air at high pressure and 300 K. The average vaporization rates of methanol droplets in dry air continuously decreased with increasing pressure up to 9 MPa ($P/Pc=1.2$), confirming the trend observed in the previous study. The same year, Chesneau et al. [27] studied the vaporization of LOX droplets in stagnant air, nitrogen and helium up to 3 MPa and 300K. The explored regime was subcritical ($Tr=2$ but $Pr<0.6$) and diffusion and buoyancy controlled. A buoyancy correction was introduced and a comparison with the predictions of the quasi-steady law was performed. This model that has a linear trend provided a good fit for his experimental data (evaporation of an n-heptane droplet in either nitrogen or helium).
1.2 Problem Definition

A good understanding of the vaporization phenomenon would help to improve the combustion process. Therefore, MD methods are being used to look at the vaporization on the molecular level. The first studies using MD looked at monatomic and diatomic species, and now the next step is to study hydrocarbon fuels.

Usually, hydrocarbon fuels (such as diesel or gasoline) are composed of a variety of different species, but it is common to use n-heptane as a simplified version of the fuel in continuum studies. Petrilla developed the MD model of n-heptane used in this study [9] [10], and vaporized an n-heptane droplet at low subcritical pressures. The goal of this thesis is to extend the use of this model to higher temperature and pressure and approach the transcritical regime.

The following chapter will present the model, as well as the process by which the droplets were vaporized, and the results of the vaporization process. First, the n-heptane model, including the molecular representation, the force calculations and the constraints, will be presented. Then, the method used to regulate the temperature and the solutions chosen to improve the efficiency of the numerical simulations are documented. Finally, the different results are presented and are followed by the conclusions and some recommendations for future work.
Chapter 2

N-HEPTANE MODEL

The system of n-heptane molecules is modeled using different concepts. First, the atomic structure has to be modeled as a “united atom” with bonds applied within the molecule. Then, the different internal forces consisting of Lennard-Jones and torsion potentials have to be taken into account. Finally, the molecular constraints have to be maintained.

2.1 Molecular Representation

To have the most accurate results possible, one would want to represent each atom within the molecule individually, and also pay attention to all the bonds associated with each atom. But this would require taking into account all the vibrational modes present and therefore would require a very large computation time, a condition that cannot be accepted in molecular dynamics. In order to reduce this computation time but still keep a fairly accurate representation of the system, some simplifications have to be made. In the case of this simulation of n-heptane, the “united atom” model will be used along with a classical formulation for the bonds associated with each atom in the molecule, due to the relatively low energy present in the system at the temperature considered [28].

2.1.1 United Atom

In this study, the “united atom” model with be used. As it can be seen in Fig. 1, this concept groups each CH$_3$ and CH$_2$ monomer into a single point mass system.
This model is widely used in MD simulations because it allows decreasing the number of computations and interactions that are necessary therefore decreasing significantly the computation time. Several studies have shown that accurate results are still obtained for thermodynamic properties and some internal structures properties when using this model [20] [21] [22] [23] [29] [30] [31].

2.1.2 Geometrical Constraints

Since it is not possible to account for all the chemical bonding by using quantum mechanics, the molecules have to be treated as rigid or semi-rigid systems. To do that, the bond lengths and the bond angles have to be constrained between monomers (in some cases, even the torsion angles can be constrained, but in our model they are free to evolve based on a torsion potential that will be presented in the following section). All the parameters associated with n-heptane that were used are presented in Tab. 1, where $\varepsilon$ is the depth of the potential “well” and $\sigma$ is the distance at which the potential is zero.

![Fig. 1: A united atom model for CH₃](image_url)
It is important to note that the bond angles $\alpha$ are maintained by constraining the distance between next nearest monomers (i.e. monomers 1 and 3 for example). A model of n-heptane with the constrained bond and length can be seen in Fig. 2.

