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Modified Embedded Atom Method with Application to Vacancy Diffusion Mechanism

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Abstract

In this diploma thesis we investigate the Modified Embedded Atom Method (MEAM) with the focus on its suitability for the simulation of vacancy diffusion in alloys, especially in dimensionally limited settings. As test system we chose $L1_2$ $FePt_3$ in order to build upon the results of Jaesong Kim, Yangmo Koo, and Byeong-Joo Lee [13]. Under these premises we have developed simulation tools which can be used as a basis for future researches. The source code of the simulation tools is included as appendix.

Zusammenfassung

In dieser Diplomarbeit beschäftigen wir uns mit der "Modified Embedded Atom" Methode (MEAM) mit dem Hauptaugenmerk auf ihrer Anwendbarkeit auf Leerstellendiffusion in Legierungen, besonders in dimensional beschränkten Situationen. Als Testsystem haben wir $L1_2$ $FePt_3$ gewählt, um auf den Ergebnissen von Jaesong Kim, Yangmo Koo, and Byeong-Joo Lee [13] aufzubauen. Unter diesen Voraussetzungen haben wir Simulation-swerkzeuge entwickelt, die auch weiterführende Untersuchungen ermöglichen. Der Quellcode der Simulationswerkzeuge befindet sich im Anhang.

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Chapter 1

Introduction

1.1 Objective

The ultimate objective of the work presented here is the simulation of atom diffusion in dimensionally limited alloy systems like thin films or nano-wires. A model for the potential is required, which can describe such a system, including at least next nearest neighbour interactions.

1.2 Options for Calculation of Potentials

1.2.1 Pair Potentials

The potential is described by the interactions of pairs of atoms. This method is no longer considered adequate, because it fails to predict known physical properties [11]:

- Pair potentials predict the Cauchy Relation for the elastic constants ($C_{12} = C_{44}$). This relation is not a good approximation in general, and is wrong for most cubic metals.
- The vacancy formation energy differs from experiment.
- An inward relaxation of the metal surface is observed in experiment, which pair potentials are incapable to reproduce.

• The melting point is overestimated about 20 %.

Pair potentials are incapable to reproduce these behaviours. Because the calculation is simple by comparison pair potentials are however still in use for some simulations.

1.2.2 Ab Initio Calculations

Ab initio calculations use the density functional theory to quantum-mechanically solve the many-body problem for the ground state [12] [16] [29]. Because the calculation method is an iterative procedure, the method involves a large computational effort and is limited to a system of at most 100 or 200 atoms. However it is the most accurate way to get the potential and results of all other methods have to be compared with the experiment and ab initio calculations.

1.2.3 Cluster Expansion

Using the cluster expansion a system of equations with correlation functions and effective energies is adjusted to known results from ab initio calculations so that new results can be successfully predicted [23] [18] [34]. The correlation functions refer to a hierarchy of increasingly complex geometrical figures representing clusters of atoms, which occur in the system, and the effective energies are contributions to the total energy from each kind of figure. This method can be applied to a wide range of the phase diagram provided that the atoms are sitting on the same crystal lattice across the whole composition range considered.

1.2.4 Virtual Neuronal Networks

A model of interacting atoms can be trained to reproduce ab initio results of energy provided that one has a large amount of data as reference, so that weight factors can be correctly adjusted. Once this training procedure has been performed, one can calculate the potential very fast and accurately [12] [16] [29], nevertheless it is expensive to produce a large enough data base for training a virtual neuronal network.

1.2.5 Many-Body Potentials

In the literature there can be found a large number of potential forms containing many-body contributions with adjustable parameters which have been proposed to calculate the potential of a solid [10] [11]. Algebraic functions save calculation time so that they can also be applied to large systems. Because there are a lot of many-body potentials one has to choose a specific function according to the requirements of the material and the problem considered.

1.3 Selection of the Modified Embedded Atom Method

We decided to use a many-body potential suitable for the simulation of large systems on and off lattice. Specifically we choose the modified embedded atom method because of the wide range of possible applications. The modified embedded atom method was successfully used for elements and alloys [20] [22] [13], for dimensionally limited systems [17] [13] [15] [24] and for the investigation of defects [14] [21]. In addition the paramters are adjusted in order to reproduce a lot of physical properties [22] (vacancy formation energy, elastic constants, inward relaxation of the surface,...). Interactions up to the second coordination shell are included.

Chapter 2

Overview

2.1 Concepts of the Method

The basic concept of all embedded atom methods is that one atom i is taken out of the host lattice and embedded into the remaining local background electronic density $\bar{\rho}_i$, which is caused by the environmental atoms. The necessary energy to do this is called embedding energy and is given by the functional $F[\bar{\rho}_i]$. Additionally all pair interactions ϕ_{ij} between the embedded atom i and the environmental atoms j are considered. This will be done for every atom in the lattice successively in order to receive the total energy E_{tot} of the system. We illustrate the idea of the concept in Figure 2.1.

$$E_{tot} = \sum_{i} \left[F[\bar{\rho}_i] + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right]$$
(2.1)

Because pure pair potentials are insufficient to calculate the total energy of an alloy the additional embedding functional includes the many-body effects.

One can consider embedding atom methods as a further development of models which were designed originally to calculate the energy needed to embed an impurity in a host lattice. When calculating the total energy of the system every atom assumes the role of an impurity.

The various embedding atom models differ mainly in the way how the embedding energy and the background electronic density are calculated. Some methods take more empirical approach and others use ab initio calculations to determine the wanted functional relationship between the energy and the density.

The so called second nearest neighbour modified embedded atom method is made up of the following components [5] [19] [13] [32]:

• For the embedding functional a logarithmic function is chosen for convenience as it is the simplest function showing the expected qualitative behaviour, Section 3.1. It includes the sublimation Energy E_s , a reference background electronic density ρ_0 and an adjustable factor A for each element included.

$$F[\bar{\rho}] = A E_s (\bar{\rho}/\rho_0) \ln(\bar{\rho}/\rho_0)$$
(2.2)

• The model for the background electronic density includes angular dependent partial electronic densities $\rho_i^{(l)}$, which consist of atomic electronic densities $\rho_i^{a(l)}$ and Legendre polynomials $L^{(l)}$ representing the angular dependence of the interactions, Section 3.2.1, 3.2.2 and 3.2.3.

$$\rho_i^{(l)} = \sum_{j \neq i} \sum_{k \neq i} \rho_j^{a(l)}(r_{ij}) \, \rho_k^{a(l)}(r_{ik}) \, L^{(l)}(\cos(\Theta_{jik}))$$
(2.3)

• The pair potentials were calculated by a universal function $E^u(R)$ derived from ab initio calculations, Section 3.3. Interactions up to the second coordination shell are considered. Z_1 and Z_2 are the coordination numbers of the first and second nearest neighbor shells, S is a screening factor and a is a scaling factor given by the quotient of the second and the first nearest neighbour distance.

$$E^{u}(R) = F[\bar{\rho}(R)] + \frac{Z_{1}}{2}\phi(R) + \frac{Z_{2}S}{2}\phi(aR)$$
(2.4)

A cut-off function f_c and a screening function S_{ikj} are applied to the components and explained in Section 3.4 and 3.5. Figure 2.2 shows the dependences of the components and a summary of the needed parameters is given in Section 2.3.



Figure 2.1: Illustration of the embedded atom method: Embed an atom *i* of the lattice in the remaining background electronic density $\bar{\rho}_i$, calculate the embedding function for it and consider the pair interactions ϕ_{ij} between the embedded atom *i* and its neighbouring atoms *j*. Do this for every atom in the lattice to obtain the total energy of the system.



Figure 2.2: The overview of the modified embedded atom method model shows the influence of the included components.

2.2 History

As it is well proven for the type of problems we have in mind we chose the second nearest neighbour modified embedded atom method for our simulation program. It is well documented and the needed parameters are published for a lot of systems [20] [22] [13]. We now give a short overview of the historical development of the method.

- **1964** Density Functional Theory: The energy of the ground state is a functional of the ground state electronic density $(E = E[\rho] \text{ for } T = 0K)$ [12].
- **1980** Quasiatom Theory: Estimation of the electrostatic interaction of an impurity with a host electronic system. The impurity ion and its screening cloud is treated as a quasiatom [30].
- **1980** Effective Medium Theory: Embedding an atom in an inhomogeneous host can be described by replacing the host with an effective homogeneous local environment [25].
- **1984** Embedded Atom Method: The total energy of an metal can be calculated by embedding each atom in the remaining host background electronic density and by considering the local pair interactions [9].
- 1989 Modified Embedded Atom Method: Modification of the background electronic density by additional angular dependent terms [5].
- **2000** Second Nearest Neighbour Modified Embedded Atom Method: Involving second nearest neighbour interactions with an additional screening function [19].
- **2003** Multistate Modified Embedded Atom Method: The model is almost exclusively using functions and data derived from ab initio calculations [6].
- **2009** Concentration dependent and composition dependent embedded atom methods [31] [28].

Almost always the quasi atom method and the effective medium theory were mentioned in the literature together, because the essential ideas are practically the same. We recommend the paper [8], model of metallic cohesion: The embedded atom method, by Murray S. Daw., to get a good idea of how the embedded atom method correlates with the previous publications and to learn about the theoretical background.

2.3 Parameters

In order to make simulations with the modified embedded atom method a set of parameters for each material is needed. We must distinguish if the parameters are determined directly from physical quantities or if they are adjusted to reproduce known material properties.

