Non-interacting lattice random walks for calculating diffusion controlled growth in solid state for dilute concentrations

Aarne Pohjonen * **Touko Puro** **
Assa Aravindh Sasikala Devi ***

* *University of Oulu, Materials and mechanical engineering department (e-mail: Aarne.Pohjonen@ Oulu.fi).*
** *Aalto University, Department of Computer Science, Konemiehentie 2, 02150 Espoo (e-mail: Touko.Puro@Aalto.fi)*
*** *University of Oulu, (e-mail: Assa.Sasikala.Devi@Oulu.fi)*

Abstract: To connect the molecular length scale phenomena to the macroscopic length scale in diffusion controlled growth in solid state, there is need to consider the movement of individual atoms in the crystal lattice and examine the length scale effect where the average density of the atoms approaches to the continuum macro scale. For this purpose a lattice random walk model has been constructed to represent the diffusion of atoms to form a precipitate. Once the atom is in contact with the precipitate surface, the precipitate grows and the atom is not anymore contributing to the random walk. Through the model, it is possible to evaluate the concentration fluctuations at different length scales in diffusion controlled growth and connect the continuum description of diffusion to the atomic level description. We connect the different length scales in theoretical description from atomistic scale through random atom movements to macroscale. In the current study, two-dimensional lattice random walks and growth are considered. The study contributes to the modelling efforts of understanding diffusion controlled precipitate growth in steels.

Keywords: Diffusion, random walk, scale bridging, atom level, continuum level, random movement probability, neb method, saddle points.

1. INTRODUCTION

Diffusion is an important phenomenon, which affects drastically the formation of several microstructural features in materials, such as formation of precipitates (Pohjonen et al., 2022), movement of phase boundaries (Pohjonen 2023), segregation of atoms to crystal defects (Cottrell and Bilby, 1949; Macchi et al., 2024; Pohjonen et al., 2022), etc. Therefore, it is of utmost practical importance to obtain the highest possible level of thorough understanding of the phenomena that affects the diffusion in atomic lattice in different conditions.

Traditionally, diffusion in macroscopic scales can be modelled using the Fick's laws of diffusion (Porter et al. , 2022). The connection of the probability of molecular movements and their macroscopic effects dates back to Brownian motion and the theoretical explanation by Einstein in ref. (Einstein (1905, 1906) and Smoluchowski in ref. (von Smoluchowski 1906) as described in (Kac, 1947). Previously, the diffusional growth of a precipitate in steels has been examined through random movements of atoms in the atomic lattice. (Larsson and Ågren, 2003) Also the activation energy that relates to the atomic movement in steels has been calculated for austenitic and ferritic/martensitic structures (Wang et al., 2021). In the current study, we describe the theory connecting these different length scales through the implementation of a random walk algorithm for diffusional atom movement in the atomic lattice. This approach provides initial step for bridging the atomistic energy, length, and time scales to macroscopic description, and it provides information on the transition, where the inherent concentration fluctuations in atomic scale diminish when increasing the length scale.

2. THEORY

The basic connection between flux of atoms and the random movement is reasonably straightforward. (Porter et al., 2022) Consider neigbouring planes of atomic sites containing diffusing atoms. If the diffusing atom on plane 1 has probability of p_{x+} to move in positive x direction to plane 2 and atom on plane 2 has probability p_{x-} to move in the negative direction to plane 1, then the net flux in x-direction $\boldsymbol{f}_x = \hat{n}_x(p_{x+}n_1 - p_{x-}n_2)/A$ where $\hat{n}_x$ is the unit normal vector in x direction. For simplicity, let us consider the movement of atoms in cubic lattice, where the atom hops from one cube to another with probability p. If the probability of the random atom movement is independent of direction x, y, z, one obtains the Fick's first law of diffusion:

$$\boldsymbol{J} = -D\nabla C \tag{1}$$

where C is the concentration of atoms, and the temperature dependent diffusion coefficient D has the connection to the atomic level probability of movement p through

