

1/26:

- Topper showed the works of Annie (FORTRAN program for simulated annealing of clusters of ammonium halides)
- Sawtooth annealing schedule (four teeth with linear decay, not one-toothed infinite exponential decay, which would be optimal)
- Saves all four final positions, and compares their energies
- Visualize clusters with Avogadro/Spartan. (Avogadro = freeware, Spartan = need Topper's license)
- Main goal: tweak parameters to achieve model extension from ammonium chlorides to ammonium fluorides.

Tasks:

- Download Avogadro
 - Email Topper for Dropbox invite
 - Research data for NH₄F crystal structure.
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1/28:

- Went to Bobst: accessed ICSD (Inorganic Crystal Structure Database). Found two articles on NH₄F crystals: from J. Chem. Phys. and Acta Crystallogr. Sect. A.
- Sent data to self in cif files.
- Annie is not compiled for PC. Topper will try to fix that.

Tasks:

- Figure out how to read cif files.
 - Read data; find N-H, H-F and N-F distances in solid NH₄F.
 - Make sure version of Annie is 4.3.1
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1/30:

- Downloaded and "compiled" Annie 4.3.1 onto TopperLab computer
- Couldn't read cif files on laptop
- Returned to Bobst to re-access ICSD. Printed pdfs of both articles, as well as the required distances.
- All files on TopperLab computer
- Helped Rachel with center of mass Visual Basic Excel Macro: set up functionality to determine the number of molecules by the number of mass-position pairs given. Remains to actually compute the center of mass of the system. Left Rachel with idea of using dot product for numerator of center of mass formula.

Tasks:

- Nothing to do but wait for Topper to get an image of Annie that compiles on PCs and let him show me how to run Annie.
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2/2:

- Topper looked at $(\text{NH}_4)\text{F}$ distances. Tried to make sense of it.
- The N-F distances don't make sense? There are different distances, but it's a symmetric structure. The F must be different/unequal... Maybe neutron diffraction data is more reliable, but paper prefers data from x-ray diffraction experiments. Topper found actual paper (Adrian and Feil) on Acta Crystallographica and is trying to make sense of it.
- Explained relationship of Annie and Spartan: Annie rules out the impossible, and currently assumes $(\text{NH}_4)\text{F}$ structure. Since we are interested at what point $(\text{NH}_3)(\text{HF})$ becomes $(\text{NH}_4)\text{F}$ (i.e., at what size of the crystal the hydrogen "transfers" from HF to the NH_3), we'd like Annie to be able to handle mixed substances: both ionic and molecular. Spartan can then fine-tune the calculations: to "put the hydrogens back" to the F and see if the resulting energy is lower.

Tasks:

- Read Chang chapter 16.
 - Wait for Topper's email: test standalone image of Annie compiled for PCs. Try to test it on multiple computers with multiple operating systems: keep track of the OSs tested on.
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2/9:

- Topper went over Ch. 16 of Chang: in particular, the intermolecular forces that most concern ammonium halides: dispersion, ion-ion, ion-induced-dipole.
- Recapped goals of research project: to find at what point small nanoclusters of particles begin to behave like bulk clusters, to find an accurate model for ammonium halides, and hopefully to find a model more general compounds
- Topper got Annie running for PCs: need to make sure she can run on different PCs with different operating systems

Tasks:

- Graph $V(r)$ equation: p.670-71 of Chang, using MatLab
 - Test Annie on multiple PCs, with different operating systems if possible.
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2/16:

- Topper went through differences: could be simply a truncation/rounding error. Code is very messy, with different data types used: double precision, real, integer, etc. Topper is fixing this
- Topper also went over idea of partial charges as the "average" of formal charges and oxidation numbers.
- MatLab: try using atomic units. The graphs dip will be at very small values of r , since they are on the order of picometers. Atomic units are made to make numbers manageable, so use them.

Tasks:

- Polish up graph with atomic units.

