A first principles kinetic Monte Carlo investigation of the adsorption and mobility of gadolinium
on the (100) surface of tungsten

Adib Samin, and Jinsuo Zhang

Nuclear Engineering Program, Department of Mechanical and Aerospace Engineering

The Ohio State University 201 W. 19th Avenue Columbus, Ohio 43210 USA

Abstract:

An accurate characterization of lanthanide adsorption and mobility on tungsten surfaces is important for pyroprocessing. In the present study, the adsorption and diffusion of gadolinium on the (100) surface of tungsten was investigated. It was found that the hollow sites were the most energetically favorable for the adsorption. It was further observed that a magnetic moment was induced following the adsorption of gadolinium on the tungsten surface and that the system with adsorbed hollow sites had the largest magnetization. A pathway for the surface diffusion of gadolinium was determined to occur by hopping between the nearest neighbor hollow sites via the bridge site and the activation energy for the hop was calculated to be 0.75 eV. The surface diffusion process was further assessed using two distinct kinetic Monte Carlo models; one that accounted for lateral adsorbate interactions up to the second nearest neighbor and one that did not account for such interatomic interactions in the adlayer. When the lateral interactions were included in the simulations, the diffusivity was observed to have a strong dependence on coverage (for the coverage values being studied). The effects of lateral interactions were further observed in a one-dimensional simulation of the diffusion equation where the asymmetry in the

surface coverage profile upon its approach to a steady state distribution was clear in comparison with the simulations which did not account for those interactions.

Introduction:

Surfaces possess distinct electronic and atomic properties when compared to the bulk of the material and are the site for a variety of processes such as redox reactions, adsorption, and catalysis among others which have indispensable technological applications [1]. Tungsten surfaces are important and have recently been investigated for a variety of reasons [2-5]. They are promising as plasma facing material and exhibit favorable properties for the divertor application in nuclear fusion reactors [6, 7]. Tungsten microelectrodes and electrodes are also used in neuroprosthetic applications and other implants which require long term viability of the tungsten surfaces and their protection against corrosion [4, 8]. In addition, tungsten surfaces are found to be stable in the range of redox potentials of various actinides thereby enhancing their promising role in pyroprocessing applications for recycling nuclear fuels [9, 10]. These surfaces also have potential applications in thermophotovoltaic systems [11] and are used to investigate the process of oxidative dissolution through the formation of complexes on the surface of the metal [12].

In pyroprocessing of used nuclear fuel treatment, it is important to separate uranium and plutonium from lanthanide fission products based on their electrochemical properties. Cyclic voltammetry is one of the primary tools currently used to investigate the kinetic and electrochemical properties of different lanthanide fission products [13, 14] in the molten salt for pyroprocessing. However, the analysis of the recorded signals is not straightforward due to the deposition of lanthanides on the electrode surface (typically tungsten). Furthermore, it was also

observed [3] that surface phenomena such as the adsorption isotherm are generally not accurately described with continuum level models since these cannot capture interatomic interactions and other atomic scale processes. Therefore, it is important to investigate the surface-related phenomena from a more fundamental point of view.

In this work, the adsorption of gadolinium (one of the lanthanide fission products) on the tungsten (100) surface will be investigated. The favorable adsorption sites on the tungsten surface will be determined. In addition, a mechanism for surface diffusion is proposed and the surface diffusion of gadolinium on the tungsten surface and the concentration profile evolution are calculated.

Computational Details:

Density Functional Theory (DFT) Calculations:

Spin polarized density functional theory calculations were carried out using the Vienna ab initio simulation package (VASP) [15, 16] with the implementation of the Projector-Augmented-Wave (PAW) pseudopotentials [17, 18]. A generalized gradient approximation (GGA) exchange correlation functional was used as parameterized by Perdew, Burke and Ernzerhov [19]. In the treatment of the electronic structure of Gd, the intra-atomic Coulomb repulsion was accounted for through the use of a Hubbard U via a GGA+U functional and the value of $U_{\text{eff}} = 6 \text{ eV}$ was utilized [20, 21]. The valence electron eigenfunctions were expanded in a plane-wave basis set with an energy cutoff of 450 eV and a Methfessel-Paxton smearing of the first order of width 0.1 eV was used in the simulations[22]. The W(100) surface was represented by a p(4×4) surface supercell and a five-layer slab which was separated by a vacuum with a thickness of about 22.19 Å to minimize interactions with slab images. The bottom three layers were fixed at bulk positions while the positions of atoms in the top two layers were allowed to relax. Reciprocal

length integrations were performed using a (3×3×1) Monkhorst-Pack [23] Γ -centered k-point grid. Convergence with respect to the cutoff energy and the k-point mesh was checked. The convergence criterion for the electronic self-consistent calculation was set to 10^{-7} eV. Furthermore, the structure was allowed to relax until the forces acting on the atoms were less than 0.01 eV/Å.

