

## **Predicting Vapor-Liquid Equilibrium for Hydrazine using Gibbs Ensemble Monte Carlo Simulations with updated OPLS Force Field Parameters**

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*Hydrazine is an important fuel that is used as a rocket propellant. Conducting experimental tests on hydrazine are difficult since hydrazine is highly reactive and dangerous. Gibbs Ensemble molecular simulations were conducted for hydrazine under high temperature conditions to obtain vapor-liquid equilibrium properties. Vapor-liquid equilibrium information is important for safety and design calculations for operations such as tank filling and isentropic compression. Prior work in our group included simulations using parameters that were determined for unsymmetrical dimethylhydrazine. In this work, updated hydrazine parameters derived from ab initio calculations for the hydrazine molecule were used. The Gibbs Ensemble Monte Carlo simulations were carried out using a simulation package from Sandia National Laboratories called Towhee (version 4.13.2). Simulations were run at multiple values of temperature to determine equilibrium pressure as well as liquid and vapor densities. The results of the simulations using the new parameters show that the new parameters yield vapor-liquid equilibrium predictions that are closer to the experimental data available than the predictions from the simulations using the old parameters values. The experimental density at 500K is 0.80g/ml (Schmidt, 2001), previous simulation results yielded a value of 1.087g/ml, and the updated simulation resulted in a value of 0.91g/ml. Predictions from the previous simulations achieved an accuracy range of 22-73%. New results had an improved accuracy of 50-88%.*

### **Introduction**

Hydrazine is a highly reactive liquid base; it is a water-soluble compound that is mainly used as a rocket propellant. Other uses include but are not limited to, the production of spandex fibers, agricultural chemicals, nickel-plating, nuclear fuel reprocessing, production of plastics and the removal of halogens from wastewater. Hydrazine has an odor similar to that of ammonia. It is manufactured by the Raschig process, which involves the oxidation of ammonia to chloramines.

Production of hydrazine in the U.S. has almost tripled since the mid 1960's from 15 million pounds to 38 million pounds. Forty percent of the hydrazine produced yearly in the United States is used for agricultural processes. The cost of anhydrous hydrazine in drum quantities in 1959 was \$7.00 per kg. The projected price, based on large-scale commercial production, was expected to be \$1.00 per kg. Because of strict environmental regulations, by 1990 NASA was paying around \$17.00 per kg for this compound (Encyclopedia Astronautica, 2005). Although hydrazine is used in a wide range of applications, its high reactivity makes it a dangerous compound to work with and therefore it is important to use alternative methods to understand how it behaves under different circumstances.

The reason why hydrazine is so reactive lies within its chemical structure. Hydrazine has a strong nucleophilicity. A nucleophile literally means "nucleus lover", it is a compound that is attracted to centers of positive charge (Holleman et al, 2001). A nucleophile participates in a chemical reaction by donating its electrons to another species in order to make a chemical bond.

Since hydrazine is so difficult to work with, there is very little published experimental property data for it. Its reactive and toxic properties not only make it an expensive but unsafe task to obtain this experimental data.

It is known that inhalation of small amounts of hydrazine will cause coughing and irritation of the throat and lungs, and even seizures. Hydrazine may also cause liver and kidney damage, or coma. Hydrazine is found in chewing tobacco and cigarettes. Tumors have been seen in many organs of animals that were exposed to hydrazine by ingestion or breathing. 1,2-Dimethylhydrazine has caused colon cancer in laboratory animals following a *single* exposure (). The Department of Health and Human Services (DHHS), The International Agency for Research on Cancer (IARC) and The Environmental Protection Agency (EPA) have all determined that several hydrazine derivatives are probable human carcinogens.

## Experimental

An alternative method to obtain the necessary information is through molecular computer simulations. Performing “experiments” with the help of computer software will provide important information about the behavior of hydrazine in a safe and cost-effective way (Palanivelu, 2005). Molecular simulations are versatile computational techniques used to determine the properties of a molecular system using either molecular dynamics or integral equation calculation methods that use pseudorandom numbers to obtain fitted data (called The Monte Carlo Method). The determination of accurate physical and thermodynamic properties such as vapor-liquid equilibrium (vapor pressure), density and heat of vaporization will be obtained. These values will then be compared with values that were calculated from the Peng-Robinson equation of state. The Peng-Robinson equation of state is one of the many equations that are currently being used to describe a compound under a specific set of conditions such as temperature, volume, and pressure. It provides a relationship between two or more state functions. Equations of state are useful in describing the properties of fluids, mixtures of fluids as well as solids, and the Peng-Robinson does a good job in predicting densities of liquids. For this reason is important to obtain data for hydrazine under a wide range of temperatures. It is our responsibility to understand and predict the behavior of such a dangerous and desirable compound.

