

Generation of optimized structures using Particle Swarm Optimization (PSO)

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Introduction

For as long as both theoretical and technological progress entitled scientists to do, there has been a wide interest to understand the nanoscopic scale of matter. Indeed, doing so makes it possible to understand the processes of transition and their results when matter is subject to changing conditions, such as pressure or temperature. It has been observed that applying new conditions could alter various variables in matter: in the case of water ices for instance, the symmetry and the number of H-bonds that are possible can be altered by the variation of pressure. Moreover, these changes can lead to variation of properties of materials, which could lead to serious issues in fields where they have expected to withstand critical infrastructure (aeronautics, nuclear powerplants, etc...). Yet, a full understanding of every material is hard to achieve: even for very common elements such as water, there is still today space for discussion over some of its solid phases [1].

Up to recently, crystalline structure for materials was obtained (or at least helped by it) through experimental studies: X-Ray diffraction (XRD) being almost the norm in order to characterize anything in Material Science. However, this implies that the crystallized experimental structure shall be accessible, which requires consequent setups in the case of extreme conditions being studied. In the case of a complete theoretical study through numerical calculations, it implies to find the global minimum of the potential energy surface of the molecule, which depends of many parameters (for a molecule containing N atoms, it can go up to $3N - 3$ degrees of freedom, including bond length, angles of rotation and torsion). Yet, as simple as the concept may seem, it hides a very complex truth: finding the global minimum of a ensemble containing many parameters, is not an easy task at all. Without any hint on initial configurations to begin optimization with, simulations can get stuck in local minima. Moreover, finding this minimum in the case of a crystalline phase is also conditioned to the right selection for the symmetry of the crystal: yet again increasing the complexity.

The quest for finding global minima in the case of molecular systems has been done through various approaches (a visual presentation is available in Figure 1):

- **Monte Carlo:** involves random changes on parameters and accept the modification using probabilistic techniques [2]
- **Simulated annealing:** the temperature of the system is increased (so that every configuration is accessible), and then slowly decreased for the system to converge to global minimum in a Monte-Carlo fashion [3]
- **Minima hopping:** perturbs the configuration at local minimum to explore near-bies ; if new configuration has lower energy, configuration is updated ; if not the perturbation module is increased [4]
- **Basin hopping:** similar to minima hopping, but focuses rather on the basins of potential energy
- **Metadynamics:** enhances the sampling of rare events, and thus permits a quasi-total sampling of the potential energy surface (PES) ; in this case the global minimum can be easily found [5]
- **Genetic algorithm:** inspired by the principles of evolution of living species, theses algorithm induce selection, mutation, and recombination to optimized configurations [6]

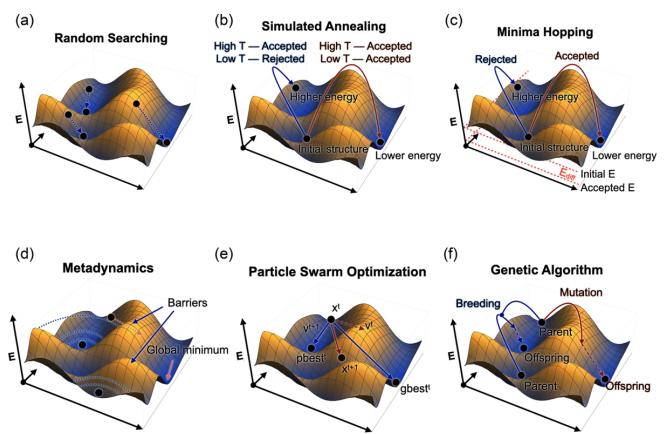


Figure 1: Schematic explanation of various crystal structure prediction methods, by Falls et al. [6]

Each method has its own advantages and inconvenients, and has been probed for the generation of configurations. Thus, there is still no consensus for a specific method, as techniques can be better in some cases.

This report, based on the publication from Naden Robinson et al. [7], tackles the application of another generalized optimization algorithm (Particle Swarm Optimization) for the purposes of potential energy surfaces exploration and the determination of the optimized geometry for extreme conditions. The study is based on the exploration of ammonia-water mixtures present inside planets of our solar system (especially Uranus and Neptune). In these mantles, there exists some particularly harsh conditions, that are not existing in our planet: indeed, high temperatures and pressure can be reached; thus accessing zones of the phase diagram of this mixture that were never explored previously. Furthermore, it is almost impossible in this case to use experiments in the first place to have first guesses, and as we have no clue about any stoichiometry, symmetry or parameters, sampling the entire potential energy surface would be very computationally expensive. Those reasons also exclude many of the above methods, that would require an initial configuration, and/or a clear final destination. As a matter of consequence, using a smart optimization technique is, of course, of high importance.