Transition states for Gd diffusion on the W(100) surface were determined using the climbing nudged elastic band method [24]. The calculation of the activation barrier on a potential energy surface was carried out using a single image with a spring constant of 5 eV/Å. Zero-point energies (ZPE's) were also quantified through calculating the normal-mode vibrational frequencies and associated zero-point energies of the adsorbate Gd and local W atoms at the minima and transition states.

Kinetic Monte Carlo (KMC) Simulations:

In kMC simulations the time evolution of the system is described by a stochastic trajectory and the system states along this trajectory are connected by processes with certain probabilities. Here, we use a lattice kinetic Monte Carlo where adsorption sites are mapped onto a lattice and the system can evolve by allowing the adsorbate Gd atoms to hop between neighboring adsorption sites. Within the quantum version of harmonic transition state theory [25] the microscopic rate constant for a hop is given by:

$$k_{IF} = \Gamma_{IF} \exp(-E_a/k_B T) \quad (1)$$

In equation (1), k_{IF} is the hopping rate from an initial site I to a final site F, Γ_{IF} is the hopping frequency at infinite temperature, k_B is the Boltzmann constant, T is the temperature of the simulation and E_a is the

activation energy barrier for hopping from the given initial site to the final site under consideration. The infinite temperature hopping rate may be estimated as [25]:

$$\Gamma_{IF} = \frac{\prod_{i=1}^3 f(h\nu_{I,i}/2k_B T)}{\prod_{j=1}^2 f(h\nu_{TS,j}/2k_B T)} \quad (2)$$

In equation (2) the function f is given by $f(x) = \sinh(x)/x$, and ν_I , and ν_{TS} are the normal mode frequencies at the initial and transition state site respectively. Finally, the activation energy barrier may be approximated as [26, 27]:

$$E_{a,IF} = E_{cl,IF} + \varepsilon_{zp}^{TS} - \varepsilon_{zp}^I + \frac{1}{2}(\Delta E) \quad (3)$$

In equation (3), $E_{cl,IF}$ is the classical energy barrier for the hop from the initial to the final state.

This classic barrier is defined by the difference in energy between the initial state and the transition state which represents a saddle point in the potential energy hypersurface. The quantities ε_{zp}^{TS} and ε_{zp}^I are the zero point energies of the system at the initial site and the transition state site respectively. Finally, the lateral Gd-Gd interactions in the adlayer were accounted for in the last term by including the effect of two-body interactions. The pair interactions were extracted from DFT calculations and the expression for ΔE is:

$$\Delta E = \epsilon_{nn} * (N_{fnn} - N_{inn}) + \epsilon_{nnn} * (N_{fnnn} - N_{innn}) + \dots \quad (4)$$

where ϵ_{nn} and ϵ_{nnn} are the interaction energy parameters for nearest neighbors and next nearest neighbors and N_{fnn} and N_{inn} are the number of nearest neighboring Gd atoms in the initial and final state and similarly N_{fnnn} and N_{innn} are the number of next nearest neighboring Gd

adsorbed atoms in the initial and final state. The interaction parameters were determined through DFT calculations via:

$$\epsilon = E^{tot}(W, Gd_2) - E_{clean} - 2[E^{tot}(W, Gd) - E_{clean}] \quad (5)$$

where E_{clean} is the total energy of the clean slab, $E^{tot}(W, Gd_2)$ is the energy of the slab with two adsorbed Gd atoms (which are either located in the nearest neighboring adsorption sites or next nearest neighbor adsorption sites), and $E^{tot}(W, Gd)$ is the total energy of the tungsten slab with one adsorbed gadolinium atom.