The physical quantities refer to groundstate properties and are:

- The sublimation energy of the equilibrium state E_{sub} . This is the energy needed to separate all atomic bonds. The parameter appears in the universal function, Section 3.3.1 Equation 3.18, and in the embedding functional, Section 3.1 Equation 3.1.
- The equilibrium nearest neighbour distance r_{eq} . The parameter appears in the universal function, Section 3.3.1 Equation 3.18, and in the atomic electronic densities, Section 3.2.3 Equation 3.17.
- The equilibrium atomic volume Ω_0 . This is the volume one atom has available if the material is in the equilibrium state. If one knows the Wigner-Seitz radius r_{ws} for example, it is possible to determine it directly with $\Omega_0 = \frac{4}{3}\pi r_{ws}^3$. Otherwise one can calculate the volume by the known properties of the unit cell also. The parameter appears in the calculation of the universal function, Section 3.3.1 Equation 3.18.
- The isothermal bulk modulus B and its derivative with respect to the pressure $\partial B/\partial p$. The parameter is needed for the calculation of the universal function, Section 3.3.1 Equation 3.18.

To determine these quantities results from experiments as well as from ab initio calculations are used. This way the semiempirical character of the modified embedded atom method becomes apparent.

The parameters which have to be adjusted to known properties are:

• The parameter of the embedding functional A, Section 3.1.

- The decay constants of the atomic electronic densities $\beta^{(0)}, \ldots, \beta^{(4)}$, Section 3.2.3.
- The weighting factors to calculate the background electronic density t_1, \ldots, t_3 , Section 3.2.1.
- The parameters C_{min} and C_{max} to calculate the screening function, Section 3.5.1 Equation 3.45.
- The atomic electronic density scaling factor $\tilde{\rho}$, Section 3.2.3. For pure elements this factor is often omitted, but for alloy systems this factor can have great effects on calculations [13].

Some of the properties one wants to reproduce with the simulation parameters are elastic constants, surface energy, vacancy formation energy, activation energy of vacancy diffusion, stacking fault energy and structural energy differences. Support for adjusting the parameters is offered by published tables [19], where the parameters and how they influence material properties are noted. Additional information about the determination of the parameters is given by M. I. Baskes [3].

For the simulation of a pure element one needs one set of physical parameters and one set of adjustable parameters. For the simulation of a binary alloy for example, one needs three sets of physical parameters. One for each involved element type and one for the alloy type, in order to calculate the universal functions. From the adjustable parameters two sets are needed, because there are two different atom types with different embedding functionals. Additionally one needs more screening function parameters, because one has to consider every possible arrangement of the atom types.

For pure elements we almost exclusively used the parameters published by Byeong-Joo Lee and M. I. Baskes [20] [22]. The physical values of these sources correspond with the tables given by James H. Rose, John R. Smith, Francisco Guinea and John Ferrante [27].

Parameters used for $L1_2$ $FePt_3$

	$E \ [eV]$	$r_{eq} \left[A \right]$	$B \ [eV/A^3]$	$\partial B/\partial p$	$\Omega_0 [A^3]$
$FePt_3$	5.49	2.72	1.635	5.73	14.20
Fe	4.29	2.48	1.080	4.95	11.74
Pt	5.77	2.77	1.800	5.98	15.00

Table 2.1: Physical quantities given by Jaesong Kim, Yangmo Koo, and Byeong-Joo [13] for $L1_2 \ FePt_3$. In this table $\partial B/\partial p$ is given instead of the parameter d, Section 6.3. Ω_0 was calculated with the help of the nearest neighbour equilibrium distance r_{eq} .

	A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	t_1	t_2	t_3	$ ho_0$
Fe	0.56	4.15	1.00	1.00	1.00	2.60	1.80	-7.20	1.00
Pt	0.90	4.92	2.20	6.00	2.20	3.90	-2.20	3.84	1.00

Table 2.2: Adjustable parameters published by Jaesong Kim, Yangmo Koo, and Byeong-Joo Leea [13] for $L1_2 \ FePt_3$.

$C_{max}(Fe)$	2.80	$C_{max}(Pt)$	2.80
$C_{min}(Fe - Fe - Fe)$	0.36	$C_{min}(Pt - Pt - Pt)$	1.53
$C_{min}(Fe - Fe - Pt)$	0.84	$C_{min}(Pt - Pt - Fe)$	0.84
$C_{min}(Fe - Pt - Fe)$	0.36	$C_{min}(Pt - Fe - Pt)$	1.53
$C_{min}(Fe - Pt - Pt)$	0.84	$C_{min}(Pt - Fe - Fe)$	0.84

Table 2.3: Screening function parameters published by Jaesong Kim, Yangmo Koo, and Byeong-Joo Leea [13] for $L1_2$ $FePt_3$.

Chapter 3

Components

3.1 Embedding Functional

The energy needed to embed an atom i in a local environment is a functional of the local background electronic density [9]. As form for the embedding functional we take the following formula [19]:

$$F[\bar{\rho}] = A E_s \left(\bar{\rho}/\rho_0\right) \ln(\bar{\rho}/\rho_0) \tag{3.1}$$

The factors one needs to calculate are: the background electronic density $\bar{\rho}$, Section 3.2.1 Equation (3.3), the background electronic density of a reference structure ρ_0 , the sublimation energy E_s and the adjustable parameter A.

The sublimation energy E_s and the parameter A depend on the type of the embedded atom i. Whereas the parameter A has to be adjusted, the sublimation Energy can determined from ab initio calculations or by experiment. As reference structure for ρ_0 the structure in equilibrium state of the material is commonly chosen. Thus the following behaviour is ensured:

• If the local background electronic density is less than in the equilibrium state, it is energetically favorable to embed another atom in the local environment $(F[\bar{\rho}] < 0)$.

- If the local background electronic density is more than in the equilibrium state, it is energetically unfavorable to embed another atom in the local environment ($F[\bar{\rho}] > 0$).
- If the local background electronic density is the same as in the equilibrium state, the embedding functional provides no contribution to the total energy $(F[\bar{\rho}] = 0)$.

The form of the embedding functional is made plausible by the following argument. When an atom participates in bonds, then with increasing number of bonds the bond length is also increasing and vice versa. The quantitative experimental values yielding this qualitative behaviour are quite well represented by a logarithmic function as illustrated in Figure 3.3.

In the case of a cubic lattice with center of symmetry it is easy to determine the background electronic density of the reference structure, because it is equal to the first partial electronic density $\rho_j^{(0)}$, Section 3.2.2 Equation (3.4). This is also the case for pure elements with a bcc or fcc structure.

In the case of alloys the background electronic density of the reference structure depends on the type of the embedded atom. For instance in $L1_0$ $FePt_3$ the background electronic density in equilibrium state differs, when an *Fe*-atom or an *Pt*-atom is embedded. Thus one needs a reference density for an *Fe*-site and one for an *Pt*-site. The different local environments are shown in Figure 3.1 and 3.2.



Figure 3.1: The equilibrium reference structure for $L1_0$ $FePt_3$ as seen from a Fe-site. The green spheres represent Fe and the bronze spheres represent Pt.



Figure 3.2: The equilibrium reference structure for $L1_0$ $FePt_3$ as seen from a Pt-site. The green spheres represent Fe and the bronze spheres represent Pt.



Figure 3.3: Change in first nearest neighbour distance $r - r_{ref}$ relative to diamond silicon as a function of ratio of number of nearest neighbours to that in diamond silicon, Z/Z_{ref} . Circles are density-functional calculations and squares are quantum-cluster calculations [2].



Figure 3.4: Embedding functional for Fe and for Pt in $L1_2$ $FePt_3$. Being in equilibrium the the local electronic densities ρ_{Fe} and ρ_{Pt} are equal to the reference densities and the embedding functionals contribute nothing to the total energy. In general, if the local densities are not too low, the forces caused by the embedding functionals point towards locations with lower electronic densities.

3.2 Density Model

3.2.1 Background Electronic Density

In order to calculate the background electronic density at the position of atom i one needs the partial electron densities $\rho_i^{(l)}$ with l = 0...3 depending on the local environment, Section 3.2.2 Equation (3.4)-(3.8), and the weighting factors $t_i^{(h)}$ with h = 1...3 depending on the type of atom i. Then the squares of the partial electronic densities are superimposed with their weighting factors to determine the gamma factor:

$$\Gamma = \sum_{h=1}^{3} t_i^{(h)} \left[\rho_i^{(h)} / \rho_i^{(0)} \right]^2$$
(3.2)

Now it is possible to calculate the background electronic density:

$$\bar{\rho} = \frac{2\rho_i^{(0)}}{1 + e^{-\Gamma}} \tag{3.3}$$

Because the gamma factor enters as an exponent the weighting factors may also be negative. In the special case of a cubic lattice with center of symmetry the gamma factor vanishes and the background electronic density becomes equal to the first partial electronic density $\rho_i^{(0)}$.

3.2.2 Partial Electronic Densities

The main progress of the modified embedded atom method was the consideration of additional angular-dependent contributions. They were calculated by the partial electronic densities $\rho_i^{(1)}$, $\rho_i^{(2)}$ and $\rho_i^{(3)}$. Their specific forms has to fulfill the following conditions [3]:

- They must be invariant to lattice translation and rotation.
- They scale in a simple manner with the atomic electronic densities for homogeneous deformation.
- They must be equal to zero for a cubic lattice with a center of symmetry.

