# DIFFUSION, THERMOTRANSPORT AND THERMODYNAMIC PROPERTIES OF NI-ZR MELTS: MOLECULAR DYNAMICS STUDY

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### Keywords

Diffusion Coefficients, Green-Kubo Formalism, Molecular Dynamics, Mori-Zwanzig Formalism, Ni-Zr Melts

### **Declaration of Authorship**

### **Statement of Originality**

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

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### **Thesis by Publication**

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20 November 2020

### Abstract

Advanced theoretical work and establishing theoretical relations is the main focus of this work and was achieved via molecular dynamics simulation. By making use of statistical mechanics and atomistic modelling, an accurate and reliable database on Ni-Zr melts and its diffusion properties is generated, in conjunction with a semiempirical many-body interatomic potential for a better understanding of thermotransport and thermodynamic properties in the melts, which are used to identify possible glass-forming alloys. Comparison of simulation results with existing experimental data confirms the molecular dynamics approach used to be quantitative, and showcases the importance of theoretical work in this field.

The developed theoretical approach within the framework of molecular dynamics, incorporates the Green-Kubo, as well as the Mori-Zwanzig formalisms, to derive expressions for diffusion properties of the melt in terms of time-correlation functions. Evaluation of self-diffusion coefficients and the kinetic part of the interdiffusion offer a detailed insight into the dynamics of Ni-Zr melts upon undercooling. A link between composition and temperature dependencies is established. Finally, the observed homogeneous dynamical slowdown of single-particle and collective diffusion dynamics in the composition range of  $0.25 \leq c_{Ni} \leq 0.5$  reveals enhanced stability of the melt against its crystallisation and therefore represents viable glass-formers.

Further investigation of cross-correlation behaviour of the interdiffusion flux and the force caused by the difference in the average random accelerations of different atoms of an alloys different components in the hydrodynamic limit  $t \rightarrow 0$  is presented. This is used to determine conditions in terms of a correction factor, *S*, and its decomposed parts, namely  $S_0$  and  $W_{12}$ . The established theory is then applied on different types of melt with i) chemical ordering and ii) phase separation tendency. The main findings conclude, that for the first type of melt:  $S < S_0$  ( $W_{12} < 0$ ); meanwhile for the second type of melt:  $S > S_0$  ( $W_{12} > 0$ ) describing the atomic ordering behaviour.

### **List of Publications**

Material from this thesis has been published to a journal in the following forms:

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Statements of co-authorship can be found in the Appendix.

In memory of Dr Alexander V. Evteev.

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# List of Symbols

$J_X$	Mass flux
c <sub>i</sub>	Mole fraction of <i>i</i>
D	Diffusion coefficient
$\mu_i$	Chemical potential of <i>i</i>
$L_i$	Phenomenological transport coefficient
t	Time
$D_0$	Exponential pre-factor
$E_A$	Activation energy
$\langle \Delta r^2 \rangle$	Mean square displacement of atoms during time <i>t</i>
$\widetilde{D}$	Interdiffusion coefficient
Н	Enthalpy
U	Internal energy
p	Pressure
V	Volume
Ν	Number of atoms
Ε	Total energy
Т	Temperature
$e_i$	Total energy of <i>i</i> -th atom
m	Mass
υ	Velocity
$F_{\mu i}$	Embedding energy of atom
$ar{ ho}_i$	Host electron density

$V_{\mu_i\mu_j}$	Pair interaction potential
k	Thermal conductivity
k <sub>B</sub>	Boltzmann constant
J	Heat current vector
Ĺ	Lagrangian function
PS	Phase space
$T_g$	Glass transition temperature
Jc	Interdiffusion flux
$Q_{C}^{*}$	Heat of transport
$Q_{C}^{*\prime}$	Reduced heat of transport
S	Correction factor
S <sub>0</sub>	Kinetic factor of the correction factor
<i>W</i> <sub>12</sub>	Collective energy generation- dissipation effect
P <sub>12</sub>	Resulting force of fluctuations between $L_c$ and $R_{12}$
R	Random force acting on atoms
$\sigma_{12}$	Dimensionless factor defining initial sign of $P_{12}$
Φ	Thermodynamic factor

## List of Abbreviations

MD	Molecular dynamics	
LAMMPS	Large-scale atomic/ molecular	
	massively parallel simulator	
K	Kelvin	
NPT	Isothermal-isobaric ensemble	
NVE	Microcanonical ensemble	
EAM	Embedded-atom-method	
HCACF	Heat current autocorrelation function	
FP	First principles	
DFT	Density functional theory	
FPMD	First principles molecular dynamics	
BO	Born-Oppenheimer	
MC	Monte Carlo	
MG	Metallic glass	

## **Chapter 1: Introduction**

This dissertation has been created for fulfilment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering. This work follows the layout of a thesis by publication including peer-reviewed work. The thesis author is the lead author of the included publication and book chapter. Detailed statements for author contributions are listed in the Appendix.

Chapter 2 talks briefly about the concepts of physical processes that are essential for this topic, and serves to familiarise the reader with fundamental background about the relationship of internal factors affecting material properties. Next, the material metallic glass is drawn out, as it possesses peculiar material properties and its production and development can be accelerated with results obtained in this study. Then, computational approaches used in this field are showcased, followed by the approach implemented in this thesis: molecular dynamics. Progress within the field of molecular dynamics simulation and how this work complements the area of research are contained in Chapter 2.

Chapter 3 gives a detailed insight into liquid binary alloys of the Ni-Zr system studied via the molecular dynamics simulation. The included publication retains its original table and figure numbering as appeared in print, with the reference list at the end of the publication. Followed by supporting material, elaborating on calculations to confirm the onset of crystallisation of the model systems and further, the calculation of the kinetic part of the interdiffusion coefficient. The chapter establishes theoretical relations that are essential for the solidification process of binary melts and enables the quantitative prediction of material properties.

Chapter 4 briefly outlines previous studies of the binary alloys of Ni-Al and Cu-Ag, and categorises them into different types of melt with i) chemical ordering and ii) phase separation tendency. This establishes a foundation used for Chapter 5.

A thorough analysis of different type behaviours of the different melts is summarised in Chapter 5 and gives detailed insights into the theoretical background. The included manuscript of the published book chapter retains its own table and figure numbering as appeared in the published manuscript, with the reference list at the end of the publication. Novel understandings for the different types of melt and their atomic ordering behaviour are established and conferred.

New insights and results are examined and put into contrast in the discussion section in Chapter 6. Lastly, Chapter 7, concludes the achieved contributions to the field of research and provides a brief outlook.

### **Chapter 2: Literature Review**

The world is developing rapidly and with it come new challenges, or, more optimistically, new opportunities. The constant drive to improve is prevalent. In sports we strive to achieve better, keep breaking personal bests, with a constant determination to set new world records. No record seems unbreakable. The ceiling of what is humanly possible is continually broken through. This is a consequence of many factors. For one, an ever increasing research of the right techniques, better training and advancements in technologies used for the equipment. In the field of engineering we see similar trends. Applications become more complex, requirements more extreme and with an ever rising demand. All of this accompanied by a need to increase the efficiency of the product while ideally decreasing time and costs of its development and production. For this reason, new technologies and materials are required. The design of new materials is subject to an often very specific set of required material properties. Those are defined by the material's microstructure. Hence it is evident that the field of materials science plays a crucial role in the research, development and design of new applications. On this matter, this thesis focuses on the microstructure of engineering materials, specifically metallic glass. Further how diffusion, thermotransport and thermodynamic properties that arise in the molten state during solidification, affect the microstructure and with it, the material properties. The content of this work establishes theoretical relations and gives insight into phenomenological correlations in the melt at atomic scale, using molecular dynamic simulation. Obtained results are collected and a self-consistent database is created. This work addresses the challenges of today and opens the door to break new records, achieve improvements and take on new opportunities.

This chapter begins with the concepts of diffusion (Section 2.1) and enthalpy (Section 2.2), to familiarise the reader with fundamentals of the physical processes. The sections are kept very short due to further elaboration in Chapters 3 and 5, where specific materials investigated are referred to. Next, the material metallic glass (Section 2.3) is identified and their key manufacturing methods, properties and uses are outlined. A brief overview about computational methods used in this field is shown (Section 2.4). Finally, the approach of molecular dynamics implemented is presented,

as it bridges the gap and advances the understanding, development and production of metallic glasses and associated fields of materials science. Sections 2.6 and 2.7 highlight implications from the discussed literature and advance the framework of this study.

### 2.1 DIFFUSION

The concept of diffusion describes the matter process of transportation within a system due to molecular motions leading to complete mixing. This type of phenomena can be seen in numerous cases. Just as when two bodies at a temperature difference are brought into thermal contact will exchange thermal energy until they reach an equilibrium, and just as two bodies at a different pressure when brought into mechanical contact will exchange volume until at an equilibrium, the two bodies at different species concentrations brought into diffusive contact will exchange particles until at a molecular equilibrium.

Principally speaking, the molecular motions are random, hence their behaviour is independent from one another. The molecules experience constant collisions during the diffusion process and as a result move towards a region of either a higher, or lower concentration, seeking equilibrium. The path of motion can be described as a random walk throughout which its mean-square distance can be calculated. Hence in a given time interval, it is possible to obtain the displacement while it is not possible to determine the direction of a molecule at that time. The diffusion process can take up a very long period of time since the speed of mixing can be slow [1,2]. Following some reference numbers of progression rates to give a rough idea on the range that these processes can happen: i) in a gas: 5 cm/min, ii) in a liquid: 0.05 cm/min, and iii) in a solid down to 0.00001 cm/min [2]. Diffusion and its importance is universal, not only limited to the field of engineering. The slow diffusion progression rate of the process is often the reason that limits the overall rate of a sequence of various processes, since it usually occurs in combination with other phenomena. For example it restricts the efficiency of distillation and industrial reactions including catalysts. In the field of biology, it limits the absorption rate of nutrients by the human intestine. More examples to showcase the universal impact of diffusion are the corrosion rate of steel,

the growth of microorganisms needed to produce penicillin, and the release of odour and flavour from food [2].

By making use of diffusion coefficients, Fick's law of diffusion describes a mathematical model of the phenomena [3]. In a multicomponent system with constant pressure and temperature, the movement of an atom of type *i* within a unit of time passing through a unit of area within a system, is described as the mass flux,  $J_x$ . Its direction moves along a concentration gradient in the direction of a reduction of concentration [4]. According to Fick's first law of diffusion:

$$J_x = -D\nabla c_i \tag{1}$$



Figure 1 Fick's first law of diffusion

Where the mass flux  $J_x$  and the concentration gradient  $\nabla c_i$  are in opposite directions, the intrinsic diffusion coefficient is presented as D. A more accurate description of its behaviour is given by its proportionality to the gradient of their chemical potential, namely  $\nabla \mu_i$ . In fact, this gradient has been identified to be the main influence on diffusion and intermixing processes of a system [2]. The Onsager formalism describes this statement with its phenomenological flux equations for an isothermal A-B system in liquid and solid phases as follows:

$$J_A = -L_{AA} \nabla \mu_A - L_{AB} \nabla \mu_B \tag{2}$$

$$J_B = -L_{AB} \nabla \mu_A - L_{BB} \nabla \mu_B \tag{3}$$

In a liquid phase the description of the flux equations are applicable in the reference frame of mean-volume where experiments are taken. In a solid phase the description of the reference frame is fixed to the atomic crystal lattice.

Diffusion processes obey the conservation law which implies that the number of diffusing atoms of each species must be conserved. Required for Fick's second law, the following equation, also known as the continuity equation stands as:

$$-\nabla J_i = \frac{\partial c_i}{\partial t} \qquad \qquad i = A, B, \dots \tag{4}$$

This equation in combination with Fick's first law results in Fick's second law:

$$\frac{\partial c_i}{\partial t} = \nabla (D \nabla c_i) \qquad \qquad i = A, B, \dots \tag{5}$$

Hence, it can be seen that the diffusion coefficient depends on the concentration of the system, therefore it is composition dependent. Though in the case of a small concentration gradient, it can be approximated as a constant value. The diffusion process is also dependent on temperature, following the Arrhenius law:

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right) \tag{6}$$

Where  $D_0$  denotes the exponential pre-factor, while  $E_A$  describes the activation energy.

In the following subsections, two different types of diffusion will be elaborated further. When looking at many-particle systems and their interactions, it is crucial to separate between single-particle and collective diffusion processes that arise in the melt.

### 2.1.1 Single-Particle Diffusion

The first type of diffusion describes the movement of individual atoms of one species within a system in terms of the self-diffusion coefficients and concentration of the tracer atoms, respectively D and  $c_i$  from Equation (5). For the evaluation of the self-diffusion coefficients, a tracer is established within a known concentration gradient. The denotation of the tracer diffusion coefficient of atoms of type i is  $D_i^*$ . In order to physically observe the process of diffusion on a macroscopic level, one needs

to establish a concentration gradient. Now, for pure metals, a radioactive tracer or isotope is used. Since the chemical concentration gradient (see Sec. 2.1.2) of the material and its tracer are equal, assuming no isotopic effect, the resulting measured process is known as the self-diffusion coefficient. As mentioned earlier, the process of diffusion describes matter transport by random particle motion at atomic scale, also known as Brownian motion [2]. This theory is closely related to the mean square displacement of atoms of different species, while the tracer diffusion coefficient,  $D_i^*$ , of atoms of species *i* is associated to the displacements of atoms of type *i* directly. Numerical and experimental methods can be used to determine the tracer and concentration gradients, the latter is considered a direct method and the former an indirect. Therefore, the computational approach used here is an indirect method to calculate diffusion properties. Indirect methods make use of microscopic model systems to obtain the mean squared displacement of atoms. On this basis and by making use of the Einstein-Smoluchowski relation describing the displacement of particles on a cubic lattice and the diffusion coefficient [5,6]. The self-diffusion coefficients are obtained with the following equation:

$$D_i^* = \frac{1}{6t} \left\langle \Delta r^2 \right\rangle \qquad (i = A, B) \tag{7}$$

With  $\langle \Delta r^2 \rangle$  describing the mean square displacement of atoms during time t. This can also be written as  $\overline{\Delta r_{\alpha}^2(t)} = 1/N_{\alpha} \sum_{i=1}^{N_{\alpha}} \Delta r_{\alpha i}^2(t)$  in order to represent the time displacement of a single atom of species  $\alpha$ , with  $N_{\alpha}$  denoting its number of atoms ( $\alpha =$ 1,2).