At each step of the kMC simulation, a gadolinium atom in the adlayer may hop from a hollow site on the W(100) surface to one of its four nearest neighbors (distance a). Each kMC move included obtaining the rates (k_i) for all the possible transitions from the current configuration. A choice for the hop was selected by generating a random number to perform the hop according to the condition:

$$\sum_{i=1}^{j-1} k_i \leq rK \leq \sum_{i=1}^j k_i \quad (6)$$

In the equation, r is the generated random number and K is the sum of the rates of all possible hopping processes. The clock is then advanced by $-\ln(\sigma)/K$ where σ is another random number. Finally, the recorded trajectory may be calculated from a kMC simulation on a surface from the equation:

$$D = \lim_{t \rightarrow \infty} \left[\frac{1}{4t} \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle \right] \quad (7)$$

Results and Discussion:

In our calculations, the lattice parameter for tungsten was determined to be 3.170 Å. This is in agreement with the experimental value of 3.165 [28] and a previous DFT calculation predicting a value of 3.172 Å [29]. Next, clean surface DFT calculations were performed and the surface energy of the W(100) surface was calculated to be 4.2 J/m² which is consistent with the value of 4.4 J/m² which was calculated by using an LDA exchange correlation functional [30].

The adsorption energies of the different sites on the W(100) surface were determined. This was computed using equation (8) and the results are included in table 1 below:

$$E_{ads} = E(W, Gd) - E_{clean} - E_{bulk}(Gd) \quad (8)$$

where $E^{tot}(W, Gd)$ is the total energy of the tungsten slab with one adsorbed gadolinium atom, and E_{clean} is the total energy of the clean slab. The results are shown in table 1 below for all symmetrically inequivalent sites on the W (100) surface:

Table 1. Ab initio calculated adsorption energies, magnetization, and distance from the tungsten surface for Gd on distinct sites on the p(4x4) W(100) surface.

Adsorption Site	On-Top	Bridge	Hollow
Adsorption Energy (eV)	-1.54	-2.62	-3.133
Magnetization (μ_B)	8.71	8.74	8.90
Distance from surface (Å)	2.55	2.04	1.92

From table 1 we conclude that the hollow sites are the most energetically favorable sites for adsorption and the on-top sites are the least energetically favorable for adsorption. However, the adsorption process is stable and favorable at all the above sites shown in table 1. Moreover, our spin-polarized calculations confirmed that the tungsten surface was non-magnetic as expected. In

addition, and considering that gadolinium has a permanent magnetic moment of $7.1 \mu_B/\text{atom}$, it appears that an additional magnetic moment is induced when a gadolinium atom is placed on the W (100) surface because the magnetization of the combined Gd/W(100) system exceeds the magnetization of the single Gd atom in bulk. Furthermore, it is observed that the calculation for the system with the hollow site Gd adsorption shows a slightly higher magnetization than the other systems considered. Next, the distance between the adsorbed Gd atom and the tungsten surface was calculated for each case. It was observed that gadolinium is closest to the surface when adsorbing to the hollow sites. In addition, the distance between the adsorbed Gd atom and the W surface was determined to be $1.92 \text{ \AA}$ which was found to be larger than the interplanar separation of $1.40 \text{ \AA}$ between the relaxed tungsten layers.

Next, we calculated the desorption energy of Gd from the hollow tungsten site by placing the Gd atom $5 \text{ \AA}$ away from the surface and applying the equation [31]:

$$E_{des} = E_{desorbed}(W, Gd) - E_{adsorbed}(W, Gd) \quad (9)$$

From this equation, we find that the desorption energy is about $(+5.174 \text{ eV})$. Hence, we observe that desorption is an energetically unfavorable process at 0 K and the adsorbed system is more stable. Furthermore, we did not observe an activation energy barrier for the desorption of the Gd atom from the surface.

From applying equation 5 we determined the values of the interaction parameters to be $\epsilon_{nn} = 0.41 \text{ eV}$ and $\epsilon_{nnn} = 0.27 \text{ eV}$. The value for the third nearest neighbor was quite smaller than the first two terms in the interaction. Therefore, only interactions up to the second nearest neighbor were accounted for in this study. The energy barrier for the hop from one hollow site to a nearest neighbor hollow site was determined to be 0.75 eV and the hopping was found to occur via the

bridge sites. These values were then used in the lattice gas kinetic Monte Carlo simulation to examine the surface diffusion process and its dependence on the temperature and the surface coverage.

