

School of Physics and Astronomy



Interacting Diffusion in Metals Second Year Report

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Abstract

Corrosion is an important process, which may severely limit the utility of an alloy. In this PhD project, I am currently developing a simple model of the way Oxygen diffuses through pure Titanium, in an effort to capture the salient features of this phenomenon. Once I am satisfied this model works, I wish to extend it to Titanium alloys in order to explain why some of them are better at resisting corrosion than others.

Signature:

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1 Introduction

I apologise for the lateness of submission of this document; I was trying to get a little more research done before submitting it, and indeed I did derive some of the formulae about lattice gas equilibria after the submission deadline. Throughout this report I will assume that the reader has already read my First Year Report, so I won't be rereferencing anything from that.

2 Progress Since First Year Report

Since the First Year Report, in which I attempted to go straight for a continuum-limit model and was largely unsuccessful, I have decided to change my approach to the problem a bit. I attended a conference on Diffusion in Dresden last September, and there I spoke with people from many different disciplines. The general feeling was that a computational lattice-based approach would be a good starting point, as this would allow me to perform calculations which I could then use to derive continuum-limit PDEs, as well as providing potentially useful information about the Titanium Dioxide/Titanium interface and its dynamics. In the following subsections, I will give a summary of my activities since last September.

2.1 Finding a Computational Framework

In order to perform Monte-Carlo lattice dynamics calculations, I could have written my own code from scratch. However, if I were to have done do that, I would have spent a lot of time working out how to implement Gillespie-like algorithms, then would have had to write and debug code and a whole host of other time-consuming things. Instead, I looked for pre-existing software packages which fulfilled my requirements.

Of those I looked into, `KMCLib`[1] looked to be the most suited to my requirements. It uses Python for configuring the calculations, and then performs them using C++ for speed and, if desired, parallelisation. I have now spent a while using this code, and after some teething problems am satisfied that it can do what I need it to do and that I can use it correctly.

2.2 Choice of Model

So, it is all very well to say that we wish to model the diffusion of Oxygen through a Titanium lattice using stochastic lattice dynamics, but what kind of model should we use? I decided to work in one-dimensional systems instead of three-dimensional systems to begin with. This is because:

- As Titanium corrodes, the oxide layer advances forward as a broad front; therefore the problem is essentially one-dimensional;
- There aren't nearly so many one-dimensional models as there are three-dimensional models; thus a one-dimensional model should have fewer free parameters, and therefore stronger predictive power;
- We can perform calculations much faster in one-dimensional models than in three-dimensional models, so if our one-dimensional model is terrible, we should find out fairly quickly!

Thus, I am in the processing of investigating the phenomenology of the following lattice model, which is about the simplest one can make which should produce the behaviour we're looking for:

- Let there be a one-dimensional chain of L lattice sites. Each site is occupied by either an Oxygen atom (denoted by O) or a Vacancy (denoted by V). For example, a particular chain of length 5 could be configured $OOVOV$.
- In a stochastic model, we randomly transition to new configurations with certain rates. In our model we would like Oxygen atoms to be able to hop into vacant spaces, imitating how Oxygen atoms move between interstitial voids in Titanium. Clearly then, we only wish to allow transitions in which adjacent Oxygens and Vacancies swap places.
- The rates for my model are as follows:

$$\begin{aligned}
 \dots VOVV \dots &\longrightarrow \dots VVOV \dots && \text{with rate } 1 \\
 \dots VOVO \dots &\longrightarrow \dots VVOO \dots && \text{with rate } 1 \\
 \dots OOVV \dots &\longrightarrow \dots OVOV \dots && \text{with rate } \lambda \\
 \dots OOVO \dots &\longrightarrow \dots OVVO \dots && \text{with rate } \lambda,
 \end{aligned}$$

as well as the 4 counterpart transitions and rates one finds by requiring left-right mirror symmetry. More simply, an Oxygen can jump forward into an empty Vacancy with rate 1 if there is a Vacancy behind its starting position, and with rate λ if the position behind it contains an Oxygen. This is supposed to indicate short-range attraction ($\lambda < 1$) or repulsion ($\lambda > 1$) between Oxygen atoms.