$$D = \frac{1}{2N}\Gamma a^2 \tag{2}$$

where N is the dimension (for 2 dimensional diffusion $N = 2$ and 3 dimensional diffusion $N = 3$) a is the lattice constant and Γ is the frequency of atom movement, which is related to the direction-independent probability p for atom to move per unit time, and the number of dimensions the atom can move during time-step.(Porter et al., 2022) For example consider k timesteps. If atom has probability p_x to move in x direction and probability p_y to move in y-direction during one time-step Δt, then the frequency of the atom movement is $\Gamma = p_x k/(k\Delta t)+p_y k/(k\Delta t) = (p_x + p_y)/\Delta t$. If probability $p_x = p_y = p$, then $\Gamma = Np/\Delta t$. The equations (1) and (2) provide the connection between average random atomic movement in bulk material and the flux of atoms. The time evolution of the concentration field can be obtained from the continuity equation by the divergence of the flux, which yields the Fick's 2nd law:

$$\frac{\partial C}{\partial t} = -\nabla \cdot \boldsymbol{J} = \nabla \cdot (D\nabla C) \tag{3}$$

At the atomistic scale, there is considerable fluctuation of concentration about the average value due to the random movement of atoms, which can be examined with random walk simulations for different cases.

In case the probability of the random atomic movement p is independent of the position $\boldsymbol{x}$, the time evolution of the concentration field is only affected by the gradient ∇C. However, if the probability $p(\boldsymbol{x})$ is function of position, the drift (i.e. advection) of atoms occurs according to the following equation:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C) = \nabla D \cdot \nabla C + D\nabla^2 C \tag{4}$$

which is the advection-diffusion equation, where the advection velocity $\boldsymbol{v} = -\nabla D = -\nabla \frac{\Gamma a^2}{2N} = -\nabla \frac{pa^2}{2\Delta t}$. Considering the position dependent probability for random atom movements $p(\boldsymbol{x})$ and compression/tension of the lattice, it becomes possible to link the atomistic phenomena to the emergent macroscopic diffusion and advection phenomena (Cottrell and Bilby, 1949).

An analytical solution is available for diffusion from point concentration (MIT, 2024), which serves as a useful test case for diffusion models (Pohjonen, 2024b,a), which we shall compare to also in the current study. For two-dimensions, the analytical solution is described by

$$C(x, y, t) = \frac{M}{4\pi Dt}\exp\left(-\frac{x^2 + y^2}{4Dt}\right) \tag{5}$$

where M is the number of atoms.

The atom movement is thermally activated process, which is caused by the random vibrations of atoms. If the diffusing atom gains enough energy, it has high probability of moving in the lattice. The probability for the atom movement from a stable lattice site to another stable site can be obtained from Arrhenius type equation:

$$p = A\exp\left(-\frac{E_A}{RT}\right) \tag{6}$$

where the activation energy barrier E_A can be calculated using atomistic simulations using the nudged elastic band method (NEB) (Wang et al., 2021). NEB method is a powerful tool to identify the microstructural evolution of a system in which defects or impurity atoms are present and they evolve interactively (Jónsson et al., 1998; Henkelman et al.. 2000, 2002) The atomic scale information such as the energies of the initial, final and transition states, can be used to identify the energy barriers and can serve as inputs to the description of mesoscale phenomena. Basically NEB method can provide a minimum energy path that describe the energy variaton of the atomic movement from an initial to final state. It is a chain of states method, to determine the minimum energy path on the potential energy surface. Each atomic configuration will be at a potential energy of 0 K, represented by a point in the configuration space, and can be determined either by empirical potentials or first principles calculations. In the NEB method the initial and final configurations will be calculated by minimizing the energy and then a linear interpolation will be carried our between the two end states to generate a finite number of replicas. Two nearby replicas will be connected by a spring, resembling an elastic band made of beads and springs. To solve the corner cutting and sliding that can arise, a force projection, such as "nudging" is employed. This procedure followed by proper optimization ensures that the elastic band converges to the minimum energy path. Further, after optimization, both the position and energy information of the configurations can be obtained. There are different variations of the basic NEB method, adapted to suit the needs of the system in use, such as extended three dimensional defects which requires a large model system with a long reaction path. This is to ensure that enough replicas are included to map the long trajectory between the saddle point and final state (Zhu et al., 2007).