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Bond Angle</th>
<th>$\sigma$</th>
<th>$\varepsilon/k_B$</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>

It is important to note that the bond angles $\alpha$ are maintained by constraining the distance between next nearest monomers (i.e. monomers 1 and 3 for example). A model of n-heptane with the constrained bond and length can be seen in Fig. 2.

2.2 Force Calculations

Since MD is based on Newton’s Second Law, it is necessary to calculate the force exerted on a monomer to track its motion. In the case of n-heptane for this simulation, both intermolecular and intermolecular forces are acting, and these forces are calculated through two potentials.

On the one hand, the Lennard-Jones (LJ) potential is an applied to all intermolecular interactions and also within a given molecule it is limited to the monomers
that are not constrained by either bond length, bond angle or through torsion forces. On the other hand, the torsion potential is applied only within the same n-heptane molecule.

### 2.2.1 Lennard-Jones Potential

The intermolecular forces are all based on the potential energy from the interacting particles. The simplest and most commonly used potential that simulates 2 body interactions is the Lennard Jones (LJ) 12-6 potential that is shown in (2):

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

The parameters \( \sigma \) and \( \varepsilon \) are determined from experimental results; the ones for n-heptane are summarized in Tab. 1. Therefore, the potential is only a function of the distance between the interacting particles. The \( r^{-6} \) term describes long range attraction while the \( r^{-12} \) one accounts for the short repulsion due to the Pauli principle [32]. A plot of the LJ 12-6 potential vs the distance between the particles for n-heptane can be seen in Fig.3:
The calculation of the Lennard-Jones potential is one of the most time-consuming operations for each time step. To save computation time, the Lennard-Jones potential is often truncated at a cut-off distance of $2.5\sigma$. At this distance, the potential is only about $1/60$ of its minimum value $\epsilon$. However, to avoid a discontinuity in the potential energy, it is usually shifted upwards a little so that the computational potential would be exactly zero at the cutoff distance. Usually, this truncation method as well as the other one consisting of adding a long-range correction to the tail have little influence on the bulk properties up to 90 percent of the critical temperature [32].
2.2.2 Torsion Potential

Bond torsion forces are intermolecular forces that accounted for twisting around one or two bonds. It is calculated in terms of the relative location 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

The force only depends on the rotation around the bond between atom i-1 and i in this group since all the bond lengths and angles are fixed. This angle is called the dihedral angle. 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 (3).

\[
\cos \theta = \frac{\left( \mathbf{d}_{i-1} \times \mathbf{d}_i \right) \cdot \left( \mathbf{d}_i \times \mathbf{d}_{i+1} \right)}{|\mathbf{d}_{i-1} \times \mathbf{d}_i| |\mathbf{d}_i \times \mathbf{d}_{i+1}|} \tag{3}
\]

Additionally the angle between bonds \( \mathbf{d}_{i-1} \) and \( \mathbf{d}_i \) is expressed by (4).

\[
\cos \alpha_i = \frac{\mathbf{d}_{i-1} \cdot \mathbf{d}_i}{|\mathbf{d}_{i-1}| |\mathbf{d}_i|} \tag{4}
\]
The torsion force on all four monomers, (i-2) through (i+1) above is calculated from the relation in (5).

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

(5)

where \( u(\theta) \) is the torsion potential given by (6).

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

(6)

Here \( k_B \) is the Boltzmann constant. The forces on subsequent sets of four monomers are calculated throughout the entire molecule until the total force on each monomer is obtained [9].

2.3 Algorithm Maintaining Constraints

Bond length and angles have to be readjusted during each time step to make up for the computation errors in the numerical integration of the equations of motion. This requires a more sophisticated treatment that the relatively simple algorithms used for monatomic systems.

The first algorithm that has been widely used to constrain molecules is the SHAKE algorithm [29] [33] [34] [35]. SHAKE [18] advances the equations of motion while constraining the bonds through the use of Lagrange multipliers, but it incorporates the same limitations found in the Verlet [19] algorithm, where the atom velocities are not used while integrating the equations of motion. Therefore, approximate values have to be
calculated following each integration step and the algorithm suffers from a greater loss of precision [36] [10].