I intend to use the model outlined above with $\lambda < 1$, so that Oxygen atoms are attracted to one another. It may not be obvious, but one can show that the above model does obey the Principle of Detailed Balance, with an “energy” proportional to the number of Oxygen-Oxygen adjacencies (one might think of these as “Oxygen bonds”).

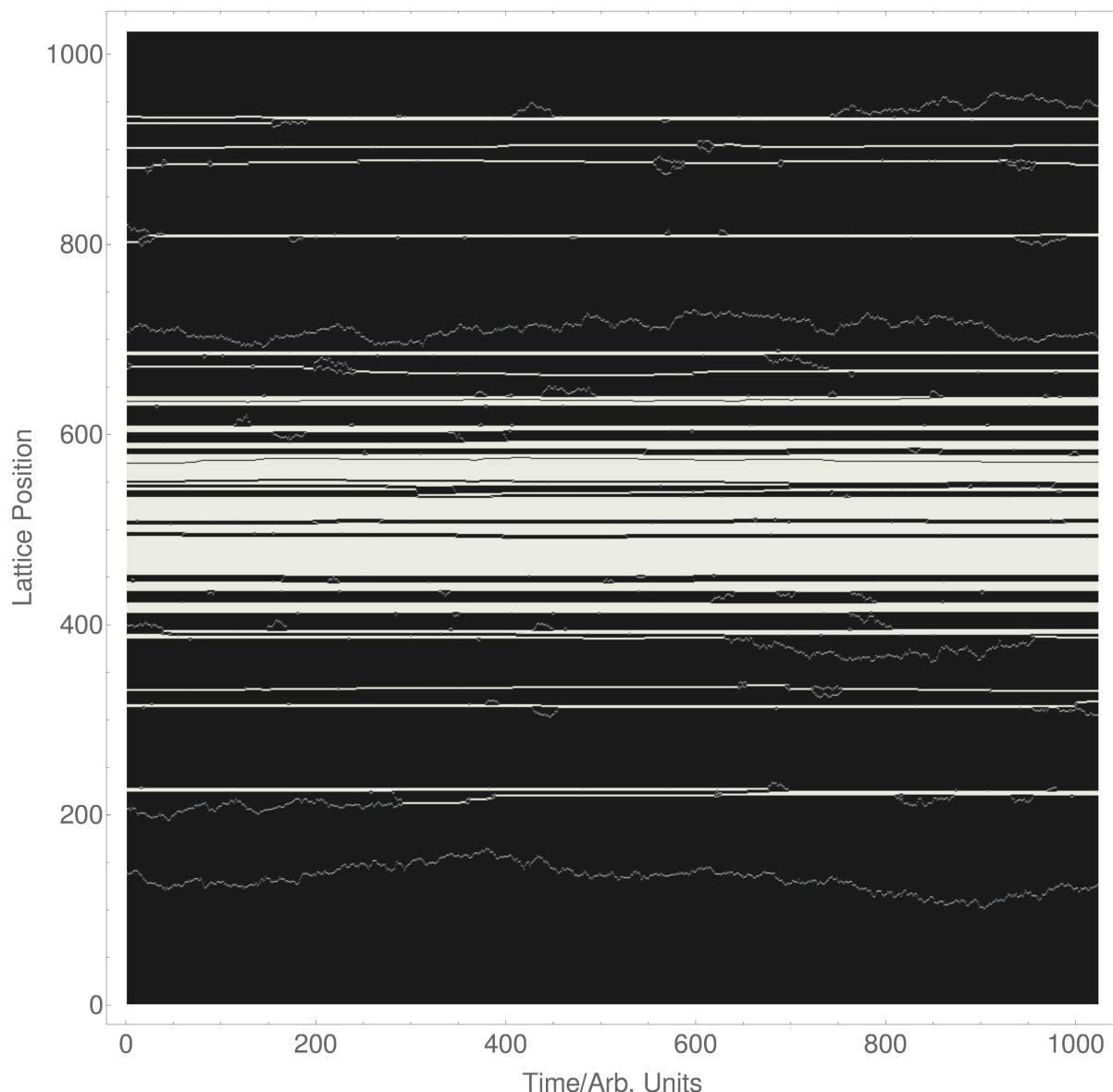


Figure 1: The time-evolution of a closed periodic system (size 1024) containing a fixed number of O and V. Each pixel is shaded according to the time-averaged occupation of that particular site during that time period (in other words, if we let the occupation be 1 if there is an O there and 0 for a V, what is the average of this occupation over a short time interval?): white indicates high average occupation, around 0; black indicates low occupation. In this case, $\lambda = 0.01$. Notice the solid blocks of Oxygen-rich material more than two Oxygens thick, often surrounded by a halo of sparse gassy individual Oxygens undergoing random walks.