Particle Swarm Optimization

Theoretical background

Particle Swarm Optimization (also called PSO) is a population-based optimization algorithm that simulates the social behavior of birds or insects, such as flocking or swarming. Every iteration, one optimization simulation's (called a particle) trajectory is inspired by its own personal local minimum (**pbest**) that it can reach through gradient descent, and the global (on all particle) minimum (**gbest**). Its application for structure discovery was introduced by Wang et al. [8], and transcribed into a software (called CALYPSO) by the same authors [9]. The particle swarm optimization presents a simple algorithm:

- Generation of one random structure per symmetry (avoids unnecessary calculations)
- Local optimization of every structure

- Exclusion of similar structures (through bond characterization matrix)
- Generation of new structures by PSO, using personal and flock's histories (see below)
- Repeating steps 2, 3 and 4 until convergence is reached
- Returns the configuration with the lowest energy

The calculation of new structures by PSO formulas is carried out for each parameter individually. For the i^{th} particle, we have the following equation for the calculation of the updated coordinates for dimension j :

$$x_{i,j}^{t+1} = x_{i,j}^t + v_{i,j}^{t+1} \quad (1)$$

With $v_{i,j}^{t+1}$ its velocity for the j^{th} dimension:

$$v_{i,j}^{t+1} = \omega v_{i,j}^t + c_1 r_1 (\text{pbest}_{i,j}^t - x_{i,j}^t) + c_2 r_2 (\text{gbest}_{i,j}^t - x_{i,j}^t) \quad (2)$$

With ω being the inertia weight (translating the importance or not of previous velocity), c_1 and c_2 being respectively the self-confidence and the swarm confidence factor, and r_i being random parameters. By changing the fixed parameters (by fixing them at first, or making them evolve throughout the simulation), it is possible to go from global jump, with long hoppings, to a precise localization of the minimum in its basin. A schematic of an iteration of generation of new coordinates for a particle on a specific coordinate is shown in Figure 2.

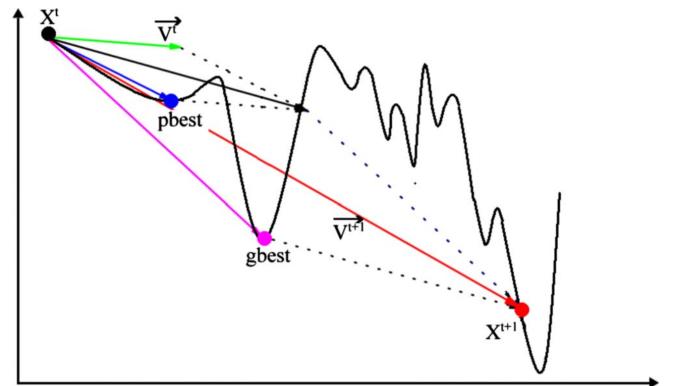


Figure 2: Schematic explanation of particle swarm optimization on one parameter, by Wang et al. [8]

The advantage of such method is thus clearly visible: by taking into account samplings at various zones of the PES, and forcing particles to travel to a zone of interest, it is possible to force particles to get out of their local minima from one hand, but also to provide a better sampling around zones

of interest (some will go further, some before the global minimum found at an iteration, which may lead to the discovery of a better minimum, etc...).

Authors announce very interesting results in both their introduction article and the presentation of CALYPSO [8, 9]: starting from scratch, and using either DFT or empirical potentials (using the GULP code), it was possible to obtain optimized structures with less than 10 PSO generations (representing around 300 structures).

Programming PSO, trial over a simple two-dimensional study case

The code that has been developped following the above instructions, is available on Github ([link here](#)). The algorithm was applied on a similar case study (yet with a lower dimensionality for the sake of simplicity): the Eggholder trial function.

$$f(x, y) = -(y + 47) \sin \left(\sqrt{\left| \frac{x}{2} + (y + 47) \right|} \right) - x \sin \left(\sqrt{\left| \frac{x}{2} - (y + 47) \right|} \right)$$

As it would be in the case of our molecular systems, the function surface is full of hills and wells, with very steep walls in between them. In the case of conventional sampling methods, it would be either very long to sample (hitting only a few units of x away from a minimum gives very different results), or quite easy to get stuck in local minima. In this example, particles were randomly placed (following a uniform distribution) in an initial area: $(x, y) \in [-512, 512]^2$ and were affected random velocities along each dimension ($|v_i| < 50$). In order to converge quickly, ω was set at 0.6 at the beginning, and linearly decreased to 0.3 until the end of the loop; c_1 and c_2 were equally defined to 1 (equal confidence).