Additionally there is a spherically symmetric partial electron density $\rho_i^{(0)}$, which will vanish only if there is no other atom within the local environment at all.

$$(\rho_i^{(0)})^2 = \left[\sum_{j \neq i} f_c S_{ij} \rho_j^{a(0)}\right]^2$$
(3.4)

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left[\sum_{j \neq i} x_{ij}^{\alpha} f_c S_{ij} \rho_j^{a(1)} \right]^2$$
(3.5)

$$(\rho_i^{(2)})^2 = \sum_{\alpha,\beta} \left[\sum_{j \neq i} x_{ij}^{\alpha\beta} f_c S_{ij} \rho_j^{a(2)} \right]^2 - \frac{1}{3} \left[\sum_{j \neq i} f_c S_{ij} \rho_j^{a(2)} \right]^2$$
(3.6)

$$(\rho_i^{(3)})^2 = \sum_{\alpha,\beta,\gamma} \left[\sum_{j \neq i} x_{ij}^{\alpha\beta\gamma} f_c S_{ij} \rho_j^{a(3)} \right]^2$$
(3.7)

$$- \frac{3}{5} \sum_{\alpha} \left[\sum_{j \neq i} x_{ij}^{\alpha} f_c S_{ij} \rho_j^{a(3)} \right]^2$$
(3.8)

with

$$x_{ij}^{\alpha} = \frac{r_{ij}^{\alpha}}{r_{ij}} \tag{3.9}$$

$$x_{ij}^{\alpha\beta} = \frac{r_{ij}^{\alpha}r_{ij}^{\beta}}{r_{ij}^2}$$
(3.10)

$$x_{ij}^{\alpha\beta\gamma} = \frac{r_{ij}^{\alpha}r_{ij}^{\beta}r_{ij}^{\gamma}}{r_{ij}^{3}}$$
(3.11)

In order to calculate all parts one has to know following factors for the neighbouring atoms j within the local environment around the embedded atom i:

- The cut-off function f_c described in Section 3.4 Equation (3.42).
- The total screening factor S_{ij} described in Section 3.5.2 Equation (3.50).
- The atomic electronic densities $\rho_j^{a(l)}$ with l = 0...3 described in Section 3.2.3 Equation (3.17).
- The angular dependent terms x_{ij}^{α} , $x_{ij}^{\alpha\beta}$ and $x_{ij}^{\alpha\beta\gamma}$ described in Equation (3.9)-(3.11), where r_{ij}^{α} is the α component of the distance vector between the embedded atom *i* and a neighbouring atom *j*.

For example, let us assume a cubic lattice with a centre of symmetry with 6 nearest neighbours in equilibrium distance r_{eq} , all having the same atom type. Let the next nearest interaction be completely screened $(S_{ij} = 0)$ and the nearest neighbour interaction unscreened $(S_{ij} = 1)$. Furthermore none of the neighbours is located within the cut-off area $(f_c = 1)$, described in Section 3.4 Figure 3.12. Then all angular dependent contributions $\rho_i^{(1)}$, $\rho_i^{(2)}$ and $\rho_i^{(3)}$ vanish and $\rho_i^{(0)}$ is equal to 6, because being in equilibrium distance the atomic electronic densities of the atoms each contribute one, compare Section 3.2.3 Figure 3.5.

One can consider the partial electronic densities as the first two terms in an expansion of spherical harmonics or as an expansion in gradients of the density [5]. The functions $L^{(l)}$ with l = 0...3 are the unnormalized Legendre polynomials and Θ_{jik} the angle between a neighbouring atoms j, the embedded atom i and a neighbouring atom k.

$$\rho_i^{(l)} = \sum_{j \neq i} \sum_{k \neq i} \rho_j^{a(l)}(r_{ij}) \rho_k^{a(l)}(r_{ik}) L^{(l)}(\cos(\Theta_{jik}))$$
(3.12)

$$L^{(0)}(z) = 1 (3.13)$$

$$L^{(1)}(z) = z (3.14)$$

$$L^{(2)}(z) = z^2 - \frac{1}{3}$$
(3.15)

$$L^{(3)}(z) = z^3 - \frac{3}{5}z$$
(3.16)

The form of Equation (3.12) differs from the Equations (3.4)-(3.8), because they are more convenient for the calculation of the density considered here, but they are mathematically equivalent [32]. Baskes, Nelson and Wright have shown the relationship between the angular dependent factors (x_{ij}^{α} , $x_{ij}^{\alpha\beta}$ and $x_{ij}^{\alpha\beta\gamma}$, Equation (3.9)-(3.11)) and the equivalent cosine terms [5].

3.2.3 Atomic Electronic Densities

Each neighbour atom of the embedded atom provides contributions to the electronic density with four atomic electronic densities. These are exponential functions $\rho_j^{a(h)}$ with h = 0...3



Figure 3.5: Atomic electronic densities for Pt. In the equilibrium distance to the embedded atom each density contributes exactly one.

which are needed for the partial electronic densities, Section 3.2.2. For each type of element one needs one set of parameters: the scaling factor $\tilde{\rho}_j$, the decay constants $\beta^{(h)}$ with h = 0...3 and the equilibrium distance r_{eq} . For pure elements one can assume $\tilde{\rho}_j$ to be equal to one for every j, but for binary systems they have to be adjusted [13]. This scaling factor and the decay constants have to be adapted when using the potential for other materials. The equilibrium distance is given by experiment and ensures the following behavior. A neighbouring atom j in equilibrium distance to the embedded atom i contributes $\tilde{\rho}_j$ to the partial electronic densities. The physical reason for this form is the exponential decay of the electron density distribution outside a "jellium" surface [1].

$$\rho_j^{a(h)} = \tilde{\rho}_j \ exp[-\beta^{(h)}(r/r_{eq} - 1)] \tag{3.17}$$

Figure 3.5 shows the atomic electronic densities for a neighbouring Pt-Atom.

3.3 Pair Potentials

3.3.1 Universal Binding-Energy Relation

If one compresses and expands the whole volume of the system, the configuration of the system, all angles, all ratio of distances and the total screening factors remain constant. This special deformation is called breathing mode. Ab initio calculations have shown that there is a universal function describing the dependence of binding energy on interatomic separation \tilde{a} for breathing modes in a metal at ground state [20] [27] [1].

$$\tilde{E}^{u}(\tilde{a}) = -(1 + \tilde{a} + d\tilde{a}^{3})e^{-\tilde{a}}$$
(3.18)

with

$$\alpha = \sqrt{9B\Omega_0/E_{sub}} \tag{3.19}$$

$$d = \frac{1}{2\alpha} \left(\frac{\partial B}{\partial p} \Big|_{T=0K} - 1 \right) - \frac{1}{3}$$
(3.20)

If one knows the equilibrium distance r_{eq} , the corresponding sublimation energy E_{sub} , the equilibrium atomic volume Ω_0 , the bulk modulus B and its derivative with respect to the pressure $\partial B/\partial p$, then the binding energy relation for breathing modes can be determined. Further information about the parameter d is given in Section 6.3.

It is possible to apply this function to a large number of metals by rescaling both coordinate axes, the axis of energy and the axis of distance.

$$\tilde{E}^u = E^u / E_{sub} \tag{3.21}$$

$$\tilde{a} = \alpha(r/r_{eq} - 1) \tag{3.22}$$

Figure 3.7 and Figure 3.8 show this behaviour using the example of Fe, Pt and $FePt_3$ [13]. This model suffers, however, from two weaknesses [1]:

1. If the breathing volume is much smaller or much greater than the equilibrium volume,

the values of the function differ from the universal form. In such a case one has to examine the function values for each metal separately.

2. If we want to examine for instance shear forces as well, we have to use an additional model. By contracting and expanding the breathing volume no shear effects occur.

Despite its weaknesses this model has a wide range of applications. It was successfully used for cohesion, adhesion, chemisorption and molecular binding [26]. In the modified embedded atom method one can use it, because the distances involved are near the equilibrium distances and the background electronic density, with its angular dependent terms, takes care of shear effects, when the parameters are appropriately adjusted.

The universal function gives the energy each atom contributes to the total energy. With it one can determine the pair potentials. The breathing volume consists of neighbouring atoms up to the second coordination shell and the energy per atom depends only on the interatomic spacing as well as the pair potentials. Because in the breathing volume the interatomic spacing scales linearly the angles, the structure and the occupation remain constant. Thus the total screening factor for a neighbouring atom remains constant too.

3.3.2 Pair Potential for a pure Element

In the case of a pure element the energy per atom E^u , Section 3.3.1 Equation (3.18), consists of the embedding functional $F[\bar{\rho}_i]$, Section 3.1 Equation (3.1), and the pair potentials ϕ of the nearest neighbours and of the next nearest neighbours.

Let Z_1 and Z_2 are the coordination numbers, *a* the factor scaling from the nearest neighbour distance to the next nearest neighbour distance. In the special case of a breathing mode, explained in Section 3.3.1, the total screening factor *S*, Section 3.5.2 Equation (3.50), remains constant and the background electronic density $\bar{\rho}$, Section 3.2.1 Equation (3.3), depends only on the interatomic spacing *R*.

$$E^{u}(R) = F[\bar{\rho}(R)] + \frac{Z_{1}}{2}\phi(R) + \frac{Z_{2}S}{2}\phi(aR)$$
(3.23)

The angular dependent terms of the partial electronic densities, Section 3.2.2 Equa-

tion (3.5)-(3.8), vanish for a cubic system with center of symmetry and we get for the background electronic density

$$\bar{\rho}(R) = Z_1 \rho^{a(0)}(R) + Z_2 S \rho^{a(0)}(aR)$$
(3.24)

where $\rho^{a(0)}$ is the first atomic electronic density from Section 3.2.3 Equation (3.17).