- Modify MatLab code to handle multiple graphs for different particle pairs. Use parameters as given in Topper Freeman 1996 paper.
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2/23:

- Presented MatLab, looked good. However, parameters lead to some bad behavior: potential diverges to negative infinity for some graphs: that shouldn't happen! They should all diverge to positive infinity.
- Went over Topper Freeman 1996 paper, cleaned up questions.
 - $V(r)$ formula includes exponential, Lennard-Jones, AND Coulombic terms. Must take all into account to get a good model for NH_4Cl . Maybe we can dump the exponential term?
 - Parameters for Topper's $V(r)$ formula: C and D parameters for NN, NH and HH are all known from a previous paper. C and D for ClCl were looked up in a different paper. By standard combination rules, C and D for HCl and NCl can be found.
 - Ising model: a lattice where there are two states, and a function is defined between neighbors: function is negative if states are the same, positive if the states are not the same. 1 and 2 dimensional lattices all have analytical solutions. 3 dimensional ones do not. Conway's Game of Life is an example.
 - Topper used an Ising model to model the orientational spins of NH_4^+ in NH_4Cl lattices. Graphs at the back of the Topper-Freeman 1996 paper illustrate his findings.
 - If you rotate one NH_4 while keeping all the others stationary, the internal energy as a function of rotation angle goes up, down, up and down again. Symmetric, like a valley. There is thus an energy barrier between getting from global minimum to local minimum
 - Heat capacity and density fluctuates as the NH_4Cl undergoes the order-disorder phase transition: expected. Heat goes into rotating the NH_4 , not heating up the molecules. The Cl cage jiggles a bit as the NH_4 moves, so molecules space out a bit.
 - "Order parameter" = measure of orderedness/chaos of the system. 1 = totally orientationally ordered. 0 = completely random. As temperature increases, order parameter falls from 1 to 0.
 - Freeman's compressible Ising model: an Ising model that allows the entities to jiggle a bit: their distances are taken into account when weighting their interactions. Went over this pretty superficially, don't really get it.
- Brainstormed and Googled a bit about how to approach actual project: modelling NH_4F ions. See below. We can use Annie and Spartan to check if our estimates for C and D are good: they will give us the lowest energy and the lowest energy structure. (How again...?)

Tasks:

- Finish reading Topper Freeman 1996 paper

- Use parameters from Topper 2011 errata for MatLab code. Convince self that the behavior is fixed (i.e. all diverge to negative infinity as r approaches 0).
 - Find article with epsilon and sigma values for FF: get citation and calculate C and D from that (use Lennard-Jones formula). Mao and Pappu 2012, "Crystal lattice properties fully determine short-range interaction parameters for alkali and halide ions"
 - Start working on fluoride ions: use C and D for HH and NN from Topper 2011 errata + C and D for FF from Mao and Pappu, and use combination rules to estimate C and D for HF and NF. These are estimates because Topper's values are for a formula with an exponential repulsion term, but Mao and Pappu do not have it!
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2/28:

- Got tasks one and two done.
 - Used Mao & Pappu values for L-J parameters to calculate C and D for F-F. Then used combination rules to estimate C and D for N-F and H-F. Had a hiccup in conversion of units, but answers make sense now. D is now on the 3rd, 4th and 6th order of magnitude, but that is to be expected, since F- ions repel each other much more.
 - Found paper by Chandrasekhar, Spellmeyer and Jorgensen that set q of F- equal to -1.0. Topper emailed to corroborate that. Paper can still be used as a reference!
 - Set A and alpha for all pairs with F- equal to 0. Ignore dispersion forces for now.
 - How do we know if the graphs are accurate though?
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3/1:

- Topper pointed out that current parameters make all graphs positive: there is absolutely no attractions, not even for pairs such as H-F pairs. This is bad.
- Probably because the H-H values we used assumed an exponential repulsive term, whereas the Mao and Pappu parameters did not. This changes parameters.
- Topper found another paper with H-H L-J parameters for function without an exponential repulsive term. Oobatake and Ooi, Prog. Theo. Phys., 1972.
- However, we may not need to find similar parameters for N-N... it depends on how things turn out with the new H-H parameters.

Task:

- Use Oobatake and Ooi to calculate C and D for H-H. This is weird because they use a different form of the Lennard-Jones potential function, and give us a strange pair of parameters, in non-atomic units.
 - Use new H-H C and D, and standard combination rules, to recalculate C and D for H-F... and maybe others? Ask Topper
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3/8:

- Coded (last-minute) a model where the ammonium was oriented such that the H was collinear with the N and F (i.e. an H "pointed" to and away from the F ion). Both graphs dipped below zero.

- This means that while NF is globally repulsive, the sum of 4 HF interactions outweighed it to make it net attractive.
- However, this did not stand up to a basic sanity test: if the value was correct, the atoms (if treated as spheres) would actually overlap one another.
- Topper decided to run Spartan calculations. Showed me the basics of how to use Spartan.

Tasks:

- Find exact value distance that minimizes potential for MATLAB model
- Use Spartan to make energy profile for NH₄F. Find corresponding minimum potential distance for the following models:
 - Semi-empirical
 - AM1
 - PM3
 - Density functional theory
 - M06
 - 6-31G*
 - Moller - Plesset
 - MP2
 - 6-31G*
 - 6-311+G(2df, 2p)
- See if they all agree...