That is why another algorithm known as RATTLE [37] had to be implemented. It implements the geometrical constraints of chain molecules as given in SHAKE but uses a two part Velocity Verlet [38] method to directly include velocities. RATTLE was developed in 1983 by Andersen [37].

The differential equation to be solved is

\[ m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \sum_j \lambda_{ij}(t) \mathbf{v}_j \mathbf{\sigma}_{ij} \]  

where the first term on the right hand side represents the sum of the LJ and torsion potentials and the second one the constraints of monomer (i) with monomer (j) (it is expressed in terms of time-dependent Lagrange multipliers \( \lambda_{RRij} \) and \( \lambda_{RVij} \)).

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 (8) and (9) respectively.

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

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

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, (10) and (11) shown below are iteratively solved to ensure the constraints are maintained, within a given tolerance.
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 (12) by recalculating the forces based on the new positions and velocities.

\[
\mathbf{r}_i(t+h) = \mathbf{r}_i(t+h) + \frac{2h^2}{m_i} \sum_j \lambda_{RRij} (t) \mathbf{r}_j(t)
\] (10)

\[
\mathbf{\ddot{r}}_i(t+h) = \mathbf{\ddot{r}}_i(t+h) - \frac{2h}{m_i} \sum_j \lambda_{RRij} (t) \mathbf{r}_j(t)
\] (11)

The Lagrange multiplier calculations for \(\lambda_{RRij}\) and \(\lambda_{avij}\) are performed for each molecule through an iterative procedure until \(\left| \mathbf{r}_j(t+h) \right|^2 - b^2_{ij}\) is within a specified tolerance of zero for all bonds as follows

\[
\lambda_{RRij} = \frac{\left| \mathbf{r}_j(t+h) \right|^2 - b^2_{ij}}{2\left| \mathbf{r}_j(t+h) \mathbf{r}_j(t) \right| \left( m^{-1}_i + m^{-1}_j \right)}
\] (14)
where $b_0$ 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 [9] [10].
Chapter 3

SIMULATION METHODOLOGY

When simulating a n-heptane system using Molecular Dynamics, one should think about two important parameters. The first one is how to regulate the system. In this case, a velocity rescaling that regulates the temperature is applied. The second one is how to reduce the simulation time. This is done through the use of periodic boundary conditions, neighbor lists and parallelization of the code. Finally, it is important to consider how to initialize the code.

3.1 Velocity Rescaling

Velocity rescaling is used to maintain a constant temperature in the system. If we decompose the velocity of each monomer, $v_i$, into the molecular center of mass velocity, $v_{cm}$, and a fluctuating component, $v_i'$, the energy of a given molecule can be expressed as

$$E_{k,mol} = \sum_i \left[ \frac{1}{2} m_i v_{cm}^2 \right] + \sum_i \left[ \frac{1}{2} m_i \left( v_i' \right)^2 \right]$$

where,

$$v_i = v_{cm} + v_i' ; \quad v_{cm} = \frac{1}{m_{mol}} \sum_{i=1}^2 m_i v_i ; \quad m_{mol} = \sum_{i=1}^2 m_i$$
Here $v_i$ is a velocity in a fixed reference frame, $m_i$ is the mass of a monomer, and $m_{mol}$ is the molecular mass. The summation is over all monomers within a given molecule.