### 2.1.2 Collective Diffusion

The second type of diffusion occurs in the presence of a gradient of chemical composition and is also known as chemical- or interdiffusion. This type of diffusion considers a large number of particles and its interactions between each other. The resulting coefficient is represented as  $\tilde{D}$ . Due to effects that arise from the chemical composition gradient, the values of self-diffusion and interdiffusion differ. According to Fick's second law, the diffusion equation in a single dimension, x, can be written as:

$$\frac{\partial c_i}{\partial t} = \widetilde{D}(c_i)\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial \widetilde{D}(c_i)}{\partial c} \left(\frac{\partial c_i}{\partial x}\right)^2 \qquad \qquad i = A, B \qquad (8)$$

With  $c_i$  describing the mole fraction related to the diffusing component. It is a function dependent on time and space, t and x respectively, while  $\widetilde{D}(c_i)$  denotes the interdiffusion coefficient. If a constant molar volume during the diffusion process is assumed such that  $\widetilde{D}(c_i) = D_0$ , then the Equation (8) term can be rewritten as:

$$\frac{\partial c_i}{\partial t} = D_0 \frac{\partial^2 c_i}{\partial x^2} \qquad \qquad i = A, B \tag{9}$$

The chemical diffusion coefficient is used to describe the changes in the concentration profiles. Atoms are affected by varying chemical environments that result during interdiffusion experiments. With a variation of the chemical composition into different diffusion zones, the diffusion coefficients may diverge as well. This collective process occurs in binary and multicomponent systems and hence depends on the composition.

Generally speaking, there are two methods used for the determination of the collective diffusion coefficient. The first option is through real experiments using phenomenological analysis on macroscopic level [7-9]. The second option takes the computational route by making use of atomistic modelling and molecular dynamics simulations [10-16].

#### 2.2 ENTHALPY

The concept of enthalpy, H, describes a thermodynamic property of a system in form of its total energy. It consists of its internal energy, U, in addition to the product of its pressure and volume, p and V respectively, given by the following equation:

$$H = U + pV \tag{10}$$

In simple terms, this property refers to the heat and work that is added/ removed from a system at a constant pressure. This extensive property cannot be measured directly, a reference point must be defined first. Then, the measured difference of energy between reference points gives physical meaning to the thermodynamic potential. Hence the change in enthalpy,  $\Delta H$ , is the common expression for the change of energy of a system denoting its transfer of energy. A negative change in  $\Delta H$  implies a loss of heat, also known as an exothermic reaction; meanwhile a positive change in  $\Delta H$  implies an addition of heat, also known as an endothermic reaction.

#### 2.3 METALLIC GLASS

The development and drive of the world of engineering is always progressing forwards and with it, the need for more advanced materials with specialised properties. To face the new tasks and challenges, new and advanced solutions are required. In a similar manner, new applications face harder and tougher conditions while it is crucial to ensure their quality and safety. It is therefore important to understand the materials creating those applications, to get the best results. One interesting range of materials with such advanced properties are metallic glasses. The materials, as result of their amorphous structure, possess a variety of amplified mechanical and electrical properties compared to crystalline materials. Metallic glass can be produced near netshape, are much stronger than steel, while also being corrosion resistant. Their unique material properties open the door to a wide range of applications, from microcomponents to structural applications.

At present however, the production of metallic glass is still very difficult. One of the reasons slowing down its progress is a lack of understanding in the field of diffusion. Processes occurring during diffusion of the different materials with each other, determine the formation of the microstructure and hence, the resulting material properties. Gaining a better understanding of thermotransport and thermodynamic properties in the melt will lead to profound knowledge of its solidification and therefore, will speed up the development and production of metallic glasses.

### 2.3.1 Historical Background

In 1960 Klement, Willens and Duwez produced the first metallic glass at Caltech [17]. The reported Au<sub>75</sub>Si<sub>25</sub> alloy was created by rapidly quenching the material from  $\sim$ 1300°C to room temperature with a cooling rate of  $\sim$ 10<sup>6</sup> K/s. The exceedingly fast cooling rate was required to avoid crystallisation within the material. The high cooling rate effectively limited the thickness of the sample within the micrometer range. In the

1960s, progress and development of metallic glass advanced with Chen and Turnbull and their work with ternary systems, producing the first bulk metallic glass with a diameter of up to 1 mm [18,19]. Constant improvement of the development method resulted in an increase of the possible sample sizes. New understandings of the material were found and used to even further increase the ability for production of metallic glasses. In 1984, the critical casting diameter of a Pd-Ni-P melt had increased to 10 mm, achieved by processing it in a boron oxide flux [20]. The next big step to improve the production even further was advanced by the discovery of a variety of multicomponent systems, where cooling rates of less than 100 K/s allowed an increase of their thickness several centimetres up to [21-23]. The pentary  $Zr_{41.2}Cu_{12.5}Ni_{10}Ti_{13.8}Be_{22.5}$  system, also known as *Vitrelov 1*, is the first commercial bulk metallic glass with a cooling rate of 1 K/s [24]. New technologies and advanced insight into materials science pushes the production of metallic glasses forward and allows the fabrication of components of several kilograms. Furthermore, it enables an increase of their critical casting thickness of more than tree orders of magnitudes, compared to the early 1990s with many multi-component systems found to be viable glass formers [25].

#### 2.3.2 Structure and Properties

The microstructure of a material relates directly to its properties, or in other words, material properties are defined by their microstructure. Understanding these relationships helps for the design of new and improved materials. Metallic glasses are usually produced by melt processing, resulting in an amorphous structure. Atoms are randomly arranged, like in a liquid. In fact, all alloys retain an amorphous structure in the molten state, the majority then crystallises when cooled down and therefore, most of the common metals possess a crystalline structure.

The crystalline structure consists of grains and grain boundaries, commonly known to be weak spots in crystalline materials. Failure of the material, i.e. cracks or corrosion, can develop and propagate through these weak-spots. Depending on the arrangement of the crystals, the material exhibits beneficial strength in only one direction. This is the case for ceramics. The nature of ceramics is brittle, while extremely strong under compression but failing fairly easy under a tensile load. An amorphous structure is densely packed. A metallic glass usually consists of two or more different elements of atoms of radii different sizes. The ratio of the mixture plays an important role of how well atoms distribute, and therefore define the packing density of the material. Atoms gridlock into a stable composition that does not plastically deform, giving the material equal strength in all directions, in contrast to ceramics which are only one-directional. This results in a brittle behaviour, similar to ceramics, which leads to catastrophic failure without plastic strain and is considered a safety risk. The impact on safety and unpredictability of the material prevents metallic glasses even today, to be a more viable option in fields of aerospace, structural and biomedical applications.

To overcome this hurdle, a better insight into atomic dynamics during solidification is needed, that define the structure and therefore the properties of the material. With a better understanding of the phenomena processes in the melt and the amorphous structure, the viability of metallic glass in a lot of different fields can be increased significantly. Some of the key material properties of metallic glass include very high strength, hardness and fracture toughness, as well as high elastic energy, corrosion resistance and wear resistance, especially under extreme conditions. Beside mechanical properties, the microstructure also grants excellent magnetic and acoustic properties, e.g. the ability to shield environmental noise or acoustic sound. One can clearly see the enormous potential of metallic glass and its applications, hence research into thermotransport and thermodynamic properties that define the microstructure is crucial for progress and development in the field of materials science, and especially for such an outstanding material like metallic glasses. On this matter, experimental approaches and numerical methodologies are used to complement each other, for a detailed and thorough investigation into the relationship of diffusion and material properties.

### 2.3.3 Production

Metallic glass is obtained through several production routes. The synthesis of the material is then followed by several different manufacturing options. This subsection gives a short overview of some of the available technologies. First, the preparation can be categorised in three different type of processes: i) vapour state processing ii) liquid state processing and iii) solid state processing. Looking into the options of vapour state processing, three variations are the most commonly used and feasible: physical vapour deposition [26,27], chemical vapour deposition [28] and ion implantation [29]. While each of the named techniques have their benefits, the most environmentally friendly and economical process option among the three is the physical vapour deposition. In general however, vapour state processes are expensive and depending on the situation, sometimes not the most viable option.

Liquid state processing is less expensive than physical vapour deposition, while also possessing a lower cooling rate. Most common options for instance are: rapid solidification processing, droplet method, jet method, surface melting techniques and splat quenching [30].

Lastly, solid state processing is usually achieved via mechanical alloying of the elements. This is a metallurgy technique using powders, developed in the 1960s [30,31]. After completion of the synthesis of the material, manufacturing routes include several forms of casting [25] and thermoplastic forming [32]. Making use of their atomic structure, the manufacturing routes allow for near net-shape processing of metallic glasses.



Figure 2 TTT-diagram schematic

Casting methods avoid crystallisation of the material, as can be seen in Figure 2, where the desired cooling rate is indicated by the red line. Novel techniques are being developed and improved to further increase the controllability of the properties of the resulting microstructure [33-35]. This results in a homogeneous microstructure within the material. With this methodology, internal stress arises within the sample, due to the rapid cooling. Thermoplastic forming, indicated by the lower blue line, benefits from the softening that occurs as a result of reheating the material above its glass transition temperature  $T_g$ . Here, the glass is kept in a metastable supercooled liquid region before crystallising, giving the material a very high formability. This novel processing technique requires very careful control of the heating and cooling rates. It also includes a greater number of production steps compared to the casting methodology, due to the extra forming and cooling processes. However, the resulting quality is far higher compared to traditional casting and provides the ability to produce very intricate shaped geometries. This increase in quality makes up for the extra effort needed.

#### 2.3.4 Applications

The peculiar structure translates into a variety of beneficial material properties, making metallic glass outstanding compared to their crystalline counterparts. This opens up a wide range of applications from military, medical to leisure and sport products. Their extremely high formability, allowing for small and intricate shaped parts, is just one of many driving factors for their use as electrode materials, sporting equipment and die material. As mentioned earlier, a better understanding of the formation processes is crucial to improve the development and production of metallic glasses, and help to overcome the hurdle of unpredictability in terms of failure and safety risks. The following section lists a few examples, showcasing the current versatility of metallic glasses.

A low elastic modulus and a high strength-to-weight ratio are perfect for many types of sport equipment i.e. golf clubs, bicycle frames, tennis rackets, marine applications or skis and snowboards. Considering their application in golf clubs, and how the material affects the performance, as an example. The amorphous structure results in a great restitution coefficient, meaning that the hysteresis loss is negligible. Where common steel clubs lose roughly 40 % of the input energy during its transfer to the ball, metallic glass golf clubs lose only around 1 %. Therefore, the ball needs less input energy to travel the same distance [36].

Next, the easily formable, strong and light material finds use in the production of casings for mobile phones. The scratch resistant materials assure good protection of expensive phones and personal electronics whilst maintaining a desirable aesthetic due to their microstructure. The material allows the production of very thin casing, that retains necessary mechanical strength to withstand operational requirements [37].

Further, medical applications are of great importance and the integration of metallic glass components that are biocompatible and non-allergic are of significant commercial interest. Wear resistance with a high strength-to-weight ratio are ideal for the use as surgical instruments and prosthetic implants. The ability to form the material down to atomic level reduces the cost of post-processing significantly, obtaining the desired surface structure and form near net-shape easily [38].

Lastly, one could say sky is the limit when it comes to the wide possible range of applications for metallic glass, closing this section with an aerospace example. On NASA's space mission Genesis in 2004 to collect solar wind samples in space, the hexagonal collector tiles needed to withstand extreme operational conditions. Fulfilling the many physical and mechanical requirements, a zirconium based multicomponent metallic glass system was chosen to measure the composition of isotopes in solar matter [39].

### 2.4 OVERVIEW OF COMPUTATIONAL APPROACHES IN THE FIELD

Making use of computational methods and simulations, it is possible to learn more about thermotransport and thermodynamic properties that arise in the melt during solidification. With an increase of the use of atomic scale modelling and its importance in industrial and commercial communities, it is becoming increasingly important to be able to quantitatively predict diffusion behaviour, obtain reliable results, and accompany experimental studies. Theoretical and computational materials science supports the development in this area and leads the way to a more profound and useful understanding using advanced simulation techniques and theoretical approaches that
enable the research, development and production of new materials and their properties. The shown approaches give insight into material properties at microscopic scale, meanwhile studying macroscopic observations of computational controlled scenarios, avoiding limitations of real-life performed experiments. An overview of the latest computational approaches is given in the following sub-sections.

# 2.4.1 First-Principles Molecular Dynamics

The first-principles (FP) or also known as *ab-initio* molecular dynamics, is a form of the molecular dynamics family and was introduced by Car and Parrinello in 1985 [40]. Making use of statistical mechanics, it allows for the study of materials on an atomic level. It is implemented when knowledge of atomic structures is limited and statistical averages of the atomic trajectories dependent on time are needed to describe the thermodynamic evolution of the system as a function dependent on temperature. In conjunction with the density functional theory (DFT), the method emerged as a powerful tool to describe the interaction of atoms and electrons using quantum mechanics. This method is a great option for calculations of ground-state properties, because it scales reasonably with system size allowing for good accuracy of properties and feasible computational cost [41,42]. More about density functional theory will follow in the next section (Section 2.4.2).

In first-principles molecular dynamics (FPMD) [42,43], atomic nuclei are treated as classical particles, which is also the case for classical molecular dynamics. The difference to classical molecular dynamics is how forces acting on atoms are handled, FPMD considers them to be quantum mechanical. Meaning, that they originate from electronic-structure calculation. As a consequence of this assumption, quality of results differs, making only the electronic subsystem precise. This is due to large mass discrepancies between nuclei and electrons. Depending on the studied system, those nuclear quantum effects can become relevant. Elements such as Hydrogen, as a result of their very low mass, are affected by the previously mentioned effects in a much stronger manner. The *ab-initio* integral can then be used for the calculations, which unfortunately is a computationally expensive process.

Characterising the physical state of the system, the Lagrangian function is used, as shown in Eq. 11. This takes into consideration the ions of the system with respect to their coordinates  $R_i$ , as well as electrons, which are defined via a set of orbitals  $\psi_i(r)$  [42]:

$$\mathcal{L}_{CP} = \mu \sum_{i} \int \left| \dot{\psi}(r) \right|^{2} dr + \frac{1}{2} \sum_{I=1}^{N} M_{I} \dot{R}_{I}^{2} - E_{tot}[\{\psi_{i}\}; \{R\}] - \sum_{ij} \lambda_{ij} \left( \int \mu \psi_{i}^{*}(r) \psi_{j}(r) dr - \delta_{ij} \right) (11)$$

Therefore, the total energy of a system in FPMD,  $E_{tot}[\{\psi_i\}; \{R\}]$ , is based on the ionic and electronic variables. This approach of the total energy represents the potential energy in classical molecular dynamics simulations. As a consequence of degrees of freedom, its analytical form is inaccessible and requires the addition of further theories. A good example of this is the use of density functional theory (see Section 2.4.2) and its theoretical model to obtain total energy and insight on the properties of a system. The total kinetic energy is shown in the second part of Eq. 11 and depends on  $R_i$ . If considering only these two terms of the Langrangian, the method could be described as Born-Oppenheimer (BO) molecular dynamics. Here, for each set of ionic coordinates the electrons lay on the ground state of the Born-Oppenheimer surface and forces calculated accordingly. According to Massobrio et al. [42] this method, which is principally feasible, needs optimisation in form of electronic structure through convergence of the orbitals to their ground state value for each time step. As a result, the computational cost and time consumption rises significantly. This can be circumvented by introducing the CP Lagrangian as can be seen in Eq. 11, where the first term describes the kinetic energy measuring the departure of the orbitals from the BO surface. With the introduction of  $\mu$ , representing a fictitious mass, a dynamical character is attributed to electronic wave functions. This creates a way to correspond between the time evolution of trajectories and the concept of systems at equilibrium from a statistical mechanics perspective. This unification of statistical mechanics and electronic structure calculations makes the CP approach a state-of-the-art technique in the field of condensed matter.