The Monte Carlo simulations were performed on a 32×32 lattice for a total of 250000 steps each and the positions of all the atoms in the adlayer were tracked throughout the simulation. The first 50000 Monte Carlo steps were not used in order to allow the simulation to reach equilibrium and the remaining 200000 steps of the generated trajectories were used in the subsequent sampling analysis. Size effects were checked by performing simulations on a 64×64 lattice and were determined to be negligible. Furthermore, and to obtain good statistic at each temperature and coverage, kMC simulations were performed on several initial configurations generated randomly, and the resulting data was averaged over the total number of configurations. A typical plot for the mean square displacement used in calculating the diffusivity is shown in figure 1.

Figure 1. A typical plot of the Mean Square Displacement from the kMC simulation plotted against time

The simulations were performed for two distinct cases; the case where lateral adsorbate-adsorbate interactions were accounted for up to the second nearest neighbor and a case where lateral interatomic interactions in the adlayer were ignored (by setting $\epsilon_{nn} = 0 \text{ eV}$ and $\epsilon_{nnn} = 0 \text{ eV}$). The diffusivity values were collected and their natural logarithm was plotted against the inverse of the simulation temperature at each coverage value. The simulation-based results are included in figure 2 along with the linear fits for each coverage case.

Figure 2. The dependence of the diffusivity on temperature shown for various surface coverages by plotting the natural logarithm of the diffusivity as a function of inverse temperature. This dependence is expected to be linear from the Arrhenius equation and the linear fits are clearly shown. The results for the case of interatomic interactions are included in figures a-d and the results for simulations neglecting the adsorbate-adsorbate interactions are included in e-h. The values of the Arrhenius parameters are derived from the linear fits and displayed in table 2. (a, e) 0.0625 ML coverage (b, f) 0.125 ML coverage (c, g) 0.25 ML coverage (d, h) 0.5 ML coverage

Linear behavior is expected in accordance with the Arrhenius equation. By performing linear fits we can extract the values of the Arrhenius equation parameters corresponding to each coverage of the surface. These results are included in table 2 below

Table 2. The Arrhenius equation fits for different coverages of the surface. The coverage is indicated as a fraction of the Monolayer (ML). The values for the parameters are indicated for two distinct cases: the case where interatomic interactions up to the second nearest neighbor are included and the case where no interatomic interactions are accounted for.

Coverage	With Interactions		Without Interactions	
	D_0 (m ² /s)	E_a (eV)	D_0 (m ² /s)	E_a (eV)
0.0625 ML	9.1×10^{-7}	0.75 ± 0.01	1.12×10^{-6}	0.75
0.125 ML	3.34×10^{-7}	0.77 ± 0.01	9.117×10^{-7}	0.75
0.25 ML	8×10^{-7}	1.00 ± 0.05	6.775×10^{-7}	0.75
0.5 ML	7×10^{-7}	1.3 ± 0.05	3.65×10^{-7}	0.75

Upon examination of table 2 and figure 2, we realize that the diffusivity decreases as the coverage of the surface increases for all cases (whether adsorbate-adsorbate interactions are included or not). However, the decrease in the diffusivity with increasing coverage is much more pronounced for the cases including the lateral interactions in the adlayer. This observation may be attributed to the increased adsorbate-adsorbate interactions in the adlayer as the coverage of the surface is increased.

After investigating the results of the calculations which included interatomic interactions we find that generally, as the surface coverage increases, the activation energy increases too. This behavior has been experimentally observed in other systems as well [32-34] and may be due to the increased repulsive interactions among the adsorbates with higher coverages, which consequently leads to a higher energy barrier for a hop. The effect of this large increase in the activation energy can be more clearly observed in the lower temperature simulations. When the lateral adsorbate interactions were included in these simulations, the surface diffusion coefficient was found to decrease by several orders of magnitude between different coverages. However, the diffusion coefficient only decreased by a factor of 2 or less between different coverages when the lateral interactions were not accounted for. Furthermore, when the adsorbate-adsorbate lateral