As told previously, the particles quickly adopt a similar behavior to a flock of birds, which is observable in Figure 3.

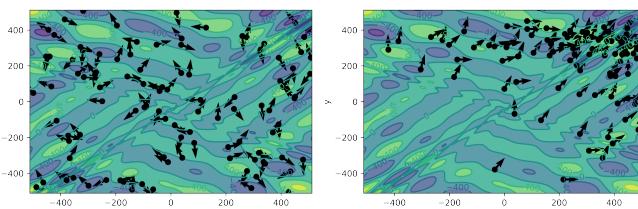


Figure 3: Visualization of particles at initial generation (left) and after one iteration (right)

Using only one PSO iteration, particles quickly moved to the `gbest` area, and allowed some further discoveries, as visible in Figure 4:

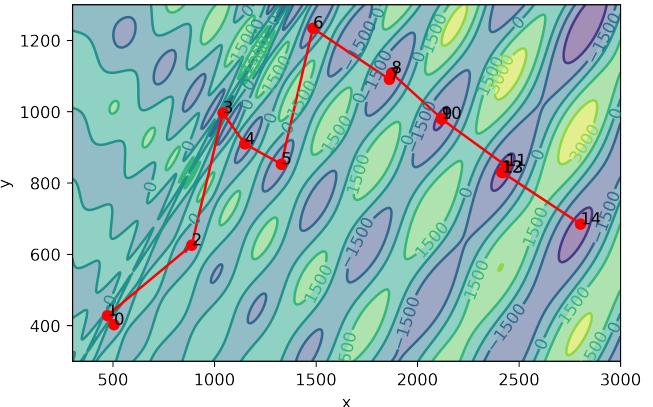


Figure 4: Displacement of global best minimum in the first iterations using the Eggholder function

In this example, the global best minimum managed to move from a basin to another without any problem, even though the spatial steps that separate every minimum are important. It becomes also clear that the more particles are considered, the easier it will be to find new global best minima, although it comes at the cost of more computational time: a compromise needs to be found to allow sufficient sampling.

Obtained results and comparison to other methods

Indeed, this method surely seems very advantageous to others when facing unknown crystal phases determination: in the considered planets (Uranus and Neptune), layers of the inner mantle are mainly composed of methane, ammonium and ice water, and are subject to pressure going from 0.1 to 2.5 Mbar [10]. It is predicted that the presence of both elements is almost equivalent, letting their stoichiometry unknown (it could be 1:1, or one element could be more used than another). However, as ammonia and water can form hydrogen-bonded networks when they are brought closer in some circumstances, it is possible to see the formation of new phases, lowered in energy. It is thus expected that the evolution of pressure might let new phases appear at high pressure. Experimental studies were conducted at a few hundreds of GPa previously, and already gave some hints about the rearrangements in place, but

In this case, only mixtures of ammonia and water

were studied, and multiple stoichiometric factors were tested, which are all supposedly possible to be observed in those planet's layers. At first, 16 formula units of $(\text{H}_2\text{O})_x(\text{NH}_3)_y$ were tried, however it was soon reduced to only four stable mixtures: ammonia monohydrate (AMH), ammonia dihydrate (ADH), ammonia hemihydrate (AHH), and ammonia quarterhydrate (AQH). The three first configurations are present on our planet at low pressures, making them easy options to consider for stable configurations. However, the last mixture turned out to present some stable crystalline phases at high pressures.

Particle Swarm Optimization that was lead on the already-known ammonia hydrates still allowed to make some new discoveries: some phases that were not present in some previously determined phase diagram are actually valid candidates for some pressures: it is the case, for instance, for AMH, with both $P4_3$ and $P2_1/m$ structures that did not appear in the litterature: using PSO in those high-pressure phase evolution studies thus allowed to discover a better stability of the crystal, before changing to the ionic phase $(\text{OH}^-)(\text{NH}_4^+)$. In previous studies, such as the one conducted by Bethkenhagen and others which was using XtalOpt, based on genetic evolution algorithm [11], came first to the conclusion with their results that all phases of AMH would be decomposed into ionic phases below 120 GPa. Thus, this shows that the latter method is less ac-

curate that PSO, as it can be expected that mutations never make it possible to sample a part of the PES. A richer phase diagram was also found for ADH, with phases being stable up to around 100 GPa. These new phases are expected due to the facilitated proton transfer that can occur in the system with the high pressure (in all mixtures): the energy of the system decreases, makes it possible to consider these phases. With usual sampling techniques, finding such phases would be a lot harder, and would require the scientist to know what to look for.