### -MONTE CARLO SIMULATIONS

Monte Carlo simulation was named for Monte Carlo, Monaco, where the primary attractions are casinos containing games that exhibit random behavior. The random behavior in games of chance is similar to how Monte Carlo simulation selects variable values at random to simulate a model. It's the same with the variables that have a known range of values but an uncertain value for any particular time or event. Most physical problems that involve interaction of molecules are usually formulated as integral equations (Perry, 1997). The Monte Carlo Method is a method uses pseudorandom numbers from 0 to 9, for this reason it is well-suited for their solution. There are five types most commonly encountered types of Monte Carlo Simulations, we will be using the "classical" Monte Carlo, or CMC (samples are drawn from a probability distribution, often the classical Boltzmann distribution) to obtain thermodynamic properties, minimum-energy structures and/or rate coefficients.

## -TOWHEE 4.13.2

MCCCS Towhee is a Monte Carlo molecular simulation code originally designed for the prediction of fluid phase equilibrium using atom-based force fields and the Gibbs ensemble with particular attention paid to algorithms addressing molecule conformation sampling. The code has subsequently been extended to several ensembles, many different force fields, and solid phases. The Monte Carlo for Complex Chemical Systems (MCCCS) program was first developed in 1994 at the University of Minnesota. In 2003 Towhee began migrating to the SourceForge site and it finished moving there completely in September of 2005. The user base has continued to swell, and new developers are leaving their mark upon the code. Sample codes for both input and force field files used to be able to run the simulations are below:

```
towhee_input          'classical'
                        ffnumber
randomseed             1
2602006               ff_filename
inputformat           /home/stokes1/cessna/towhee-
'Towhee'              4.13.2/ForceFields/towhee_ff_NMSU
ensemble              classical_potential
'nvt'                 'Lennard-Jones'
temperature           classical_mixrule
500.0d0               'Geometric'
nmolty                lshift
1                     .false.
nmolectyp             ltailc
261                   .true.
numboxes              rmin
2                     0.5d0
stepstyle             rcut
'cycles'              10.0d0
nstep                 rcutin
500                   10.0d0
printfreq             coulombstyle
100                   'ewald_fixed_kmax'
blocksize             kalp
250                   5.6d0
moviefreq             kmax
100000               5
backupfreq            dielect
1000                  1.0d0
runoutput             nfield
'full'                0
pdb_output_freq       isolvtype
0                     0
loutdft               linit
.false.               T
loutlamps             initboxtype
.false.               'dimensions'
pressurefreq          initstyle
20                    'full cbmc'
trmaxdispfreq         'full cbmc'
1000                  initlattice
volmaxdispfreq        'simple cubic'
10                    'simple cubic'
chempotperstep        initmol
10                    1
potentialstyle         260
```

inix	inix	iniz			pmavb2ct
1	1	1			1.0d0
7	7	7			avb2rad
hmatrix					10.0d0
45.0d0	0.0d0	0.0d0		pmavb3	
0.0d0	45.0d0	0.0d0		0.0d0	
0.0d0	0.0d0	45.0d0			pmavb3mt
30.0d0	0.0d0	0.0d0			1.0d0
0.0d0	30.0d0	0.0d0			pmavb3ct
0.0d0	0.0d0	30.0d0			1.0d0
pmvol					avb3rad
0.1d0					10.0d0
	pmvlpr			pmcb	
	1.0d0			0.4d0	
	rmvol				pmcbmt
	0.1d0				1.0d0
	tavol				pmall
	0.5d0				0.0d0
pmcell				pmback	
0.0d0				0.0d0	
	pmcellpr				pmbkmt
	1.0d0				1.0d0
	pmcellpt			mpivot	
	0.5d0			0.0d0	
	rmcell				mpivmt
	1.0d0				1.0d0
	tacell			pmconrot	
	0.5d0			0.0d0	
pm2boxrbswap					pmcrmt
0.2d0					1.0d0
	pm2rbswmt			pmcrback	
	1.0d0			0.0d0	
	pm2rbswpr				pmcrbmt
	1.0d0				1.0d0
pm2boxcbswap				pmplane	
0.1d0				0.0d0	
	pm2cbswmt				pmplanebox
	1.0d0				0.0d0 1.0d0
	pm2cbswpr				planewidth
	1.0d0				3.0d0
pm1boxcbswap				pmrow	
0.1d0				0.0d0	
	pm1cbswmt				pmrowbox
	1.0d0				0.0d0 1.0d0
pmavb1					rowwidth
0.0d0					3.0d0
	pmavblin			pmtraat	
	0.5d0			0.0d0	
	pmavblmt				pmtamt
	1.0d0				1.0d0
	pmavblct				rmtraa
	1.0d0				0.5d0
	avblrad				tatraa
	10.0d0				0.5d0
pmavb2				pmtracm	
0.0d0				0.67d0	
	pmavb2in				pmtcmt
	0.5d0				1.0d0
	pmavb2mt				rmtrac
	1.0d0				0.5d0