3/22:

- Didn't really understand how to use Spartan: there was "wrap around" behavior...
- Topper re-explained how to use Spartan: don't constrain NH₄ distances, let them be. Profile HF distance, and run MMFF on it. Then run quantum mechanics calculations.

Tasks:

- Re-run Spartan calculations.
- See if they agree with each other, and with the MATLAB results.

3/23:

- Re-ran Spartan calculations
- Ran into trouble with density functional theory calculation: SCF error. Topper said to use keyword GUESS=CORE when submitting the calculation. SCF = self contained field. Basically, adjust the initial guess to something else: the calculation is getting stuck in some bad loop/finding the wrong maxima, etc. (like a failure of the Newton-Raphson method)
- All the density functional and Moller-Plesset calculations give a graph that has the right shape and behavior, but values for energy that have been displaced by some -40000 kJ/mol... In other words, the minima appears to be in the right place, but the values for energy are all massively negative, which doesn't seem to make intuitive sense... There

ought to be some H-F distances that cause the structure to be overall unstable. This might just be Spartan doing weird stuff again.

- A more worrying observation would be that the minima (1-1.5 Angstrom) doesn't agree with the minimum that we calculated with MATLAB a few weeks ago (somewhere around 6 Bohr). I'm under the impression that the quantum calculations from Spartan are more reliable than the ad-hoc MATLAB calculations I did based on your potential equation... but I'm not sure what this means for the next step in the research.
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3/26:

- Emailed Topper with results; he emailed back with further calculations that needed to be done: DFT M06-2X/6-31G**, MP2 aug-cc-pVTZ.
 - Also wanted the DFT calculations to be done on NH₄Cl cluster, for which he has an interaction model to compare.
 - MP2 aug-cc-pVTZ calculation did not work out: SCF convergence error that could not be resolved with GUESS = CORE. Topper said to try to run MP2/6-31G** and then run aug-cc-pVTZ. That worked, but gave an anomalous point. Subsequent attempts to re-run the calculation threw the same SCF convergence error.
 - Put everything on Excel and plotted relevant graphs.
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4/5:

- Topper looked at graphs and tables.
- "Terrific work"
- Quantum calculations agree very well with one another.
- SYBYL and MMFF (molecular mechanical methods) give differing results, with MMFF giving results that agree much better with quantum mechanics than SYBYL: this is because MMFF has been parameter-optimized to agree with quantum results
- So, now we change the parameters of the MATLAB interaction model so that it agrees with quantum results too.
- First port of call: the partial charges on ammonium. Why? We have a reference for everything else, so we can blame someone else if things don't work out! :D

Tasks:

- Modify MATLAB code to test out a battery of tests and calculate the interaction energies for a range of possible partial charge.
 - If time allows, re-run Spartan calculations with SYBYL and MMFF, with a "rigid NH₄" structure.
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4/9:

- Modified MATLAB code to not only graph the functions, but to calculate the N-F length that gives the minimum interaction energy, and to do so for a range of possible charge values.

dVal	HCharge	NCharge	minLength
0.00	1.00	-3.00	5.3551
0.05	0.95	-2.80	5.3907
0.10	0.90	-2.60	5.4290
0.15	0.85	-2.40	5.4706
0.20	0.80	-2.20	5.5161
0.25	0.75	-2.00	5.5662
0.30	0.70	-1.80	5.6218
0.35	0.65	-1.60	5.6843
0.40	0.60	-1.40	5.7556
0.45	0.55	-1.20	5.8384
0.50	0.50	-1.00	5.9371
0.55	0.45	-0.80	6.0594
0.60	0.40	-0.60	6.2206
0.65	0.35	-0.40	6.4602
0.70	0.30	-0.20	6.9672
0.75	0.25	0.00	3.1691E+29
0.80	0.20	0.20	3.1691E+29
0.85	0.15	0.40	3.1691E+29
0.90	0.10	0.60	3.1691E+29
0.95	0.05	0.80	3.1691E+29
1.00	0.00	1.00	7.9363

- Generally good results: reasonable distances are generated for all delta values, except for those charges for which the N partial charge (q_N) are non-negative...
- That is kind of to be expected: if the partial charges on both H and N were both positive, then ammonium would a) be overall repulsive and not be stable in the first place, so that doesn't make sense, and b) be basically a positive cluster of charges. Thus, we'd expect

that, as we move a negative F⁻ ion around it, the interaction energy would just asymptote to zero as the N-F distance went to infinity: no diving below the x axis, no local minima, no nothing. Something like the behavior of $y = 1/x$. The large numbers that MATLAB spits out is an indication that something computationally has gone wrong: its probably assuming that there *is* a minimum, and throwing up its hands and giving us the “best number” it can find, which is massive.