2.3 Model Predictions

I originally intended to quickly investigate the way the Oxygen flows through a one-dimensional chain, by imposing boundary conditions equivalent to different concentrations at different ends of the chain and measuring how rapidly the Oxygen flows with different concentration gradients and in different average-concentration environments. However, it then occurred to me that this system might exhibit some phase equilibrium

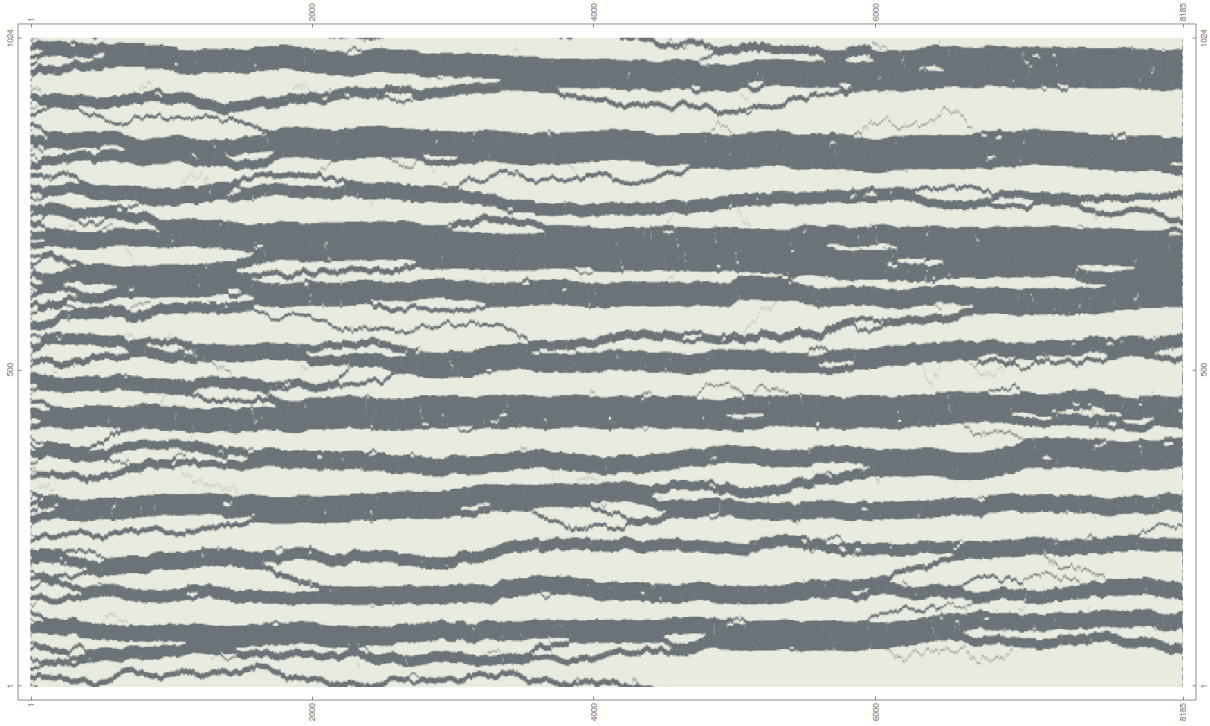


Figure 2: A plot done using the same technique as Figure 1, again with periodic boundary conditions. This computation was performed with a similar value of λ but over a much longer time period. In this case, the initial configuration had a random 50:50 mix of O and V. Notice how the Vacancy-rich regions form streams which walk randomly whilst retaining roughly the same width, occasionally coalescing and splitting.

phenomena, which would be best investigated by considering the problem to have periodic boundary conditions and simply setting up a mixtures of Oxygen and Vacancies and then seeing how they behave for a given value of λ . In order to check that the simulations are proceeding as desired, I have put some effort into being able to record and view the system's behaviour over time; a visualisation of an example system's time evolution is displayed in Figure 1. As of writing this paper, this numerical work is still ongoing; the code needs to be refactored a little before it is ready for bulk use.