Our strategy is now to solve Equation (3.23) to get the wanted pair potential ϕ . Because it is used with two different arguments one can not do this directly. In order to solve this problem another pair potential ψ was introduced [20].

$$\psi(R) = \phi(R) + \frac{Z_2 S}{Z_1} \phi(aR)$$
 (3.25)

Now it is possible to rewrite Equation (3.23) and solve the equation for a given R value to get the pair potential $\psi(R)$.

$$E^{u}(R) = F[\bar{\rho}(R)] + \frac{Z_{1}}{2}\psi(R)$$
 (3.26)

$$\psi(R) = \frac{2}{Z_1} \left(E^u(R) - F[\bar{\rho}(R)] \right)$$
(3.27)

Once $\psi(R)$ is determined one can make use of an expansion that can be derived from recursive relations to calculate ϕ by successive approximation.

$$\bar{\phi}(R) = \psi(R) + \sum_{n=1}^{n_{max}} (-1)^n (\frac{Z_2 S}{Z_1})^n \psi(a^n R)$$
(3.28)

We begin by calculating an approximate $\bar{\phi}$ by taking $n_{max} = 1$. Now one has to increase n_{max} successively by one until $\bar{\phi}(R)$ is approximately equal to $\phi(R)$. Thus one has to choose an exit condition as follows:

$$E^{u}(R) = F[\bar{\rho}(R)] + \frac{Z_{1}}{2}\phi(R) + \frac{Z_{2}S}{2}\phi(R)$$
(3.29)

$$\bar{E}^{u}(R) = F[\bar{\rho}(R)] + \frac{Z_{1}}{2}\bar{\phi}(R) + \frac{Z_{2}S}{2}\bar{\phi}(R)$$
(3.30)

$$\| E^u(R) - \bar{E}^u(R) \| \leq \varepsilon$$

$$(3.31)$$

This procedure is described Byeong-Joo Lee and M. I. Baskes [19] and our simulation program shows in Figure 3.6 the same functional behaviour of ψ and ϕ as they reported. In the present work we chose an exit condition $\varepsilon = 0.001$.

Because one has to recalculate $\phi(R)$ for every R we recommend to save the values of the wanted pair potential $\phi(R)$ in a data file. Then it is possible to fit a simple function to the datapoints and one can calculate derivatives easily as well.

3.3.3 Pair Potentials for Binary Alloys

Knowing the universal function of the alloy and the pair potentials of the pure elements ϕ_{AA} and ϕ_{BB} , one can determine the pair potential of the elements with different types ϕ_{AB} . The pair potentials of the pure elements were determined as described in Section (3.3.2).

This treatment can be illustrated by the example of $L1_2 \ FePt_3$. We have to distinguish if it is an Fe-atom or an Pt-atom which is embedded. The energy per atom of each site is made up of the pair potentials ϕ_{ij} and the corresponding embedding functional, $F_{Fe}[\rho_{Fe}]$ or $F_{Fe}[\rho_{Pt}]$. As mentioned before in Section 3.1 one has to use different reference structures when calculating the background electronic densities, $\bar{\rho}_{Fe}$ or $\bar{\rho}_{Pt}$, because of the different local environments . Z_1 and Z_2 are the coordination numbers and S_{Fe} and S_{Pt} are the total screening factors, Section 3.5.2 Equation (3.50), of an Fe neighbouring atom and of an Ptneighbouring atom. The total screening factors are constant, but they can differ for each neighbour, because of different screening function values S_{ikj} , Section 3.5.1 Equation (3.45).

$$E_{Fe}(R) = F_{Fe}[\rho_{Fe}(R)]$$
(3.32)

+
$$\frac{Z_1}{2}\phi_{FePt}(R) + \frac{Z_2}{2}S_{Fe}\phi_{FeFe}(aR)$$
 (3.33)

$$E_{Pt}(R) = F_{Pt}[\rho_{Pt}(R)]$$
 (3.34)

+
$$\frac{Z_1 - 4}{2}\phi_{PtPt}(R) + \frac{4}{2}\phi_{PtFe}(R) + \frac{Z_2}{2}S_{Pt}\phi_{PtPt}(aR)$$
 (3.35)

Accordingly the energy per atom of the alloy is made up in the proportion 1 : 3 as follows:

$$E_{FePt_3}(R) = \frac{1}{4} \cdot E_{Fe}(R) + \frac{3}{4} \cdot E_{Pt}(R)$$
(3.36)

$$E_{FePt_3}(R) = \frac{1}{4} F_{Fe}[\rho_{Fe}(R)] + \frac{3}{4} F_{Pt}[\rho_{Pt}(R)]$$
(3.37)

+
$$\frac{Z_1}{2} \Big[\frac{1}{2} \phi_{FePt}(R) + \frac{1}{2} \phi_{PtPt}(R) \Big]$$
 (3.38)

+
$$\frac{Z_2}{2} \left[\frac{1}{4} S_{Fe} \phi_{FeFe}(aR) + \frac{3}{4} S_{Pt} \phi_{PtPt}(aR) \right]$$
 (3.39)

By setting $Z_1 = 12$ and $Z_2 = 6$ one finally obtains the pair potential of *Fe*-atoms and *Pt*-atoms [13].

$$\phi_{FePt}(R) = \frac{1}{3} E^{u}_{FePt_3}(R) - \frac{1}{12} F_{Fe}[\rho_{Fe}(R)] - \frac{1}{4} F_{Pt}[\rho_{Pt}(R)]$$
(3.40)

$$- \phi_{PtPt}(R) - \frac{1}{4}S_{Fe}\phi_{FeFe}(aR) - \frac{3}{4}S_{Pt}\phi_{PtPt}(aR)$$
(3.41)

This calculation is representative for all $L1_2$ systems. Figure 3.10 illustrates the pair potentials ϕ_{FeFe} , ϕ_{PtPt} and ϕ_{FePt} for $FePt_3$.



Figure 3.6: The potentials ψ and ϕ for Fe reproduced by our simulation program. It shows the same behaviour published originally by Byeong-Joo Lee and M. I. Baskes [19] using the identical parameters.



Figure 3.7: Binding energy relation of Fe, Pt and $FePt_3$ for breathing modes at ground state.


Figure 3.8: Universal form of the binding energy relation of Fe, Pt and $FePt_3$ for breathing modes at ground state. Axes are rescaled and the units are dimensionless.



Figure 3.9: Embedding functionals for Fe and Pt in $L1_2$ $FePt_3$ as a function of interatomic spacing applying breathing modes to the system. In this case the embedding energies only depend on the interatomic spacing r.



Figure 3.10: Pair potentials for $L1_2$ $FePt_3$ extracted out of the universal functions $(E_{Fe}^u, E_{Pt}^u \text{ and } E_{FePt}^u)$ and the embedding functionals $(F_{Fe}[\bar{\rho}_{Fe}] \text{ and } F_{Pt}[\bar{\rho}_{Pt}])$. The pair potentials ϕ_{FeFe} and ϕ_{PtPt} were first calculated for the pure elements. Then ϕ_{FePt} was calculated from Equation (3.40). The additional local minimum for ϕ_{FePt} is caused by the second partial electronic density $\rho_{Pt}^{(2)}$, which does not vanish by embedding a Pt-atom within its quilibrium environment in the $L1_2$ system.

3.4 Cut-Off Function

To save calculation time we follow previous authors [19] and calculate the embedding energy and the contributions of pair potentials only within a local environment around the embedded atom with cut-off radius r_c . Interactions near the margin and further away are negligible and are adjusted to zero by the cut-off function f_c shown in Figure 3.11. Its argument ξ is the control parameter described by Equation (3.43).

$$f_c(\xi) = \begin{cases} 1 & 1 \le \xi \\ \left[1 - (1 - \xi)^4\right]^2 & 0 < \xi < 1 \\ 0 & \xi \le 0 \end{cases}$$
(3.42)

The cut-off area with the width Δr is between the cut-off radius r_c and $r_c - \Delta r$ [19] as shown in Figure 3.12.

$$\xi = (r_c - r)/\Delta r \tag{3.43}$$



Figure 3.11: Behaviour of the cut-off function f_c within the cut-off area.



Figure 3.12: The orange area discribes the cut-off area $r_c-\Delta r.$

3.5 Screening

The interaction between the embedded atom i and one of its neighbours j also depends on the local environment of both atoms. Another neighbour atom can intervene and screen the interaction. This screening can be described by two spheroids through the atoms i and j as shown in Figure 3.13.

The screening function is a sufficient factor to describe the influence of intervening atoms on the second nearest-neighbour interaction. It appears as a factor both in the pair potentials, Section 3.3, and in the atomic electronic densities, Section 3.2.3. We have to mention that there is sometimes a third nearest-neighbour interaction as well. But in most cases these are negligibly small [19].

3.5.1 The Screening Function S_{ikj}

Let i and j be two atoms which interact with each other and k an atom of the local environment which screens the interaction.

The implicit equation of an ellipse is given by:

$$x^{2} + \frac{1}{C}y^{2} = (\frac{1}{2}r_{ij})^{2}$$
(3.44)

Here (x, y) are the point coordinates with (0, 0) being the center of the coordinate system. The distance between atom *i* and atom *j* is given by r_{ij} . *C* is the parameter which determines the aspect ratio of an ellipse. Rotating the ellipse around the line through atom *i* and atom *j* gives a spheroid.