- A exception to this happens when we use the oxidation numbers: in that case, the hydrogens have a partial charge of 0, so its as if they don't exist at all, and the above reasoning should still apply. I don't know why we get a nice, finite 7.9363 for the N-F distance then... MATLAB should give a massive positive number... Oh well, its doesn't matter much.
- Another note: the N-F distances were heavily dependent on the initial guess I fed to the MATLAB's minimization function. I used a guess of 5 bohr every time, but if I change it, the values of the “optimum N-F distance” for the non-negative q_N cases would change (but they're nonsense anyways, so we don't care).
- The only worrying observation I made was that if I supplied a guess of 1 bohr, *all* N-F distances would become 0.7682, non-negative q_N or not. Maybe the interaction graph really *does* have a local minimum at that point, and we just don't know it because we haven't graphed it to such extremes? Not sure here, but again, since we know (?) that the optimum N-F distance is a continuous function, we can stick this under the carpet for now and move on.
- Here comes the clincher: even after having recognizing all the above caveats to the data, we now look at the “valid” stuff and realize that the values of 5-7 bohr that MATLAB is giving us is nowhere near the 1-1.5 Angstrom (2-2.5 bohr) that Spartan gave us. So that means that it's not just the partial charges that need to be optimized to fit quantum results: at least one of the other parameters also has to be adjusted if the interaction model is to agree with Spartan.
- I'm not sure which parameter we should hit up next... I recorded the sources of all the parameters, and they're from all over the place. We'll have to look at that on Tuesday and see which one we want to focus on next... Perhaps some parameters were derived on some assumptions, while other parameters were derived with other assumptions... or something...

4/12:

- Read Topper's reply emails: he had suspected that just changing the charges wouldn't be enough, so now we have two options.
 - Change C/D parameters for the Lennard-Jones potential until the distance of minimum energy agrees with quantum calculations
 - Introduce a new term into the force field: it would look like a Lennard Jones 6-12, except now the attractive term would have an exponent of 10, not 6. Also, the term would be multiplied by a $\cos^2(\theta)$, where θ = angle between acceptor, hydrogen and donor. This would slow ANNIE down galactically

- So, we turn to optimizing the CD parameters. We limit ourselves to the CD values of HF pairs. Why?
- We can to make the distance of minimum energy SHORTER, so we should make the C (attractive) parameter larger, or the D (repulsive) parameter smaller.
- A can of worms will open: tampering with C and D can place the minimum at the right place, but it WON'T ensure that the depth of the well will match quantum calculations! That's a problem for later, though. One step at a time.

Tasks:

- Modify MATLAB code to optimize C (and maybe D) values. Find the optimum values of C and D.

4/18:

- Modified MATLAB code. Ran it three times, increasing search domain for C and D each time. Found optimum length and well depth for every single (C, D) pair.
- But what are the target values of the length and depth? Spartan values, but WHICH ONES? Ask Topper
- Once we have that, we can use a Euclidean distance metric to find

4/19:

- Presented stuff to Topper. He cleared stuff up. Lots of work to do

Tasks:

- Massage Moller-Plesset MP2 6-311+G(2df, 2f) data so that it has the same qualitative behavior as the interaction model:
 - So, use Spartan to calculate the asymptotic energy (i.e. the energy of an isolated NH_4^+ and F^-)
 - Shift Spartan data points up by the absolute energy of the current minimum
 - Shift Spartan data points down by the difference between the asymptotic energy (2 above) and the absolute energy (1 above), so that it achieves a nice minimum
 - MAY WANT TO SAMPLE MORE DATA POINTS FOR THIS
- Once all Spartan data is shifted, we can calculate the well depth that Spartan predicts, and finally compare it to the data we got in MATLAB, using Excel. Use Euclidean distance to measure how close the predicted value is to the target value. Minimize Euclidean distance.
- Try to match target and predicted values to within 0.1 kJ/mol (for well depth) and 0.01 Å (for distance).
- ALTERNATIVE: Topper suggested that for every (C, D) pair, we generate the potential curve, and compare the data points on the curve to the data points produced by Spartan. Then perform a least squares regression and find the best (C, D) pair that gives the curve that fits closest to the data. This is a more conventional way of doing it; the way outlined above is unconventional. However, it takes a lot of computation: for every single

(C, D) pair, generate a curve. For every single curve, calculate the sum of squares of differences.