# 2.4.2 Density Functional Theory

One rapidly developing approach is the already mentioned density functional theory, introduced by Hohenberg and Kohn [44] in 1964 and also by Kohn and Sham [45] in 1965. DFT is a numerical model from first principles. Most models apply broad assumptions, examining comparatively macroscopic statistical average of particle

thermodynamics. Here, DFT attempts to directly model at a level very close to the building blocks of all matter. Its application is very useful for the modelling of diverse materials in the field of materials science, engineering, physics and chemistry. The theory uses the quantum behaviour of atoms and molecules to model larger physical phenomena, such as diffusion kinetics. One could say the solution of the Schrödinger equation, is achieved through settings of practical value via the DFT approach. This description is an incredible step towards a fundamental understanding of the underlying meaning of the Schrödinger equation, relating to the theory of matter, describing our universe and its existence. A brief introduction to the technique and governing equations is discussed in this section.

Representing a many body problem, the interaction of N electrons in a system is investigated. The interactions take place between all electrons, as well as the atom nucleus. By making use of the exchange-correlation potential, these interactions are replaced by an approximate potential, acting on one single electron. For the description of the energy of molecules or atoms and how it changes when they are in motion, one needs to define the position of the nucleus and the electrons of atoms. As a result, fixed positions for atomic nuclei need to be solved with equations that describe the motion of electrons. According to the Hohenberg- Kohn theorem [44], the fundamental energy of a system is determined by a functional of the electronic density.

The Born-Oppenheimer approximation is then used, which reduces the degrees of freedom. Due to the big difference of the nuclei and electrons, their dynamics can be decoupled. Hence, it separates mathematical problems of nuclei and electrons in their ground state, the lowest energy state. In quantum mechanics, the wave function describes the quantum state of a set of particles in an isolated system. Here, the electronic wave function is now depending upon the nuclear positions, but not their velocities. Making use of the adiabatic potential energy surface of atoms function one can approach the question of how the energy changes once atoms are in motion. One way of dealing with this, is by utilising an approach of the Schrödinger description, shown in Eq. 12:

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}V(r_i) + \sum_{i=1}^{N}\sum_{j(12)$$

With *m* describing the mass of the electron. The first term inside the brackets define the kinetic energy for each electron, the second term the interaction energy between each electron and the collection of atomic nuclei and lastly the third term is the interaction energy between different electrons. In this case [46], the Hamiltonian was chosen with  $\psi$ , the electronic wave function, that represents a function of each of the spatial coordinates of each of the *N* electrons. Hence  $\psi = \psi(r_1, ..., r_N)$ , with *E* describing the lowest energy state of the electrons. Since the energy of the electrons ground state is independent of time, it represents the time-independent Schrödinger equation.

Further, the density of electrons at a certain position n(r) is closely related and is a function of three coordinates. The individual electron wave function can then be written as:

$$n(r) = 2\sum_{i} \psi_i^*(r) \psi_i(r)$$
(13)

In Eq. 13 all wave functions from individual electrons occupied by electrons are covered by the summation; meanwhile the part inside of the summation describes the energy of an electron in its individual wave function  $\psi_i(r)$  to be located at position r.

Application of the Hohenberg- Kohn theorem implies, that the ground-state properties of the system are determined by the electron density. Consequently, the total ground-state energy of a many-body system consisting of many electrons, is a unique functional of the electron density. Finally, to find the ground state electron density, the functional needs to be minimized. While the wave functions are related to the electronic density, when using the density function theory approach, they are used as a mathematical tool for determination of density. Kohn- Sham equations [45], a set of Schrödinger-like equations, address the reformulated problem statement for the electronic density. These are solved self-consistently with the average potential depending on the electronic density. The developed theory investigates the ground state properties and therefore, is not valid for electronic excitations. This leads to under-estimation of the electronic gap, and van der Waals interaction is not well defined.

This approach is a powerful tool to obtain insights into intrinsic properties of a wide range of important materials, and pursue further understanding of predictive

materials science, bridging the gap between simulation and experiments. This technique is widely used in advancing studies around the world and is bound to become even stronger due to its diversity. In conjunction with FPMD [42,43], this approach is advantageous for the prediction of materials behaviour and phenomena at atomic scale as it has been demonstrated by Massobrio *et al* in [42]. The quality and accuracy of this approach is excellent for predictive purposes to describe properties of even very complex materials.

# 2.4.3 Monte Carlo Simulations

The concept of Monte-Carlo (MC) simulations can be described as a type of risk analysis. This is performed via the creation of models of possible outcomes by substitution of a probability distribution for any uncertain factors. Then, it re-calculates new results based on computational algorithms, making use of a different set of random values of the probability functions. This mathematical approach gives a model of risk or uncertainty of a system and is often used to solve problems of optimisation, numerical integration, or different cases related to probability distributions. In the world of physics, the MC method simulates systems with multiple degrees of freedom, i.e. disordered materials, fluids, solids and cellular structures where particles of the system interact with each other. The mathematical technique evaluates multidimensional definite integrals with complex boundary conditions. In the field of engineering it is used to predict system failures.

For the evaluation of multivariable integrals in statistical physics, one of the originating problems of a system, is its unknown Hamiltonian, at a given temperature and following Boltzmann statistics. To compute a solution, one needs to obtain the mean value of macroscopic variables, i.e. A over a phase space PS. By making use of the Boltzmann distribution, the mean value of A is calculated by:

$$\langle A \rangle = \int_{PS} A_{\vec{r}} \frac{e^{-\beta E_{\vec{r}}}}{Z} d\vec{r}$$
(14)

Where  $E(\vec{r}) = E_{\vec{r}}$  describes the energy of the system for a state that is given by a vector  $\vec{r}$ , with all degrees of freedom and  $\beta \equiv 1/k_BT$ . Then for the partition function:

$$Z = \int_{PS} e^{-\beta E_{\vec{r}}} \, d\vec{r} \tag{15}$$

Solving this approach requires an exact enumeration of all possible configurations of the systems, to then calculate averages at will. This method is used in exactly solvable systems and simulations of simple systems with only few particles. In realistic systems those numbers are significantly higher, hence an exact enumeration is very challenging if not impossible to implement. This size limitation strongly influences the computation time, a more realistic system would become very expensive in computational costs, making most simulation infeasible.

However, approaches that make use of MC algorithms can still be worked with very efficiently to perform a variety of simulations. Therefore it is considered to be an effective tool to obtain insights into phenomena inaccessible through experiments, helping to close the gap between experiments and theory. A recent study used this method for the evaluation of self-diffusion in a triple-defect A-B binary system and to demonstrate the importance of atomic jumps to next-nearest neighbour vacancies [47].

#### 2.5 MOLECULAR DYNAMICS

The following section talks about the used approach in the scope of this thesis. It is placed as part of the literature review, to allow a more structured layout of the remaining thesis and its included publications. Therefore, the developed methodology to obtain the results and relations of this study is presented in detail in this section, building the groundwork of the computational approach. Further elaboration will follow in the different chapters according to their aims, where needed.

Diffusion dynamics and thermal transport phenomena have a major impact on the molecular structure of the melt as it solidifies, and hence play a major role in shaping the properties of the final material. Therefore, improved knowledge and control of these factors allow for better control of the properties of the final material, and hence paves the way for the design of highly specialised materials. This field has been an attractive research topic for a long time with molecular dynamics as one of the most important methods for a numerical investigation of thermotransport- and thermodynamic properties at atomic scale. With the molecular dynamics method it is possible to compute the material properties of a classical many-body system, making it a powerful method to support experimental work. The process of a simulation is actually very close to the setup of real world experiments, since the aim of a simulation model is always to reflect real world as close as possible. The experiment usually starts with the preparation of a material sample that gets connected to a measuring application. Then its properties are being measured over a certain time interval. For the simulation, a model system of a certain size is chosen. To investigate its properties computationally, Newton's equation of motion is applied until the system reaches equilibrium. Hence the properties will not change with time, then the measurement of the properties is carried out. The step of equilibration can be compared with the reduction of statistical noise of experimental results. Longer simulation times help to reduce error of fluctuations. Another crucial step to guarantee high quality simulations with reliable results is the correct preparation of all its inputs. Similar to experimental studies, it is important to prepare the sample or model system correctly, choose applicable potentials, ensembles, conditions, and the right theoretical treatment of the data. This allows for simulation to be a powerful tool that helps to explain and therefore to better understand a physical process providing a high level of information.

Modern technologies and industry extensively utilise the principles of materials science for appropriate material selection, processing route and treatment. To obtain desired material properties that depend on the microstructure, it is crucial to understand several phenomena, especially the ones of heat and material transport, which arise during solidification of alloys. Molecular dynamics are an effective tool to obtain insights into the structure at atomic scale.

# 2.5.1 Simulation Methodology

Molecular dynamics is a branch of computational methods commonly used to simulate diffusion based processes. The chosen methodology for molecular dynamics simulation of the Ni-Zr system in the scope of this thesis is very useful for the investigation of transport- and thermodynamic properties of binary melts. The embedded-atom method potential used was developed by Pun *et al* [48] and is successfully applied to a binary study of the Ni-Al system [14].

With the idea of obtaining an extensive picture of material properties during solidification of the Ni-Zr model system, a wide composition range is chosen, namely: Ni, Ni<sub>87.5</sub>Zr<sub>12.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub>, Ni<sub>37.5</sub>Zr<sub>62.5</sub>, Ni<sub>25</sub>Zr<sub>75</sub>, Ni<sub>12.5</sub>Zr<sub>87.5</sub>, and pure Zr. The thorough study of the two pure materials as well as seven compositions allows for evaluation of high accuracy composition dependencies of their properties. The studied temperature ranges from 2200 K down to 1200 K to ensure the capturing of significant diffusion dynamics in the melt during its solidification. By making use of the Verlet algorithm [49], the time evolution of the model system is calculated via numerical integration of Newton's equation of motion with a time step  $\Delta t = 1.5$  fs. The simulations are performed using the large-scale atomic/ molecular massively parallel simulator (LAMMPS) code [50]. Within a zero-momentum reference frame, the total momentum of the used model system is kept at a zero value, hence the velocity reference frame relatively fixed to the centre of mass of the system. Size of used simulation cell ranges for different models between 4000-4394 atoms using periodic boundary conditions. Models are initialised with liquid states in the NPT ensemble at a temperature of 4000 K and zero pressure for a period of 6 ns. Instigated in LAMMPS code, a Nosé-Hoover thermostat and barostat are included. Additional equilibration runs of the length of 6 ns are performed after switching MD models to the NVE ensemble.

After completion, renormalisation of velocities of atoms at next considered temperature of 3000 K followed by the same sequence of runs to equilibrate the model systems. After reaching 2200 K, the temperature step is decreased significantly down to 50 K to obtain thorough insight into the arising transport dynamics of the melts at different temperatures. The resulting cooling rate is approximately 4 K ns<sup>-1</sup>. At considered temperatures, the equilibrations go along with three consecutive production runs, each lasting 9 ns in the *NVE* ensembles. Achieving a high quality of results, the outcomes of these production runs are averaged. The in-depth simulation with a total number of time origins of  $1.8 \times 10^7$  is used to calculate the following: i) autocorrelation function of the interdiffusion flux and ii) mean-squared displacements of atoms of different species.

The here described simulation methodology talks about the fundamentals established and is followed by a further elaborated methodology that can be found at the start of the included publication and book chapter, Chapters 3 and 5 respectively.

Further understanding of theoretical background is closely related to the framework of the carried out studies, thus elaborated within their respective chapters of this work.

# 2.5.2 Thermodynamic Ensembles

The molecular dynamics method is used to study the time evolution of N-body of particles classical system in a volume, while its total energy remains constant. Due conservation of energy in a system, the microcanonical ensemble (NVE), is the most reliable. In it, the number of atoms N, volume of the system V and the total energy E, are fixed. Hence the quantities of pressure and temperature of the system fluctuate. The ensembles can easily be changed to find and calculate other quantities. With help of thermostats and barostats, the temperature and pressure can be set in different ensembles respectively, see simulation methodology in Chapter 3.

For representation of a mechanical system in thermal equilibrium with a constant temperature, the canonical ensemble (NVT) is used. Here, the number of particles N, volume V and temperature T are fixed. While it is not possible for matter, the energy of the system can transfer across boundaries between system and its surroundings. Lastly, the isothermal-isobaric ensemble (NPT), is given by a constant number of particles N, pressure p and temperature T. This statistical mechanical ensemble is essential when describing the Gibbs free energy of a system, due to its ability to represent the possible work of a system under the conditions of constant pressure and temperature. This approach models closely to real life experiments. Here, often those experiments are performed under constant pressure. Thus, if one aims to computationally calculate the composition effect of a solvent and properties of the system, the volume in the NVT ensemble needs to be attuned to ensure a remaining constant pressure. In this case a change of the ensemble makes more sense in a way, where the pressure is fixed and finally the volume is considered a dynamical variable.

Within the simulation method used to obtain results on the binary Ni-Zr model system, the use of the different statistical mechanical ensembles *NPT* and *NVE* is necessary to obtain insights into transport and thermodynamic kinetics in the melt. The included investigations in Chapters 3 and 5 elaborate on the importance and necessity of the switches between ensembles.

## 2.5.3 Boundary Conditions

The model system in MD simulation is structured as a simulation cell, consisting of thousands of atoms. Due to limitations of the molecular dynamics technique, one can use periodic boundary conditions to counteract problems with boundary effects that arise owing the finite size of the simulation cell. Symmetry planes are used to account for the finite nature of the simulated control volume and to decrease computational expense. Hence, a central cell is used, periodic images of itself that surround the central cell in x-y-z directions copy the movement of particles of the original cell as can be seen in Figure 3. When a particle moves outside of the central cell, it re-enters again on its opposite side. This method preserves the number density of atoms as well as the momentum of the system. This procedure is repeated to simulate the evolution of the system without influence of external surfaces, providing correct measurements of bulk properties. Periodic boundary conditions are essential to keep computational cost reasonably low, allowing the simulation of a few hundred atoms to imitate the behaviour of a simulation of infinite size removing surface effects. Therefore the simulated behaviour of the internal structure will not be affected by wall effects.



