CHEM 4305 Term Project: Simulating Molecular Liquids

Stage 3: Calculate the Properties of the Liquid

23. Find Literature Values

Find experimental values for the density, enthalpy of vaporization, self-diffusion coefficient, and dielectric constant at 298 K. Record the citation(s) of these values according to the ACS Style Guide (http://pubs.acs.org/isbn/9780841239999). Enter these data in the following table.

Property	Calculated	Experimental [a]
ρ (kg/m^3)		
Δ_{vap}H (kJ/mol)		
D (cm^2/s)		
ε		

a. Citation for experimental values.

24. Run a Production MD Simulation of Your Liquid

Change to the directory where you ran the equilibriation. Copy the NAMD input file, `production.namd`, to this directory.

```
$ cp ~crowley/chm4305/production.namd .
```

Edit `production.namd` to match the file names for your simulation

```
# input
coordinates             moleculefill.pdb
bincoordinates          moleculefill.coor
extendedSystem          moleculefill.xsc
structure               moleculefill.psf
parameters              molecule.prm
paratypecharmm          on

# output
set output              production
outputname              $output
dcdfile                 ${output}.dcd
xstFile                 ${output}.xst
dcdfreq                 1000
xstFreq                 1000
binaryoutput            no

binaryrestart           no
outputEnergies          100
restartfreq             1000

fixedAtoms              off
```

```
# Basic dynamics
exclude                 scaled1-4
1-4scaling              1
COMmotion               no
dielectric              1.0

# Simulation space partitioning
switching               on
switchdist              9
cutoff                  10
pairlistdist            12

# Multiple timestepping
firsttimestep           0
timestep                1
stepspercycle           20
nonbondedFreq           2
fullElectFrequency      4

# Temperature control

set temperature         298
temperature             $temperature;  # initial temperature

# Langevin Dynamics
langevin            on;  # do langevin dynamics
langevinDamping     1;   # damping coefficient (gamma) of 1/ps
langevinTemp        $temperature;   # bath temperature
langevinHydrogen    no; # don't couple langevin bath to hydrogens
seed                    12345

# Pressure control
langevinPiston          on
langevinPistonTarget    1.01325; # in bar -> 1.01325 bar = 1 atm
langevinPistonPeriod    2000
langevinPistonDecay     100
langevinPistonTemp      $temperature
useFlexibleCell         no
useGroupPressure        no
fixedAtomsForces        off

# PBC
wrapAll                 on
PME                     yes
PMEGridSpacing          1.0

# Scripting
reinitvels          $temperature
run                 5000000
```

Write a submission script for your job and submit it to the queue,

```
$ nano script-3.sh
```

```
#!/bin/bash
#$ -l h_rt=48:00:00
#$ -pe openmp* 4
#$ -cwd

module load namd/2.9-smp
namd2 +p4 production.namd 1> production.out 2> production.err
```

```
$ qsub script-3.sh
```

25. Calculate the Density and Dielectric Constant of the Liquid

To calculate the density and dielectric constant, you need a program called dcd2prop-rev. This program will read the .psf and the .dcd files generated from your production NVT simulation.

```
$ ~crowley/chm4305/dcd2prop-rev -p thiophenefill.psf -t production.dcd
epsinf= 1.000000 0.000000 136.254790 eps = 1.494838
density = 1025.317754 (kg/m^3)
```

26. Calculate the Internal Energy of Your Liquid

You now have the `production.out` file that you need to use to calculate the enthalpy of vaporization of the liquid. A python script (`internalenergy.py`) is provided to extract this property from the output file for you

In this example, the output file (`production.out`) and the number of molecules in the unit cell (`203`) are given as arguments to this script.

```
$ ~crowley/chm4305/internalenergy.py production.out 203
INTERNAL ENERGY = 40.8700776536  kJ/mol
```

Record this value ($\langle U \rangle_{\text{liquid}}$) for use in calculating the enthalpy of vapourization.

27. Calculating the Internal Energy in the Gas Phase.

Next, we have to calculate the enthalpy of the gas phase. To do this, we run an md simulation Change to the directory where you ran `antechamber` in Stage 1. Make a new directory and copy necessary files to it. Follow the commands below to copy the files you need into the gas phase directory. Note that you are copying the pdb and psf files for a single molecule generated using `antechamber/charmm`.

```
$ cd antechamberdemo
$ mkdir gas_phase
$ cp thiophene.pdb gas_phase/
$ cp thiophene.psf gas_phase/
$ cp thiophene.prm gas_phase/
$ cp ~crowley/chm4305/onemolecule.namd gas_phase/
$ cd gas_phase/
```

The simulation of a single molecule is fast enough to run on the command line. Edit `onemolecule.namd` so that the file names match those of your molecule then run the MD simulation.

```
$ nano onemolecule.namd
$ module load namd
$ namd2 onemolecule.namd > onemolecule.out
```

Run the internalenergy.py script to determine the internal energy.

```
$ ~crowley/chm4305/internalenergy.py onemolecule.out 1
INTERNAL ENERGY = 11.37456344 kJ/mol
```

Record this value ($\langle U \rangle_{gas}$) for use in calculating the enthalpy of vaporization.

