Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Artem Samtsevich

PhD Program: Materials Science and Engineering

Title of Thesis: Simulation of mechanisms of solid-solid phase transition

Supervisor: Professor Artem Oganov

The thesis document includes the following changes in answer to the external review process.

Dear Reviewers,
I would like to express my gratitude for your comments and suggestions to all of you! I found them very useful and implemented them in my thesis. Also, I would consider them in my future research work. Please find the responses to your comments.

Sincerely,
Artem Samtsevich

Reviewer: Anatoly Belonoshko

Comment 1. *In some cases the suggested methods are not applicable and some cases are not even mentioned.*

Response*:* I suggest you mean a diffusive solid-solid phase transition that often proceeds through a liquid/amorphous/disordered (intermediate) state and whether approaches presented in the thesis apply to treat such transitions. The short answer to this question – yes. The presented workflow with the geometrical and topological approaches have been used for reconstructive phase transitions. Nevertheless, it also can be used for diffusive phase transitions. As for liquid/amorphous transition states – it also can be covered by the presented workflow. However, after NEB calculation, simulation by transition path sampling (TPS) must be performed, which governs nucleation processes because it works in large supercell (thousands of atoms).

Reviewer: Xavier Gonze

Comment 1. *I strongly suggest the candidate to separate each chapter from the previous one in the text, and label them explicitly as "Chapter XYZ" in the text. Also, the candidate should number the sections inside the chapters, and possibly should number subsections. The table of content should be updated accordingly.*

Response: The labels of chapters in the thesis have been updated and the numeration of sections and subsections have been added too. The table of content also has been updated.

Comment 2. *I find also a bit strange that the "Introduction" chapter also includes two sections that are more advanced than usual introductory material, entitled "Theories of phase* *transitions" and "Transition State Theory". Perhaps they should be included in Chap. 2, that should then be renamed "Theoretical background" ?*

Response: The previous *Introduction* chapter has been split into two chapters – *Introduction* and *Theoretical Background.*

Comment 3. *It is not clear whether there is somewhere a list of previous first-principles investigations of solidsolid phase transitions. Actually, methods are listed indeed, but some brief mention of the specific transitions studied in these works might be useful. This is to complete the state of the art : what people were able to do before the current work ? There is actually the mention of one specific system at p25 : graphite to diamond.*

Response: I have added more examples of previous studies of phase transitions in solids that have been studied by metadynamics and NEB-based methods.

Comment 4. *Many English mistakes are present (often words are missing), and also the bibliographical references need to be "cleaned" (many need to be completed). Some figures need also to be clarified. To help in this respect, I have noted some of these and will transmit them to the candidate.*

Response: Thant you for careful reading, the text of the dissertation was proofread.

Reviewer: Stefano Leoni

Comment 1. *I found several images from chapter 1 (1.2, 1.3, 1.4 1.5) and chapter 2 (2.4) not duly referenced, this must be fixed. There are also several of our contribution to solid-solid phase transitions that are not cited, I was surprised by this choice.*

Response: The images in all chapters have been checked and for some of them (where it is need) have been added references. Sorry for missing these studies, I added examples on the usage of TPS to phase transition simulation. The contribution to the solid-solid phase transition investigation has been mentioned – added reference to Metashooting method and usage of TPS to various solids.

Comment 2. *The discussion of TST follows the reference to TPS, I think that the connection between the two should be better clarified – also Chandler is the original author of the TPS method, this cannot be attributed to Bolhuis alone, like it is currently the case on p. 12.*

Response: Added a more specific explanation of the connection between TST and TPS. Also, fixed reference to the authors of TPS.

Comment 3. *The problem of mapping two crystal structure onto each other, in a way that the resulting pathway is meaningful, is a non-trivial problem, particularly in the absence of a relationship of a group to an isotropic subgroup. Examples are made, but it would improve clarity and didactic message if the candidate would illustrate a full set of topological mappings and the meaningful geometric models that can be connected thereof – I found the explanation of the topological mapping sound but somehow too much biased by the content and approach of the original publications (Blatov et al.) – it would help, maybe for the first system studied, to provide details of actual and even unlikely, rejected mappings, and how the mapping choice may affect the final results.*

Response: The geometrical representation of atom-to-atom mapping for transition in CrN has been added. There is shown how interatomic contacts are mapped onto each other. As for unlikely mappings – the case is presented in the end of the *Topological mapping* subsection. There are presented the real case of wrong (non-periodic) mapping in the rutile-anatase transition of TiO_2 (it is out of scope of the presented thesis since the results are not published yet).