tatract	2
0.5d0	improper torsion
pmrotate	0
1.0d0	unit ntype qqatom
pmromt	6 'H' 0.375d0
1.0d0	vibration
rmrot	1
0.05d0	2
tarot	improper torsion
0.5d0	0
cbmc_style	
'coupled-decoupled'	
coupled_decoupled_form	
'Coupled to pre-nonbond'	
cbmc_setting_style	
'Martin and Frischknecht'	
inpstyle hydrazine	
2	
nunit	
6	<b>towhee_ff</b>
nmaxcbmc	towhee_ff Version
6	13
lpdbnames	Number of Nonbonded Types
F	2
forcefield	Potential Type
'NMSU'	Lennard-Jones
charge_assignment	Classical Mixrule
'manual'	Geometric
unit ntype qqatom	Atom Type Number
1 'NT~2' -0.75d0	1
vibration	Nonbond Coefficients
3	0.
2 3 4	0.
improper torsion	0.
0	0.
unit ntype qqatom	Mass
2 'NT~2' -0.75d0	1.0079
vibration	Element
3	H
1 5 6	Bond Pattern
improper torsion	s
0	Base Charge
unit ntype qqatom	0.
3 'H' 0.375d0	Polarizability
vibration	1.0
1	Force Field Name
1	NMSU
improper torsion	Atom Names
0	H
unit ntype qqatom	H
4 'H' 0.375d0	H
vibration	H
1	H
1	Atom Type Number
improper torsion	2
0	Nonbond Coefficients
unit ntype qqatom	3.29999995
5 'H' 0.375d0	85.5468243
vibration	3.29999995
1	42.7734122

Mass	108.9
14.007	17516.092
Element	Force Field Name
N	NMSU
Bond Pattern	Number of Atoms with Same
sp3	Parameters
Base Charge	1
0.	Atom Names
Polarizability	NT NT H
1.0	Angle Type Number
Force Field Name	2
NMSU	Angle Style
Atom Names	1
NT~2	Angle Coefficients
NT	106.8
NT	22022.619
NT~	Force Field Name
Number of Bonded Terms	NMSU
2	Number of Atoms with Same
Bond Type Number	Parameters
1	1
Bond Style	Atom Names
2	H NT H
Bond Coefficients	Number of Torsion Terms
1.437	1
215780.611	Torsion Type Number
Force Field Name	1
NMSU	Torsion Style
Number of Atoms with Same	2
Parameters	One-Four Nonbond Logical
1	T
Atom Names	One-Four Coulombic Scaling
NT NT	0.5
Bond Type Number	Torsion Coefficients
2	0.
Bond Style	0.
2	75.4824921
Bond Coefficients	Force Field Name
1.014	NMSU
277122.925	Number of Atoms with Same
Force Field Name	Parameters
NMSU	1
Number of Atoms with Same	Atom Names
Parameters	H NT~ NT~ H
1	Number of Improper Terms
Atom Names	0
H NT	Number of Angle-Angle Terms
Number of Angle Terms	0
2	Number of One-Five Types
Angle Type Number	0
1	Number of Bond Increments
Angle Style	0
1	
Angle Coefficients	

## Results

Below are the values of the molecule parameters that were used for the simulations. Both previous and updated angle bond and angle constants were compared (Table 1.1) as well as the bond force and bond constants (Table 2.1). The values for degrees, lengths and constants were inserted into the Towhee software code.

