

HEXANE WATER RESULTS LOG

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1. 1/8/2018

- (1) Ran a simulation of the hexane-water interface using LAMMPS. Set up for 1M time steps, but only got through 745,200 due to time limit of 24 hrs.
- (2) Ran a simulation of the hexane-water interface in DASH, using the python script "interface.py" in the dash-work/interface folder. The run was for 4,000,000 time steps, printing a configuration every 50,000 steps. Below are snapshots of the 0th timestep and the 3,950,000 time step.

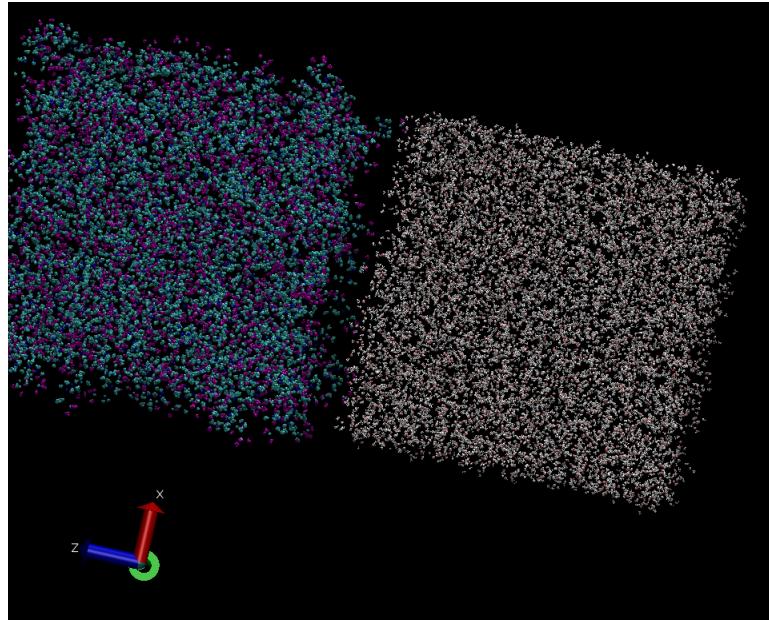


FIGURE 1. DASH simulation of the TAFFI - q-TIP4P/F interface. Arithmetic mixing, 4,000,000 time steps. This is the 0th timestep.

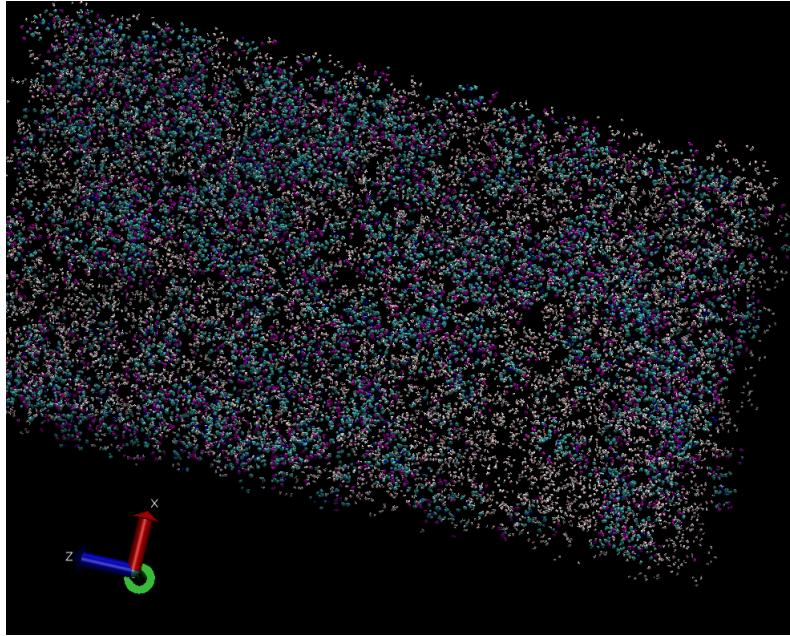


FIGURE 2. DASH simulation of the TAFFI - q-TIP4P/F interface. Arithmetic mixing, 4,000,000 time steps. This is the 3,950,000th timestep.

- (3) This is in stark contrast to the amount of mixing that we observed in OPLS + TIP4P/2005 in LAMMPS, which was the appropriate amount of mixing, i.e., very little mixing. So, there are several possible things going on here. One is that there is an error in the code. Another is that there is an error in DASH. And third is that there is a problem with the interaction parameters between the two force fields. So, here are the following tests that we are going to run to narrow down the problem:

Run TAFFI + TIP4P/F in LAMMPS using arithmetic, geometric, and Waldman-Hagler mixing rules and using both TAFFI and OPLS parameters for hexane

Run TAFFI + TIP4P/F in DASH using geometric and Waldman-Hagler mixing rules using both TAFFI and OPLS parameters and using 1 bead versus 8 beads

Run OPLS + TIP4P/F in DASH using geometric mixing rules and using 1 bead versus 8 beads