The effect of elastic lattice distortions can bias the random movement of the atoms and give rise to net drift of interstitial atoms towards tensile stress and away from compression. The dependence of the random movement probability on the local strain can be quantitatively examined with ab-initio based NEB methods, and the emerging flux and the random fluctuations can be examined with the random walk simulations.

In certain temperature range, it is energetically favourable for the atoms to coalesce and form a precipitate, which then grows due to diffusion of more atoms to the surface of the precipitate (Larsson and Ågren, 2003; Pohjonen et al., 2022).

3. NUMERICAL ALGORITHM

A random walk algorithm was implemented to simulate the random movements of atoms in two-dimensional lattice, and their coalescence to a precipitate, which is located in the center of the simulation domain. When the atom coalesces to the precipitate surface, the precipitate radius will grow and the coalescing atoms are removed from the random walk simulation. As a result of this, the concentration is lowered near the precipitate, which then implicitly causes net flux of atoms towards the negative of the concentration gradient. Periodic boundaries were applied in the simulation.

The random walk algorithm has two main stages. First, it moves the atoms based on the random probability of movement, and secondly, it will remove the atoms from calculation when they are within the precipitate radius,

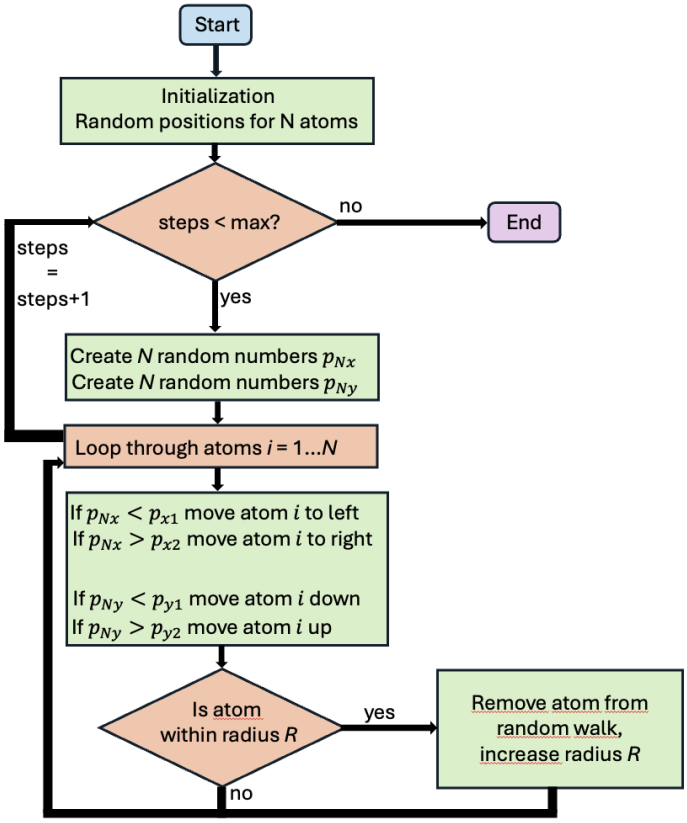

Fig. 1. Flow chart depicting the operation of the random walk and precipitate growth algorithm.

which grows each time an atom is located there within. A flow chart depicting the operation of the algorithm is shown in Fig. 1.

The local density of atoms was calculated by dividing the simulation domain to rectangular subdomains and calculating the number of atoms within each subdomain, and dividing the number of atoms by the size of the subdomain (area in 2D).

To speedup the simulations we accelerated the random walk algorithm to run on GPUs by writing our algorithm directly in CUDA. In the following, we refer readers unfamiliar with CUDA and GPU terminology to (NVIDIA, 2024). The random walk algorithm is straightforward to parallelize and accelerate, because except for growing the precipitate radius the atoms do not affect each others. In the performed simulations it was found that atoms coalescing to the precipitate surface is rare enough that performance-wise the radius expansion can be performed with GPU atomic operations.

Atomic operations guarantee that no other atomic operations happen while the atomic operation is being performed. Thus they prevent race conditions that would otherwise happen when multiple threads try to write to the same variable. Naturally atomic operations are more costly than normal operations, especially if many of them are being performed on the same memory address, since the operations have to be synchronized in some manner.