Its influence is described by a factor called screening function S_{ikj} . The formula of the screening function is equivalent to the cut-off function, Section 3.4 Equation 3.42).

$$S_{ikj}(\xi) = \begin{cases} 1 & 1 \le \xi \\ \left[1 - (1 - \xi)^4\right]^2 & 0 < \xi < 1 \\ 0 & \xi \le 0 \end{cases}$$
(3.45)

But they differ in the way how the argument is calculated.

$$\xi = \frac{C - C_{min}}{C_{max} - C_{min}} \tag{3.46}$$

$$C = \frac{2(X_{ik} + X_{jk}) - (X_{ik} - X_{jk})^2 - 1}{1 - (X_{ik} - X_{jk})^2}$$
(3.47)

$$X_{ik} = \frac{r_{ik}}{r_{ij}} \tag{3.48}$$

$$X_{jk} = \frac{r_{jk}}{r_{ij}} \tag{3.49}$$

The argument of the screening function depends on the distances of the atoms $(r_{ij}, r_{ik},$ and $r_{jk})$ and the parameters C_{min} and C_{max} , which describe the two spheroids in Figure 3.13. C determines where atom k is located [4]. We can summarize the behaviour of the screening function as follows:

- When k is outside the bigger spheroid the interaction between atom i and atom j is unscreened $S_{ikj} = 1$ (Figure 3.14).
- If k located in the space between the smaller and the bigger one, then the interaction is partially screened $0 < S_{ikj} < 1$ (Figure 3.15).
- Being within the smaller one the interaction is totally screened $S_{ikj} = 0$ (Figure 3.16).

Both parameters C_{min} and C_{max} depend on the atom types involved. C_{max} is usually considered to be the same constant (2.80) for all cases [20] [22] [13]. For pure elements one has to determine only one value for C_{min} . In binary alloys one has to consider the different atom types A and B. There are six cases for i-k-j: A-A-A, B-B-B, A-B-A, B-A-B, A-B-A = B-B-A and B-A-A = A-A-B.

3.5.2 The Total Screening Factor S_{ij}

Considering the whole environment around atom i and j one gets the total screening factor S_{ij} . In other words one has to calculate the screening factor S_{ikj} for every atom k within

the local environment which screens the interaction. Then one has to multiply the values to get the total screening factor.

$$S_{ij} = \prod_{k \neq i,j} S_{ikj} \tag{3.50}$$

- When all screening atoms k within the local environment are outside the bigger spheroid then the interaction is unscreened $(S_{ij} = 1)$.
- If at least one screening atom is within the space between the smaller and the bigger one, then the interaction is screened $(0 \le S_{ij} < 1)$.
- The interaction is completely screened, when at least one atom is within the smaller spheroid $(S_{ij} = 0)$.



Figure 3.13: two spheroids through atom i and atom j described by the parameters C_{min} and C_{max}



Figure 3.15: atom k screens the interaction between atom i and j: 0 < S < 1



Figure 3.14: atom k leaves the interaction between atom i and j unscreened: S = 1



Figure 3.16: atom k screens the interaction between atom i and j completely: S = 0

Chapter 4

Results

In this work a computer code was developed and tested to calculate the atomic interaction for $L1_2$ $FePt_3$ with the modified embedded atom method. It is possible to simulate the bulk material as well as dimensionally limited systems like thin films or nanowires. One only has do adapt the periodic boundary conditions to the corresponding situation. Positions of single atoms can be manipulated and also the whole calculation cell can be compressed and expanded. The energy which each atom contributes to the total system and the forces which affect each atom can be calculated. Interactions up two the second coordination shell are included. The total energy can be updated each time when the configuration of the system changes. In order to save calculation time, only those partial volumes of the calculation cell are considered where changes take place. Additional programs were implemented in order to validate the method and to examine the behaviour of the system. The two output formats XYZ and XFS are supported to investigate the calculation cell and the local environments with common structure visualisation programs like RasMol, VMD or XCrySDen. The code is particularly suitable for $L1_2$ alloys and for *bcc* and *fcc* pure element structures. For other cubic systems like $L1_0$ the calculation of the pair potentials has to be adapted.

4.1 Energy per Atom of the Equilibrium State

The energy each atom contributes to the total system consists of the embedding energy needed to embed the atom within its local environment and of the pair interactions with its surrounding neighbouring atoms. For the equilibrium bulk system of $L1_2$ $FePt_3$ only the pair interactions contribute, because the background electronic density of each element is equal to its corresponding reference density, compare Section 3.1 Figure 3.4, 3.1 and 3.2. We expect a mean energy contribution of $-5.49 \ eV$ for every atom, which is exactly the sublimation energy of the system. This energy per atom is obtained by calculating the total energy of the system divided by the number of atoms within the calculation cell.

For the bulk system in equilibrium state every Fe-atom is surrounded by the same local environment. Ditto for Pt-atoms. In our simulation program an embedded Fe-atom contributes $-4.74 \ eV$ to the total energy and an Pt-atom $-5.74 \ eV$. Provided that the calculation cell is occupied by Fe- and Pt-atoms in the ratio of 1:3, we obtain the mean energy contribution indipendent of the size of the calculation cell and all forces on the atoms vanish within given accuracy limits of 10^{-6} .

$$\frac{1 \times (-4.74) \ eV + 3 \times (-5.74) \ eV}{4} = (-5.49) \ eV \tag{4.1}$$

4.2 Confirmation of Physical Quantities

What we expect from the model is at least to be capable to reproduce the physical parameters, which were given as input parameters. We did this by compressing and expanding the simulation cell in order to validate the universal relationship between the binding energy and the interatomic spacing, Section 3.3.1 Equation (3.18). As a test candidate $L1_2$ -ordered $FePt_3$ was chosen as well as the constituent elements, body centered cubic Fe and face centered cubic Pt. We have to mention, however, that by applying breathing modes to the system the cut-off function, Section 3.4 Equation (3.42), causes some points of discontinuity. This is understandable, because the pair potentials, Section 3.3.2 and 3.3.3, were extracted by considering the ideal case without the need of a cut-off function. Nevertheless, as one can see in the Figure 4.1, 4.2 and 4.3, we were able to reproduce the universal functions quite well. The points of discontinuity can be reduced by increasing the cut-off radius and can be smoothed by increasing the cut-off area. One obtains the equilibrium bulk modulus B_0 and the derivative of it with respect to the pressure, $\partial B_0/\partial p$ by fitting the universal function E^u to the data points. The sublimation energy E_0 and the equilibrium atomic volume Ω_0 one gets directly out of the energy minimum. Another possibility is to fit the Birch-Murnaghan equation of state, Equation (4.2), to the data points [7]. One has to rescale the nearest neighbour distance r to the atomic volume Ω by dividing the volume of the unit cell by 4 for fcc systems and by 2 for bcc systems. Figure 4.4 shows the results for $L1_2$ FePt₃.

$$E(\Omega) = E_0 + \frac{9\Omega_0 B_0}{16} \left\{ \left[\left(\frac{\Omega_0}{\Omega}\right)^{\frac{2}{3}} - 1 \right]^3 \frac{\partial B_0}{\partial p} + \left[\left(\frac{\Omega_0}{\Omega}\right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{\Omega_0}{\Omega}\right)^{\frac{2}{3}} \right] \right\}$$
(4.2)



Figure 4.1: A bcc Fe calculation cell with 128 atoms compressed and expanded to validate the universal function E_{Fe}^u dependent on the atomic volume Ω . Ω_0 is the atomic volume at equilibrium state. Within the interval of [0.8,0.9] the energy values deviate more from the universal function, because of the cut-off function described in Section 3.4. For the cut-off function we chose $r_c = 3.0$ and $\Delta r = 0.05$. Periodic boundary conditions are applied in all three dimensions. The points of strong discontinuity caused by the cut-off function are marked with a circle.



Figure 4.2: A fcc Pt calculation cell with 256 atoms compressed and expanded to validate the universal function E_{Pt}^{u} dependent on the atomic volume Ω . Ω_{0} is the atomic volume at equilibrium state. For the cut-off function we chose $r_{c} = 2.4$ and $\Delta r = 0.05$. Periodic boundary conditions are applied in all three dimensions.



Figure 4.3: A $L1_2$ $FePt_3$ calculation cell with 256 atoms compressed and expanded to validate the universal function $E_{FePt_3}^u$ dependent on the atomic volume Ω . Ω_0 is the atomic volume at equilibrium state. For the cut-off function we chose $r_c = 2.4$ and $\Delta r = 0.05$. Periodic boundary conditions are applied in all three dimensions.



Figure 4.4: A $L1_2$ $FePt_3$ calculation cell with 256 atoms compressed and expanded to calculate energy values dependent on the atomic volume Ω . The Birch-Murnaghan equation of state is fitted to extract the equilibrium bulk modulus, $B_0 = 1.63 \ eV/A^3$, and the derivative of it with respect to the pressure, $\partial B_0/\partial p = 5.74$. The sublimation energy, $E_0 = -5.49 \ eV$, and the equilibrium volume, $\Omega_0 = 14.20 \ A^3$, are constant parameters in the fit and are given by the potential minimum. For the cut-off function we chose $r_c = 2.4$ and $\Delta r = 0.05$. Periodic boundary conditions are applied in all three dimensions.

4.3 Vacancy Formation Energy

Also we introduced a vacancy into the system of the alloy and of the pure elements to investigate the forces around the vacancy site and to calculate energy profiles for some nearest neighbour jumps into the vacancy site.