Comment 4. *NEB methods also suffer from local PES rugosity, meaning that a sufficiently high local energy barrier can prevent bands to fully relax – I think some discussion on how NEB copes with this problem will be appropriate. Towards doing so, several stages of band relaxation could be presented and discussed.*

Response: Since the NEB-based methods have improved by climbing image method, there is no problem with full band relaxation. The proper location of transition state using band optimization can be solved easily by combining NEB and climbing image approaches.

Comment 5. *In general, while nucleation is indicated as the main mode of solid-solid first order phase transitions, the method of interest in this thesis does not allow nucleation – this is discussed. I would welcome some reasoning about the extent to which a collective mechanism can still represent a nucleation-based one, where phase coexistence and interfaces are present.*

Response: The transition mechanism obtained by the NEB method can be interpreted as the first approximation to real one and such collective transition mechanism can be used as input for transition path sampling (TPS) simulation, but with larger cell (thousands of atoms), where the coexistence of solids, interfaces between solids, and the process of new phase nucleation can be investigated.

Reviewer: Sergey Levchenko

Comment 1. *This is a confusing description of metadynamics. While using collective variables may reduce the effort to evolve system to another state, the main driving force is the modification of the potential that pushes the system out of the well.*

Response: The description of metadynamics has been corrected, where I have shown what role bias potential plays in the metadynamics simulation and how it is related to collective variables. Also, I have extended the description of metadynamics by several examples of its usage. Additionally, I have provided a description of another landscape-explore method, called Stochastic Surface Walking, which is an advanced version of metadynamics.

Comment 2. *"The vibrational prefactor nu, which describes the characteristic atomic vibrational frequencies at the minimum and the saddle point, can be calculated explicitly to capture entropic contributions to the transition rate. The prefactor nu is small if the passageway at the saddle point is narrow and large if it is wide." - The prefactor mainly reflects the number of escape attempts per time unit. This should be mentioned as well. Similarly, in other places where entropic contribution is mentioned, I am not sure if you actually mean entropic contributions or the frequency of escape attempts through the saddle point, or perhaps both.*

Response: Has been fixed to “The vibrational prefactor ν is related to the width of the potential energy well at the minimum and the energy valley at the saddle point and is a characteristic atomic vibrational frequency. It can be calculated explicitly to capture entropic contributions to the transition rate. The prefactor ν is small if the passageway at the saddle point is narrow and large if it is wide.” In other places, where entropic contribution is mentioned, I mean entropic contributions.

Comment 3. *There are parts of the text that repeat in different words what was already said previously. For example, paragraphs starting with "The picture of rare transitions between two stable states can be described in the language of statistical mechanics as two free energy minima separated by a high activation barrier" and "Figure 2.2 illustrates a simple PES as a hilly landscape with peaks..." discuss what was already discussed previously. This can be organized much better.*

Response: The starting part of the *Energy Landscapes* paragraph has been rationalized by adding references to previous-written sections. Other parts of the text were proofread and optimized as well.

Comment 4. *"For the particular structure, several topologies can be defined depending on the bond length cutoff parameter." - Please explain the role of cutoff parameter. When there are two minima that differ by small displacements of atoms relative to each other, one would need to tune the cutoff parameter to distinguish the topology of the two minima. How is it done in practice?*

Response: The interatomic contacts for a particular crystal structure can be defined using the distance-based approach with cutoff parameter and using approaches based on or involved Voronoi decomposition. For example, in case of distance based approach, we can consider the case of graphite – if cutoff will be large, we will 3D connected topology, which is wrong. In those crystal structures, which have been studied in this thesis, I used Voronoi-Dirichlet approach for CN and topology determination and for well-optimized structures there were no problems to define topology. Finally, two crystal structures may have the same topology, since the structures are geometrically close to each other, like α and β-quartz or deferent perovskites.

Comment 5. *It would be good to illustrate the section describing supernets and subnets by examples.*

Response: Added detailed description of what is a subnet with respect to topologies and has shown how subnets can be generated with several illustrations.

Comment 6. *"The main result of this thesis is the development of the topology-based approach for the initial path generation and the adaptation of the geometrical mapping approach with its further application for MEP search." - This should be discussed much more across the thesis than it is now. The introduction is too long, with a lot of repetitions and details whose relation to the work done in the thesis is not clear. More details should be given specifically on the proposed unified workflow and its implementation. Similarly, when you write "My contribution to this work was investigating the phase transition mechanism from Pnma-CrN to newly predicted P-6m2-CrN.", the discussion should be focused more on this, rather than on the detailed results on convex hulls for Cr-N system.*

Response: Added more detailed description of phase transition investigation in CrN systems, like the geometrical representation of atom-to-atom mapping for transition in CrN, which has been generated from topological one. There is shown how interatomic contacts are mapped onto each other and how it is related to the geometries of both structures.

