**Modeling Interfacial Tensions in Tight Formations Using Molecular Simulations Documentation**

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**Abstract**

This document serves as documentation of the research setup utilized to conduct molecular simulations for the paper in progress: *Modeling Interfacial Tensions in Tight Formations Using Molecular Simulation.* There are detailed instructions to properly setup a machine to perform molecular simulations with the RASPA software package and to run customized simulations of bulk densities of single alkane systems beyond critical pressure. Additional to the documentation, all research conducted is available privately on GitHub to further investigate and expand upon the findings shown here.

1. **Installation**

RASPA allows for numerous types of molecular simulations (i.e. Grand Canonical Monte Carlo,

Molecular Dynamics, Radial Distributions, and more) and operates through the Command Line. The machine used to develop this documentation was running Mac OSX 11.6.5 with an Intel i7 chip and 16GB RAM. To properly install the software package RASPA onto a compatible machine the following steps were used in the Terminal command line:

Download the GitHub repository into your home folder:

git clone <https://github.com/iRASPA/RASPA2>

Move into the ‘RASPA2’ folder and compile and install the package as follows:

cd RASPA2

rm -rf autom4te.cache

mkdir m4

aclocal

autoreconf -i

automake –add-missing

autoconf

export CFLAGS=”-Wall -03 -mfpmath=sse -fomit-frame-pointer -ftree-vectorize -funroll-loops -ffast-math”

export CC=”gcc”

./scripts/CompileScript/make-gcc-local

make

make install

If the commands above result in any errors, it means that certain packages are not installed on the current machine and need to be to perform simulations properly. Commonly for Mac OS, XCode is required for its Command Line Tools package and Homebrew allows for simple installation of other necessary packages. The compilation and installation process should take roughly ten minutes and should not present any errors to ensure accurate simulations moving forward.

1. **Simulation Structure**

To run a simulation of any kind, the most necessary components are the ‘run’ file and ‘simulation.input’ file. The ‘simulation.input’ file operates by defining the specifics of the simulation that is to be run. Here is an example of an input file for bulk density of fluid methane:

SimulationType MonteCarlo

NumberOfCycles 5000

NumberOfInitializationCycles 2000

PrintEvery 100

RestartFile no

Forcefield ExampleMoleculeForceField

Box 0

BoxLengths 100 100 100

ExternalTemperature 298.0

ExternalPressure 2.97e7

ComputeMolecularPressure yes

VolumeChangeProbability 0.05

Component 0 MoleculeName methane

MoleculeDefinition ExampleDefinitions

TranslationProbability 0.5

RotationProbability 0.5

ReinsertionProbability 0.5

CreateNumberOfMolecules 256

This input file for bulk density of fluid methane specifies the type of simulation, how many cycles, how many molecules, and the operating pressure. Different types of simulations require additional or different parameters to complete successfully. The simulations in this paper were based off of the RASPA documentation to complete the Non-Basic example of NPT simulations for propane, which can be in the ‘examples/Non-Basic/2\_MC\_NPT\_Propane’ directory of RASPA. The example ‘simulation.input’ files provided in the RASPA2/examples folder are great resources for tailoring input files to specific situations and understanding the syntax of the files.

A common error that occurs with these simulations is with the box cutoff length being longer than the box lengths:

ERROR: (System (0) Cutoff smaller than half of one of the perpendicular boxlengths !!!

Cutoff: 12.000000 perpendicular boxlengths: 23.976919 23.976919 23.976919

This is typically solved by increasing the box lengths from 30 to 100 or by increasing the number of fluid molecules in the box from 100 to 150 or 256. This results in a longer simulation run time, however it almost always guarantees a successful run and the numbers can be modified to improve accuracy or runtime.

The ‘run’ file is identical for all simulations and is structured as follows:

#! /bin/sh -f

export RASPA\_DIR=${HOME}/RASPA/simulations/

export DYLD\_LIBRARY\_PATH=${RASPA\_DIR}/lib

export LD\_LIBRARY\_PATH=${RASPA\_DIR}/lib

$RASPA\_DIR/bin/simulate $1

This file calls the necessary locations of RASPA files needed to run simulations and link different forcefields, molecules, and frameworks. To initiate any simulation, the command **./run** is entered into the Command Line inside of a simulation’s respective folder.

To structure the files properly in separate folders, the name of the folder should describe what simulation is being done and subfolders should describe the molecules or distinct parameters used in the simulations to help avoid confusion. The output files of the completed simulation provide this information as well, but it is simpler to add this for less time spent searching for certain results. The file structure shown in the GitHub repository at: <https://github.com/amoghcharan/IFT-RASPA/> is a proper example of this. Additionally, to improve workflows a shell script was created for each simulation to automate the simulation runs and track progress for each molecule in the research conducted. This script can be called with the command **bash fluid.sh** where the fluid is specific to the simulation being run.

1. **Simulation Data**

After a simulation is ran, the directory will now contain resulting ‘Movies’, ‘Output’, ‘Restart’, and ‘VTK’ subdirectories containing the simulation data. Different output files provided will contain data to create visualizations, tables, charts, and more. For the purpose of the fluid bulk density studies, the resulting data is found in the ‘Output’ folder and provides a breakdown of the simulation at numerous intervals. The search functionality of the file viewer is the quickest method to find distinct parameters. For the bulk density plots generated, searching for ‘average density’ in the output file provides the overall average density of the fluid during the simulation and its standard deviation.

Average density:

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Block[ 0] 524.52480 [kg/m^3]

Block[ 1] 521.21182 [kg/m^3]

Block[ 2] 520.94172 [kg/m^3]

Block[ 3] 525.88760 [kg/m^3]

Block[ 4] 520.30588 [kg/m^3]

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Average 522.57437 [kg/m^3] +/- 3.06932 [kg/m^3]

The average bulk density for fluid propane at twice the critical pressure is 522.574 kg/m3 or 11.850 mmol/cm3. In comparison the NIST data claims this value to be 11.612 mmol/cm3 which is only a 2.04% error. The simulated data is shown against the NIST dataset in Figures 1-5 of the Appendix and Figure 6 shows the original simulations performed with the older MuSiC software package.

1. **Appendix**

**Figure 1. GCMC of Fluid Bulk Density for Methane at 298 K**

**Figure 2. GCMC of Fluid Bulk Density for Propane at 298 K**

**Figure 3. GCMC of Fluid Bulk Density for Butane at 298 K**

**Figure 4. GCMC of Fluid Bulk Density for Hexane at 298 K**

**Figure 5. GCMC of Fluid Bulk Density for Ethane at 298 K**

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**Figure 6. Original GCMC of Fluid Bulk Density for Single Alkane Systems**

1. **References**

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