Check for any errors in the DASH input scripts

TAFFI + TIP4P/F in DASH using one bead

- (4) So, the first step we are going to take is to run TAFFI + q-TIP4P/F in LAMMPS using arithmetic mixing rules. Let's first take a look at the simulation of TAFFI + TIP4P/2005 and see what that snapshot looks like. At timestep zero:

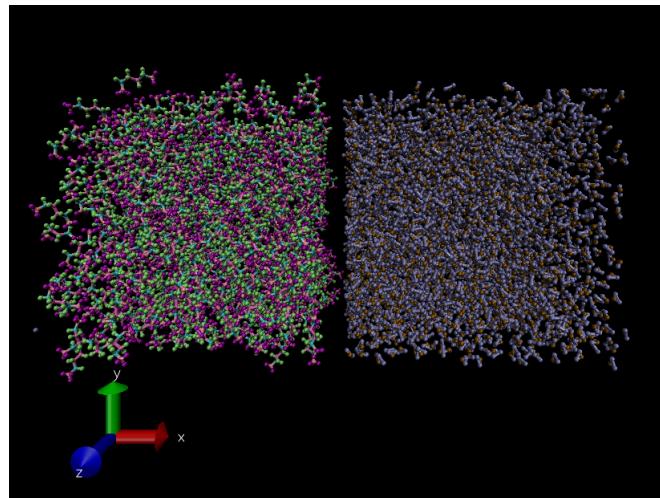


FIGURE 3. Lammps simulation of the TAFFI - TIP4P/2005 interface. Arithmetic mixing, 200,000 time steps. This is the 0th timestep.

After 200,000 time steps:

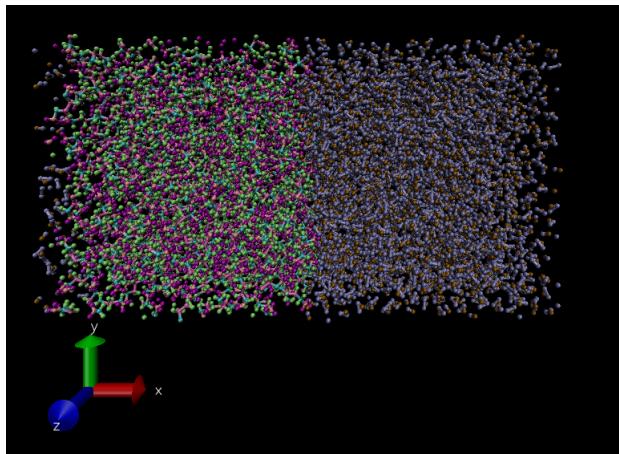


FIGURE 4. Lammps simulation of the TAFFI - TIP4P/2005 interface. Arithmetic mixing, 200,000 time steps. This is the 199,000th timestep.

For more direct comparison, here is the dash version of TAFFI + TIP4P/F at 200,000 steps:

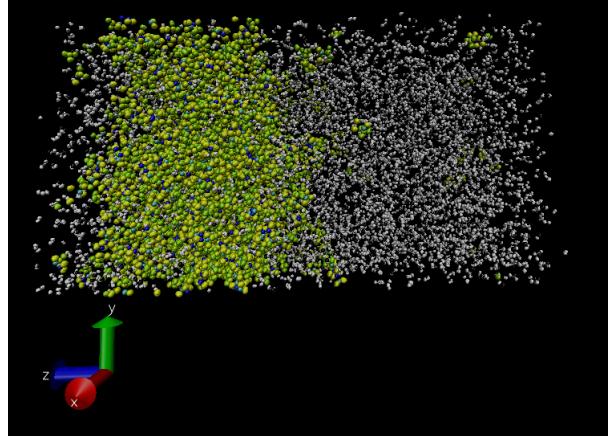


FIGURE 5. DASH simulation of the TAFFI - q-TIP4P/F interface. Arithmetic mixing, 4,000,000 time steps. This is the 3,950,000th timestep.

- (5) Now, we are going to construct the TIP4P/F in LAMMPS. The starting point is the TIP4P/2005 classical rigid water model, which we have already implemented. The next step is to add a quartic expansion of a Morse potential for the OH stretch:

$$V_{OH}(r) = D_r \left[\alpha_r^2(r - r_0)^2 - \alpha_r^3(r - r_0)^3 + \frac{7}{12}\alpha_r^4(r - r_0)^4 \right], \quad (1.1)$$

where $D_r = 116.09$, $\alpha_r = 2.287$, and $r_0 = 0.9419$.

And then we add a simple harmonic potential for the bond angle:

$$V_{HOH}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2, \quad (1.2)$$

where $k_\theta = 87.85$, and $\theta_0 = 107.4$.

- (6) In LAMMPS, then, we will try using `bond_style class2` for the quartic expansion of the Morse potential for the OH stretch:

$$E = K_2(r - r_0)^2 + K_3(r - r_0)^3 + K_4(r - r_0)^4, \quad (1.3)$$

where $r_0 = r_{eq}$, $K_2 = \alpha_r^2 = 5.23$, $K_3 = -\alpha_r^3 = -11.962$, and $K_4 = \frac{7}{12}\alpha_r^4 = 15.958$.