28. Calculate the Enthalpy of Vaporization.

Use the internal energies calculated from your simulations to calculate the enthalpy of vaporization of your liquid. Record this value in your Table.

$\Delta H_{vap} = RT + \langle U \rangle_{gas} - \langle U \rangle_{liquid}$

29. Run a Production NVE MD Simulation of Your Liquid

The calculation of the diffusion coefficient requires a trajectory from an NVE simulation where PBC wrapping is turned off. Wait until the NVT production simulation is complete. Change to the directory where you ran the production simulation of your liquid. Copy the `production-nve.namd` file to this directory.

```
$ cp ~crowley/chm4305/production-nve.namd .
```

Write a submission script for this calculation and submit it to the queue.

```
$ nano script-4.sh
```

```
#!/bin/bash
#$ -l h_rt=24:00:00
#$ -pe openmp* 4
#$ -cwd

module load namd/2.9-smp
namd2 +p4 production-nve.namd 1> production-nve.out 2> production-nve.err
```

```
$ qsub script-4.sh
```

Wait for the simulation to finish. One it is complete, you can use VMD with an extension for calculating the diffusion coefficient (D). Copy this script (`diffusion_coefficient.tcl`) to this directory, then run `VMD` to calculate the diffusion coefficient.

```
$ cp ~crowley/chm4305/diffusion_coefficient.tcl .
$ module load vmd
$ vmd
vmd> source diffusion_coefficient.tcl
vmd> package require diffusion_coefficient
vmd> mol new moleculefill.psf
Info) Using plugin psf for structure file moleculefill.psf
psfplugin) no cross-terms defined in PSF file.
```

```
Info) Analyzing structure ...
…
vmd> mol addfile production-nve.dcd
dcdplugin) detected standard 32-bit DCD file of native endianness
dcdplugin) CHARMM format DCD file (also NAMD 2.1 and later)
Info) Using plugin dcd for coordinates from file production-
nve.dcd
0
vmd > Info) Coordinate I/O rate 1374 frames/sec, 55 MB/sec, 6.9
sec
Info) Finished with coordinate file production-nve.dcd.
vmd> diffusion_coefficient -selection "name C1" -msd 1000
Computing: 100% done
Ready
145.94395560285034
```

The number printed is the MSD of the system at time τ in units of Å^2. Use the following equation to solve for the diffusion coefficient, where τ is 1000 times the timestep of your MD simulation (timestep (fs)) times the number of steps between the frequency at which configurations were saved to the trajectory file (dcdfreq). Record the calculated diffusion coefficient in your table.

$$\left\langle \left| r(t+\tau) - r(t) \right|^2 \right\rangle = 6D\tau$$

See this website for more information:
http://multiscalelab.org/utilities/DiffusionCoefficientTool

Graduate Students Only

30. Calculation of the Surface Tension

The surface tension of a liquid can be calculated from the averages of the pressure tensor on a system that contains a slab of the liquid in the XY plane, with vapour phases above and below this slab on the Z axes. This can be created by using the equilibrated unit cell of the liquid and using it to initiate a new simulation where the cell basis vector along the Z axis is elongated to create the vapour layers.

A general input file for this simulation can be copied from the chm4305 directory.

```
$ cp ~crowley/chm4305/interface.namd .
```

Edit this input file to take the cell dimensions from the production.xsc file and enter them in the x and y cell vector fields.

```
# input
coordinates             moleculefill.pdb
bincoordinates          production.corr
```

```
structure               moleculefill.psf
parameters              molecule.prm
paratypecharmm          on

cellBasisVector1 39.7349 0 0
cellBasisVector2 0 39.7349 0
cellBasisVector3 0 0 72
```

$$\gamma = \frac{1}{2} L_z \left[\langle P_{zz} \rangle - \frac{1}{2} \left(\langle P_{xx} \rangle + \langle P_{yy} \rangle \right) \right]$$

L_z is the length of the simulation cell along the Z-axis (72 Å). P_{xx}, P_{yy}, and P_{zz} are the xx, yy, and zz components of the pressure tensor. Their averages can be extracted from the interface.log file using the script pressuretensor.py.

Part 3 Complete

Submit a PDF file containing the table of the computed density, enthalpy of vaporization, and diffusion coefficient in the Term Project Dropbox on D2L.