

Evaluation of the Ph.D. Dissertation
“Atomistic simulation of mass transport phenomena in inhomogeneous intermetallic systems”
by Piotr Sowa

Wien, am 13.09.2017

Piotr Sowa's dissertation concerns development of simulation methods for modelling of atomic migration in crystalline solids. The presentation begins with introduction and general description of mass transport mechanisms operating in condensed matter, sketching of experimental and simulation techniques in dynamics studies and the motivation for the study. Already at this point I want to stress why I was so pleased to read this work: although it is, broadly speaking, a theoretical work, it is very closely linked with experimental studies of the same system. Here it is the binary intermetallic compound β -NiAl which still remains an extremely interesting material from technological point of view.

The thesis stresses the importance of two fundamental processes in highly ordered alloys which are self-diffusion and order-order relaxations. Since both processes result from thermally activated atomic jumps, one would expect that they will exhibit similar temperature behavior. It was, however, not the case in β -NiAl where resistometric measurements of ordering or disordering relaxations performed by the group of Prof. Kozubski revealed much lower activation energies than that of atomic diffusion. This long-standing controversy has been one of the basic motivations for this thesis.

The thesis then describes in-depth in three main parts different aspects of the simulation techniques and the simulation results. Part I is devoted to the detailed description of the theoretical background of the atomistic diffusion, Part II to the applied models and techniques of Monte Carlo simulations and Part III presents the results. The chapter “Elements of the theory of diffusion” is a compact but amazingly detailed, informative and logically designed introduction into phenomenological description of diffusion including tracer, interdiffusion, the Kirkendall effect and the Darken equation as the simplest model connecting inter- and self-diffusion coefficients (further completed by the vacancy-wind factor). Then follow a non-equilibrium approach and an atomistic description of atomic motion including correlation effects which at the end applied to the description of order-order relaxations. The equations and references into original papers and into the text books are very detailed and present a lot of important and useful information. In order to demonstrate that the text was examined in depth following typographical errors and other minor editorial issues should be addressed (the true reason for that will be elucidated close to the end of my evaluation):

- The author provides a list of most common diffusion mechanisms in chapter 2.1 properly addressing a vacancy mechanism as a dominant one in most metallic systems. It sounds pedantic but for the sake of completeness one should mention apart from interstitial also interstitialcy mechanism. This curious mechanism would be not worth mentioning if not operating in such very important class of materials like semiconductors.
- In Eq. (2.1) on page 26 probably “ J_i and ...” is missing.
- In Eq. (2.80) on page 39 the distance λ of the jump shall be (for a bcc structure) presumably $a_0 \sqrt{3}/2$.

- Spacing after Eq. (2.93) on page 41 is not necessary and the sentence “The vacancy availability factor ...” on page 42.
- In Eqs. (2.103) on page 43 should stay probably τ_A^{-1} as well as N_B in the second text line.
- The figure 3.1 from the next chapter is already necessary few text pages before. It simplifies reading if it will appear earlier.

The chapter “Model of an alloy and research methods” describes in detail computational techniques and algorithms of the simulation methods which are the heart of the author’s research. It is clear that the author of the thesis used methods and/or algorithms developed by former PhD students like Biborski, Oramus or Kozłowski. However, the elaboration of the simulation mechanism of the vacancy generation/annihilation due to dislocation climbing is author’s independent achievement. In the next chapter “Direct simulation of interdiffusion” the author proves on model systems that this mechanism works and provides in simulations essentially better results compared to former, simpler simulation methods.

Only two typographical errors have been noticed:

- In Eq. (3.41) on page 56 should stay variance factors θ_{BB} and θ_{AA} .
- The standard definition of the Boltzmann transformation in Eq. (3.46) is different, namely $\zeta = x/\sqrt{t}$.