To calculate the total Energy $E_{tot}[N]$ of the system containing one vacancy and N atoms. one has to know the energy contribution ε_i for each element *i* in the system. This is the energy per atom for the pure elements in equilibrium state. N_i being the number of type *i* atoms.

$$E_v^f = E_{tot}[N] - \sum_i N_i \varepsilon_i \tag{4.3}$$

We calculated the unrelaxed vacancy formation energy E_v^f for bcc Fe and fcc Pt and compared the values with known relaxed results [20] [22]. Additionally we examined the unrelaxed vacancy formation energies for $L1_2$ $FePt_3$ as well. Table 4.1 shows that the unrelaxed values for Fe and Pt are about 13% and 11% greater than the relaxed reference values. For the alloy no reference values were available for comparison but one can see that a vacancy on a Fe-site is favoured by about 0.05 eV compared to a vacancy on a Pt-site. Further investigations of neighbouring atoms jumping to the vacancy site, Section 4.6, correspond with this result.

System	Vacancy Site	$E_v^f \ [eV]$	relaxed expected value $[eV]$
BCC Fe	Fe	1.98	1.75
FCC Pt	Pt	1.66	1.50
$L1_2 \ FePt_3$	Fe	1.84	-
$L1_2 \ FePt_3$	Pt	1.89	-

Table 4.1: Vacancy formation energies E_v^f for pure Fe, pure Pt and a $L1_2 \ FePt_3$ alloy. The reference values [20] [22] for the pure elements are smaller, because our values are not relaxed. In the alloy it costs less energy to produce a vacancy on a Fe-site in comparison to a vacancy on a Pt-site.

4.4 Calculation of the Force

The calculation of the force of the potential entails derivatives of all parts containing the position of the atom like the cut-off function, the screening function, the partial electronic densities et cetera. In order to validate the results of this algebraically somewhat involved calculation, we compared every derivative for each component with its corresponding difference quotient.

$$\frac{\Delta f(x)}{\Delta x} = \frac{f(x + \Delta x) - f(x)}{\Delta x}$$
(4.4)

This can be done for every derivative by output routines, which were implemented particularly for this purpose.

In Section 4.4.1 we illustrate the force affecting an Fe-atom, which jumps into a vacancy on a Pt-site in $L1_2$ $FePt_3$. In general the results correspond quite well. Only a few values show a greater deviation from each other, compare Figure 4.6. 4.4.1 Force during Atom Jump: Fe-Atom Jumps to Vacancy on Pt-Site in $L1_2FePt_3$



is compared with its difference quotient. The x-component is equivalent to the y-component of the force because of symmetry reasons. Figure 4.5: In a $L1_2$ FePt₃ system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt site. The Fe-atom jumps within the $(\tilde{1}, \tilde{1}, 0)$ -plane and the (0, 0, 1)-plane in [1, 1, 0]-direction. The x-component of the force, which affects the jumping atom, The arrows mark the positions of the potential minimum and maximum. The potential minima are almost at the ideal lattice positions. Points of strong discontinuity caused by the cut-off function are marked with circles.



Figure 4.6: In a $L1_2 \ FePt_3$ system a Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt site. The Fe-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in [1, 1, 0]-direction. The z-component of the force, which affects the jumping atom, is compared with its difference quotient. The component has to vanish because of symmetry reasons. Remarkable are the relative high deviation of the values within the interval of [25%, 75%]. The reasons therefore are not completely clarified so far. Points of strong discontinuity caused by the cut-off function are marked with ellipses.

4.5 Forces around a Vacancy

It is possible to calculate the forces exerted on each atom of the system. If for example we take out an atom, producing a vacancy, all surrounding atoms feel forces, which deform the lattice within a local environment.

We have calculated the forces acting on the neighbouring atoms of a vacancy, for bcc Fe, for fcc Pt and for $L1_2$ $FePt_3$. The naive expectation is that the forces always point towards the vacancy site, but this turns out not always to be the case.

- $BCC \ Fe$ with vacancy: The forces on the nearest neighbours point towards the vacancy and the forces which affect the next nearest neighbours point away, Section 4.5.
- FCC Pt with vacancy: All forces point towards the vacancy, Section 4.5.
- $L1_2$ FePt₃ with vacancy on Fe-site: The forces which affect the nearest neighbours point away of the vacancy and the forces which affect the next nearest neighbours point towards it, Section 4.5.
- $L1_2$ FePt₃ with vacancy on Pt-site: All forces point towards the vacancy, Section 4.5.

In general one can say, that the embedding functional causes a component of the force, which is directed towards the vacancy, and the pair potentials cause a component of the force, which points away from the vacancy. Altogether the direction of the force depends on which component prevails.

Forces around a Vacancy in BCC Fe

Atom	DV_{VA}	r [A]	$E \ [eV]$	$F_y \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Fe	(2, 0, 0)	2.86	-4.17	0.17	0.00	0.00
Fe	(-2, 0, 0)	2.86	-4.17	-0.17	0.00	0.00
Fe	(0, 2, 0)	2.86	-4.17	0.00	0.17	0.00
Fe	(0, -2, 0)	2.86	-4.17	0.00	-0.17	0.00
Fe	(0, 0, 2)	2.86	-4.17	0.00	0.00	0.17
Fe	(0, 0, -2)	2.86	-4.17	0.00	0.00	-0.17

Table 4.2: Second nearest neighbour atoms around a vacancy in bcc Fe. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r[A]	$E \ [eV]$	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Fe	(1, 1, 1)	2.48	-4.13	-0.42	-0.42	-0.42
Fe	(-1,-1,-1)	2.48	-4.13	0.42	0.42	0.42
Fe	(1, 1, -1)	2.48	-4.13	-0.42	-0.42	0.42
Fe	(1,-1,1)	2.48	-4.13	-0.42	0.42	-0.42
Fe	(-1, 1, 1)	2.48	-4.13	0.42	-0.42	-0.42
Fe	(-1, -1, 1)	2.48	-4.13	0.42	0.42	-0.42
Fe	(-1, 1, -1)	2.48	-4.13	0.42	-0.42	0.42
Fe	(1,-1,-1)	2.48	-4.13	-0.42	0.42	0.42

Table 4.3: Nearest neighbour atoms around a vacancy in bcc Fe. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Forces around a Vacancy in FCC Pt

Atom	DV_{VA}	r [A]	$E \ [eV]$	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Pt	(2, 0, 0)	3.92	-5.77	-0.41	0.00	0.00
Pt	(-2, 0, 0)	3.92	-5.77	0.41	0.00	0.00
Pt	(0, 2, 0)	3.92	-5.77	0.00	-0.41	0.00
Pt	(0, -2, 0)	3.92	-5.77	0.00	0.41	0.00
Pt	(0, 0, 2)	3.92	-5.77	0.00	0.00	-0.41
Pt	(0, 0, 2)	3.92	-5.77	0.00	0.00	0.41

Table 4.4: Second nearest neighbour atoms around a vacancy in fcc Pt. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r [A]	E [eV]	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Pt	(1, 1, 0)	2.77	-5.63	-0.20	-0.20	0.00
Pt	(-1, -1, 0)	2.77	-5.63	0.20	0.20	0.00
Pt	(1,-1,0)	2.77	-5.63	-0.20	0.20	0.00
Pt	(-1, 1, 0)	2.77	-5.63	0.20	-0.20	0.00
Pt	(1, 0, 1)	2.77	-5.63	-0.20	0.00	-0.20
Pt	(-1, 0, -1)	2.77	-5.63	0.20	0.00	0.20
Pt	(1, 0, -1)	2.77	-5.63	-0.20	0.00	0.20
Pt	(-1, 0, 1)	2.77	-5.63	0.20	0.00	-0.20
Pt	(0, 1, 1)	2.77	-5.63	0.00	-0.20	-0.20
Pt	(0,-1,-1)	2.77	-5.63	0.00	0.20	0.20
Pt	(0, 1, -1)	2.77	-5.63	0.00	-0.20	0.20
Pt	(0, -1, 1)	2.77	-5.63	0.00	0.20	-0.20

Table 4.5: Nearest neighbour atoms around a vacancy in fcc Pt. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r[A]	$E \ [eV]$	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Fe	(2, 0, 0)	3.84	-4.74	-0.14	0.00	0.00
Fe	(-2, 0, 0)	3.84	-4.74	0.14	0.00	0.00
Fe	(0, 2, 0)	3.84	-4.74	0.00	-0.14	0.00
Fe	(0, -2, 0)	3.84	-4.74	0.00	0.14	0.00
Fe	(0, 0, 2)	3.84	-4.74	0.00	0.00	-0.14
Fe	(0, 0, -2)	3.84	-4.74	0.00	0.00	0.14

Forces around a Vacancy in $L1_2$ $FePt_3$ sitting on a Fe-Site

Table 4.6: Second nearest neighbour atoms around a vacancy in $L1_2 \ FePt_3$. The vacancy sits on a Fe-site. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r [A]	$E \ [eV]$	$F_X \ [eV/A]$	$F_Y \ [eV/A]$	$F_Z \ [eV/A]$
Pt	(1, 1, 0)	2.72	-5.59	0.06	0.06	0.00
Pt	(-1, -1, 0)	2.72	-5.59	-0.06	-0.06	0.00
Pt	(1,-1,0)	2.72	-5.59	0.06	-0.06	0.00
Pt	(-1, 1, 0)	2.72	-5.59	-0.06	0.06	0.00
Pt	(1, 0, 1)	2.72	-5.59	0.06	0.00	0.06
Pt	(-1, 0, -1)	2.72	-5.59	-0.06	0.00	-0.06
Pt	(1, 0, -1)	2.72	-5.59	0.06	0.00	-0.06
Pt	(-1, 0, 1)	2.72	-5.59	-0.06	0.00	0.06
Pt	(0, 1, 1)	2.72	-5.59	0.00	0.06	0.06
Pt	(0,-1,-1)	2.72	-5.59	0.00	-0.06	-0.06
Pt	(0, 1, -1)	2.72	-5.59	0.00	0.06	-0.06
Pt	(0,-1,1)	2.72	-5.59	0.00	-0.06	0.06