- (7) We will use `angle_style harmonic` for the simple harmonic potential for the bond angle:

$$E = K(\theta - \theta_0)^2, \quad (1.4)$$

where $K = \frac{1}{2}k_\theta$ and $\theta_0 = \theta_{eq} = 107.4$.

- (8) Then, we created a `data_water_flexible.txt` file, which is a data file describing a single TIP4P/F water molecule for lammps. I then created an `in.water_flexible` file, a lammps input file to run the flexible water model simulation. I modified this from the TIP4P/2005 input file by removing the fix shake command and

- adding the bond_style class2 command. I then ran lammps_molecule_replicator_water.py in order to get 3650 flexible water molecules on an initial lattice.
- (9) I tried running a lammps simulation using in.water_flexible, but I am getting the error that the program does not recognize class2. Turns out that this belongs to the LAMMPS package CLASS2, which might not be compiled for in my folder. So checking that now.
 - (10) Compiled LAMMPS with CLASS2, and now able to run the flexible water model. However, massive forces seem to be appearing as I am getting the error: "Out of range atoms - cannot compute PPPM). It works better if I make the timestep minuscule, but it still breaks eventually. Sometimes says missing bonds or atoms. My guess is that I shouldn't be using the command pair_style lj/cut/tip4p/long. So perhaps for next time, what I need to do is just implement the water model irrespective of that particular pair style command, and instead I need to input all of the specifications by hand.
 - (11) Setting that aside for now, let's turn to DASH again, and try different parameter sets here. Let's first work just in the classical world, with one bead. First, let's run TAFFI + TIP4P/F in DASH using TAFFI parameters, geometric mixing, and 1 bead.
 - (12) This is currently running.
 - (13) Now, let's run TAFFI + TIP4P/F in DASH using TAFFI parameters, arithmetic mixing, and 1 bead. Just to check/be consistent.
 - (14) This is also currently running.

1.1. 2/23/2018.

- (1) NOTICED AN ERROR: MISSING FACTOR OF 116 IN THE BOND POTENTIAL. FIX THIS NEXT.

1.2. 2/27/2018.

- (1) Fixed this problem, added the missing factor of 166.09 in the bond potential where it was due. Saved the resulting new input file. Currently, running an NPT system of 3650 water molecules in order to generate an initial configuration for the test interface of q-TIP4P/F and TAFFI in LAMMPS.
- (2) The TAFFI + TIP4P/F in DASH using TAFFI parameters, arithmetic mixing, and 1 bead finished running. There is too much mixing going on. Here is a snapshot at time zero:

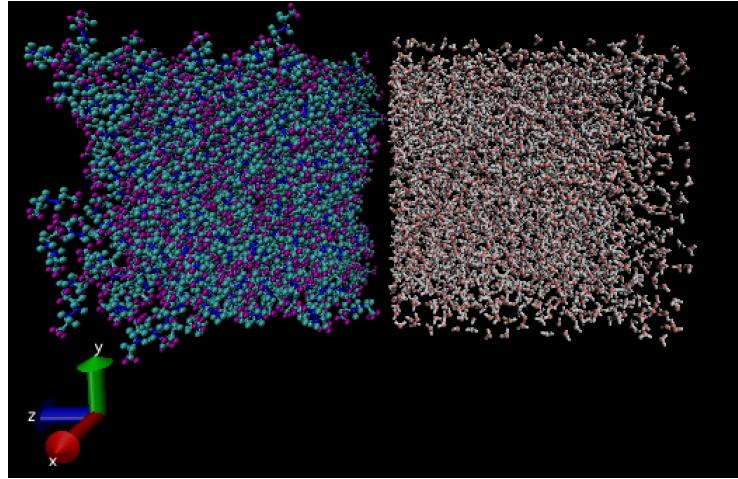


FIGURE 6. DASH simulation of the TAFFI - q-TIP4P/F interface. Arithmetic mixing, 4,000,000 time steps, 1 bead. This is the 0th timestep.

(3) Here is a snapshot after 4,000,000 timesteps of length 0.5:

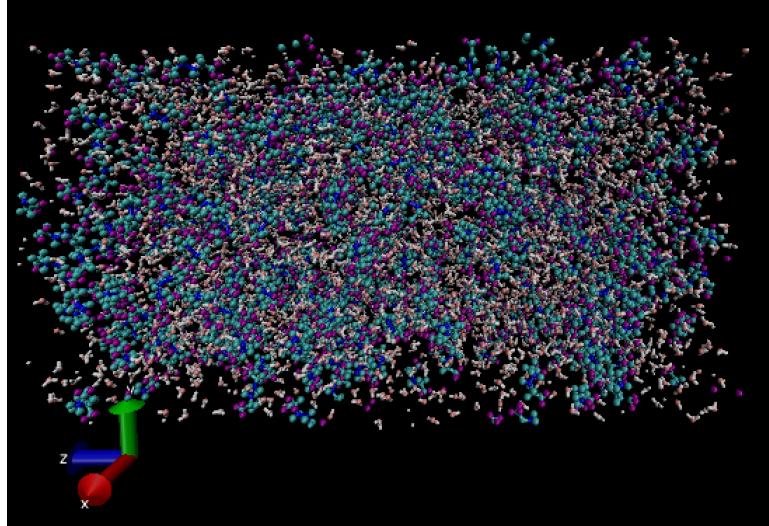


FIGURE 7. DASH simulation of the TAFFI - q-TIP4P/F interface. Arithmetic mixing, 4,000,000 time steps, 1 bead. This is the 3950000th timestep.

(4) The TAFFI + TIP4P/F in DASH using TAFFI parameters, geometric mixing, and 1 bead also finished running. There is too much mixing. Here is a snapshot at time zero:

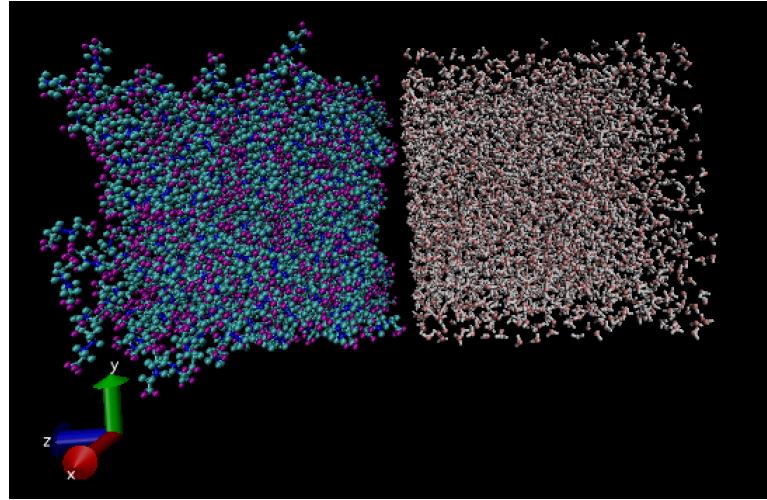


FIGURE 8. DASH simulation of the TAFFI - q-TIP4P/F interface. Geometric mixing, 4,000,000 time steps, 1 bead. This is the 0th timestep.

(5) Here is after 4,000,000 timesteps of length 0.5:

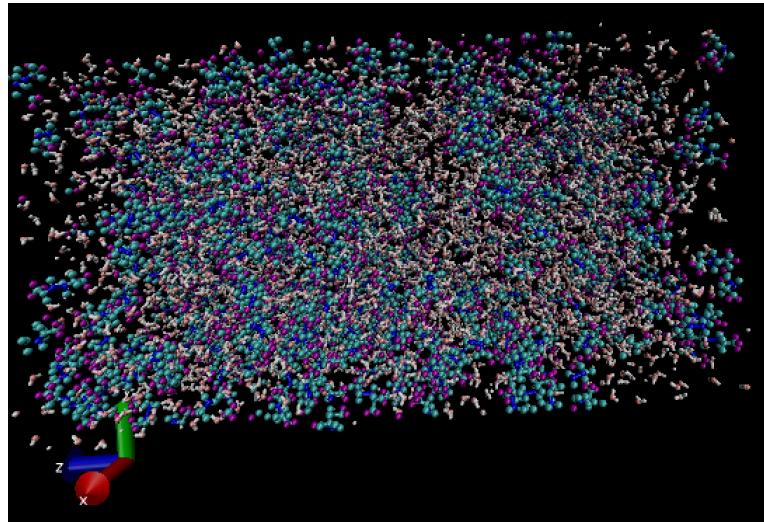


FIGURE 9. DASH simulation of the TAFFI - q-TIP4P/F interface. Geometric mixing, 4,000,000 time steps, 1 bead. This is the 3950000th timestep.

1.3. 3/5/2018.

- (1) Downloaded the trajectory file, dump.water_flexible.lammpstrj, from the lammps_water/water folder to check the performance of the TIP4P/F in LAMMPS. The trajectory looks good. Moreover, the density of the system reached a final value instantaneous value, at step 200,000, of 0.98752919. The output file produced, output_water_flexible_preequil.txt, taken after the final 200,000th step in the simulation, also looks reasonable:

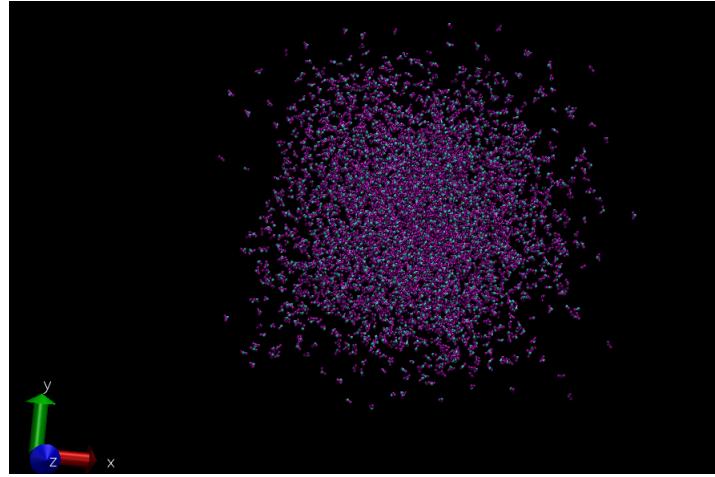


FIGURE 10. LAMMPS simulation of TIP4P/F water. Geometric mixing, 200,000 timesteps, this is the final step.

- (2) Now, we will follow steps from before to simulate the TAFFI - q-TIP4P/F interface in LAMMPS.
- (3) First, move output_water_flexible_preequil.txt into the interface folder. Also move the file hexane_restart_modified.txt, which is a preequilibrated slab of TAFFI hexane. Now, we have two preequilibrated slabs - one with 500 TAFFI hexane molecules, and the other with 3650 TIP4P/F water molecules.
- (4) Second, move original molecular data file descriptions of single molecules of TAFFI hexane (i.e. data_webb_hexane_modified.txt) and TIP4P/F water (data_water_flexible.txt) to the interface folder.
- (5) Run the file lammmps_molecule_replicator_tip4pwater_webbhexane.py in order to produce a mixed system template that can be used as the -dataoriginal input file in the lammmps_restart.py program. This is what this original file looks like:

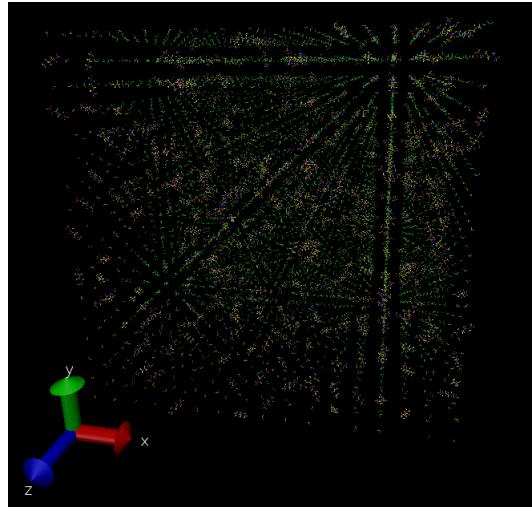


FIGURE 11. Image of datafileoriginal for TAFFI and TIP4P/F.

Run the lammps_restart.py file using -data1=hexane_restart_modified.txt, -data2=output_water_flexible_preequil.txt, and -dataoriginal=datafileoriginal_taffi_tip4pF.txt. This produces the initial configuration for the hexane-water TAFFI-TIP4P/F system in LAMMPS:

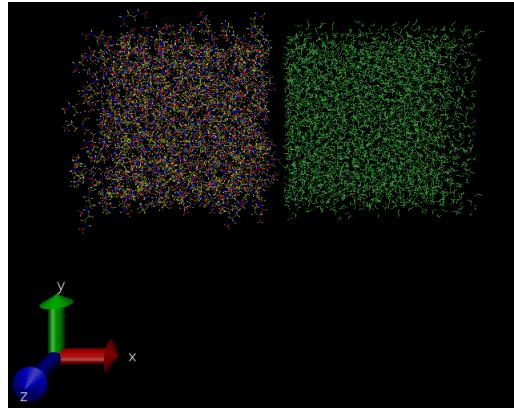


FIGURE 12. Image of input file for TAFFI and TIP4P/F.

- (6) Finally, adjust the input_restart_taffi_tip4pF file to have a Bond Coeffs style that is compatible with bond_style class2.
- (7) HYPOTHESIS: All of my previous LAMMPS simulations of the interface were NPT, while in DASH, they were NVT. Perhaps this is a difference? I must do all simulations in both to check...
- (8) I am now running a LAMMPS simulation of the hexane-water interface: 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT, 200,000 steps of time 1.0.
- (9) I am now also running an NVT LAMMPS simulation of the hexane-water interface: 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NVT, 200,000 steps of time 1.0.

1.4. 3/6/2018.

- (1) These are snapshots of the NPT simulations:

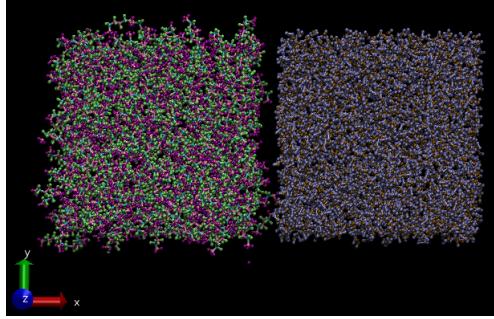


FIGURE 13. LAMMPS simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT at $T = 300$ and $P = 1$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at the same T and P . Cutoff = 12.0, pppm/tip4p 1e-4, special bonds 0 0 0. This is the 0th timestep.