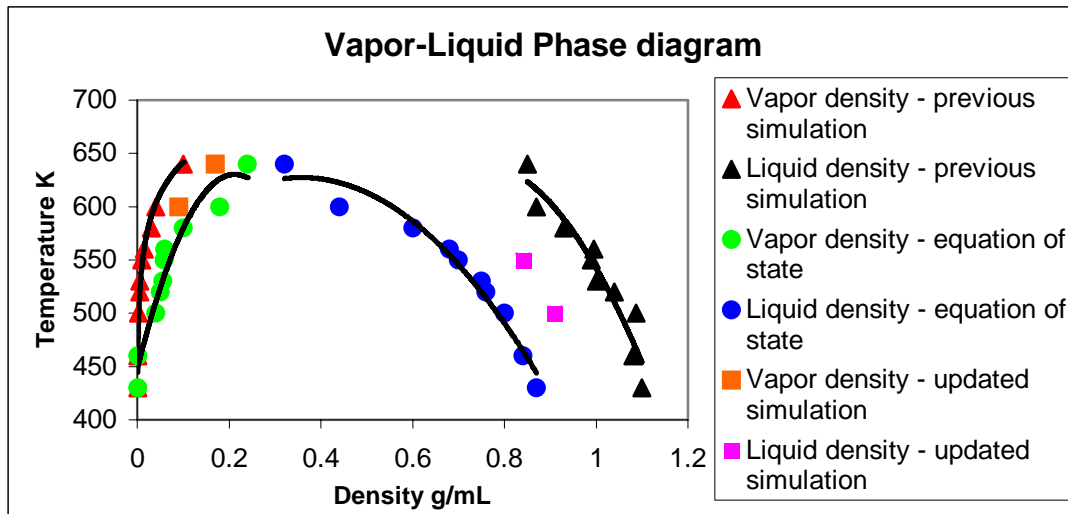
Parameter type	Angle Bond	Degrees	Constant, K/rad <sup>2</sup>
Old parameter	N-N-H	109.5	17612.6
New parameter	N-N-H	108.9	17516.092
Old parameter	H-N-H	106.4	21940.2
New parameter	H-N-H	106.8	22022.619

Table 1.1. Comparison of angle bond and angle constant values

Parameter type	Bond	Length, Å	Constant, K/Å <sup>2</sup>
Old parameter	N-N	1.445	176125.8
New parameter	N-N	1.437	215780.611
Old parameter	N-H	1.01	218396
New parameter	N-H	1.014	277122.925

Table 1.2. Comparison of bond lengths and bond constant values

The various simulations yielded the following data points that were plotted against previous works and actual experimental data.



Graph 1. Vapor-Liquid Phase diagram will all simulations and experimental data

The four data points that were obtained for the value of density (two data points for liquid density and two for vapor density) are shown in the graph above (Graph 1).

## **Discussion and Conclusion**

This project was started by a graduate student who wanted to see how accurate molecular simulations were when trying to find vapor-liquid equilibrium properties. The molecular parameters had to be found in order to accomplish the simulation, but for some reason the hydrazine parameters were not found. Instead, the parameters of dimethylhydrazine (a derivative of hydrazine) were implemented. Just last year, a chemical engineering student found the parameters for the hydrazine molecule that needed to be used. This research took these 'new' parameters and ran the whole simulation again with the objective of obtaining more accurate numbers that were closer to actual experimental values. The input codes were updated and changed and the simulation itself ran for about a day and a half at three different temperatures: 500, 550 and 600K. From the diagram above we can observe that our new parameter values changed our results significantly, our new numbers are now closer to the experimental values at the same temperature.

Experimental value of density at 500K is about 0.80g/ml, this new simulation yielded a value of 0.91g/ml which is far more accurate than the previous simulation that yielded 1.87g/ml. Another simulation at 650K resulted in a density of 0.17 for an experimental value of 0.32g/ml and previous simulations displayed a value of 0.85g/ml. In general, new simulations showed an improved accuracy range of 50-88% versus the 22-73% for the previous work.

Even though the parameter values, new compared to old, are very similar, there is a significant shift in property values towards the experimental curve. This is a good sign that shows us that the molecular simulation that was executed is more accurate than the previous one.

## **Future Work**

The work presented will be further extended to better determine the accuracy of the numbers obtained. The results will be compared to approximations given by an equation of state such as the Peng-Robinson equation. More simulations will be completed at different temperatures to be able to complete the new phase envelope.

This work could also be extended to other carcinogenic derivatives of hydrazine and other dangerous compounds that are useful, but dangerous to work with. This method will not only take less time and money, but will also help save human lives and unfortunate accidents that are prone to happen when it is necessary to work with dangerous compounds.

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