Table 4.7: Nearest neighbour atoms around a vacancy in $L1_2$ $FePt_3$. The vacancy sits on a Fe-site. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r [A]	E [eV]	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Pt	(2, 0, 0)	3.84	-5.74	-0.32	0.00	0.00
Pt	(-2, 0, 0)	3.84	-5.74	0.32	0.00	0.00
Pt	(0, 2, 0)	3.84	-5.74	0.00	-0.32	0.00
Pt	(0, -2, 0)	3.84	-5.74	0.00	0.32	0.00
Pt	(0, 0, 2)	3.84	-5.74	0.00	0.00	-0.55
Pt	(0, 0, -2)	3.84	-5.74	0.00	0.00	0.55

Forces around a Vacancy in $L1_2$ $FePt_3$ sitting on a Pt-Site

Table 4.8: Second nearest neighbour atoms around a vacancy in $L1_2 \ FePt_3$. The vacancy sits on a Pt-site. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

Atom	DV_{VA}	r [A]	$E \ [eV]$	$F_x \ [eV/A]$	$F_y \ [eV/A]$	$F_z \ [eV/A]$
Fe	(1, 1, 0)	2.72	-4.54	-0.01	-0.01	0.00
Fe	(-1, -1, 0)	2.72	-4.54	0.01	0.01	0.00
Fe	(1,-1,0)	2.72	-4.54	-0.01	0.01	0.00
Fe	(-1, 1, 0)	2.72	-4.54	0.01	-0.01	0.00
Pt	(1, 0, 1)	2.72	-5.60	-0.41	0.00	-0.17
Pt	(-1, 0, -1)	2.72	-5.60	0.41	0.00	0.17
Pt	(1, 0, -1)	2.72	-5.60	-0.41	0.00	0.17
Pt	(-1, 0, 1)	2.72	-5.60	0.41	0.00	-0.17
Pt	(0, 1, 1)	2.72	-5.60	0.00	-0.41	-0.17
Pt	(0,-1,-1)	2.72	-5.60	0.00	0.41	0.17
Pt	(0, 1, -1)	2.72	-5.60	0.00	-0.41	0.17
Pt	(0,-1,1)	2.72	-5.60	0.00	0.41	-0.17

Table 4.9: Nearest neighbour atoms around a vacancy in $L1_2$ $FePt_3$. The vacancy sits on a Pt-site. Atom type, direction vector DV_{VA} from the vacancy to the atom, distance r, energy contribution E and the components of the force F_x , F_y and F_z affecting the neighbour atom are shown.

4.6 Atom Jumps to the Vacancy Site

In general we are interested in energy barriers for Monte Carlo simulations. Thus we calculated energy profiles of some unrelaxed atom jumps of neighbouring atoms into the vacancy position in order to test the behaviour of the potential and the forces. This was carried out for bcc Fe, fcc Pt and $L1_2 FePt_3$. Although the system is unrelaxed the jumping profiles show expected qualitative behaviours. Points of interest are marked with arrows. Points of strong discontinuity caused by the cut-off function are marked with circles.

- Atom jumps which leave the state of long-range order of the alloy constant have got the same energies at the initial state and at the final state, Section 4.6.1, 4.6.2 and 4.6.5.
- Atom jumps which change the state of long-range order of the alloy show different energies at the initial state and at the final state, Section 4.6.3 and 4.6.4.
- At the equilibrium state and at a potential maximum the forces vanish.
- In the presence of a vacancy the equilibrium state does not lie exactly at the ideal lattice positions, because the vacancy causes small forces shifting the equilibrium distance of the jumping atoms a little bit, compare Section 4.5. The direction of the shift depends on the local environment and on the vacancy site.
- The jump path in Section 4.6.5 is energetically unfavourable. The forces on the atom do not vanish at the half-way point, because of the atomic occupation of four-atom window consisting of common nearest neighbours to the initial and the final position. The *Pt*-atom jumps through a window consisting of two *Pt*-atoms and two *Fe*-atoms side by side, which introduces asymmetry, compare Section 3.1 Figure 3.2. The energetically favourable path generally depends on the configuration of this four-atom window.
- A vacancy on a Fe-site in $L1_2$ $FePt_3$ is energetically favoured, Section 4.6.3 and 4.6.4, which corresponds with the results of Section 4.3 Table 4.1.

In order to make quantitative comparisons and conclusions one has to relax the positions of the atoms in a certain environment of the defect, seeking a minimum of the total energy of the system.

4.6.1 Fe-Atom jumps to Vacancy on Fe-Site in BCC Fe



jumps within the $(1, \overline{1}, 0)$ -plane in $[\overline{1}, \overline{1}, \overline{1}]$ -direction. The potential of the system during the jump is shown. The arrows mark the positions Figure 4.7: In a bcc Fe system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Fe-site. The Fe-atom of the potential minimum and maximum. The potential minima are shifted a little bit apart from the ideal lattice positions, at 0% and 100%, towards the vacancy site. Initial and final state are energetically equivalent and the jumping path is symmetric. Points of strong discontinuity caused by the cut-off function are marked with circles.



jumps within the $(1, \overline{1}, 0)$ -plane in $[\overline{1}, \overline{1}, \overline{1}]$ -direction. The x-component of the force affecting the jumping atom during the jump is shown. The component is equivalent to the y-component and the z-component of the force, because of symmetry reasons. The arrows mark the positions of the potential minimum and maximum. The force are approximately zero at these points. The potential minima are shifted a little bit apart from the ideal lattice positions, at 0% and 100%, towards the vacancy site. The jumping path is symmetric and points of Figure 4.8: In a bcc Fe system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Fe-site. The Fe-atom strong discontinuity caused by the cut-off function are marked with circles.

4.6.2 *Pt*-Atom jumps to Vacancy on *Pt*-Site in FCC *Pt*



jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The potential of the system during the jump is shown. The arrows mark the positions of the potential minimum and maximum. The potential minima are shifted a little bit apart from the ideal lattice positions, at 0% and 100%, towards the vacancy site. Initial and final state are energetically equivalent and the jumping path is Figure 4.9: In a fcc Pt system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom symmetric. Points of strong discontinuity caused by the cut-off function are marked with circles.



during the jump is shown. The component is equivalent to the y-component of the force, because of symmetry reasons. The arrows mark Figure 4.10: In a fcc Pt system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The x-component of the force affecting the jumping atom the positions of the potential minimum and maximum. The force are approximately zero at these points. The potential minima are shifted a little bit apart from the ideal lattice positions, at 0% and 100%, towards the vacancy site. Initial and final state are energetically equivalent and the jumping path is symmetric. Points of strong discontinuity caused by the cut-off function are marked with circles.



Figure 4.11: In a fcc Pt system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The z-component of the force affecting the jumping atom during the jump is shown. The component has to vanish because of symmetry reasons.
4.6.3 Fe-Atom jumps to Vacancy on Pt-Site in $L1_2$ $FePt_3$



Fe-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in [1, 1, 0]-direction. The potential of the system during the jump is shown. The arrows mark the positions of the potential minimum and maximum. The potential minima are almost at ideal lattice positions, at Figure 4.12: In a L_{12} FePt₃ system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The 0% and 100%. The vacancy on the Fe-site is energetically favoured and the jumping path is asymetric because the atom jump orders the alloy.



atom during the jump is shown. The component is equivalent to the y-component of the force, because of symmetry reasons. The arrows mark the positions of the potential minimum and maximum. The force are approximately zero at these points. The potential minima are almost at ideal lattice positions, at 0% and 100%. The point of strong discontinuity caused by the cut-off function is marked with a circle. Figure 4.13: In a L_{12} FePt₃ system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Fe-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in [1, 1, 0]-direction. The x-component of the force affecting the jumping



Figure 4.14: In a $L1_2$ $FePt_3$ system an Fe-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Fe-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in [1, 1, 0]-direction. The z-component of the force affecting the jumping atom during the jump is shown. The component has to vanish because of symmetry reasons.

4.6.4 *Pt*-Atom jumps to Vacancy on *Fe*-Site in $L1_2$ *FePt*₃



Figure 4.15: In a L_{12} FePt₃ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Fe-site. The Pt-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The potential of the system during the jump is shown. The arrows mark the positions of the potential minimum and maximum. The potential minima are shifted a little bit apart from the ideal lattice positions. At 0% it is shifted away from the vacancy site and at 100% it is shifted towards the vacancy site. The vacancy on the *Fe*-site is energetically favoured and the jumping path is asymetric because the atom jump orders the alloy. Points of strong discontinuity caused by the cut-off function are marked with circles.



Figure 4.16: In a L_{12} FePt₃ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Fe-site. The Pt-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The x-component of the force affecting the jumping atom during the jump is shown. The component is equivalent to the y-component of the force, because of symmetry reasons. The arrows mark the positions of the potential minimum and maximum. The force is approximately zero at these points. The potential minima are shifted a little bit apart from the ideal lattice positions. At 0% it is shifted away from the vacancy site and at 100% it is shifted towards the vacancy site. The jumping path is asymetric because the atom jump orders the alloy. Points of strong discontinuity caused by the cut-off function are marked with circles.



Figure 4.17: In a $L1_2$ $FePt_3$ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Fe-site. The Pt-atom jumps within the $(1, \overline{1}, 0)$ -plane and the (0, 0, 1)-plane in $[\overline{1}, \overline{1}, 0]$ -direction. The z-component of the force affecting the jumping atom during the jump is shown. The component has to vanish because of symmetry reasons.