The first term in (15) is the pure translational component and the second term corresponds to internal motions. For n-heptane, we have 3 translational and 7 internal degrees of freedom [20]. If we perform a sum of the translational component over all the molecules in the system, we arrive at the global kinetic temperature

$$T_{\text{kin}} = \frac{2}{3} \frac{1}{Nk_B} \sum_j \left( \sum_{i=1}^7 \frac{1}{2} m_i v_{i,\text{cm}}^2 \right)$$

(18)

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 by

$$T_{\text{int}} = \frac{2}{7} \frac{1}{Nk_B} \sum_j \sum_{i=1}^7 \left[ \frac{1}{2} m_i \left( v_{i}^\prime \right)^2 \right]$$

(19)

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 (17) and (18). 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. Both phases are treated in the same fashion.
3.2 Simulation Refinements

Since MD simulations require very large amounts of computation time as well as memory, one would want to use methods that greatly reduce it. The most widely used of these are to employ periodic boundary conditions, use what is known as a neighbor list, and use parallel processing.

3.2.1 Periodic Boundary Conditions

The use of periodic boundary conditions has two main purposes. The first one is to overcome surface effects (that was done by Born and von Karman in 1912 [39]). The second one is to simulate the effect of a much larger bulk system without increasing the actual size of the system, and therefore not increase computation time.

The basic principle of periodic boundary conditions is that if a molecule moves through a boundary on one edge of the domain, it will return to it from the opposite edge. Fig. 5 shows an example of a two dimensional square domain. Each molecule can leave and reenter the domain from the mirror one on the other side.
3.2.2 Neighbor Lists

Besides the use of periodic boundary conditions, another way to reduce simulation time is the use of neighbor lists when calculating the LJ potential. This method was proposed by Verlet in 1967 [19]. A cutoff distance of $2.5\sigma$ is used for the calculation of the LJ forces. He thought that creating a list for each molecule that keeps track of which molecules fall within a $2.5\sigma$ radius would be better than determining whether or not each
pair of molecule have LJ interactions each time step. The number of calculations done during the force calculation is significantly reduced when using this method.

Rather than updating the neighbor list each time step it would be better to update it less often. Allen and Tildesley [8] stated that the cutoff distance for the neighbor list was varied to improve the performance of the calculation and $3.1\sigma$ was found to be the optimal cutoff distance for the system being looked at. Petrilla [10] found that the optimal update period for the neighbor list was 80 time steps.

Fig. 6: Neighbor list with a cutoff for the LJ potential $R_c$ and a neighbor list cutoff $R_n$
3.2.3 Parallelization

Parallel programming uses multiple processors to split the computation performed each time step and therefore decreases simulation time. The code must be altered to allow message passing between processors. The standard used for this simulation is MPI2 (Message Passing Interference).

The calculations are split up by using “atom or molecule decomposition” [40]. This method splits up the molecules evenly without regard to their location within the system. In our simulation case, this method was more efficient than the other method (“domain decomposition”) because of the very uneven distribution of molecules in the case of droplet vaporization.

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. Both phases were given an initial temperature and were allowed to evolve over time until thermal equilibrium was achieved. Then the two phases were combined to form the initial droplet vaporization setup.

3.3.1 Gas Phase

The gas phase was initialized at two different temperatures of 471 K and 550 K depending on the set of simulations. Initially, the gas phase was placed in a cubic domain with periodic boundary conditions. A density of 2.586 kg/m$^3$ was used for this phase at 1
atm of pressure and 471 K. All gas densities were calculated using the ideal gas law. The molecules were arranged on a BCC lattice, as suggested by Rapaport [28].

3.3.2 Liquid Phase

The liquid phase was initialized at 293.15 K, and a density of 679.5 kg/m\(^3\) was chosen at 1 atm of pressure. The densities were obtained from reference 41. An additional modification was required for the liquid phase, which consists of placing the monomers in a helical shape arrangement for each molecule. This was done to ensure the correct liquid density is achieved without having overlapping monomers. This structure was chosen to reduce the linear length of each molecule such that large repulsive forces were not experienced. The initial helical setup for the system is shown in Fig. 7. An initial random velocity was then given to all monomers.
After both phases were initialized on the BCC lattice and were assigned initial random velocities, the separate systems were allowed to evolve through the use of the RATTLE algorithm. Velocity rescaling was used for the first half of these simulations to ensure that a constant system temperature was maintained. Then velocity rescaling was shut off after the system had relaxed to a random state. Kinetic and internal temperatures were compared to ensure thermal equilibration and therefore make sure the simulation could be stopped.