Figure 3 Periodic boundary conditions for the main simulation cube

# 2.5.4 Limitations of Molecular Dynamics

Every simulation method comes with their own advantages and limitations. The molecular dynamics method is mainly affected by time, size and temperature limitations. In particular:

- a) The tendency of a system to slow down around phase transitions affects the simulation time. It should therefore be longer than the relaxation time of the quantities. This happens usually within 1 μs and is the most common limitation [51]. For numerical stability of the simulation a short time step is required.
- b) Increasing or diverging correlation lengths around phase transitions may alter simulation results when the size of the simulation cell becomes equivalent. Length scales should therefore be within the range of 1 nm to 1  $\mu$ m [52].
- c) To apply the classical description of atomic dynamics, the simulation temperature should be above the critical temperature of the system. This way, quantum effects become important in any system at low temperatures, hence a wide temperature range can be considered [51].

# 2.5.5 Embedded-Atom Method

To describe the energy between atoms, Daw and Baskes introduced a semiempirical approach in 1984, the so called embedded- atom method (EAM) [53]. In this method, which is widely used in MD, each atom embeds in a host lattice, generally describing atomic bonding in a metallic system. The approximation depends not only on the separation between pairs of atoms, but also how neighbouring atoms are located around each other, thus their atomic environment. It defines the energy between atoms as an interatomic potential as shown in Eq. 16.

$$e_{i} = \frac{1}{2} m_{i} v_{i}^{2} + F_{\mu_{i}}(\bar{\rho}_{i}) + \frac{1}{2} \sum_{j(\neq i)} V_{\mu_{i}\mu_{j}}(r_{ij})$$
(16)

Where

$$\bar{\rho}_i = \sum_{j(\neq i)} \rho_{\mu_j} \left( r_{ij} \right) \tag{17}$$

The total energy of an atom *i* is dependent on the mass of the atom given by  $m_i$ , absolute value of the velocity vector v,  $F_{\mu_i}$  the embedding energy of the atom as a function of the host electron density  $\overline{\rho}_i$  induced at site *i* by all other atoms in the system. Finally,  $V_{\mu_i\mu_j}$ , represents the pair interaction potential as a function of distance  $r_{ij}$  between atoms *i* and *j*. Its relation to the second moment approximation to the Finnis-Sinclair model [54] and is highly accurate for simulation of metallic systems, makes this method a widely used technique for MD simulations.

# 2.5.6 Green-Kubo Formalism

The heat of transport in equilibrium MD simulations can be expressed as an integral of the time correlation function between the matter flux and the heat flux. This expression is commonly known as the Green-Kubo formulae, and is an effective tool to obtain the thermal conductivity and phonon transport properties of a material [55-59].

The Green-Kubo method gives the thermal conductivity k in terms of the time integral of the heat current auto-correlation function (HCACF),  $\langle J(t)J(0) \rangle$  as:

$$k = \frac{1}{{}_{3Vk_BT^2}} \int_0^\infty \langle J(t)J(0) \rangle dt,$$
 (18)

Where V gives the simulation cells volume,  $k_B$  the Boltzmann constant, T the absolute temperature, J the heat current vector and t the time. The heat current vector is generally described as follows:

$$J = \frac{d}{dt} (\sum_{i} e_{i} r_{i}) = \sum_{i} e_{i} v_{i} + \sum_{i} r_{i} \frac{de_{i}}{dt},$$
(19)

Where summations cover the atoms in the system with  $e_i$ ,  $r_i$  and  $v_i$  representing respectively total energy, radius vector and the velocity vector of the *i*-th atom. The first summand on the right side of the equation takes into consideration the convection, the second summand the conduction. While this method has no effect on the atomic dynamics, the temperature of the system is uniform and constant. Thus allowing for calculation of the temperature dependence of the thermal conductivity k.

# 2.5.7 Function

Overall, the shown computational approach of molecular dynamics is capable to access thermotransport and thermodynamic properties of the material at atomistic level. The developed methodology using atomistic modelling and statistical mechanics, allows to establish a relationship between the microstructure and diffusion properties and hence, create principles for atomic-scale engineering. The outcome of the simulations can be used to gain control of the design of mechanical properties of materials, for instance metallic glass. Obtained results build the foundation for future research in this field and can help to reduce time and cost for the development and production of new advanced materials.

# 2.6 SUMMARY AND IMPLICATIONS

The previously covered topics of the concept of diffusion, the fundamentals of enthalpy, metallic glass, computational approaches in the field and the molecular dynamics simulation method, build the foundation of this research. These topics were described to familiarise the reader with principle concepts this research is based on. An in-depth exploration of each relevant topic is included in the following chapters, which divide the subject of the study further in form of binary melts with different types of atomic ordering. In the framework of molecular dynamics simulation in conjunction with a semi-empirical many-body interatomic potential, the developed approach uses molecular dynamics calculations, atomistic modelling, and statistical mechanics. The statistical part is based on the Green-Kubo formalism, a generalisation of the Langevin Equations and the Mori-Zwanzig formalism. In addition, new theoretical relations for the fluctuation-dissipation theorem for collective energy were established and further advanced. The importance of gaining a better understanding of diffusion, thermotransport and thermodynamic properties on Ni-Zr melts and other case studies, like the systems of Ni-Al and Cu-Ag, lies in their wide range of applications. While materials of the studied alloys are already being used in sports equipment [36], aerospace applications [39,60] or micro-forming applications [61], general technological interest is very high due to their versatility and excellent material properties [62].

For the design of metallic glass materials with desired properties, it is crucial to understand dynamics in the melt during solidification that directly affect the microstructure and therefore the properties of a material. Laboratories perform experiments to study microscopic behaviour to learn more about the solidification of alloys. After thorough analysis of literature, it was found that the existing experimental research lacks results in certain fields of diffusion, thermotransport and thermodynamics properties due to external factors that reduce the reliability of their quality or simply make experiments physically impossible to perform. Measuring accurate transport and thermodynamic properties of liquid alloys in experimental studies is heavily affected by chemical reactivity, high temperatures or crystallisation of the melt in contact with the container walls. For instance, especially in the case of Ni-Zr alloys in experiments, the high reactivity of the melt with the container interferes with the outcome of the study, decreasing the reliability of results. New ways to perform studies reducing occurring limitations are constantly being worked on and developed, i.e. the method of processing the melt without the use of a container using electrostatic levitation [63]. This methodology allows the study of atomic dynamics in the melts by quasielastic neutron scattering at the time of flight [7]. However by reducing the limitations, experiments often spike up in terms of their costs and time consumption.

Aiming to push research further and support experimental studies, the approach using molecular dynamic simulation carried out in this thesis, is a powerful tool to obtain insights into solidification processes that arise in the melt at atomic level. It is important to mention that currently, approaches using phase-field modelling are based on the limited existing experimental data for transport and thermodynamic properties, but are crucial for prediction of material properties. This method allows for a reliable way of producing results that can be used to verify the scarce experimental data. Additionally, outcome of simulation projects like the included case studies, can be used to determine quantitative outcomes for experiments. They play a major role in the decision making process of experiments with the opportunity of reducing their cost and time. This will help with the correct choice of processing routes and also to improve quality of alloys in solid state. This allows for more extensive research in the design of new materials on the basis of a strong understanding of microscopic phenomena at atomic scale, while using a method free of the existing experimental limitations.

For this matter, focus lies on the evaluation of various diffusion properties by making use of the Onsager coefficient for mass transport within the framework of the Mori-Zwanzig formalism of statistical mechanics. diffusion properties include but are not limited to i) self-diffusion coefficients,  $D_{1,2}$ , based on the mean-squared displacement of atoms of different species and ii) the kinetic part of interdiffusion,  $\tilde{L}_{CC}$ , based on the interdiffusion flux,  $J_{C}$ . While establishing new relations expressing microscopic cross-correlation effects in the kinetics of collective diffusion, the quality and precision of results obtained is crucial. In terms of the diffusion coefficient for example, if the value only varies by a few times, or simply not considering its temperature and composition dependence, will lead to a significant change in quality of prediction for the microstructure [64]. Advanced focus then is placed on establishing theoretical relations on thermotransport properties. Those basically describe the tendency of segregation of a system of a minimum of two components under a temperature gradient, also known as the Soret effect, ultimately changing the viscosity dependent on the temperature gradient. In case of solidification, thermotransport affects the structure and composition of the solidification front of the alloy.

# 2.7 OBJECTIVES

The aim of this research is to elucidate material properties of diffusion, thermotransport and thermodynamics in binary melts of Ni-Zr. Furthermore, the melts of Ni-Al and Cu-Ag are analysed and their diffusion dynamics evaluated. Results group the different melt systems into melts with different types of atomic ordering. By making use of computational methodology, the obtained results and established relations help, to close the existing knowledge gap related to mass- and thermal transport phenomena. To fill this gap, detailed insights into the following must be obtained, and is addressed separately in Chapter 6:

- Self-diffusion coefficients
- Interdiffusion coefficients
- Decoupling behaviours
- Correction factor
- Time-correlation functions
- Enthalpy
- Collective energy generation-dissipation effect

The diffusion coefficients in liquid alloys are a major factor for the control of the crystalline microstructure during solidification and are crucial input parameters in phase field modelling [65,66]. Developing theoretical relation between the different mass transport coefficients enables quantitative prediction of material properties. This allows to express unknown coefficients in terms of other, during experiments reliably measurable coefficients [67]. In studied many-body systems, transport and dynamical properties are expressed via time-correlation functions of physical variables. A one-sided Fourier transformation can be used to express the frequency dependent thermal conductivity and diffusion coefficients in terms of the time-correlation functions of heat and mass currents. The control of transport and dynamical properties of many-body systems is a crucial step towards closing the existing gap via modelling and analysis of the time correlation functions. This is addressed with the developed approach using concepts of the Brownian motion [59,68], the discussed collective energy fluctuation- dissipation theorem [59,68], Langevin equation [59,68], as well as the Mori-Zwanzig formalism [69-72].

Additionally, this computational approach aims to eliminate limitations that occur in experimental approaches, as previously discussed in Section 2.6, and can influence the decision making process for future experiments, processing and manufacturing routes. The identification of a composition range with desired diffusion dynamics via the developed simulation technique, will drastically reduce time and costs of experiments, by determining the best alloy to fulfil given requirements for a certain application. The molecular dynamics methodology developed, is an excellent tool to support experimental studies in the field. Opportunities are countless, hence the additional study of a number of different model systems with the idea, to also investigate cross-system behaviours. The considered case studies, namely Ni-Zr [10], Ni-Al [14] and Cu-Ag [16], where chosen due to a variety of reasons. They are of high technological importance in the world of engineering, which relates to their peculiar atomistic behaviours in terms of crystallisation, diffusion and heat transfer properties. Indicating different types of behaviours, the different melts can be grouped into binary liquid alloys with i) mixing tendency and ii) demixing tendency. Novel insights are obtained and discussed for the different type of melts in Chapter 5.

This work elaborates further on following topics:

- Establishing theoretical relations
- Single-particle and collective diffusion dynamics
- Thermotransport properties
- Thermodynamic properties
- Stability of different types of melt

These topics are studied in-depth in the following chapters, novel theoretical treatment is derived and established. Dependencies between material properties, dynamics in the melt and the microstructure are shown. Concluding a state-of-the-art approach and creating an innovative database on material properties. Predictions based on obtained results are given in this work.

# Chapter 3: Diffusion in Ni-Zr Melts: Insights from Statistical Mechanics and Atomistic Modeling

# 3.1 INTRODUCTION

This chapter introduces the simulation method used to obtain insights into diffusion properties of Ni-Zr melts over a wide composition and temperature range. Delivering thermotransport properties, describing single-particle and collective diffusion, a self-sufficient database is generated. A statistical mechanical approach is used to study cross-correlation between the interdiffusion flux,  $J_c(0)$ , and the force,  $R_{12}(t)$ , that results of atoms of different species and their difference in their average random accelerations in the short time limit  $t \rightarrow 0$ . The lack of available experimental results points out the importance of the theoretical approach developed. This is a consequence of various difficulties that occur when performing experiments as previously shown in Chapter 2. The high accuracy of calculations achieved via this study helps predict outcomes of expensive or even impossible to perform experiments.

The temperature range 2200 K to 1200 K is investigated and results for the two self-diffusion coefficients of Nickel and Zirconium,  $D_{Ni}$  and  $D_{Zr}$  respectively, obtained. The simulation method in the framework of the molecular dynamics method in conjunction with a semi-empirical many-body potential gives results in good agreement with results available through experiments. Additionally, by making use of the Green-Kubo formalism, the kinetic part of interdiffusion,  $\tilde{L}_{CC}$ , is calculated using the Onsager Coefficient for mass transport,  $L_{CC}$ , via the time integral of the autocorrelation function of the interdiffusion flux,  $C_{CC}(t)$ , describing collective diffusion. More detailed derivation of the methodology including visualisation for several composition and temperatures is shown in the publications supporting material section after the reference list. Going forward with the diffusion properties and the Mori-Zwanzig formalism, an expression for cross-correlation effects in the kinetics of collective diffusion is developed. Furthermore, initial behaviour of the binary Ni-Zr melt with tendency for chemical ordering is examined and new theoretical relations

introduced, that help to describe the relative change of stability of atomic ordering of the system upon undercooling. This is particularly important for a better understanding of the response of the system and its initial reaction in short time limit  $t \rightarrow 0$  when pushed out of equilibrium.

This chapter provides new understandings on diffusion properties of binary Ni-Zr melts, investigating single-particle and collective diffusion dynamics and their contribution into the glass-forming ability of an alloy with atomic ordering. Furthermore, the correlation of  $J_c(0)$  and  $R_{12}(t)$  is found to develop over time. Hence, the initial sign of  $P_{12}(t)$ , is depending on the novel dimensionless factor,  $\sigma_{12}$ . The new findings, as well as theoretical understanding of diffusion dynamics in the melt, result in identification of the composition range  $0.25 \leq c_{Ni} \leq 0.5$  exhibiting dynamical homogeneous slowdown of single-particle and collective diffusion dynamics in the melt. Suggesting that this dynamical behaviour indicates better stability of the melt against its crystallisation upon undercooling, ultimately emerging enhanced glassforming ability within this composition range.

# **3.2 PUBLICATION**

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The statement of co-authorship can be found in Appendix A.

Diffusion

# Diffusion in Ni–Zr Melts: Insights from Statistical Mechanics and Atomistic Modeling

Andreas Kromik, Elena V. Levchenko, Carlo Massobrio, and Alexander V. Evteev\*

An accurate database of diffusion properties of Ni-Zr melts is generated within the framework of the molecular-dynamics method in conjunction with a semi-empirical many-body interatomic potential. The reliability of the model description of Ni-Zr melts is confirmed via comparison of the simulation results with the existing experimental data on diffusion properties of Ni-Zr melts. A statistical mechanical formalism is employed to understand the behavior of the cross-correlation between the interdiffusion flux and the force caused by the difference in the average random accelerations of atoms of different species in the short time limit  $t \rightarrow 0$ . This theoretical description is exploited to analyze the simulation data on the diffusion properties of Ni-Zr melts. On this basis, it is found that in the composition range  $0.25 \lesssim c_{\text{Ni}} \lesssim 0.5$ both single-particle and collective diffusion dynamics slow down homogeneously upon undercooling of Ni-Zr melts. Furthermore, it is inferred that such homogeneous dynamical slowdown is related to the enhanced stability of undercooled melt against crystallization. As a consequence, Ni-Zr alloys within this composition range are identified as viable glass formers.