interactions were completely ignored, we observed that the activation energy did not change with different values of the surface coverage and the pre-exponential factor was found to decrease with increasing coverage. These findings are also consistent with the literature and were reported by Yang et al. [2] in their study of hydrogen diffusion on the tungsten (001) surface. The authors of that study conducted a kinetic Monte Carlo simulation but did not include the lateral adsorbate interactions and reached a similar conclusion. The authors also reported pre-exponential factors in the order of ($10^{-7} \text{ m}^2/\text{s}$) consistent with our results. In reviewing the literature, we found similar studies on similar materials which we also used for comparison purposes. Loburets et al. [35] conducted an experimental study on the diffusion of dysporium (a lanthanide) on the (112) plane of molybdenum. The authors of that study reported diffusivity values in the same order of magnitude as ours. Moreover, the authors reported activation energies for the diffusion ranging between 0.5 eV and 1.5 eV for various values of the surface coverage also consistent with our reported results. Finally, the activation energy for Ni diffusing on the W(100) surface was reported at 1.01 eV for temperatures ranging from 337 to 376 K [36].

Next, we perform a two-dimensional linear interpolation between the available data points for the two distinct simulation cases (with and without lateral interactions). The resulting surfaces which emerge from the interpolation show the dependence of the natural logarithm of the surface diffusion coefficient on temperature and surface coverage and these surface plots are included in figure 3 below.

Figure 3. The surface plot illustrates the dependence of the surface diffusion on surface coverage and temperature (a) for the case accounting for lateral adsorbate interactions up to the second nearest neighbor (b) for the case ignoring lateral interatomic interactions in the adlayer.

In order to develop a further fundamental understanding of the effects of lateral interaction among the adsorbates, we will track the evolution of the surface concentration profile for the case with and without including the lateral interaction. This will be accomplished by examining the one-dimensional transport of the adsorbate gadolinium on the W (100) surface which is described by the diffusion equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left(D(\theta) \frac{\partial \theta}{\partial x} \right) \quad (10)$$

In equation (10), the diffusivity (D in units of cm^2/s) is a function of the surface coverage which itself is a function of the position. The surface coverage (θ) is described in units of the monolayer (ML). The simulation is performed for a fixed temperature along a length of $L = 0.1$ cm of tungsten and the values for the diffusivity are obtained via linear interpolation and extrapolation of the data generated in the previous section. Moreover, Neumann (no flux) boundary conditions were used at both ends and an initial linear profile of the form

$\theta(x) = \theta_0(L - x)$ was used for all simulation (with $\theta_0 = 0.25 \text{ ML}$). The equation was solved numerically using forward-time central-space finite differencing approach with ghost points to describe the boundary conditions more accurately. The simulations were converged with respect to the mesh size and the time step and were terminated when a steady state profile began to emerge. The results are included in 4 below:

Figure 4. The surface concentration profile as a function of time (a) $T = 500$ K without interactions (b) $T = 500$ K with interactions (c) $T = 750$ K without interactions (d) $T = 750$ K with interactions.

Upon inspection of figure 4 we find that the simulations including the effects of lateral interactions clearly show that the transport of gadolinium in areas of high coverage is significantly slower than the transport of gadolinium in the low coverage regimes. This consequently leads to the asymmetry in the surface coverage profile as it evolves towards a steady state. In the simulations neglecting lateral interactions, this effect is not obvious as there is

not a big difference between diffusivity values at a fixed temperature for the coverage values being explored. Hence, the surface coverage profile appears symmetric in its approach to a steady state profile and further reaches the steady state distribution much faster than the case with lateral interactions. This asymmetry in the evolution of the surface coverage profile may be significant in the characterization of the role of adlayer lateral interactions for the materials being examined.

Finally, it is important to remember the limitations under which this study was conducted. In this study, a lattice gas Monte Carlo model was employed and we only considered hopping amongst the most stable surface adsorption sites. However, the other sites may contribute to the surface mobility of gadolinium. In addition, the lateral interactions were included up to the second nearest neighbor only. However, it may be important to consider further interactions.

Nevertheless, and in the scarcity of experimental data on this system, the computational studies are significant in furthering our understanding of such systems.