Then, the liquid and gas phases were combined to begin the droplet vaporization. A spherical droplet was cut from the gas phase and placed in the center of the gas.
domain. Any gas molecules that occupied liquid space were removed so that no overlap would occur. The initial setup is shown in Fig. 8.

![Initial setup of a 1524 molecules droplet vaporization simulation](image)

Fig. 8: Initial setup of a 1524 molecules droplet vaporization simulation

During the droplet vaporization, velocity rescaling was applied again, but this time for the entire simulation time (only near the boundaries so that a constant bulk gas temperature was maintained). The system was run until thermal equilibrium is achieved and the droplet vaporizes.
Chapter 4

RESULTS

4.1 Equilibration of Gas and Liquid Phases

The initial setup of both liquid and gas phases were discussed in the previous chapter. During the equilibrium process both the liquid and gas phases used a time step of 1.25 femtosecond (fs). Velocity rescaled is applied for a period of 0.125 nanosecond (ns), then it was shut off and then system was allowed to evolve for another 0.125 ns to ensure it had reached equilibrium. The total simulation time was therefore 0.25 ns. The final position of a 1000 molecules liquid system can be seen in Fig. 9.
To confirm that thermal equilibrium was achieved, the internal and kinetic temperatures of the system were compared. From the equipartition theorem, when a system is in equilibrium, all degrees of freedom should contain $1/3k_B T$ kinetic energy. Therefore, when the system is in equilibrium the kinetic and internal temperatures should be equivalent. The kinetic and internal temperatures for a 1000 molecules liquid system can be seen in Fig. 10.
Fig. 10: Temperature plot for a 1000 molecule system. The average kinetic temperature of the system after rescaling is 293.58 K. The average internal temperature after rescaling is 293.72 K.

The difference between the two averages is only 0.18 K and it can also be seen that the graph is lacking any temperature drift after the rescaling period, so thermal equilibrium has been reached.

4.2 Droplet Vaporization

After equilibrating the gas and liquid phases the droplet vaporization could proceed. Four cases were run at a temperature of 471 K (since the critical temperature is Tc=540 K, the ratio of the temperatures T/Tc is equal to 0.87) of approximately 1500
molecules at pressure of 1, 2, 5 and 9 atmospheres. 6 other cases were run at a
temperature of 550 °K and pressures ranging from 1 to 25 atm (also approximately 1500
molecules). For n-heptane, the critical pressure is 27 atm and the critical temperature is
540 °K. Tab.2 lists each case and the conditions at which they were run.

Tab. 2: Summary of each droplet vaporization

<table>
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<th>Case</th>
<th>P(atm)</th>
<th>Environment Total Number of Molecules</th>
<th>Vapor</th>
<th>Liquid</th>
<th>Vapor</th>
<th>Liquid</th>
<th>Vapor</th>
<th>Liquid</th>
<th>Vapor</th>
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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. Fig. 11 through Fig. 20 show contour plots for the first through the
fourth cases respectively. Each plot has an overlay of the center of mass of each molecule
in the system. Additionally, for conciseness only one cross sectional plane is presented
for each case as the cross sections for the two other dimensions 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 [42] on argon droplets and Kaltz [43] on oxygen droplets, these plots do not have nicely shaped droplets or temperature distributions. The difference is due to the much smaller size of the system as well as the presence of internal motions within each molecule. The plots of the net forces acting within the droplet, Fig. 11 through Fig. 20, show that these droplets are too small to stay spherical throughout the vaporization. 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 [42] and Kaltz et al. [12,43]. Instead, one can see a more random distribution of the forces as the droplet shape evolves over time. The higher pressure cases show that the droplet totally disappears quickly.
Fig. 11: Contour plots for 1529 molecules system at 1 atm and 471 K vs. time
Fig. 12: Contour plots for 1526 molecules system at 2 atm and 471 K vs. time
Fig. 13: Contour plots for 1517 molecules system at 5 atm and 471 K vs. time
Fig. 14: Contour plots for 1500 molecules system at 9 atm and 471 K vs. time
Fig. 15: Contour plots for 1527 molecules system at 1 atm and 550 K vs. time
Time