#### 1. Introduction

Binary Ni–Zr alloys have attracted great interest as reference systems for understanding the properties of an important class of multicomponent Zr-based bulk metallic glasses (BMGs).<sup>[1–11]</sup> The BMGs are typically produced by melt processing and their excellent glass-forming ability is strongly determined by peculiarities of atomic dynamics in the liquid state.<sup>[12,13]</sup> In this context, it was previously noted that the Ni self-diffusion coefficients measured by quasi-elastic neutron scattering in binary glass-forming Ni<sub>36</sub>Zr<sub>64</sub>, Ni<sub>50</sub>Zr<sub>50</sub>, and Ni<sub>64</sub>Zr<sub>36</sub> liquid alloys are well comparable to those measured in the multicomponent Zr-based metallic glass-forming melts.<sup>[4,5,7]</sup> Although glass-forming abilities and

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liquidus temperatures for the binary and multicomponent alloys exhibit relatively large differences, the absolute values of the Ni self-diffusion coefficients were found to be similar at the same temperature.

Furthermore, theoretical analysis<sup>[11]</sup> of simultaneous radiotracer diffusion measurements of <sup>57</sup>Co (which is conveniently used to assess Ni diffusion) and 95 Zr in the binary Ni<sub>36</sub>Zr<sub>64</sub> melt<sup>[10]</sup> as well as in a Zr-based multicomponent Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> glass-forming melt<sup>[8]</sup> revealed additional indication of similar diffusion behavior in the alloys by including into consideration the Zr self-diffusion coefficients. In particular, in refs. [10,11], it was recognized that a significant component decoupling (with the ratio of Ni and Zr self-diffusion coefficients as large as four,  $D_{\rm Ni}/D_{\rm Zr} \approx 4$ ) observed in Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> melt near its liquidus temperature of 1050 K is in

accordance with the ratio  $D_{\rm Ni}/D_{\rm Zr}\approx 1$  observed in  $\rm Ni_{36}Zr_{64}$  melt above its liquidus temperature of 1283 K. Indeed, the ratio  $D_{\rm Ni}/D_{\rm Zr}$  decreases to a factor of less than two when the self-diffusion coefficients of Ni and Zr in  $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$  glass-forming melt are extrapolated above 1200 K according to the Arrhenius law. Moreover, a small but notable composition dependence of the ratio  $D_{\rm Ni}/D_{\rm Zr}$  was determined, this ratio increasing with increasing Ni content from  $Ni_{36}Zr_{64}$  toward  $Ni_{64}Zr_{36}$  melt composition. $^{[10,11]}$ 

These findings indicate that the strong chemical short-range order in the binary Ni–Zr and multicomponent Zr-based melts can cause a dynamical decoupling of the self-diffusion coefficients of the components, which is expected to become stronger with decreasing temperature.<sup>[8,10,11]</sup> It was suggested that such a dynamical behavior might be due to a saturation effect among Ni–Zr nearest-neighbor pairs and an increased amount of less strongly interacting Ni–Ni pairs toward Ni-rich compositions.<sup>[11]</sup> As a result, the binary Ni–Zr melts are currently recognized as realistic model systems for understanding microscopic dynamics of the multicomponent Zr-based bulk metallic glass formers.<sup>[10,11]</sup>

Given the above premises, we study in this contribution, the diffusion properties of Ni–Zr melts by using molecular dynamics (MD) implemented with a semi-empirical many-body interatomic potential developed in ref. [14]. This interatomic potential is based on accurate potential functions for pure Zr and pure Ni,<sup>[15,16]</sup> previously developed within the framework of the embedded atom method (EAM) formalism.<sup>[17]</sup> In this potential, two additional cross-interaction functions are constructed within the framework of the Finnis-Sinclair formalism<sup>[18]</sup> by seeking the best agreement with ab initio and experimental data for crystal and liquid phases of two stoichiometric NiZr<sub>2</sub> and NiZr alloys.<sup>[14]</sup> In particular, it is important to note that the interatomic potential is able to correctly reproduce experimental data on the enthalpies of mixing (formation) of the NiZr<sub>2</sub> and NiZr liquid alloys as well as on the stability and melting temperatures of the C16-NiZr<sub>2</sub> and B33-NiZr crystal phases.<sup>[14]</sup> Tabulated forms of the potential functions entering the interatomic potential employed in our work are available for download from http://www.ctcms.nist.gov/potentials/.<sup>[14]</sup> Our choice of adopting interatomic potentials within a classical MD framework is mostly due to the requirement of extended temporal trajectories underlying the proper evaluation of diffusion properties. We remind that first-principles MD has also been employed to model metallic liquid alloys.<sup>[19]</sup> The diffusion properties of the MD models of Ni–Zr melts, which are considered in the present work, include the selfdiffusion coefficients of Ni and Zr atoms,  $D_{Ni}$  and  $D_{Zr}$ , as well as the Onsager coefficient for mass transport,  $\tilde{L}_{cc}$ , which characterizes the kinetics of collective diffusion under a composition gradient. We present an extensive and self-consistent database of these diffusion properties generated over a wide temperature and composition ranges for the MD models of Ni–Zr melts. This allows achieving a comprehensive understanding of the atomic dynamics in such systems.

This article is organized as follows. In Section 2, we describe our simulation methodology. In Section 3, we discuss theoretical relations between diffusion properties of a binary melt. We present equations expressing the diffusion properties in terms of the time-correlation functions of appropriate physical variables within the framework of the Green-Kubo and Mori-Zwanzig formalisms. We derive the explicit expression for the crosscorrelation function between the interdiffusion flux and the force caused by the difference in the average random accelerations of atoms of different species in the short time limit. In Section 4, we report our MD results for the diffusion properties of Ni–Zr melts. Analyzing these data on the basis of theoretical relations of Section 3, we are able to establish a link between temperature and composition dependencies of the diffusion properties of Ni-Zr melts and their glass-forming ability. In Section 5, we formulate conclusions.

# 2. Simulation Methodology

The methodology of MD simulations, which we advance in this work for Ni–Zr melts, is in general very promising for systematic studies of thermodynamic and transport properties of binary melts. In particular, it is also proved to be successful for the MD models of Ni–Al melts<sup>[20]</sup> with the EAM potential developed in ref. [21]. Specifically, we consider nine compositions across the binary Ni–Zr system: pure Ni, Ni<sub>87.5</sub>Zr<sub>12.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub>, Ni<sub>37.5</sub>Zr<sub>62.5</sub>, Ni<sub>25</sub>Zr<sub>75</sub>, Ni<sub>12.5</sub>Zr<sub>87.5</sub>, and pure Zr. The diffusion properties of the models of Ni–Zr melts are studied over a wide temperature range 2200–1200 K.

The MD simulations were performed with the LAMMPS code<sup>[22]</sup> using the Verlet algorithm<sup>[23]</sup> for numerical integration of the equations of motion with a time step  $\Delta t = 1.5$  fs. The total momentum of the model systems was conserved at a zero value,

ensuring a velocity reference frame fixed relative to the center of mass of the system (the zero-momentum reference frame). The initial liquid states of the models were equilibrated in cubic simulation cells of about 4000 atoms (for different models the number of atoms varies slightly within the range 4000-4394) with periodic boundary conditions in all three directions using NPT ensemble dynamics at the temperature 4000 K and zero pressure, P = 0, for 6 ns. We adopted a Nosé–Hoover thermostat and a Nosé-Hoover barostat as implemented in the LAMMPS code.<sup>[22]</sup> Then, the studied MD models were switched to the NVE ensemble and additional equilibration runs of length 6 ns were performed. After this, the velocities of the atoms were renormalized to the next considered temperature 3000 K and the same sequence of runs (a 6 ns NPT run followed by a 6 ns NVE run) were employed to bring the systems to equilibrium. Starting from 2200 K, this procedure was implemented at each new temperature by cooling down the systems with a temperature step of 50 K. Accordingly, the average cooling rate below 2200 K can be estimated to be about 4 K  $ns^{-1}$ .

The equilibrations at the considered temperatures were followed by three successive production runs lasting 9 ns each in the *NVE* ensembles. The reported results were averaged over these three production runs. The total number of time origins (about 1.8 × 10<sup>7</sup>) were used for calculations of: (i) the autocorrelation function of the interdiffusion flux  $J_c(t)$ ,  $C_{cc}(t) = \langle J_c(t)J_c(0) \rangle$ , and (ii) the mean-squared displacements,  $\langle \Delta \mathbf{r}_1^2(t) \rangle$  and  $\langle \Delta \mathbf{r}_2^2(t) \rangle$ , of Ni (species 1) and Zr (species 2) atoms (*t* is the time and  $\langle \cdots \rangle$  means the statistical time average at thermal equilibrium). Throughout the article, we assume that Ni is species 1 while Zr is species 2.

# 3. Theoretical Background

The self-diffusion coefficients of Ni and Zr atoms were calculated according to the well-known Einstein relation,  $^{\left[24\right]}$  as

$$D_{\alpha} = \lim_{t \to \infty} \frac{\overline{\langle \Delta \mathbf{r}_{\alpha}^{2}(t) \rangle}}{6t} \tag{1}$$

where the mean-squared displacements of Ni and Zr atoms are given by

$$\overline{\Delta \mathbf{r}_{\alpha}^{2}(t)} = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \Delta \mathbf{r}_{\alpha i}^{2}(t)$$
<sup>(2)</sup>

with  $\Delta \mathbf{r}_{\alpha i}(t) = \mathbf{r}_{\alpha i}(t) - \mathbf{r}_{\alpha i}(0)$  representing the timedisplacement of a single atom of species  $\alpha$  and  $N_{\alpha}$  denoting the number of atoms of species  $\alpha$  ( $\alpha = 1, 2$ ) in the considered model system.

In order to analyze the collective diffusion process in the models of Ni–Zr melts, we consider the interdiffusion flux  $J_c$  which can be calculated in a binary melt as

$$J_{c}(t) = \frac{N}{V} c_{1} c_{2} \left( \mathbf{v}_{1}(t) - \mathbf{v}_{2}(t) \right) = c_{2} J_{1}(t) - c_{1} J_{2}(t)$$
(3)

where  $N = N_1 + N_2$  is the total number of atoms in the system volume *V*,  $c_{\alpha} = N_{\alpha}/N$  ( $c_1 + c_2 = 1$ ) is the atomic (mole)

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fraction of species  $\alpha$ ,  $\mathbf{v}_{\alpha}(t)$  is the mean velocity of species  $\alpha$  relative to the center of mass of the system, and  $J_{\alpha}(t) = \frac{N}{\nabla}c_{\alpha}\mathbf{v}_{\alpha}(t)$  is the flux of species  $\alpha$  in a velocity reference frame fixed relative to the center of mass of the system. Since the velocities of both species are referred to the center of mass of the system, the fluxes  $J_1(t)$  and  $J_2(t)$  are not independent and a linear relation exists between the fluxes which in the zero-momentum reference frame is  $m_1 J_1(t) + m_2 J_2(t) = 0$ , where  $m_{\alpha}$  is the mass of atoms of species  $\alpha$ . Thus in a binary melt there exists only one independent matter flux

$$J_{c}(t) = \frac{m}{m_{2}} J_{1}(t) = -\frac{m}{m_{1}} J_{2}(t) = \frac{m}{m_{2} V} \sum_{i=1}^{N_{1}} \boldsymbol{v}_{1i}(t)$$
$$= -\frac{m}{m_{1} V} \sum_{i=1}^{N_{2}} \boldsymbol{v}_{2i}(t)$$
(4)

where  $m = c_1 m_1 + c_2 m_2$  is the total mass per atom of the system, while  $\mathbf{v}_{\alpha i}(t)$  denotes the velocity of a single atom of species  $\alpha$ . The invariance of the interdiffusion flux with respect to the choice of reference frame arises from the fact that it describes the fluxes of components  $J_1(t)$  and  $J_2(t)$  relative to each other. Furthermore, the fluctuation of an atomic velocity,  $\mathbf{v}_{\alpha i}(t)$ , in thermal equilibrium is a stationary Gaussian process with the mean velocity equal to zero,  $\langle \mathbf{v}_{\alpha i} \rangle \equiv \langle \mathbf{v}_{\alpha i}(t) \rangle = 0$ , and the thermal velocity given by the Maxwell-Boltzmann distribution as  $\langle \mathbf{v}_{\alpha i}^2 \rangle = 3k_{\rm B}T/m_{\alpha}$  (where *T* is the temperature and  $k_{\rm B}$  is the Boltzmann constant). Then, it follows that the fluctuation of the interdiffusion flux given by Equations (3) and (4) in the form of the linear combination of the atomic velocities is also a stationary Gaussian process with  $\langle \mathbf{J}_c \rangle \equiv \langle \mathbf{J}_c(t) \rangle = 0$  and the effective thermal velocity given by [<sup>25,26</sup>]

$$V^2 \langle \boldsymbol{J}_c^2 \rangle = 3 N c_1 c_2 \frac{k_{\rm B} T}{m_{\rm c}}$$
<sup>(5)</sup>

where  $m_c = m_1 m_2/m$  is the effective mass (per atom) carried by the interdiffusion flux as it follows from Equation (4). It is also important to note that the fluctuations of the interdiffusion flux are characterized by  $3Nc_1c_2$  degrees of freedom as it can be seen from Equation (3).