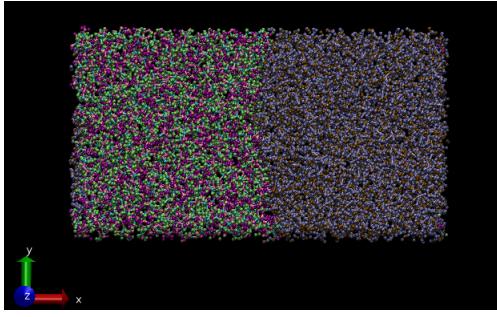


FIGURE 14. LAMMPS simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT at $T = 300$ and $P = 1$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at the same T and P . Cutoff = 12.0, pppm/tip4p 1e-4, special bonds 0 0 0. This is the 200,000th timestep.

- (2) So, the TAFFI-TIP4P/F interface in LAMMPS appears to be stable under NPT conditions. The final density of this simulation was around 0.854.
- (3) These are snapshots of the NVT simulations:

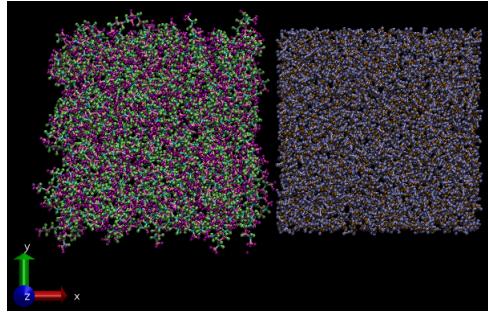


FIGURE 15. LAMMPS simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NVT at $T = 300$ and $V = (4.722, 5.62, 6.26) \times (113.25, 64.29, 64.71)$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at the same T and $P = 1.0$. Cutoff = 12.0, pppm/tip4p 1e-4, special bonds 0 0 0. This is the 0th timestep.

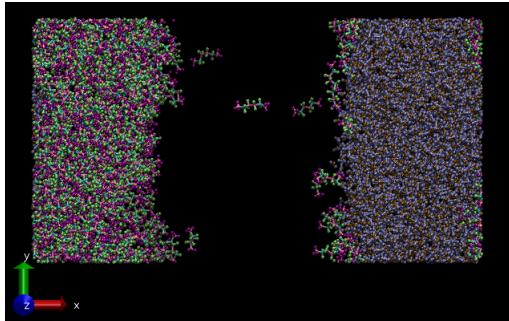


FIGURE 16. LAMMPS simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NVT at $T = 300$ and $V = (4.722, 5.62, 6.26) \times (113.25, 64.29, 64.71)$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at the same T and $P = 1.0$. Cutoff = 12.0, pppm/tip4p 1e-4, special bonds 0 0 0. This is the 200,000th timestep.

- (4) I have chosen, as usual, the box bounds to be the outermost atoms. It appears as though this results in a box that is too large for NVT to produce an actual interface in the middle. However, an interface does exist at the x-boundaries, which appears to be stable. The final NVT density of the simulation was around 0.4855.
 - (5) In order to check my new hypothesis, I want to run a classical simulation in DASH of the TAFFI-TIP4P/F interface under NPT conditions.
- These are snapshots of the NPT result:

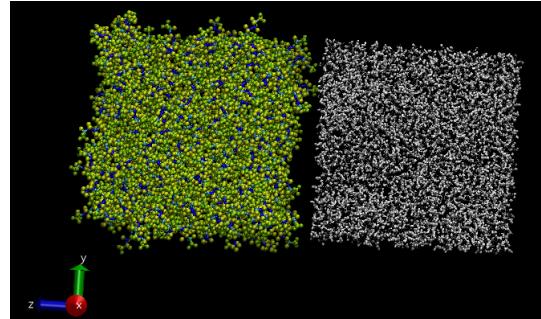


FIGURE 17. DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 300$ and $P = 1$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at 298.15K and same P. Cutoff = 12.0, Ewald summation. This is the 0th timestep.

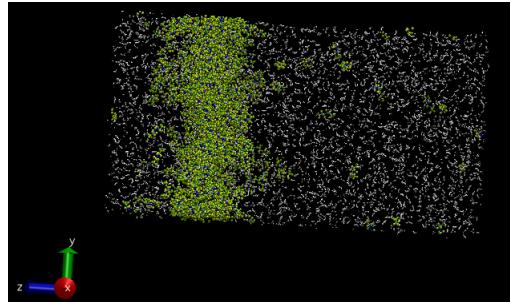


FIGURE 18. DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 300$ and $P = 1$, 200,000 timesteps of length 1.0 fs, NPT pre-equilibration of each slab at 298.15K and same P. Cutoff = 12.0, Ewald summation. This is the 200000th timestep.