0.025 ns  0.375 ns  0.750 ns

Translational Kinetic Energy

Internal Temperature

Average Force

Fig. 16: Contour plots for 1524 molecules system at 2 atm and 550 K vs. time
Fig. 17: Contour plots for 1514 molecules system at 5 atm and 550 K vs. time
Fig. 18: Contour plots for 1493 molecules system at 10 atm and 550 K vs. time
Fig. 19: Contour plots for 1475 molecules system at 20 atm and 550 K vs. time
Time
0.025 ns                      0.175 ns

Translational Kinetic Energy

Internal Temperature

Average Force

Fig. 20: Contour plots for 1420 molecules system at 25 atm and 550 K vs. time
Further analysis of the simulation results was done by using the Amsterdam method to determine the number of molecules in the liquid droplet. The Amsterdam method requires that a minimum of 4 molecules be present within a certain distance for the molecule to be considered part of the droplet. Petrilla [10] used values of $1.7\sigma$, $1.9\sigma$ and $2.1\sigma$ for the vaporization of n-heptane, and compared those to a reference value of $1.6$. He found that the value of $2.1\sigma$ is the more accurate for this study. Fig. 21 and Fig. 22 show the evaporation rate for the four different cases using a $2.1\sigma$ Amsterdam cutoff radius. N represents the number of molecules in the droplet.

![Fig. 21: Number of molecule in the droplets at 471 K and different pressures vs. time](image-url)
Fig. 22: molecule in the droplets at 550 K and different pressures vs. time

Each case was also compared to the D² law that 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 obtained by taking the number of droplet molecules present and raising it to the two-thirds power. Then all systems are scaled to 1. The results can be seen in Fig. 23 and Fig. 24.
Fig. 23: Comparison of 1500 molecules droplet at 471 K to the D² law
Fig. 24: Comparison of 1500 molecules droplet at 550 K to the D² law

All cases adhere to the D² law fairly well, with some variations between runs. It can be noticed that the vaporization rate is increasing with the ambient pressure. This can be explained as the result of an increase of the heat flux into the droplet from the gas region for higher pressure cases.

The evaporation constant is defined as the slope of the variation of the squared droplet diameter in the quasi-steady evaporation period [24]. In our case, the slope of the rescaled vaporization rate was calculated. The results are presented in Fig. 25 and Fig. 26.
Fig. 25: Evaporation constant vs. reduced pressure at $T=471$ K

Fig. 26: Evaporation constant vs. reduced pressure at $T=550$ K
It can be seen that the evaporation constant increases linearly with the pressure. This tends to confirm the results and predictions by Chesneau [27]. He introduced a buoyancy corrected average model for the evaporation constant. This model that has a linear trend provided a good fit for his experimental data (evaporation of an n-heptane droplet in either nitrogen or helium).

The results of these simulations show that even a micrometer 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 [11] 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. Ten 1500 molecules system cases were looked at including a system at 471 K and 1, 2, 5 and 9 atmospheres of pressure as well as another system at 550 K and a pressure ranging from 1 to 25 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 molecule. 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, D^2 behavior was observed for all ten cases. Also, the evaporation constant was calculated and it appears that it is increasing linearly with pressure.

This important first step showed that using MD to simulate droplet vaporization is possible. Additionally, it confirmed that even in very small droplets, D^2 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 these 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.
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