4.6.5 *Pt*-Atom jumps to Vacancy on *Pt*-Site in $L1_2$ $FePt_3$



jumps within the $(0, \overline{1}, 1)$ -plane and the (0, 1, 0)-plane in $[0, \overline{1}, \overline{1}]$ -direction. The potential of the system during the jump is shown. The external arrows mark the positions of the potential minimum. The arrow in the middle is not a maximum of the potential, because the Figure 4.18: In a $L1_2$ FePt₃ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom force differs from zero. The potential minima are shifted a little bit apart from the ideal lattice positions, at 0% and 100%, towards the vacancy site. Initial and final state are energetically equivalent and the jumping path is symmetric. Points of strong discontinuity caused by the cut-off function are marked with circles.



Figure 4.19: In a L_{12} $FePt_3$ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom jumps within the $(0, \overline{1}, 1)$ -plane and the (0, 1, 0)-plane in $[0, \overline{1}, \overline{1}]$ -direction. The x-component of the force affecting the jumping atom during the jump is shown. The component has to vanish because of symmetry reasons.



Figure 4.20: In a $L1_2$ $FePt_3$ system an Pt-atom jumps to the neighbouring vacancy position. The vacancy sits on a Pt-site. The Pt-atom jumps within the $(0, \bar{1}, 1)$ -plane and the (0, 1, 0)-plane in $[0, \bar{1}, \bar{1}]$ -direction. The y-component of the force affecting the jumping atom during the jump is shown. The component is equivalent to the z-component of the force, because of symmetry reasons. The external arrows mark the positions of the potential minimum, where the force approximately vanishes. The arrow in the middle is not a maximum of the potential, because the force differs from zero. The jumping path is symmetric. Points of strong discontinuity caused by the cut-off function are marked with circles.

Chapter 5

Conclusions and Outlook

At the present state of work the question, if the modified embedded atom method is suitable for Monte Carlo simulation of diffusion of atoms in dimensionally limited systems, cannot be resolved. It is not possible to make appropriate statements about its applicability without at least a working algorithm for the elastic relaxation of atoms, which was beyond the scope of this work. Probably the main weakness of the method is that the parameters are adjusted mostly to macroscopic physical quantities, which may turn out to be insufficient to reproduce behaviour at the atomic scale. Particularly near surfaces and if one needs to calculate energy barriers for atom jumps this could be crucial. Scruples about the method occur because some forces we calculated acting on atoms in the neighbourhood of a vacancy point away from the vacancy. To further clarify this problem one should implement a relaxation algorithm to have the possibility to compare with relaxed jump profiles from ab initio calculations. If then the method is confirmed to contradict first principle calculations one has to decide if the method can be improved or has to be discarded for the purposes envisioned.

Chapter 6

Appendix

6.1 The Calculation of the Force

6.1.1 Gradient of the Total Energy

The force affecting an atom i' is given by the negative gradient of the total energy E_{tot} .

$$F_{i'} = -\nabla_{i'} E_{tot} = -\nabla_{i'} \left[\sum_{i} F[\rho_i] + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \right]$$
(6.1)

If one derives with respect to the atom i' different terms of the total energy are affected:

$$\nabla_{i'} E_{tot} = \nabla_{i'} F[\bar{\rho}_{i'}] + \frac{1}{2} \sum_{j \neq i'} \nabla_{i'} \phi_{i'j} + \sum_{j \neq i'} \left[\nabla_{i'} F[\bar{\rho}_j] + \frac{1}{2} \nabla_{i'} \phi_{ji'} \right]$$
(6.2)

$$= \nabla_{i'} F[\bar{\rho}_{i'}] + \sum_{j \neq i'} \nabla_{i'} F[\bar{\rho}_j] + \sum_{j \neq i'} \nabla_{i'} \phi_{i'j}$$

$$(6.3)$$

- Because atom i' is embedded one has to derive the embedding functional $F[\bar{\rho}_{i'}]$ and the pair potentials $\phi_{i'j}$ which describe the interactions between atom i' and all neighbouring atoms j.
- Because the neighbrouring atoms j of the atom i' are embedded as well one has to derive the embedding functional $F[\bar{\rho}_j]$ and the pair potential $\phi_{i'j}$ which interacts with atom i' for every neighbouring atom j.

• Furthermore the screening function S_{ikj} , Section 3.5.1 Equation 3.45, and the cut-off funcition f_c , Section 3.4 Equation 3.42, cause additional terms.

6.1.2 Gradient of the Screening Factor

Let *i* be an atom which is located in the center of a local environment. Let *j* be one of its neighbours, which interact with it. Let atom *k* be one of the atoms, which screens the interaction. To know the force which affects an atom \tilde{i} we have to derive with respect to atom \tilde{i} . Therefore we have to consider three cases. In each case there is an different derivative of the screening function.

1. Atom \tilde{i} is the atom located in the center of the local environment ($\tilde{i} = i$). One must consider the derivative with respect to the atom in the center:

$$\nabla_i S_{ij} = \sum_{k \neq i,j} \left[\nabla_i S_{ikj} \prod_{k' \neq i,j,k} S_{ik'j} \right]$$
(6.4)

2. Atom \tilde{i} is the atom which interacts with the atom in the center i ($\tilde{i} = j$). One must consider the derivative with respect to a neighbour atom which is interacting with the atom in the center:

$$\nabla_j S_{ij} = \sum_{k \neq i,j} \left[\nabla_j S_{ikj} \prod_{k' \neq i,j,k} S_{ik'j} \right]$$
(6.5)

This formula is mathematically equivalent to the formula in case two. Only the role of atom i and atom j is interchanged.

3. Atom \tilde{i} screens the interaction between the atom in the center i an another neighbour atom j ($\tilde{i} = k$). One must consider the derivative with respect to a screening atom:

$$\nabla_{k'} S_{ij} = \nabla_{k'} S_{ik'j} \prod_{k \neq i,j,k'} S_{ikj}$$
(6.6)

6.2 Periodic Boundary Conditions

As the memory and the calculation power of computers are limited, the size for the calculation cell must be limited, too. To simulate an infinite solid periodic boundary conditions are used. Let us imagine the calculation cell as a cube bounded by its six faces, so that for instance face number one shall be opposite to number six. As in a conveyor belt, the two ends are joined. Particles leaving the cell by crossing the surface on one side reenter on the opposite side.

- For simulating a bulk phase one must apply the periodic boundary conditions in all three dimensions.
- For simulating a thin film one must apply the periodic boundary conditions in two dimensions.
- For simulating a quantum wire one must apply the periodic boundary condition in only one dimension.

In our simulation program we have to consider periodic boundary conditions in two cases especially. When the position of an atom moves over the edge, and when we have to calculate the distance between two atoms. The vectors of position and distance have to be adapted accordingly. This is especially important when one is looking for the nearest neighbours of an atom. With periodic boundary conditions one particle sitting on the edge of the simulation box could be the nearest neighbour of an atom on the other side of the cell, whereas without periodic boundary conditions this would not be the case. For further informations we refer to the book Computational Physics by Franz J. Vesely [33].

Implementation of the Periodic Boundary Conditions

Periodic boundary conditions for a cubic system can be found in our simulation program within the modules in PBC_CUBIC_SWITCH. With the "use" directive it is possible to choose the dimensions which should be affected. Provided that cell size is initialized with INI_PBC_CUBIC the subroutines PBC_POSITION and PBC_DISTANCE adjust the vector of position and the vector of distance, respectively. The values one needs for calculation are the atom position \tilde{x} , the distance $\Delta \tilde{x}$ and the size of the calculation cell L.

PBC_DISTANCE:

$$\Delta x = \Delta \tilde{x} - L \cdot int(\frac{\Delta \tilde{x}}{L/2}) \tag{6.7}$$

PBC_POSITION: Because in Fortran 90/95 and in C++ there is no modulus operator for floating type numbers we have to implement $x = (\tilde{x} + 2L) \mod L$ like:

$$\bar{x} = (\tilde{x} + 2L)/L \tag{6.8}$$

$$x = \bar{x} - real(int(\bar{x})) \cdot L \tag{6.9}$$

6.3 Calculation of the Parameter d

The universal function is given by [20]:

$$E^{u}(a^{*}) = -E_{sub}(1+a^{*}+da^{*3})e^{-a^{*}}$$
(6.10)

$$\tilde{a} = \alpha(r/r_{eq} - 1) \tag{6.11}$$

$$\alpha = \sqrt{9\Omega_0 B/E_{sub}} \tag{6.12}$$

By knowing $\Omega_0 = \frac{4}{3}\pi r_{ws}^3$ we can calulate [27]:

$$\frac{\partial B}{\partial P}\Big|_{T=0\,K} = 1 - \frac{r_{ws}}{3l} \frac{E^{u'''}(0)}{E^{u''}(0)}$$
(6.13)

$$l = \sqrt{\frac{E_{sub}}{12\pi B r_{ws}}} \tag{6.14}$$

$$E^{u''}(0) = E_{sub}$$
 (6.15)

$$E^{u'''}(0) = -E_{sub}(6d+2) \tag{6.16}$$

$$\frac{r_{ws}}{l} = \alpha = \sqrt{(9\Omega_0 B)/E_{sub}} \tag{6.17}$$

Finally we get an simple expression of the parameter d.

$$d = \frac{1}{2\alpha} \left(\frac{\partial B}{\partial P} \Big|_{T=0 K} - 1 \right) - \frac{1}{3}$$
(6.18)

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