- However, it's good to know that an alternative is there.

4/20:

Moller-Plesset MP2 6-311+G (2df, 2p):

- Isolated NH_4^+ energy = -149087.84 kJ/mol
- Isolated F^- energy = - 261827.69 kJ/mol

- Asymptotic energy = isolated NH_4^+ energy + isolated F^- energy = - 410915.53 kJ/mol
- Minimum energy = -411538.56 kJ/mol
- ^ This energy may not actually be the “minimum”... Only 10 data points were taken, it is possible that the minimum is between the 2nd and 3rd, or 3rd and 4th, data points... We will see.

- Well depth = minimum energy - asymptotic energy = 623.03 kJ/mol
- (Asymptotic energy of interaction model = 0 kJ/mol)

So,

H-F Distance (A)	Rigid Rel E (kJ/mol)
0.5	1992.18
0.833	-346.64
1.167	-623.03
1.5	-609.75
1.833	-547.81
2.167	-485.17
2.5	-431.99
2.833	-388.44
3.167	-352.69
3.5	-323.04

- But this means that (C, D) ~ (1, 1000) ?????
 - This is weird: something wrong probably happened. Needs more inspection.
-

4/24:

- Went back into code and spotted a MASSIVE typo in the definition of Utot... I accidentally typed UHN instead of UHF. Will need to re-run calculations of dCharge_Opt and CD_Opt.

dCharge_Opt:

dVal	HCharge	NCharge	optLength
0	1	-3	5.806
0.05	0.95	-2.8	5.8163
0.1	0.9	-2.6	5.8268
0.15	0.85	-2.4	5.8377
0.2	0.8	-2.2	5.849
0.25	0.75	-2	5.8606
0.3	0.7	-1.8	5.8726
0.35	0.65	-1.6	5.8851
0.4	0.6	-1.4	5.898
0.45	0.55	-1.2	5.9114
0.5	0.5	-1	5.9254
0.55	0.45	-0.8	5.9399
0.6	0.4	-0.6	5.9551
0.65	0.35	-0.4	5.9709
0.7	0.3	-0.2	5.9874
0.75	0.25	0	6.0047
0.8	0.2	0.2	6.0229
0.85	0.15	0.4	6.0421
0.9	0.1	0.6	6.0622
0.95	0.05	0.8	6.0836
1	0	1	6.1061

- MUCH BETTER: optLength is a continuous function of d, and there's none of that wild jumping around, as before.
- However, the optLengths are still nowhere near what they're meant to be, so we push on with the CD optimization: we let $d = 0.5$, as before,
- CD optimization now gives a non-weird result: there now seems to be some actual optimization that needs to be done. Will do several attempts, to see where this whole Euclidean distance idea goes...
- Found a nice search domain:
 - for $C = 1:5:70$
 - for $D = 300:100:2000$
- This gives a proper minimum! As in, there is a minimum, and there are points greater than it all around.
- $(C, D) = (26, 1000) \rightarrow \text{length} = 3.9028, \text{depth} = -0.97216, \text{euclidean} = 1.8497$
- $(C, D) = (31, 1000) \rightarrow \text{length} = 3.86, \text{depth} = -1.0638, \text{euclidean} = 1.8496$
- $(C, D) = (16, 300) \rightarrow \text{length} = 3.6877, \text{depth} = -1.0732, \text{euclidean} = 1.7019$

4/26:

- Showed Topper fixed code and "best" minimum possible.
- He suggested one of two things:
 - Use a switch function on the entire Utot function: this has the effect of shifting the ENTIRE V-r curve. $S(r) = 1/(1/\exp(\beta r))$, where β is a parameter that must be optimized.
 - Change the 6-12 potential to a 6-14 potential: make the repulsive forces decay away faster, so that bond length gets shorter.
- At this point, we prioritize getting a good N-F distance over getting a good well depth. This is because Annie and Spartan can cope with an incorrect well depth better than an incorrect bond length.

Tasks:

- WRITE REPORT. Outline what I did and how I did it.
 - Try out the $S(r)$ idea, if time permits.
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- It turns out that I've been comparing apples to oranges... In Spartan, I constrained and drove the HF distance. However, in MATLAB, I optimized the NF distance. They should be off by 1.012 angstrom, ASSUMING A RIGID AMMONIUM ION.
 - This makes the agreement MUCH better, but still not perfect... The agreement is still not within our prescribed tolerances. So, the $S(r)$ idea is still fair game.