**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/m3) |  |  |
| ΔvapH (kJ/mol) |  |  |
| D (cm2/s) |  |  |
| ε |  |  |

1. 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.

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| $ **cp ~crowley/chm4305/production.namd .** |

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

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| --- |
| # 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,

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| $ **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.

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| $ **~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.

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

Record this value () 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.

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| $ **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.

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| $ **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 () 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.

**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.

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| $ **cp ~crowley/chm4305/production-nve.namd .** |

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

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| $ **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.

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| $ **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 Å2. 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.



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.

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| $ **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.

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| --- |
| # 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 |

Lz is the length of the simulation cell along the Z-axis (72 Å). Pxx, Pyy, and Pzz 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.