Using the Onsager formalism of the thermodynamics of irreversible processes,<sup>[27,28]</sup> it can be generally shown that for an isotropic binary melt the phenomenological coefficient for mass transport,  $L_{cc}$  (or its renormalized counterpart  $\tilde{L}_{cc}$ ),<sup>[29]</sup> which links the interdiffusion flux to the conjugate thermodynamic force, is related to the ratio of the interdiffusion coefficient,  $D_c$ , and the thermodynamic factor,  $\Phi$ , as

$$\tilde{L}_{cc} = \frac{Vk_{\rm B}T}{Nc_1c_2}L_{cc} = \frac{D_c}{\Phi}$$
(6)

Both  $D_c$  and  $\Phi$  are in principle accessible in experiment. We note that the thermodynamic factor,  $\Phi$ , is related to the second derivative of the molar Gibbs free energy G/N with respect to the composition at constant temperature *T* and pressure *P*, as

$$\Phi = \frac{c_1 c_2}{k_{\rm B} T} \left( \frac{\partial^2 G/N}{\partial c_{\alpha}^2} \right)_{T,P} = \frac{c_{\alpha}}{k_{\rm B} T} \left( \frac{\partial \mu_{\alpha}}{\partial c_{\alpha}} \right)_{T,P}$$
(7)

where  $\mu_{\alpha}$  denotes the chemical potential of species  $\alpha$ . Therefore, incorporating the driving force for chemical diffusion due to the difference in the chemical potential, the interdiffusion coefficient characterizes collective mass transport in a binary system under a composition gradient. In MD simulations, the Onsager coefficient for mass transport,  $L_{cc}$ , can be conveniently evaluated within the framework of the Green–Kubo formalism via the time integral of the autocorrelation function of the interdiffusion flux,  $C_{cc}(t)$ ,<sup>[20,25,26,29–37]</sup> as

$$L_{cc} = \frac{V}{3k_{\rm B}T} \lim_{t \to \infty} \int_{0}^{t} C_{cc} \left(t'\right) dt'$$
(8)

Taking into account Equations (5) and (6), Equation (8) can be rewritten for  $\tilde{L}_{cc}$ , as

$$\tilde{L}_{cc} = \frac{k_{\rm B}T}{m_c} \lim_{t \to \infty} \int_0^t \varepsilon_c \left(t'\right) dt' \tag{9}$$

where  $\varepsilon_c(t) = \langle J_c(t) J_c(0) \rangle / \langle J_c^2 \rangle = m_c V^2 C_{cc}(t) / 3 N c_1 c_2 k_B T$  $(C_{cc}(0) = \langle J_c^2 \rangle, \ \varepsilon_c(0) = 1)$  is the normalized autocorrelation function of the interdiffusion flux.

Moreover, it can be shown<sup>[26]</sup> that in a binary melt there exists a relation between  $D_1$ ,  $D_2$ , and  $\tilde{L}_{cc}$  which can be presented in the form of the so-called Darken–Manning equation,<sup>[38]</sup> as

$$\tilde{L}_{cc} = \frac{D_c}{\Phi} = S(c_2 D_1 + c_1 D_2)$$
(10)

This equation was originally introduced in 1948 by Darken to describe data on interdiffusion in a binary crystal coupled via the vacancy mechanism primarily on the basis of macroscopic arguments which resulted in an oversight of the factor S.<sup>[39]</sup> Later, in 1961, Manning put forward an extension of the Darken equation, in the general context of chemical diffusion in crystals, ingeniously demonstrating that a certain correction factor of the microscopic kinetic origin, *S*, must be included into the equation.<sup>[40]</sup>

Recently, an analytical expression for the Onsager coefficient for mass transport and two self-diffusion coefficients of species in a binary melt has been derived<sup>[26]</sup> within the framework of the Mori–Zwanzig formalism of statistical mechanics,<sup>[34,41–44]</sup> using the generalized Langevin equations for the atomic velocities and the interdiffusion flux. The derived expression accounts for the manifestation of microscopic (dynamic) cross-correlation effects in the kinetics of collective diffusion in the form

$$S = \frac{\tilde{L}_{cc}}{c_2 D_1 + c_1 D_2} = S_0 \left( 1 + \frac{W_{12}}{k_B T} \right)$$
(11)

where the kinetic factor  $S_0$  (0 <  $S_0 \le 1$ ) is given by

$$S_0 = \frac{m^2 D_1 D_2}{m^2 D_1 D_2 + c_1 c_2 (m_1 D_1 - m_2 D_2)^2}$$
(12)

while

$$W_{12} = \int_{0}^{\infty} P_{12}(t)dt$$
 (13)

is related to a collective energy generation–dissipation effect due to the correlations between fluctuations of the interdiffusion flux and the force,  $\mathbf{R}_{12}(t)$ , caused by the difference in the average random accelerations of atoms of different species, as given by

$$P_{12}(t) = \frac{V}{3 N c_1 c_2} \langle \boldsymbol{R}_{12}(t) \boldsymbol{J}_c(0) \rangle$$
(14)

Accordingly, this force can be expressed as

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$$R_{12}(t) = Nc_1 c_2 m_c \left( \frac{\bar{R}_1(t)}{m_1} - \frac{\bar{R}_2(t)}{m_2} \right)$$
(15)

where

$$\bar{R}_{\alpha}(t) = \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} R_{\alpha i}(t)$$
(16)

denotes the average random force acting on atoms of species  $\alpha$  at time t, while  $\mathbf{R}_{\alpha i}(t)$  is the usual random force in the generalized Langevin equation for an atomic velocity of species  $\alpha$ , which: i) vanishes in the mean,  $\langle \mathbf{R}_{\alpha i}(t) \rangle = 0$ , and ii) is uncorrelated with the atomic velocity, so that  $\langle \mathbf{R}_{\alpha i}(t) \mathbf{v}_{\alpha i}(0) \rangle = 0$  for all times.<sup>[33,34,43,44]</sup>

As it has been pointed out in ref. [26],  $W_{12}$  is related to the average amount of generated–dissipated energy due to the correlations between fluctuations of  $R_{12}$  and  $J_c$ . Hence, it follows that, in thermal equilibrium, the absolute value of  $W_{12}$  cannot exceed the characteristic thermal energy,  $k_B T$ , per each degree of freedom (out of  $3Nc_1c_2$  degrees of freedom related to the fluctuations of  $J_c$  and  $R_{12}$ ), according to the equipartition law, so that  $|W_{12}| \leq k_B T$ .

Furthermore, in ref. [26], it has been indicated that in binary mixing melts exhibiting chemical ordering  $R_{12}(t)$  should create (on average over the correlation time) an obtuse angle with  $J_c(0)$ , tending to effectively suppress its deviation from equilibrium during fluctuations. As a result, it can be expected that  $W_{12} < 0$  for binary mixing melts exhibiting chemical ordering (i.e., a large negative enthalpy of formation). In contrast, for binary melts with demixing tendency, it can be expected that  $W_{12} > 0$  since  $R_{12}(t)$  should create (on average over the correlation time) an acute angle with  $J_c(0)$ , tending to effectively stimulate its deviation from equilibrium during fluctuations.

Moreover, we should note that the relations given by Equations (11)–(13) follow, as the hydrodynamic limit  $(t \to \infty)$ , from a Volterra type convolution equation derived in ref. [26]. This equation relates to each other  $\varepsilon_c(t)$ ,  $P_{12}(t)$  and the two so-called memory kernels (functions) ultimately defined via the auto-correlation functions of the random forces,  $\mathbf{R}_{\alpha i}(t)$  ( $\alpha = 1, 2$ ), within the framework of the Mori–Zwanzig formalism as  $K_{\alpha}(t) = \langle \mathbf{R}_{\alpha i}(t) \mathbf{R}_{\alpha i}(0) \rangle / m_{\alpha}^2 \langle \mathbf{v}_{\alpha i}^2 \rangle = \langle \mathbf{R}_{\alpha i}(t) \mathbf{R}_{\alpha i}(0) \rangle / 3m_{\alpha} k_{\rm B} T.^{[33,34,43,44]}$  Specifically, it can be presented in the form

$$\frac{P_{12}(t)}{k_{\rm B}T} = \frac{d\varepsilon_c(t)}{dt} + \int_0^t \left[ c_2 \frac{m_2}{m} K_1(t-t') + c_1 \frac{m_1}{m} K_2(t-t') \right] \varepsilon_c(t') dt' \quad (17)$$

Since  $\varepsilon_c(t)$ ,  $K_1(t)$ , and  $K_2(t)$  are autocorrelation functions, they must be even functions of time by the definition. Then, it follows from Equation (17) that  $P_{12}(t)$  is an odd function of time, so that  $P_{12}(-t) = -P_{12}(t)$ . Consequently, it can be expanded in an odd power Taylor series in time evaluated at t = 0, as

$$P_{12}(t) = \sum_{n=0}^{\infty} \frac{t^{2n+1}}{(2n+1)!} P_{12}^{(2n+1)}(0)$$
(18)

where  $P_{12}^{(2n+1)}(0)$  denotes the (2n + 1) derivative of  $P_{12}(t)$  evaluated at t = 0. Hence, the value of  $P_{12}(t)$  in the short time limit  $t \rightarrow 0$  can be approximated using expression for the first derivative of  $P_{12}(t)$  evaluated t = 0 by means of Equation (17), as

$$\frac{P_{12}(0)}{k_B T} = \frac{1}{k_B T} \left. \frac{d P_{12}(t)}{d t} \right|_{t=0} = c_2 \frac{m_2}{m} \Omega_1^2 + c_1 \frac{m_1}{m} \Omega_2^2 - \Omega_c^2$$
(19)

where

$$\Omega_{\alpha}^{2} = K_{\alpha} (0) = \frac{\langle \mathbf{R}_{\alpha i}^{2} \rangle}{3m_{\alpha}k_{\mathrm{B}}T} = \frac{m_{\alpha} \langle \dot{\boldsymbol{v}}_{\alpha i}^{2} \rangle}{3k_{\mathrm{B}}T}$$
(20)

is the so-called Einstein frequency, at which a tagged atom of species  $\alpha$  ( $\alpha = 1, 2$ ) would vibrate on average if it were undergoing small oscillations in the potential wells produced by the surrounding atoms when maintained at their mean equilibrium positions around the tagged atom.<sup>[34]</sup> Meanwhile,

$$\Omega_c^2 = -\ddot{\varepsilon}_c (0) = -\left. \frac{d^2 \varepsilon_c(t)}{dt^2} \right|_{t=0} = \frac{m_c V^2 \langle j_c^2 \rangle}{3 N c_1 c_2 k_{\rm B} T}$$
(21)

can be similarly interpreted as an effective Einstein frequency associated with each degree of freedom related to the fluctuations of the interdiffusion flux. It should be noted that the instantaneous values of  $\dot{\boldsymbol{v}}_{\alpha i} = \frac{d\boldsymbol{v}_{\alpha i}(t)}{dt} = -m_{\alpha}^{-1}\nabla_{\alpha i}U$  and  $\dot{\boldsymbol{J}}_c = \frac{dJ_c(t)}{dt} = (-1)^{\alpha}m_c^{-1}\sum_{i=1}^{N_{\alpha}}\nabla_{\alpha i}U$  (where *U* is the total potential energy of the system) for a given atomic configuration are routinely evaluated in MD simulations in terms of the interatomic interactions. Thus, in the short time limit  $t \to 0$ ,  $P_{12}(t)$  can be approximated as

$$\frac{P_{12}(t)}{k_{\rm B}T} \approx \sigma_{12} \Omega_c^2 t \tag{22}$$

where

$$\sigma_{12} = \frac{c_2 m_2 \Omega_1^2 + c_1 m_1 \Omega_2^2}{m \Omega_c^2} - 1$$
(23)

is the dimensionless factor which defines the initial sign of  $P_{12}(t)$  as the correlation between  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$  starts to develop with time. As a result,  $\sigma_{12} < 0$  and  $\sigma_{12} > 0$  indicate that  $\mathbf{R}_{12}(t)$  tends to initially create with  $\mathbf{J}_c(0)$  obtuse and acute angles, respectively. In addition, we should note that  $\lim_{c_\alpha \to 0} \Omega_c = \Omega_\alpha$  as it follows from Equations (4), (20), and (21), so that  $\lim_{c_\alpha \to 0} \sigma_{12} = 0$  ( $\alpha = 1, 2$ ).

It can be expected that for a binary mixing melt exhibiting chemical ordering in the normal liquid state (i.e., above its liquidus temperature), one should observe that both  $\sigma_{12} < 0$  and  $W_{12} < 0$ . In other words, an initial ( $t \rightarrow 0$ ) obtuse angle ( $\sigma_{12} < 0$ ) between  $R_{12}(t)$  and  $J_c(0)$  should remain predominantly obtuse

over the correlation period to ensure, according to Equation (13), a negative value of  $W_{12}$  which is naturally expected from the thermodynamic point of view for the normal liquid state of a binary mixing melt exhibiting chemical ordering. However, one may assume that, in some cases, the short-range atomic ordering, which is inherent in the normal liquid state of a binary mixing melt, can promptly become unfavorable in the undercooled liquid state of the binary melt. Hence, it is reasonable to expect in such a case that an initial obtuse angle between  $R_{12}(t)$  and  $J_{c}(0)$  may principally transform to an acute angle to promote the evolution of an undercooled binary mixing melt toward a more thermodynamically stable state with a somewhat different type of atomic ordering. As a result, one may observe  $W_{12} > 0$  in the undercooled liquid state of a binary mixing melt exhibiting chemical ordering. Moreover, at sufficiently large undercooling of some binary mixing melts exhibiting chemical ordering, W12 may even exceed the upper bound of its equilibrium range, demonstrating diverging behavior, so that  $W_{12} > k_{\rm B}T$ . Therefore, we may conclude that  $\sigma_{12} < 0$  and  $W_{12} < 0$  can be considered as necessary conditions for a binary mixing melt exhibiting chemical ordering to be in thermodynamic equilibrium. Meanwhile, a relative change in  $W_{12}$  can be used to characterize variation in dynamical stability of atomic ordering in a binary mixing melt upon undercooling.

# 4. Results and Discussion

The temperature of 2200 K, below which the cooling rate of about 4 K ns<sup>-1</sup> was implemented in our MD simulations of Ni-Zr melts, is well above the equilibrium melting temperature,  $T_{\rm m} \approx 2109$  K, for the model of body-centered cubic zirconium (BCC Zr).<sup>[15]</sup> The equilibrium melting temperature for the model of face-centered cubic nickel (FCC Ni) is  $T_{\rm m} \approx 1728~{
m K}.^{[16]}$  Both melting temperatures are reproduced in close agreement with the target experimental values of 2128 K and 1728 K for BCC Zr and FCC Ni, respectively.<sup>[15,16]</sup> We should note that at the considered cooling rate the first crystallization was detected for the model of  $Ni_{75}Zr_{25}$  melt at 1650 K. Meanwhile, for the models of pure Zr and Ni melts crystallizations were observed, respectively, at 1550 K and 1150 K, that is, at the reduced temperatures  $(T/T_m)$ approximately equal to 0.74 and 0.67. Furthermore, at 1150 K we also detected the onset of crystallization in the models of Ni<sub>12.5</sub>Zr<sub>87.5</sub> and Ni<sub>87.5</sub>Zr<sub>12.5</sub> melts, while no crystallization was noticed during the quenching of the models of Ni<sub>25</sub>Zr<sub>75</sub>, Ni<sub>37.5</sub>Zr<sub>62.5</sub>,  $Ni_{50}Zr_{50}$  and  $Ni_{62.5}Zr_{37.5}$  melts down to 0 K.