To minimize the costs of the atomic operations we use a common technique of first combining all atomic updates inside a threadblock into a variable in shared memory and make a single atomic update from the threadblock into the variable in global memory that is shared across all threads. This cuts down the amount of atomic operations to variables in global memory significantly and atomic operations to variables in shared memory are significantly faster due to them being closer in memory and due to the need of synchronizing only between the threads in the current threadblock.

Due to this optimization and the radius updates being rare we found the atomic operations to be a solution that is easy to implement for growing the radius. This implementation did not have measurable effect on the performance of the kernels. The rarity of the coalescing motivated optimization, where instead of synchronizing between a single update of each atom, we update each atom n steps and then synchronize. This cuts down memory traffic by a factor of n since we can reuse the values loaded to local memory. The only difference between synchronizing between each step and every n steps is that the radius size lags after the first update done after synchronizing in the second scheme, but if the number of radius updates is small enough this difference is negligible. We found that on the tested hardware, a single RTX A2000 8GB Laptop GPU, synchronizing after every second step gave a performance improvement of 30 percent.

4. NUMERICAL TEST CASES

4.1 Diffusion from initial point source

To test the connection between the random movements and the macroscopic diffusion equation, we compared the random walk simulation from initial point concentration to corresponding diffusion calculation. Consider a two-dimensional case where all atoms are initially located at the origin. The random movement is assumed to occur in two dimensional square lattice with lattice constant $a = 1$. Also, timestep is chosen as $\Delta t = 1$, i.e. dimensionless units were used, as this is mathematical study, not directly connected with physical properties. The atoms have 50 % probability to move within time-step in x-direction, and the same probability for y-direction. If they move, they have equal probability to move either in positive or negative direction. Since the diffusing atom can move both x and y direction within timestep with 50% chance in each direction, the frequency for the atom movement during timestep is $\Gamma = (0.5 + 0.5)/\Delta t = 1/\Delta t$, and according to equation (2) the diffusion coefficient in this case becomes $D = \Gamma/(2N) = 1/4$. The simulation results and comparison to analytical continuum solution, equation (5), are shown in Fig. 2. To see the effect of the random fluctuations, the simulation was repeated ten times and the standard deviation for each plotted datapoint was calculated. The standard deviations are indicated as error bars in the figure. The small difference between the simulated results and the analytical solution arises because of the differences between the analytical continuum description and the discrete random walk results, and also due to chosen area where the atoms are averaged over when calculating the results from the simulations.

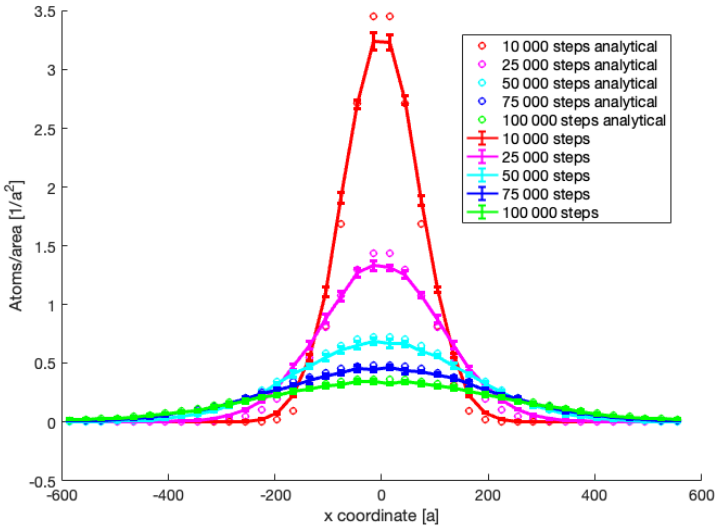

Fig. 2. Diffusion from initial point concentration. The lines show the simulation results averaged over 10 separate simulations and the error bars indicate the standard deviation. The markers show the corresponding analytical solution described by equation (5).