Comment 7. *"...with U-J=1 eV (see Figure 4.6). Details of the calculations can be found in related publication 193." - All important details of calculations should be described in the thesis. It was never mentioned that Hubbard U correction approach was used. Explain how a particular value of U_eff was chosen.*

Response: The description of Hubbard U-term correction usage has been added. Also, has been added the logic of U-J value choice.

Other comments: the text of the dissertation was proofread.

Reviewer: Roman Martonak

Comment 1: *The problem with the Ehrenfest classification is different - it ignores the singularity of the free energy in case of continuous (2nd order) transitions.*

Response: Provided more detailed description and restrictions of Ehrenfest classification.

Comment 2: *"Homogeneous nucleation is described by classical nucleation theory (CNT)29" there is also non classical nucleation theory, see B. Moran, Y. Chu, and G. Olson, International Journal of Solids and Structures 33, 1903 (1996)*

Response: Added description of non-classical nucleation theory.

Other comments response: fixed/added proper description of metadynamics, correlation function and Pareto optimization. The formula of strain components in VCNEB method has been updated.

Question 1. *p. 57 In Fig 4.9 a P-T phase diagram is shown where the transition pressure decreases from 12 GPa at T=0 to zero at T=200 K. Such large Clapeyron slope appears surprising. Is there a particular reason for such behaviour, e.g. a soft phonon mode in the high-temperature phase resulting in large entropic contribution?*

Response: This issue was not studied in detail in my thesis, but the possible reason is much faster increase of entropic contribution in more symmetric WB structure at higher pressures compared to low-symmetry low-temperature phase.

Question 2 *p.64 What is the reason to analyze the pathway from a more stable structure A to a less stable structure B (e.g. kyanite → sillimanite at both 0 and 10 GPa)? Such transition is unphysical.*

Response: Evidently, the way of plotting is less appealing than it should be and seems like the transition goes from less stable to more stable structure. Also, as presented in the review of Whitney, 2019, there are numerous cases when two or three polymorphs of Al_2SiO_5 are found coexisting in the same rock. Thus, we studied such phase transitions to prove that the origin of phases coexistence lay in high barriers and complex topological reorganization of structures.

Reviewer: Alexander Shapeev

Comment 1. *The quality of English is rather good and I did not trouble understanding almost all the details. However, I advise the author to re-read and fix some of the issues with English*

Response: the text of the dissertation was proofread

Comment 2. *Figure 1.1. is slightly misleading: as if MD simulations cannot capture atomic vibrations*

Response: Added more details into the description of MD application and timescales.

Comment 3. *The algorithmic details, like what is a supernet and subnet, could perhaps be better explained on an example of a crystal (even a toy-2D crystal) by identifying which bonds are part of supernet/subnet.*

Response: Added more detailed description of what is a subnet with respect to topologies and has shown how subnets can be generated with several illustrations.

Question 1. *I would expect that the transformation between phases, in many cases, would not occur everywhere in the bulk at the same time, but would start somewhere from a nucleus. In other words, one should be concerned about the energy barrier of nucleating a small grain of the phase from the old phase. Can the candidate please comment how relevant would his method be to predict the mechanism and the likelihood of such transformation happening (e.g., by computing the "bulk energy barrier" in eV/atom) in this case.*

Response: The real solid-solid transformation goes via nucleation and growth – this is true. Such processes must be simulated in larger cells (hundreds and thousands of atoms) and can be done only by more advanced techniques, such as transition path sampling (TPS). The results of presented solid-solid phase transitions can be used as input for TPS simulation. The presented workflow for phase transition simulation should give results close or identical to a full global search, which will be energetically close to the TPS simulation.

Comment 2. *How can experimentalists use the results of this work?*

Response: The presented work results shed light on the atomistic description of solid-solid phase transition and provided an energy profile of such transformation. However, the simulation of nucleation and growth in solids must be simulated in larger cells (hundreds and thousands of atoms) and more advanced techniques, such as transition path sampling (TPS), must be used. The results of the simulation can be interpreted into the kinetics from the correlation function. The energy barrier height can be used to estimate the heating parameters need to perform solid-solid transformation. Also, presented approaches for solid-solid phase transition investigation can be used for new phases prediction, which also can be addressed to experimentalists for confirmation of existence of these new phases. Also, presented atomistic description can be used for the understanding of topotactic reactions in solids.