Conclusions:

Efficient implementation of pyroprocessing technology demands developing an accurate and complete understanding of the thermodynamic and transport properties of lanthanide fission products on the tungsten surface. In this work, the behavior of gadolinium on the (100) plane of tungsten was investigated via a multi-scale simulation. It was found that the hollow sites were most energetically favorable for adsorption. It was also determined that the magnetization of gadolinium may be enhanced following its adsorption on the tungsten surface. Additionally, the diffusion of gadolinium on the surface was found to occur between the hollow sites through the bridge site that separates them. The calculated diffusion coefficients were found to depend

strongly on the surface monolayer coverage and by fitting the calculated diffusivities to the Arrhenius equation it was observed that the activation energy increased with the surface coverage. The role of lateral interactions was further observed in a one-dimensional simulation of the diffusion equation.

Acknowledgements:

The authors would like to acknowledge funds available through the U.S. Department of Energy Project DOE-NEUP 14-6489. This work was possible via the use of computational resources allocated in part by the Idaho National Laboratory Supercomputing Center.

References:

1. Bechstedt, F., *Principles of surface physics* 2003, Berlin; New York: Springer.
2. Yang, X. and Hassanein, A., *Kinetic Monte Carlo simulation of hydrogen diffusion on tungsten reconstructed (0 0 1) surface*. Fusion Engineering and Design, 2014. **89**(11): p. 2545-2549.
3. Samin, A. J. and Zhang, J., *A multi-scale study of the adsorption of lanthanum on the (110) surface of tungsten*. Journal of Applied Physics, 2016. **120**(4): p. 045305.
4. Patrick, E., Orazem, M. E., Sanchez, J. C., et al., *Corrosion of tungsten microelectrodes used in neural recording applications*. Journal of Neuroscience Methods, 2011. **198**(2): p. 158-171.
5. Trufanov, D., Marenkov, E., and Krashennnikov, S., *The Role of the Adatom Diffusion in the Tungsten Fuzz Growth*. Physics Procedia, 2015. **71**: p. 20-24.
6. Faiza, S., Karl, D. H., Niklas, J., et al., *Tungsten surface evolution by helium bubble nucleation, growth and rupture*. Nuclear Fusion, 2013. **53**(7): p. 073015.
7. Khripunov, B. I., Koidan, V. S., Ryazanov, A. I., et al., *Study of Tungsten as a Plasma-facing Material for a Fusion Reactor*. Physics Procedia, 2015. **71**: p. 63-67.
8. Sanchez, J. C., Alba, N., Nishida, T., et al., *Structural modifications in chronic microwire electrodes for cortical neuroprosthetics: A case study*. IEEE Transactions on Neural Systems and Rehabilitation Engineering, 2006. **14**(2): p. 217-221.
9. Choi, E.-Y. and Jeong, S. M., *Electrochemical processing of spent nuclear fuels: An overview of oxide reduction in pyroprocessing technology*. Progress in Natural Science: Materials International, 2015. **25**(6): p. 572-582.
10. Merwin, A. and Chidambaram, D., *Alternate Anodes for the Electrolytic Reduction of UO₂*. Metallurgical and Materials Transactions A, 2015. **46**(1): p. 536-544.
11. Sai, H. and Yugami, H., *Thermophotovoltaic generation with selective radiators based on tungsten surface gratings*. Applied Physics Letters, 2004. **85**(16): p. 3399-3401.
12. Trifonova, E. N., Mukhanova, A. A., Stepanov, A. I., et al., *Complex Formation on the Surface of Tungsten on Its Chlorination in DMF Medium*. Russian Journal of Coordination Chemistry, 2005. **31**(6): p. 410-414.
13. Tang, H. and Pesic, B., *Electrochemistry of ErCl₃ and morphology of erbium electrodeposits produced on Mo substrate in early stages of electrocrystallization from LiCl-KCl molten salts*. Electrochimica Acta, 2014. **133**: p. 224-232.