4.2 Concentration fluctuations as function of system size

Fluctuations in small systems are inherent due to random movement of discrete particles. It was examined how the concentration fluctuations in a two dimensional system depend on the system size. To achieve this, the length of the square domain and the number of atoms were both scaled by scaling factor sf, which was altered in the simulations. The atoms were initialized to random positions and the random walk simulation was ran for 1000 timesteps. In each simulation the domain was divided in to 40x40 square subdomains. The 2d concentration was calculated as number of atoms/area for each subdomain. Then standard deviation of the subdomain concentrations was calculated. The standard deviation as function of the scaling factor is shown in Fig. 3. The result shows that the standard deviation depends on the scaling factor approximately proportional to $1/sf$. Increasing the system size in the random walk simulations up to $sf = 12$ still showed noticeable fluctuations, and was not much different from the case $sf = 6$.

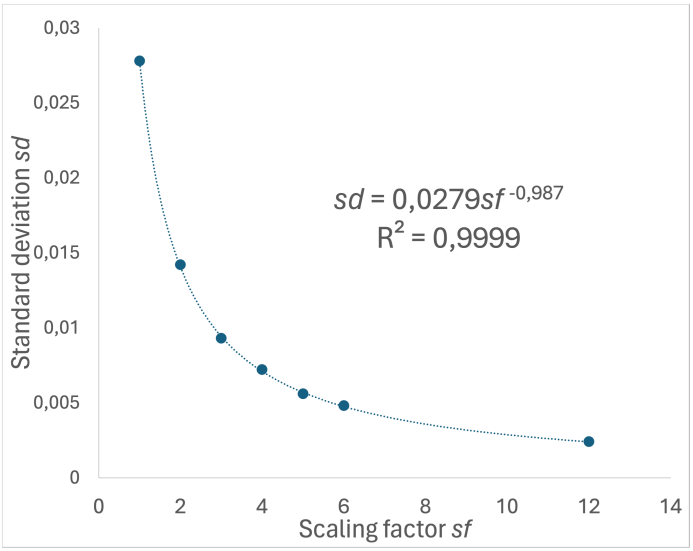

Fig. 3. The standard deviation sd of the concentrations of 40 by 40 subdomains as function of system scaling factor sf

The result shows that the concentration near the precipitate becomes depleted as atoms are being removed from the diffusion to increase the precipitate radius, which is a realistic effect (Porter et al., 2022).

4.3 Diffusion controlled growth of precipitate

To test the random walk simulation in a more interesting case, a coupled precipitate growth and diffusion simulation was performed. The atoms, which were initially located randomly at the domain, were moved randomly similar to the previous case, but if they arrived within a radius, the precipitate radius grew and the atom was removed from the random walk. The simulation results from small scale simulations are shown in Fig. 4, where a) shows the concentration of atoms in the whole simulated two dimensional domain and b) shows the plot of concentration of atoms along the horizontal line which passes throught the origin, where the growing precipitate is located. The area increase of preciptate due to attachment of atom was set as $A_{\mathrm{at}} = \pi(a/6)^2$.