- (6) There is a significant difference in the LAMMPS and DASH simulations, suggesting that something is amiss in the DASH program.
- (7) I will now check over the interface_NPT.py script to see if there are any possible sources of error. We should check: relationship of bulk hexane and water to temperature in DASH, and compared to LAMMPS, as well as specifications of both models, i.e. charge and other parameters.
- (8) Went through the interface_NPT.py file in detail. Did not find any errors.
- (9) Now, I am going to run the interface_NPT.py file with pure water, removing the hexane component, and check the resulting density at various temperatures. I will then do the same with hexane, removing the water. Unless I've found the error at this point, I will then do the same calculations in LAMMPS and compare.
- (10) It looks like there is an issue with the water. So, we will start tomorrow with an exploration of what is going on with the pure water restart. The goal will be to create a water restart within the interface framework that does not have any issues.

1.5. 3/7/2018.

- (1) Looking into pure water simulations in DASH.
- (2) First, starting in dash_work/water folder, running a test version of in.tip4pF.py.
- (3) Ran the simulation for 100,000 steps using time length 0.5. Density approached values around 0.98/0.99 by at least before 50,000 steps. Simulation video looked reasonable.
- (4) Ran a restart simulation for 50,000 steps, starting at the previous simulation's 50,000th step. Density approached 0.985 after the 50,000 steps, which is good. Video also looks very reasonable.
- (5) Tomorrow, I will start with the file in.tip4pF_restart7.5.py and build from it the hexane-water simulation, checking videos/densities at each step to see where things go wrong!

1.6. 3/15/2018.

- (1) Solved the problem. The Ewald summation fix was not being activated. ALL fixes must be activated in DASH.
- (2) To confirm, currently running: DASH simulation of 500 TAFFI hexane, 4650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 298.15\text{ K}$ and $P = 1.0$, 400,000 simulation steps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15 K and 1.0 atm. Potential cutoff at 12.0, long-range Ewald summation. Classical simulation, no path integrals.

1.7. 3/22/2018.

- (1) Simulation above finished. Results are shown below. The simulation looks clean:

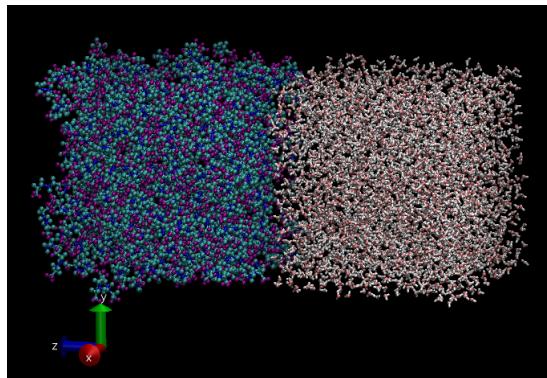


FIGURE 19. DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 298.15\text{K}$ and $P = 1\text{ atm}$, 240,000 timesteps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15K and same P. Cutoff = 12.0, Ewald summation. Classical simulation, no path integrals. This is the 0th timestep.

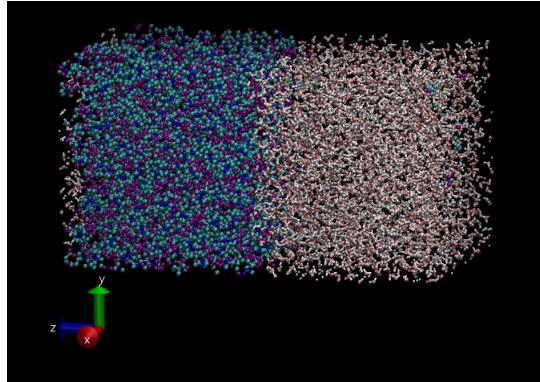


FIGURE 20. DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 298.15\text{K}$ and $P = 1 \text{ atm}$, 240,000 timesteps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15K and same P. Cutoff = 12.0, Ewald summation. Classical simulation, no path integrals. This is the 400,000th timestep.

1.8. 3/26/2018.

- (1) Added a python operation to interface.py that collects densities information. Ran a test: DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 298.15\text{K}$ and $P = 1.0 \text{ atm}$, 400,000 timesteps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15K and same P. Cutoff = 12.0, Ewald summation. Classical simulation, no path integrals.
- (2) After 400,000 steps, the density profiles converge to the following: 0.9858, 1.0191, 0.9989, 1.0086, 0.7922, 0.0233, 0, 0, 0, 0.1867, which are values for the z-axis cut into 10 slices, starting from the water end at negative z and moving in the positive z direction. Took about 200,000 steps to converge to this density profile. Next time, we will do a more fine-grained one, check how they are actually computed in papers, then run this and plot the result and compute the 90-10 width!

T

1.9. 3/27/2018.

- (1) From Patel, section C.1.: "The density profiles are computed from the average molecular density in 0.5 Angstrom slabs parallel to the liquid-vapor interface. The average profile is block averaged over 200 ps trajectory blocks from a total run of 3 ns."
- (2) We will begin first with "simple" block averaging. We will do 200,000 fs of system equilibration and then 3,000,000 fs of system run. In terms of the program, what we need to do is just write the densities in 0.5 Angstroms slabs parallel to the z-axis. FOR THE TIME BEING, I'm going to do this in NVT, simply because constant volume will lend itself better to a consistent way of computing density profiles. However, we will do the initial equilibration in NPT.

