CHEM 6004: Theoretical and Physical Methods, Profs. Snyder and Foley

Simulated Annealing: A Materials Science Inspired Optimization Technique

A key technique used in purifying materials is annealing. Briefly, annealing is a technique involving heating then re-cooling in order to purify and/or increase the crystallinity of the material. Essentially, annealing is a physical method for “optimizing” a material: you take a material in a “local minimum” of being partially purified and partially crystallized, heat it up to mobilize impurities and allow the material to escape from its locally minimized state, and then slowly cool the material down to allow it to recrystallize in a pure state.

The process of annealing can be simulated computationally, and those simulations can be used as an optimization technique: heating a system removes it from a local minimum and cooling it allows it to relax into a global minimum. An example of simulated annealing that captures how physical annealing increases crystallinity is the use of simulated annealing to minimize changes in color in a random image: the resulting “energy minimized” image has larger “crystalline” domains of homogeneous color than the original image just as a physical annealing increases the crystallinity and homogeneity of materials. You may wish to explore this example of simulated annealing at <https://www.nayuki.io/page/simulated-annealing-demo>. You may also wish to compare what you learn about simulated annealing (e.g. as you explore it at the above example or in this computational exercise) with the discussion in your textbook in Section 3.6.

Simulated annealing, however, need not so closely simulate physical annealing. If you have an “energy” defined for a system as well as a “temperature” somehow related to an average energy, you can use a simulated annealing technique to minimize that “energy”. In this computational exercise, you will use simulated annealing to find the lowest energy geometry of the FHF- anion. Building upon your previous exercises exploring the HF molecule, the Jupyter notebook for this lab constructs a simplified (and not exactly accurate, for what it’s worth) model of FHF-: this model has two localized energy minima: one in which the hydrogen is covalently bonded to a fluorine atom at the origin and hydrogen bonded to a fluorine atom a fixed distance away from the origin (which we’ll denote as F-H…F) and another in which the hydrogen is hydrogen bonded to the fluorine atom at the origin and covalently bonded to the other fluorine atom (which we’ll denote as F…H-F). In our model F-H…F will have lower energy than F…H-F, and there is an energy barrier between these two states.

Simple minimization methods will identify one or other of the local minima as *the* minimum: which minima is so identified will depend on the starting configuration of the system … if the hydrogen atom is originally closer to the fluorine atom at the origin, F-H…F will be correctly identified as the lowest energy configuration. On the other hand, simple minimization methods (such as “steepest descent”) will identify F…H-F as the minimum if the hydrogen is initially placed further away from the fluoride atom at the origin.

Given an appropriate heating/cooling schedule, simulated annealing techniques (there are many ways of actually implementing simulated annealing: you can use so-called Monte Carlo methods, Langevin dynamics or other approaches) will generally be able to escape local minima and find a system’s global minimum (or at least a better local minimum than could be found with simple energy minimization methods). In this computational exercise, you will vary parameters (such as the heating/cooling schedule) of a simulated annealing run and see how changing simulated annealing parameters affects your ability to identify the correct configuration of the FHF- anion.

Simulated Annealing Questions

Our model system has two local minima, one at approximately 1.9 atomic units and another at approximately 2.4 atomic units.

1. Set the r\_init to 1.8 atomic units (i.e. somewhat near the minimum of the energy landscape for the system) and run the simulation a few times.
   1. Does the final value for the position of H always, usually, sometimes or rarely converge to the “equilibrium” value?
   2. Does the final value for the position of H ever converge to the other, non-global local minimum in the energy landscape?
   3. How well, in general, does the final value for the potential energy match the minimum of the energy landscape?
2. Set the r\_init to 2.4 atomic units (i.e. very near the other, non-global local minimum in the energy landscape) and run the simulation a few times.
   1. Does the final value for the position of H always, usually, sometimes or rarely converge to the “equilibrium” value?
   2. Does the final value for the position of H ever converge to the other, non-global local minimum in the energy landscape (i.e. does the position of H ever end up more or less where it started, even after “exploring” positions with lower energy?)?
   3. How well, in general, does the final value for the potential energy match the minimum of the energy landscape?
3. Note that the value of g used in this week’s exercise is higher than the value of g used in the previous computational exercise (which itself was on the high side for Langevin dynamics).
   1. What effect, if any, does lowering the value of g have? In particular, when you start with r\_init being 2.4 atomic units, do you often see the position of H explore values near the global energy minimum in the landscape and then return to the local minimum occurring when the position of H is near 2.4 atomic units?
   2. What does lowering the value of g mean, conceptually speaking? Do your observations of what happens when you lower the value of g make sense in terms of what g means as a “drag” parameter?
4. Convert the initial temperature and hot temperature to kelvin (using the conversion factor ): what would actually happen if you heated an aqueous solution of HF to the hottest temperature used in our simulation?
5. Change the value of g back to 0.02 and change the initial temperature and hot temperature to 0 (essentially using the drag term in the Langevin equation to minimize energy). How do your answers to the questions in parts 1 & 2 above change? In particular, if you start with r\_init = 2.4 atomic units, does the position of H ever converge to the global minimum? You may also want to try using a hotter temperatures than you did with your first