Moreover, using PSO also made it possible to discover the stability of another ammonia-water mixture: ammonia quarterhydrate (AQH). This phases begins to exist at already high pressures (starting from 8.5 GPa), and decomposes back into ices again around 300 GPa.

In the end, it was also shown that no stoichiometry other than AMH, ADH, AHH or AQH would ever be stable, by using a convex hull diagram (which consists in representing the difference of enthalpy of formation between the considered ammonia-water crystal and the seperated constituents). Indeed, other proportions systematically lead to the dissociation into the previously listed phases, or the basic constituents. This can be observed by the fact that, for other proportions only, structures which were predicted were never able to get a negative difference, making it unstable.

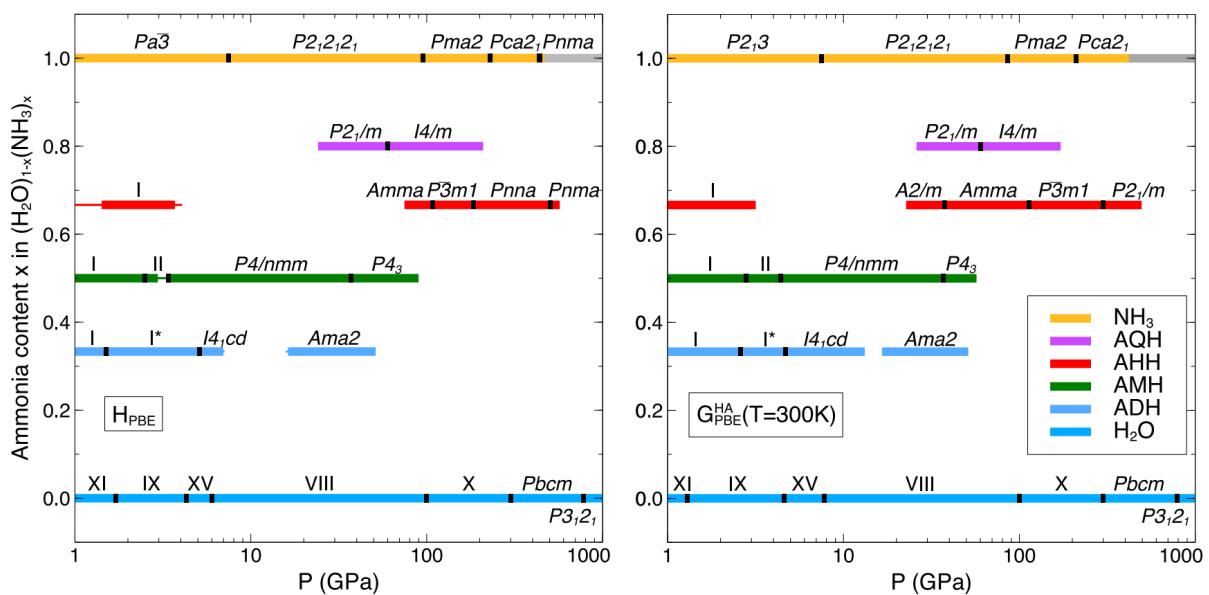


Figure 5: Phase stability ranges for binary ammonia-water mixtures as a function of pressure, for the ground state (left) and at $T = 300 \text{ K}$ (right), by Naden Robinson et al. [7]

Conclusion

The sampling of various binary ammonia-water mixtures using Particle Swarm Optimization, Naden Robinson et al. managed to discover new phases, extending the domain of stability that was initially found in previous researches. As a matter of consequence, this sampling technique has showed its advantages, as being more rigorous

than others, and permitting an efficient sampling (less time is spent in the upper part of the hills of the PES). Yet, it is still important to note that in the case of the presence of experimental data allowing to get a good start for theoretical studies (such as XRD does) ; this method might not be the most efficient. There is no gold standard, each person has to get the best compromise for their studies.

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