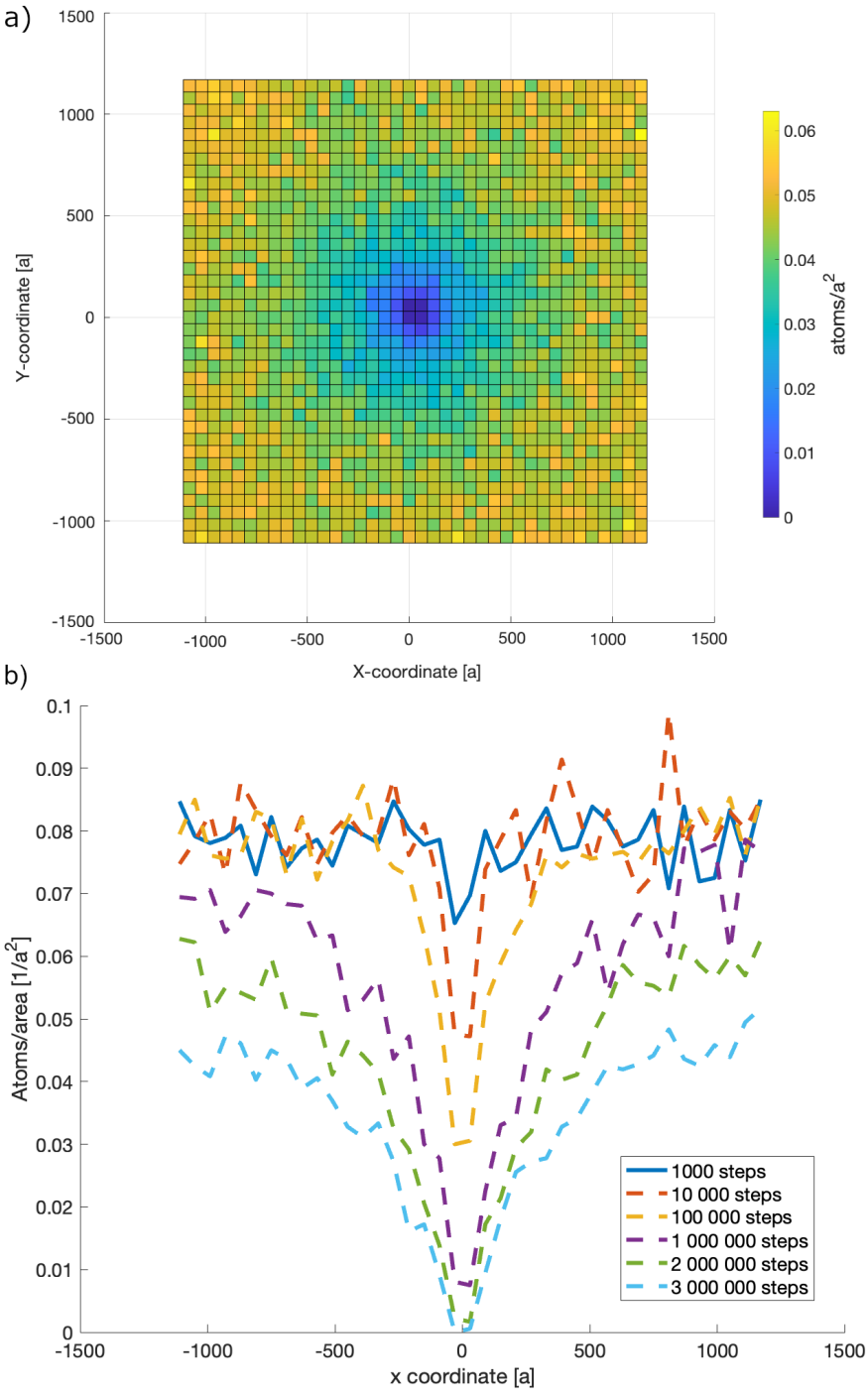

Fig. 4. a) The concentration of atoms per subdomain area after 3 000 000 timesteps, b) Plot of concentration along the horizontal line which passes the origin at several different time-steps.

5. CONCLUSIONS

A theory linking random movement (i.e. random walk) of atoms in crystalline material to the activation barrier of atom hopping from stable lattice cite to another was described and also the link between the diffusion equation and the random movement probability was presented. The random random walk model describing diffusional movement of atoms in a lattice was constructed and parallelized using GPU. The model was compared to a continuum analytical solution for diffusion from an initial point concentration, and it was applied for mathematical calculation of diffusion controlled growth of a precipitate.

In future studies, the probabilities and their dependence on different factors, such as local stress/strain state, can be obtained from nudged elastic band (NEB) calculations and the model can be parameterized using physical data. The NEB calculations combined with atomistic ab-initio density functional theory simulations have the capability for providing the energy barriers for atomic mobility, and hence they could be used in future for theoretic prediction of the of atomic scale effects of diffusion, precipitation and partitioning phenomena. Such effects are very difficult to observe directly experimentally, which makes phenomenological parameterization of models difficult. The theoretical calculations can also provide explanations connected with these practically very important metallurgical phenomena.

ACKNOWLEDGEMENTS

Authors acknowledge financial support from the AID4GREENEST project (AI powered characterization and modelling for green steel technology) funded by Horizon Europe Research and Innovation Program, Grant Agreement No. 101091912. We would also like to thank Jane and Aatos Erkko (J&AE) Foundation and Tiina and Antti Herlin (TAH) Foundation for their financial supports on Advanced Steels for Green Planet project.