14. Samin, A., Wang, Z., Lahti, E., et al., *Estimation of key physical properties for LaCl₃ in molten eutectic LiCl–KCl by fitting cyclic voltammetry data to a BET-based electrode reaction kinetics model*. Journal of Nuclear Materials, 2016. **475**: p. 149-155.
15. Kresse, G. and Furthmüller, J., *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*. Computational Materials Science, 1996. **6**(1): p. 15-50.
16. Kresse, G. and Furthmüller, J., *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*. Physical Review B, 1996. **54**(16): p. 11169-11186.
17. Blöchl, P. E., *Projector augmented-wave method*. Physical Review B, 1994. **50**(24): p. 17953-17979.
18. Kresse, G. and Joubert, D., *From ultrasoft pseudopotentials to the projector augmented-wave method*. Physical Review B, 1999. **59**(3): p. 1758-1775.
19. Perdew, J. P., Burke, K., and Ernzerhof, M., *Generalized Gradient Approximation Made Simple*. Physical Review Letters, 1996. **77**(18): p. 3865-3868.
20. Ma, P.-W. and Dudarev, S., *Dynamic magnetocaloric effect in bcc iron and hcp gadolinium*. Physical Review B, 2014. **90**(2): p. 024425.
21. Melissa, P., Jürgen, H., and Martijn, M., *Structural, electronic and magnetic properties of Gd investigated by DFT+ U methods: bulk, clean and H-covered (0001) surfaces*. Journal of Physics: Condensed Matter, 2006. **18**(30): p. 7021.
22. Methfessel, M. and Paxton, A. T., *High-precision sampling for Brillouin-zone integration in metals*. Physical Review B, 1989. **40**(6): p. 3616-3621.
23. Monkhorst, H. J. and Pack, J. D., *Special points for Brillouin-zone integrations*. Physical Review B, 1976. **13**(12): p. 5188-5192.
24. Henkelman, G., Uberuaga, B. P., and Jónsson, H., *A climbing image nudged elastic band method for finding saddle points and minimum energy paths*. The Journal of chemical physics, 2000. **113**(22): p. 9901-9904.
25. Katz, L., Guinan, M., and Borg, R. J., *Diffusion of H₂, D₂, and T₂ in Single-Crystal Ni and Cu*. Physical Review B, 1971. **4**(2): p. 330-341.
26. Van Bavel, A. P., Hermse, C. G. M., Hopstaken, M. J. P., et al., *Quantifying lateral adsorbate interactions by kinetic Monte-Carlo simulations and density-functional theory: NO dissociation on Rh(100)*. Physical Chemistry Chemical Physics, 2004. **6**(8): p. 1830-1836.
27. Du, Y. A., Rogal, J., and Drautz, R., *Diffusion of hydrogen within idealized grains of bcc Fe: A kinetic Monte Carlo study*. Physical Review B, 2012. **86**(17): p. 174110.
28. *CRC Handbook of Chemistry and Physics 96th edition 2015-2016*. [Accessed August 5th, 2015]; Available from: <http://www.hbcpnetbase.com/>.
29. Heinola, K. and Ahlgren, T., *Diffusion of hydrogen in bcc tungsten studied with first principle calculations*. Journal of Applied Physics, 2010. **107**(11): p. 113531.
30. Wang, J. and Wang, S.-Q., *Surface energy and work function of fcc and bcc crystals: Density functional study*. Surface Science, 2014. **630**: p. 216-224.
31. Pavlova, T. V., Andryushechkin, B. V., and Zhidomirov, G. M., *First-Principle Study of Adsorption and Desorption of Chlorine on Cu(111) Surface: Does Chlorine or Copper Chloride Desorb?* The Journal of Physical Chemistry C, 2016. **120**(5): p. 2829-2836.
32. Inderwildi, O. R., Lebedez, D., Deutschmann, O., et al., *Coverage dependence of oxygen decomposition and surface diffusion on rhodium (111): A DFT study*. The Journal of chemical physics, 2005. **122**(3): p. 034710.
33. Naumovets, A. G., Poplavsky, V. V., and Vedula, Y. S., *Diffusion and phase transitions in barium monolayers on the (011) plane of tungsten*. Surface Science, 1988. **200**(2): p. 321-334.

34. Gomer, R., *Diffusion of adsorbates on metal surfaces*. Reports on Progress in Physics, 1990. **53**(7): p. 917.
35. Loburets, A. T., Naumovets, A. G., and Vedula, Y. S., *Diffusion of dysprosium on the (112) surface of molybdenum*. Surface Science, 1998. **399**(2): p. 297-304.
36. Kellogg, G. L., *The mobility and structure of nickel atoms on the (100) plane of tungsten*. Surface Science, 1987. **192**(2): p. L879-L886.