We can also make progress using analytics. So far, I have managed to derive the mean-field theory, with a little help from Martin Evans. If $\rho_i(t)$ is the mean-field average occupation of the i^{th} site at time t , then it should obey

$$\frac{\partial \rho_i}{\partial t} = (1 - \rho_i) [(1 - \zeta \rho_{i-2}) \rho_{i-1} + (1 - \zeta \rho_{i+2}) \rho_{i+1}] - \rho_i [2\zeta \rho_{i-1} \rho_{i+1} - (3 - \zeta) (\rho_{i-1} + \rho_{i+1}) + 2], \quad (1)$$

where $\zeta = 1 - \lambda$ seems to be the most appropriate way to express the degree of nonlinearity in the system. If we let the spacing between the lattice sites be a , and promote $\rho_i(t)$ to $\rho(x, t)$, a continuous spacetime variable, then we find that in the long-wavelength limit it should obey

$$\frac{\partial \rho}{\partial t} = \frac{1}{2} a^2 \left[(2 - 2\zeta \rho (4 - 3\rho)) \frac{\partial^2 \rho}{\partial x^2} - \zeta (2 - 3\rho) \left(\frac{\partial \rho}{\partial x} \right)^2 \right] + \mathcal{O}(a^4). \quad (2)$$

Later on, I would like to use these PDEs to help simulate large-scale aspects of the Titanium/Titanium Dioxide problem.

Finally, it possible to make limited predictions about equilibrium. As I have stated, the number of Oxygen-Oxygen “bonds” makes a god candidate for the energy of the system. Thus, we may be able to use this to tell if phase separation has occurred or not. By making a few simplifying assumptions, one can show that for a closed sample with Oxygen number density ρ_0 , the average number of bonds per Oxygen is

$$1 + \frac{\lambda(\rho_0 - 1)}{\rho_0}, \quad (3)$$

so long as $\lambda < \rho$. Exploring the validity of this theory is one of the immediate goals of my current numeric work.

3 Courses, Publications, and Plans

Given that KMCLib has a Python frontend, a language with which I was not familiar, I took SUPA Python course this year. Other than that, I have attended no other courses, since, including that, I believe I have already met all of my SUPA requirements.

As of yet, I have no publications. However, I would like to be ready to publish on the subject of the phenomenology of the one-dimensional lattice model described in 2.2 by the end of the Summer. In order to do this, I have the following short-term goals:

1. Get the code working properly and stably. The input files have become a bit of a mess as I have experimented with them and need to be cleaned. Also the computations are currently memory-limited, which is not a great situation from a scaling-up perspective, so I need to develop cleverer ways of taking, storing and processing results.
2. I need to work out how to port the code to some cluster in order to perform large-scale calculations; currently I am just running it on my laptop. I believe Eddie3 would be a good choice of machine. In order to be able to run on such a system, I will need to tweak the code further.
3. Once I have the capability to do lots of calculations fairly fast, I would like to firmly establish what the system does in equilibrium (as in, does it obey equation 3?), and then move onto investigating dynamical behaviour in which Oxygen is driven through the system via concentration gradients. At that point we can compare to the mean-field long-wavelength PDE in equation 2.

Once I have done these things, I think that will be enough to publish in a paper.

I’m not entirely sure what to do after that; I will probably be in a better position to plan my next moves once this is done. Certainly I would like to extend the model to include alloying atoms such as Nickel, and it would also be good to extend the model to three-dimensions, to make sure the behaviour isn’t that different from that observed in one-dimension. I would like to have at least made the Nickel extension by the end of my PhD.

References

- [1] Mikael Leetmaa and Natalia V Skorodumova. KMCLib: A general framework for lattice kinetic monte carlo (kmc) simulations. *Computer Physics Communications*, 185(9):2340–2349, 2014.