- (3) Wrote a temporary program, interface_densities.py, that records the density profiles using 200 bins. It has NPT equilibration for 400,000 steps and then computes density profiles every 1000 steps for 200,000 steps in NVT conditions. This is running now.
- (4) I also wrote density_profile_analysis.py which will plot the density profile.
- (5) So, the next step will be to check this result in the density profile analysis tool and then develop the full machinery for analyzing the water density profile, followed by other profiles etc. more rigorously.

1.10. 3/29/2018.

- (1) Need to write a program that can take the hexane_restart.txt file and the output_interface.xml file as inputs and restart a simulation of the interface. This way, we can avoid the time-consuming problem of doing pre-equilibration. Pre-equilibration can be done as just one run. This process shouldn't be too hard.
- (2) Performed the following simulation: DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, arithmetic mixing, NPT Andersen/Berendsen at $T = 298.15\text{ K}$ and $P = 1.0\text{ atm}$, 300,000 timesteps of length 0.5 fs equilibration followed by 1000 production steps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15 K and same P. Cutoff = 12.0, Ewald summation. Classical simulation, no path integrals. During production run, computed density of water in 200 parallel slabs along the z-direction every 10 simulation steps. We obtain the following density profile of water:

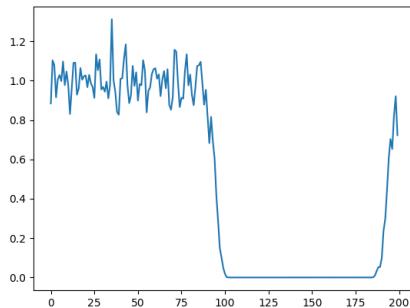


FIGURE 21. Density of water component across 200 bins in the interface normal direction.

We then fit to the error function profile as described in Patel et. al (2006), and obtain the following parameters: $\rho_W = 0.997$, $h_W = 94.212$, $w_c = 1.87\text{ Angstroms}$, which is in good agreement with previous simulations and experiments. A plot of the fit is shown below:

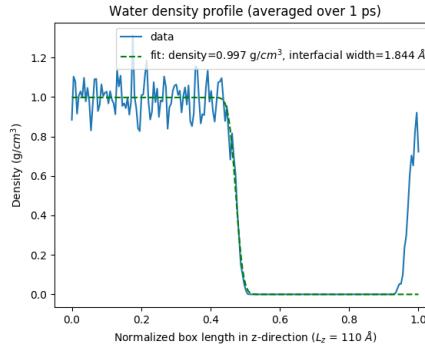


FIGURE 22. Density of water component across 200 bins in the interface normal direction.

1.11. 4/5/2018.

- (1) I checked that hexane.in.settings, which contains the intramolecular mixing rules for TAFFI hexane, exhibits Waldman-Hagler mixing:

$$\epsilon_{ij} = 2\sqrt{\epsilon_i \epsilon_j} \left(\frac{\sigma_i^3 \dot{\sigma}_j^3}{\sigma_i^6 + \sigma_j^6} \right)^{\frac{1}{6}} \quad (1.5)$$

$$\sigma_{ij} = \left(\frac{\sigma_i^6 + \sigma_j^6}{2} \right)^{\frac{1}{6}}$$

- (2) I added the following functionality to interface.py: collecting densities for both water and hexane, and deciding standard versus waldman-hagler mixing, number of equilibration and production steps, the output filenames. Below is a preliminary figure of combined density profiles taken from just 2000 simulation steps:

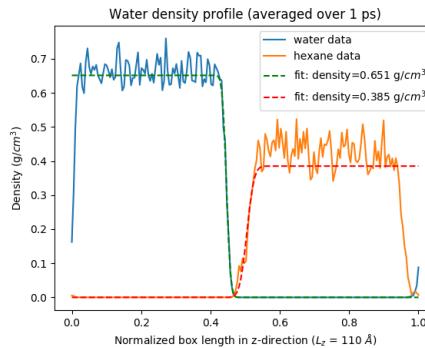


FIGURE 23. Double density profile test.

- (3) I am now running : DASH simulation of 500 TAFFI hexane, 3650 TIP4P/F water, standard mixing, NPT Andersen/Berendsen at T = 298.15 K and P = 1.0 atm, 300,000 timesteps of length 0.5 fs equilibration followed by 100000 production steps of length 0.5 fs, NPT pre-equilibration of each slab at 298.15

K and same P. Cutoff = 12.0, Ewald summation. Classical simulation, no path integrals. During production run, computing density of water in 200 parallel slabs along the z-direction every 100 simulation steps.

- (4) For waldman, I am now running the same as above except waldman mixing, 400,000 equilibration steps only 1000 production, no density calculation.

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