We are not aware of any simulation data on the equilibrium melting properties of Ni<sub>12.5</sub>Zr<sub>87.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, and Ni<sub>87.5</sub>Zr<sub>12.5</sub> alloys with the interatomic potential developed in ref. [14]. Nevertheless, experimental data<sup>[45]</sup> on the liquidus temperatures of Ni<sub>12.5</sub>Zr<sub>87.5</sub> (1810 K) and Ni<sub>87.5</sub>Zr<sub>12.5</sub> (1540 K) alloys allow for estimation of the reduced crystallization temperatures of the models of Ni<sub>12.5</sub>Zr<sub>87.5</sub> (0.64) and Ni<sub>87.5</sub>Zr<sub>12.5</sub> (0.75) melts which are in reasonably good agreement with the abovementioned similar data for the models of pure Zr and Ni melts. Then, the liquidus temperature of the reduced crystallization temperature of 0.75 for the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub> melt. This is the model with the closest alloy composition to the model of Ni<sub>75</sub>Zr<sub>25</sub> melt for which we

have an assessment of the reduced crystallization temperature at the cooling rate of about 4 K ns<sup>-1</sup>. As a result, we estimate the liquidus temperature of the model of Ni<sub>75</sub>Zr<sub>25</sub> melt as about 1650/0.75  $\approx$  2200 K. This is about 29% higher than the experimental value of 1700 K.<sup>[45]</sup>

The fact that the three liquidus temperatures of Ni<sub>12.5</sub>Zr<sub>87.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, and Ni<sub>87.5</sub>Zr<sub>12.5</sub> alloys are predicted by the employed interatomic potential<sup>[14]</sup> at this reasonable level of accuracy demonstrates the good transferability to other alloy compositions besides pure Ni and Zr, as well as NiZr<sub>2</sub> and NiZr alloys included in the potential fit. The largest discrepancy, which is estimated for Ni<sub>75</sub>Zr<sub>25</sub> alloy, is at the typical level of accuracy expected for the prediction of materials properties not included in the potential fit within the framework of either EAM or Finnis–Sinclair formalism.<sup>[14–18,21]</sup> In Appendix A (see Supporting Information online), we show for illustration purpose the pair distribution functions calculated for the model Ni, Zr, Ni<sub>87.5</sub>Zr<sub>12.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, and Ni<sub>12.5</sub>Zr<sub>87.5</sub> systems at temperatures in the vicinity of the onset of crystallization.

The composition dependencies of all the diffusion properties reported here are primarily evaluated in the temperature range between 2200 and 1200 K. Meanwhile, the fit of the data according to the Arrhenius law  $D_0 \exp(-E_A/k_B T)$  (where  $E_A$  is the activation energy of the diffusion process and  $D_0$  is the temperatureindependent prefactor) is mainly performed in the temperature range between 2200 and 1400 K, since below 1400 K some notable deviations from the Arrhenius law are observed for a number of the studied model systems. Due to the crystallization observed in the models of Ni<sub>75</sub>Zr<sub>25</sub> and Zr melts at 1650 K and 1550 K, respectively, only the data extrapolated (according to the Arrhenius law) from high temperatures are available for these melts below 1700 K and 1600 K, respectively.

In Figure 1a, we show the temperature dependence (an Arrhenius-type plot) of the self-diffusion coefficients of Ni and Zr in the models of pure Ni and Zr melts, respectively. These simulation results are shown along with available (in the temperature range about 1726  $\pm$  200 K) experimental measurements for pure Ni melt.<sup>[46,47]</sup> In **Table 1**, the calculated values of the selfdiffusion coefficients are presented with the temperature step of 100 K. Meanwhile, in Table 2, we give the results of the fit of the data between 2200 and 1400 K according to the Arrhenius law. As it can be seen in Figure 1a, comparison of the simulation and experimental data for the self-diffusion coefficient of Ni in pure Ni melt reveals a good agreement. The fit of experimental data for Ni according to the Arrhenius law gives  $E_A \approx 0.47$  eV and  $D_0 \approx 0.77 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ .<sup>[48]</sup> Both the activation energy and the exponential prefactor extracted from experimental data are in close agreement with our simulation results  $E_A \approx 0.45$  eV and  $D_0 \approx 0.73 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  (see Table 2). We are not aware of relevant experimental data for pure Zr melt. Meanwhile, it is important to note that the calculated (between 2200 and 1600 K) values of the self-diffusion coefficient of Zr in the model of pure Zr melt as well as its Arrhenius parameters,  $E_{\rm A} \approx 0.49$  eV and  $D_0 \approx 0.77 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ , turn out to be fairly close to those for the self-diffusion coefficient of Ni in the model of pure Ni melt (see Figure 1a and Tables 1 and 2).

In Figure 1b–d, we show the temperature dependence of the self-diffusion coefficients of Ni and Zr in the models of Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub>, and Ni<sub>37.5</sub>Zr<sub>62.5</sub> melts, respectively. These

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**Figure 1.** Arrhenius plot of the self-diffusion coefficients of Ni,  $D_{Ni}$ , (open squares) and Zr,  $D_{Zr}$ , (open diamonds) in the models of: a) pure Ni and Zr melts, b) Ni<sub>62.5</sub>Zr<sub>37.5</sub> melt, c) Ni<sub>50</sub>Zr<sub>50</sub> melt, and d) Ni<sub>37.5</sub>Zr<sub>62.5</sub> melt. The lines display the fits of the simulation data. a) The half-solid squares show experimental data for Ni,<sup>[46,47]</sup> while the thin line displays the fit of the experimental data according to ref. [48]. b) The solid squares and diamonds show experimental data for  $D_{Ni}$  and  $D_{Zr}$  in Ni<sub>64</sub>Zr<sub>36</sub> melt, respectively.<sup>[5,10]</sup> c) The solid squares show experimental data for  $D_{Ni}$  in Ni<sub>50</sub>Zr<sub>50</sub> melt.<sup>[5]</sup> d) The solid squares and diamonds show experimental data for  $D_{Ni}$  in Ni<sub>50</sub>Zr<sub>50</sub> melt.<sup>[5]</sup> d) The solid squares and diamonds show experimental data for  $D_{Ni}$  in Ni<sub>50</sub>Zr<sub>50</sub> melt.<sup>[5]</sup> d) The solid squares and diamonds show experimental data for  $D_{Ni}$  in Ni<sub>50</sub>Zr<sub>50</sub> melt.<sup>[5]</sup> d) The solid squares and diamonds show experimental data for  $D_{Ni}$  and  $D_{Zr}$  in Ni<sub>36</sub>Zr<sub>64</sub> melt, respectively.<sup>[5,10]</sup>

alloy compositions are chosen in Figure 1b–d to facilitate comparison of our simulation results with available experimental measurements of the self-diffusion coefficients of Ni and Zr in Ni–Zr melts.<sup>[5,10]</sup> Meanwhile, in **Figure 2**, we show our simulation results for the kinetic part of the interdiffusion coefficient  $\tilde{L}_{cc}$ (see Equations (9) and (10), as well as Appendix B in Supporting Information online for details) in the same models of Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub> and Ni<sub>37.5</sub>Zr<sub>62.5</sub> melts. We are not aware of any relevant experimental data to be included in Figure 2. For all the studied alloy compositions the calculated diffusion coefficients,  $D_{Ni}$ ,  $D_{Zr}$ , and  $\tilde{L}_{cc}$ , are presented in Table 1 with the temperature step of 100 K, while the results of the fit of the data according to the Arrhenius law are summarized in Table 2. In Figure 1b, it can be seen that a very good agreement with the experimental data<sup>[5,10]</sup> is observed for both  $D_{Ni}$  and  $D_{Zr}$  in the model of Ni<sub>62.5</sub>Zr<sub>37.5</sub> melt. For the models of Ni<sub>50</sub>Zr<sub>50</sub> and Ni<sub>37.5</sub>Zr<sub>62.5</sub> melts the calculated values of  $D_{Ni}$  are also in close agreement with experiment (see Figure 1c,d). The simulation data for  $D_{Ni}$  somewhat overestimate the experimental measurements for these alloy compositions.<sup>[5]</sup> Experimental data for  $D_{Zr}$  in Ni<sub>50</sub>Zr<sub>50</sub> melt are not available in the literature, while the experimental data<sup>[10]</sup> for  $D_{Zr}$  in Ni<sub>36</sub>Zr<sub>64</sub> melt are tightly spread (within the error of the experimental measurements) around our simulation data for  $D_{Zr}$  in Ni<sub>37.5</sub>Zr<sub>62.5</sub> melt, as it can be seen in Figure 1d. In contrast to the model of pure Ni (see Figure 1a), it can be seen in Figures 1b–d and 2, that a notable deviation from the Arrhenius law is observed in the models of Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub>, and Ni<sub>37.5</sub>Zr<sub>62.5</sub> melts for all three diffusion coefficients  $D_{Ni}$ ,  $D_{Zr}$ , and  $\tilde{L}_{cc}$  below 1400–1350 K.

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**Table 1.** Diffusion coefficients (in units of  $10^{-9}$  m<sup>2</sup> s<sup>-1</sup>) calculated for the model Ni–Zr system in the liquid state.

Temperature [K	]	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200
Pure Ni	D <sub>Ni</sub>	0.94	1.34	1.78	2.24	2.83	3.36	4.01	4.68	5.36	6.06	7.09
	D <sub>Ni</sub>	0.41	0.72	1.11	1.53	2.08	2.67	3.27	3.80	4.73	5.37	6.18
Ni <sub>87.5</sub> Zr <sub>12.5</sub>	$D_{Zr}$	0.12	0.27	0.50	0.79	1.07	1.43	1.92	2.34	2.92	3.62	4.01
	Ĩ <sub>cc</sub>	0.22	0.39	0.62	0.88	1.23	1.65	1.94	2.54	2.95	3.39	4.00
	D <sub>Ni</sub>	—	—	—	—	—	1.96	2.37	3.02	3.61	4.36	5.15
Ni <sub>75</sub> Zr <sub>25</sub>	$D_{Zr}$	—	—	—	—	—	0.89	1.19	1.63	1.96	2.47	3.03
	Ĩ <sub>cc</sub>	—	—	—	—	—	0.99	1.22	1.54	1.91	2.27	2.72
	D <sub>Ni</sub>	0.19	0.42	0.74	1.13	1.55	2.06	2.59	3.14	3.79	4.45	5.19
Ni <sub>62.5</sub> Zr <sub>37.5</sub>	$D_{Zr}$	0.10	0.26	0.46	0.71	1.04	1.35	1.79	2.14	2.62	3.16	3.56
	Ĩ <sub>cc</sub>	0.12	0.24	0.41	0.62	0.88	1.19	1.40	1.74	2.05	2.46	2.85
	D <sub>Ni</sub>	0.41	0.72	1.09	1.56	2.01	2.57	3.15	3.81	4.45	4.97	5.82
Ni <sub>50</sub> Zr <sub>50</sub>	$D_{Zr}$	0.31	0.54	0.83	1.17	1.57	1.97	2.41	2.94	3.45	3.99	4.45
	Ĩ <sub>cc</sub>	0.28	0.48	0.70	0.94	1.26	1.60	1.91	2.29	2.63	3.09	3.51
	D <sub>Ni</sub>	0.61	0.97	1.40	1.94	2.44	3.04	3.53	4.32	4.97	5.75	6.46
Ni <sub>37.5</sub> Zr <sub>62.5</sub>	$D_{Zr}$	0.48	0.77	1.12	1.54	1.96	2.43	2.92	3.48	4.01	4.64	5.36
	Ĩ <sub>cc</sub>	0.44	0.70	1.01	1.36	1.75	2.13	2.53	2.99	3.43	3.93	4.61
	D <sub>Ni</sub>	0.80	1.18	1.73	2.21	2.84	3.45	4.10	4.92	5.65	6.46	7.07
Ni <sub>25</sub> Zr <sub>75</sub>	$D_{Zr}$	0.57	0.88	1.29	1.69	2.13	2.67	3.21	3.78	4.36	5.01	5.51
	Ĩ <sub>cc</sub>	0.63	0.97	1.38	1.82	2.30	2.76	3.33	3.82	4.44	5.11	5.62
	D <sub>Ni</sub>	0.82	1.40	1.99	2.47	3.13	3.66	4.17	5.39	5.80	6.66	7.60
Ni <sub>12.5</sub> Zr <sub>87.5</sub>	$D_{Zr}$	0.50	0.90	1.32	1.73	2.23	2.76	3.35	3.83	4.43	5.16	5.88
	Ĩ <sub>cc</sub>	0.84	1.26	1.69	2.23	2.80	3.28	3.89	4.10	5.27	6.06	6.65
Pure Zr	$D_{\rm Zr}$	—	—	—	—	1.95	2.67	3.24	3.76	4.32	5.01	5.76

**Table 2.** Arrhenius parameters of the diffusion coefficients evaluated for the model Ni–Zr system in the liquid state. Except the models of Ni<sub>75</sub>Zr<sub>25</sub> and Zr melts, the Arrhenius fit is performed in the temperature range between 2200 and 1400 K. For the models of Ni<sub>75</sub>Zr<sub>25</sub> and Zr melts, the Arrhenius fit is performed in the temperature ranges of 2200–1700 K and 2200–1600 K, respectively.

Model	Sel	f-diffusion Ni	Sel	f-diffusion Zr	Collective diffusion		
	E <sub>A</sub> [eV]	D <sub>0</sub> [10 <sup>-7</sup> m <sup>2</sup> s <sup>-1</sup> ]	E <sub>A</sub> [eV]	D <sub>0</sub> [10 <sup>-7</sup> m <sup>2</sup> s <sup>-1</sup> ]	E <sub>A</sub> [eV]	D <sub>0</sub> [10 <sup>-7</sup> m <sup>2</sup> s <sup>-1</sup> ]	
Pure Ni	0.45	0.73	_	_		_	
Ni <sub>87.5</sub> Zr <sub>12.5</sub>	0.56	1.24	0.69	1.58	0.60	0.94	
Ni75Zr25	0.63	1.41	0.77	1.72	0.65	0.83	
Ni <sub>62.5</sub> Zr <sub>37.5</sub>	0.63	1.49	0.67	1.26	0.63	0.84	
Ni <sub>50</sub> Zr <sub>50</sub>	0.55	1.09	0.56	0.86	0.54	0.60	
Ni <sub>37.5</sub> Zr <sub>62.5</sub>	0.50	0.88	0.50	0.75	0.49	0.59	
Ni <sub>25</sub> Zr <sub>75</sub>	0.47	0.87	0.48	0.72	0.46	0.65	
Ni <sub>12.5</sub> Zr <sub>87.5</sub>	0.46	0.85	0.49	0.76	0.45	0.72	
Pure Zr	_	_	0.49	0.77	_	_	

In **Figure 3**a–c, we show, respectively, the composition dependence of  $D_{\rm Ni}$ ,  $D_{\rm Zr}$ , and  $\tilde{L}_{cc}$  in the models of Ni–Zr melts evaluated at 2200, 2000, 1700, 1400, and 1200 K using the Arrhenius parameters obtained from our simulation data (see Table 2). A set of two Arrhenius parameters allows us to conveniently encode the temperature dependence of a diffusion coefficient. As a result, one can use the Arrhenius parameters in Table 2 for smoothing and interpolation of the discrete calculation data within the temperature range of fitting (see the open symbols in Figure 3a–c).