The last part of the thesis comprises preprints of two papers with Piotr Sowa as the first author and a long chapter describing in detail results of direct simulations of interdiffusion using the author’s model of vacancy source/sinks. Two papers published in Philosophical Magazine in 2013 (vol. 93, p. 1987) and 2017 (vol. 97, p. 1375) have been already reviewed and any detailed analysis here are about to become obsolete. Just a brief comment:

In the paper Sowa et al. 2013 experimentally found relation between the order-order kinetics activation energy lower than the diffusion activation energy have been confirmed in the simulation of a triple-defect binary system using kinetic Monte Carlo technique with a temperature dependent vacancy concentrations calculated by the semi-grand Canonical Monte Carlo method. The pair-interaction energies for the kinetics simulations have been rather arbitrary chosen creating, however, a B2-orderd superstructure with a clear tendency for a triple-defect formation. In the Sowa et al. 2017 the same model system have been used, but this time the simulation was accompanied by the detailed atomistic models for both activation energies including activation energy for the tracer correlation factor, antisite atom formation and for migration. A similar model was elaborated for the order-order relaxation energy, see Eqs. (2.98) and (2.105). The comparison of both activation energy models with the simulation results is especially compelling. Moreover, it was shown by the author that the inequality of ordering energies is characteristic *only* for triple-defect systems. Side note: there were a lot of discussions with Prof. Pfeiler, former member of our group “Dynamics of Condensed Systems”, who used an experimental method of residual resistivity to study order-order relaxation in intermetallics. The aim of our discussions was to build a bridge between diffusion and relaxation studies, i.e. to find a common factor between our research fields: order relaxation and atomistic diffusion. Needless to say, that no consensus could be reached and only now it is clear that such a link is rather complex and by no means can be considered self-evident.

The last chapter “Direct simulations of interdiffusion”, which apparently is not yet published, is well suited for a high-impact journal. It contains tricky atomistic simulations of the diffusion couple assuming that the vacancy concertation equilibrates much faster than the atomic configuration. The values of the interdiffusion coefficients are analyzed by two methods: indirectly by kinetic Monte Carlo correlation factors or directly by the Boltzmann-Matano fits to concentration profiles. The author proofs that both methods provide equivalent results. The binary systems used in simulations, one without long-range order and one with a B2 order have been simulated using rigid lattices. Before the publication is finalized, I recommend Mr. Sowa consider several questions raised by the results and their interpretation, e.g. how one can introduce elastic stress from dislocations in the model or what is the impact of stress on interdiffusion in the frame of applied model (diffusion and stress are currently particularly popular research areas).

In the figure caption 5.8 should stay probably “DIS-ASY” instead of “SYM-ASY”.



I was very pleased and excited to read this work, even though I was already familiar with the publications which formed the fourth chapter. Thesis quality and research quality is absolutely excellent. The dissertation is clearly written and it properly places the findings in the context of current progress in the field. The layout of the thesis is exceptionally well organized and thesis proceeds in natural, logical fashion. There is substantial amount of background provided for readers to place the research in broader context.

Due to this I would strongly recommend to make this thesis accessible to broad readership publishing e.g. in the series *Springer Theses – Recognizing Outstanding Ph.D. Research*.

I am of the opinion that the thesis by Piotr Sowa is clearly an excellent scientific work, presenting new and original, cutting-edge research in a very clear and detailed fashion. Overall, the extent and quality of the research easily meet standards for a Ph.D. dissertation in Poland. My final conclusion on the thesis that I place in the top 10% of all known PhD thesis is definitely positive, and I rate it as “very good”. I want also to suggest that Mr. Sowa’s dissertation should be awarded with commendation.

Sincerely,

A handwritten signature in blue ink, appearing to read 'B Sepiol', with a long, sweeping flourish extending to the right.

Bogdan Sepiol



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Wniosek o wyróżnienie rozprawy doktorskiej
magistra Piotra Sowy "Atomistic simulation of
mass transport phenomena in inhomogeneous
intermetallic systems"

Wiedeń, 13.09.2017

Rozprawa doktorska Piotra Sowy zajmuje się opracowaniem metod symulacji migracji atomowej w krystalicznych ciałach stałych. Szczegółowa analiza doktoratu zawarta jest w recenzji. Jestem zdania, że rozprawa doktorska Piotra Sowy jest znakomitą pracą naukową, przedstawiającą oryginalne badania w bardzo czytelny i szczegółowy sposób. Praca jest jasno napisana i w kontekście obecnego postępu w tej dziedzinie wiedzy, jest bardzo aktualna. Spora część wyników albo została już opublikowana albo zostanie opublikowana w najbliższym czasie. Zarówno zakres jak i jakość badań zdecydowanie spełniają standardy dla prac doktorskich. Osobiście umieszczam tę pracę wśród najlepszych 10% wszystkich znanych mi prac doktorskich. Z wyżej wymienionych powodów chciałbym wnioskować o wyróżnienie rozprawy doktorskiej mag. Piotra Sowy.

Z wyrazami uszanowania

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