REFERENCES

Cottrell, A.H. and Bilby, B.A. (1949). Dislocation theory of yielding and strain ageing of iron. *Proceedings of the Physical Society. Section A*, 62(1), 49.

Einstein, A. (1906). Zur theorie der brownschen bewegung. *Annalen der Physik*, 324(2), 371–381. doi:10.1002/andp.19063240208.

Einstein, A. (1905). Über die von der molekularkinetischen theorie der wärme geforderte bewegung von in ruhenden flüssigkeiten suspendierten teilchen. *Annalen der physik*, 4.

Henkelman, G., Jóhannesson, G., and Jónsson, H. (2002). Methods for finding saddle points and minimum energy paths. *Theoretical methods in condensed phase chemistry*, 269–302.

Henkelman, G., Uberuaga, B.P., and Jónsson, H. (2000). A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of chemical physics*, 113(22), 9901–9904.

Jónsson, H., Mills, G., and Jacobsen, K.W. (1998). Nudged elastic band method for finding minimum energy paths of transitions. In *Classical and quantum dynamics in condensed phase simulations*, 385–404. World Scientific.

Kac, M. (1947). Random walk and the theory of brownian motion. *The American Mathematical Monthly*, 54(7P1), 369–391.

Larsson, H. and Ågren, J. (2003). A random-walk approach to diffusion controlled growth. *Scripta Materialia*, 49(6), 521–526. doi:10.1016/S1359-6462(03)00364-6.

Macchi, J., Teixeira, J., Danoix, F., Geandier, G., Denis, S., Bonnet, F., and Allain, S.Y. (2024). Impact of carbon segregation on transition carbides and cementite precipitation during tempering of low carbon steels: Experiments and modeling. *Acta Materialia*, 272, 119919. doi:10.1016/j.actamat.2024.119919.

MIT (2024). Lecture notes on diffusion, accessed 10.6.2024, massachusets institute of technology. URL `http://web.mit.edu/1.061/www/dream/THREE/THREETHEORY.PDF`.

NVIDIA (2024). Cuda c++ programming guide. URL `https://docs.nvidia.com/cuda/pdf/CUDA_C_Programming_Guide.pdf`.

Pohjonen, A. (2023). Full field model describing phase front propagation, transformation strains, chemical partitioning, and diffusion in solid–solid phase transformations. *Advanced Theory and Simulations*, 6(3), 2200771.

Pohjonen, A. (2024a). Application of two-grid interpolation to enhance average gradient method for solving partial differential equations. *The Journal of Physics: Conference series*, 2701(2), 97–111.

Pohjonen, A. (2024b). Solving partial differential equations in deformed grids by estimating local average gradients with planes. *The Journal of Physics: Conference series*, 2701(2), 97–111.

Pohjonen, A., Babu, S.R., and Visuri, V.V. (2022). Coupled model for carbon partitioning, diffusion, cottrell atmosphere formation and cementite precipitation in martensite during quenching. *Computational Materials Science*, 209, 111413.

Porter, D.A., Easterling, K.E., and Sherif, M.Y. (2022). *Phase transformations in metals and alloys 4th Edition*. CRC press.

von Smoluchowski, M. (1906). Zur kinetischen theorie der brownschen molekularbewegung und der suspensionen. *Annalen der Physik*, 326(14), 756–780. doi:10.1002/andp.19063261405.

Wang, S., Kistanov, A.A., King, G., Ghosh, S., Singh, H., Pallaspuro, S., Rahemtulla, A., Somani, M., Kömi, J., Cao, W., et al. (2021). In-situ quantification and density functional theory elucidation of phase transformation in carbon steel during quenching and partitioning. *Acta Materialia*, 221, 117361.

Zhu, T., Li, J., Samanta, A., Kim, H.G., and Suresh, S. (2007). Interfacial plasticity governs strain rate sensitivity and ductility in nanostructured metals. *Proceedings of the National Academy of Sciences*, 104(9), 3031–3036.