Moreover, the Arrhenius parameters allow for extrapolation of the calculation data from the temperature range of fitting down to lower temperatures (see the crossed symbols in Figure 3a–c). The extrapolated data along with the actual calculated data (see the grey-filled symbols in Figure 3a–c) are used to conveniently visualize the influence of composition on the dynamical slowing down upon melt undercooling (it should be recalled that undercooling of the models of  $Ni_{75}Zr_{25}$  and Zr melts is interrupted by crystallization at 1650 and 1550 K, respectively). ADVANCED SCIENCE NEWS www.advancedsciencenews.com



**Figure 2.** Arrhenius plot of the kinetic part of the interdiffusion coefficient,  $\tilde{L}_{cc}$ , in the models of Ni<sub>62.5</sub>Zr<sub>37.5</sub> (downward-facing triangles), Ni<sub>50</sub>Zr<sub>50</sub> (diamonds), and Ni<sub>37.5</sub>Zr<sub>62.5</sub> (upward-facing triangles) melts. The lines display the fits of the simulation data.

In Figure 3a,b, we also show the relevant experimental data on the composition dependence of  $D_{Ni}$  and  $D_{Zr}$  in Ni–Zr melts, respectively. The solid squares and diamonds in Figure 3a show the interpolation of experimental data to 1700 and 1400 K, respectively, according to the Arrhenius fits presented in refs. [5,46–48]. Meanwhile, the solid diamonds in Figure 3b show the experimental data at 1388 K presented in refs. [10,11]. It can be seen in Figure 3a,b that in both cases a close agreement with the experimental data is observed. Overall, we predict similar minima in the composition dependencies of  $D_{Ni}$ ,  $D_{Zr}$ , and  $\tilde{L}_{cc}$  located in the region of 0.625  $\,< c_{\rm Ni} <$  0.75. Furthermore, a fairly flat maximum can be noticed in the composition dependence of  $D_{Zr}$  in the vicinity of  $c_{\text{Ni}} \approx 0.125$ . Another common trend among  $D_{\text{Ni}}$ ,  $D_{\text{Zr}}$ , and  $\tilde{L}_{cc}$  is that the larger values of the diffusion coefficients are observed in the models of Zr-rich melts compared to the models of Ni-rich melts. However, it should be noted that this asymmetrical behavior is less pronounced in the case of  $D_{\rm Ni}$ . In addition, we point out that the most notable dynamical slowing down upon undercooling is observed for the model of  $Ni_{62.5}Zr_{37.5}$  melt in the case of which the ratios of the extrapolated and actual calculated values of  $D_{\text{Ni}}$ ,  $D_{\text{Zr}}$ , and  $\tilde{L}_{cc}$  at 1200 K reach, respectively, 1.7, 1.9, and 1.5 (see also Figures 1b-d and 2).

In **Figure 4**, we show the composition dependence of the ratio of the self-diffusion coefficients  $D_{\rm Ni}/D_{\rm Zr}$  in the models of Ni– Zr melts evaluated at 2200, 2000, 1700, 1400, and 1200 K using values of  $D_{\rm Ni}$  and  $D_{\rm Zr}$  reported in Figure 3a,b, respectively. As it can be seen in Figure 4, our simulation results reveal a considerable decoupling of the self-diffusion coefficients of Ni and Zr in the models of Ni-rich Ni–Zr melts. In particular, it is observed that the calculated ratio  $D_{\rm Ni}/D_{\rm Zr}$  can exceed a factor of three upon melt undercooling, reaching about 3.3 for the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub> melt at 1200 K just before the onset of its crystallization at 1150 K. Probably, as it may follow from the data in Figure 4 extrapolated down to 1200 K, even stronger decoupling would be observed for the model of Ni75 Zr25 melt if its undercooling were carried out with a higher cooling rate, sufficient to avoid crystallization between 1650 and 1200 K. These findings are in both qualitative and quantitative agreement with an assessment of the ratio  $D_{\rm Ni}/D_{\rm Zr}$  in Ni<sub>36</sub>Zr<sub>64</sub> and Ni<sub>64</sub>Zr<sub>36</sub> melts made in refs. [10,11] on the basis of experimental data (see, for illustration, the solid diamonds with error bars in Figure 4).<sup>[5,10,11]</sup> Although the pronounced chemical short-range order in Ni-Zr melts should apparently suppress diffusion decoupling, it was argued in refs. [10,11] that with an increasing amount of Ni content in the melts, the fraction of strongly interacting Ni–Zr pairs is saturated above a certain composition due to the limited number of Zr atoms and only the fraction of Ni-Ni pairs can increase further. Therefore, the saturated fraction of heterogeneous Ni-Zr pairs leads to an increased amount of excess less-strongly coupled Ni atoms which, as a result, exhibit an enhanced diffusion mobility in Ni-rich melts.<sup>[10,11]</sup>

Overall, it can be observed in Figure 4 that the calculated ratio  $D_{\rm Ni}/D_{\rm Zr}$  is always greater than one within the composition and temperature ranges considered in the present study. As it was pointed out in ref. [10], such behavior may indicate that the bonds of Zr atoms with the nearest neighbors are on average stronger than the bonds of Ni atoms. As a result, more thermal energy is needed to break the bonds of more reactive Zr atoms. Consequently, as temperature goes down the available thermal energy becomes smaller and motion of more reactive Zr atoms should be slowed down by energy landscape more rapidly than motion of Ni atoms. Thus, the stronger decoupling of the self-diffusion coefficients of Ni and Zr at lower temperatures observed in Figure 4 can be attributed to the transition from simple liquid-like motion to diffusion behavior approaching the energy landscape controlled regime.<sup>[10,49]</sup>

In this context, it is also important to note a significant component decoupling observed in Zr-based multicomponent Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> glass-forming melt with the ratio  $D_{
m Ni}/D_{
m Zr} pprox$  4 near its liquidus temperature of 1050 K.<sup>[8]</sup> In fact, as it was pointed out in ref. [10], the ratio  $D_{\rm Ni}/D_{\rm Zr}$  decreases to a factor of less than two when the self-diffusion coefficients of Ni and Zr in Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> glass-forming melt are extrapolated above 1200 K. In terms of the energy landscape, this can be explained by significant decay of the diffusion barriers for Zr atoms at higher temperatures.<sup>[10]</sup> The most remarkable is that the extrapolated ratio is in close agreement with the decoupling factor of the self-diffusion coefficients of Ni and Zr which we observe in our models of Zr-rich Ni-Zr melts at 1200 K (see Figure 4). It can also be seen in Figure 4 that the smallest decoupling of the self-diffusion coefficients of Ni and Zr (1.2  $\leq D_{\rm Ni}/D_{\rm Zr} \leq 1.3$ ) is observed in our simulations in the composition range of 0.375  $\lesssim$  $c_{\rm Ni} \lesssim 0.5$ . Furthermore, it is interesting to note that inside this composition range the ratio  $D_{\rm Ni}/D_{\rm Zr}$  is practically independent of temperature within the considered temperature range. Hence, one may conclude that the effect of the energy landscape on the decoupling of the self-diffusion coefficients of Ni and Zr should be smallest for Ni–Zr melts in this composition range.

In **Figure 5**a, we show the composition dependence of the correction factor in the Darken–Manning equation,  $S = \tilde{L}_{cc}/(c_{\text{Zr}} D_{\text{Ni}} + c_{\text{Ni}} D_{\text{Zr}})$ , evaluated for the models of Ni–Zr

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**Figure 3.** Composition dependence of the self-diffusion coefficients of a) Ni,  $D_{Ni}$ , and b) Zr,  $D_{Zr}$ , as well as of c) the kinetic part of the interdiffusion coefficient,  $\tilde{L}_{cc}$ , evaluated at temperatures 2200 K (open upward-facing triangles), 2000 K (open circles), 1700 K (open squares), 1400 K (open diamonds), and 1200 K (crossed downward-facing triangles) by making use of the Arrhenius parameters given in Table 2. The crossed diamond and the crossed downward-facing triangles indicate the data extrapolated down to 1400 K and 1200 K, respectively. The grey-filled, downward-facing triangles show the actual calculated values of a)  $D_{Ni}$ , b)  $D_{Zr}$ , and c)  $\tilde{L}_{cc}$  at 1200 K. The lines serve as a guide for the eye. a) The solid squares and diamonds show the interpolation of experimental data to 1700 K and 1400 K, respectively, according to the Arrhenius fits.<sup>[5,46–48]</sup> b) The solid diamonds show the experimental data for Ni<sub>36</sub>Zr<sub>64</sub> and Ni<sub>64</sub>Zr<sub>36</sub> melts at 1388 K.<sup>[10,11]</sup>

melts at the same temperatures using values of  $D_{\text{Ni}}$ ,  $D_{\text{Zr}}$ , and  $\tilde{L}_{cc}$  reported in Figure 3a–c, respectively. At high temperatures (i.e., in the normal liquid state) the composition dependence of *S* has similar trends to those which were previously observed for Ni–Al melts.<sup>[20,26,35,50–52]</sup> In particular, as in the case of Ni–Al melts it can be seen in Figure 5a that in the normal liquid state of the models of Ni–Zr melts we have S < 1 for all compositions as it can be expected for binary liquid alloys with mixing tendency in accordance with our discussion in the previous section. Furthermore, it is generally expected that collective diffusion kinetics in non-demixing binary liquid alloys should slow down

upon increasing the concentration of the minority species toward the equi-atomic composition.<sup>[20,26,50–52]</sup> In accordance with this suggestion, a minimum in the composition dependence of *S* in Figure 5a is located somewhere in the range of 0.5  $\leq c_{\rm Ni} \leq 0.625$ . The minimum value of the correction factor *S* for the models of Ni–Zr melts in the normal liquid state is practically independent of temperature and it can be estimated as about  $S_{\rm min} \approx 0.67$ . Again, we should note that the position and depth of the minima in the composition dependencies of *S* for the models of Ni–Zr and Ni–Al melts in the normal liquid state reveal very similar values (see also refs. [20,26]).

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**Figure 4.** Composition dependence of the ratio of the self-diffusion coefficients of Ni and Zr,  $D_{\text{Ni}}/D_{\text{Zr}}$ , evaluated at temperatures 2200 K (open upward-facing triangles), 2000 K (open circles), 1700 K (open squares), 1400 K (open diamonds), and 1200 K (crossed downward-facing triangles) by making use of the Arrhenius parameters given in Table 2. The crossed diamond and the crossed downward-facing triangles indicate the data extrapolated down to 1400 and 1200 K, respectively. The grey-filled, downward-facing triangles show the actual calculated values of  $D_{\text{Ni}}/D_{\text{Zr}}$  at 1200 K. The lines serve as a guide for the eye. The solid diamonds with error bars show an assessment of  $D_{\text{Ni}}/D_{\text{Zr}}$  in Ni<sub>36</sub>Zr<sub>64</sub> and Ni<sub>64</sub>Zr<sub>36</sub> melts at 1388 K which is made in refs. [10,11] on the basis of experimental data.<sup>[5,10,11]</sup>

Overall, as in the case of the models of Ni–Al melts,<sup>[20]</sup> it is observed that the composition dependence of the correction factor for the models of Ni-Zr melts in the normal liquid state has a shape which is similar to the composition dependence of their enthalpy of mixing. In Figure 6, we show the enthalpy of mixing calculated per atom,  $h_{\rm m} = h - c_{\rm Ni} h_{\rm Ni}^* - c_{\rm Zr} h_{\rm Zr}^*$  (where *h* denotes the total enthalpy of the models of Ni–Zr melts, while  $h_{Ni}^*$  and  $h_{Zr}^*$ denote the enthalpies of the models of pure Ni and Zr melts), for the models of Ni-Zr melts along with the assessment of enthalpy of mixing of Ni-Zr melts on the basis of experimental thermodynamic data.<sup>[53]</sup> It can be seen in Figure 6 that the enthalpy of mixing of the models of Ni-Zr melts is practically temperatureindependent in the temperature range between 2200 and 1600 K. We should note that, because of crystallization of the model of pure Zr melt at 1550 K, our simulation data for  $h_{\rm m}$  are only available down to 1600 K. Also, it can be seen in Figure 6 that one point  $(c_{\rm Ni} = 0.75)$  is missed at 1600 K due to crystallization of the model of Ni<sub>75</sub>Zr<sub>25</sub> melt at 1650 K. Altogether, our simulation data for  $h_{\rm m}(c_{\rm Ni})$  are in good agreement with the experimental results, especially on the Ni-rich side. Although, some deviations between the experimental and simulation data on the Zr-rich side as well as a somewhat more pronounced displacement of the minimum in the simulation curve from equi-atomic composition toward Nirich side can be noted.

In Figure 5b,c, we show the composition dependence of  $S_0$  and  $W_{12}/k_BT$ , respectively. According to Equation  $S_0 = [1 + c_{\rm Ni} c_{\rm Zr} (m_{\rm Ni} D_{\rm Ni} - m_{\rm Zr} D_{\rm Zr})^2 / m^2 D_{\rm Ni} D_{\rm Zr}]^{-1}$ (11).and  $W_{12}/k_{\rm B}T = (S - S_0)/S_0$  ought to characterize the factorization of S into the contributions due to single-particle kinetic effects and a collective energy generation-dissipation effect. One of the important differences between the models of Ni-Zr and Ni-Al melts is that in the models of Ni-Zr melts the lighter Ni species  $(m_{\rm Ni}/m_{\rm Zr} \approx 58.69/91.22 \approx 0.64)$  possess the larger self-diffusion coefficient while in the models of Ni-Al melts the heavier Ni species  $(m_{\rm Ni}/m_{\rm Al} \approx 58.69/26.98 \approx 2.18)$  possess the larger self-diffusion coefficient. Therefore, in the normal liquid state of the models of Ni-Zr melts, the single-particle kinetic effects due to an increase of the ratio  $D_{\rm Ni}/D_{\rm Zr}$  above unity (it varies between 1.2 and 1.8 at high temperatures) are effectively damped by the mass ratio  $m_{\rm Ni}/m_{\rm Zr} \approx 0.64$  resulting in  $S_0 \approx 1$ over the whole composition range. This is in contrast to our previous results obtained for the models of Ni-Al melts,<sup>[26]</sup> for which the single-particle kinetic effects due to an increase of the ratio  $D_{\rm Ni}/D_{\rm Al}$  above unity are further amplified by the mass ratio  $m_{\rm Ni}/m_{\rm Al} \approx 2.18$ , resulting in a considerable reduction of  $S_0$  below unity at all compositions. For instance, in the normal liquid state of the models of Ni–Al melts S<sub>0</sub> reaches its minimum value of 0.85 in the vicinity of equi-atomic composition. Nonetheless, a considerable reduction of  $S_0$  below unity is also observed in Figure 5b for the models of Ni-rich Ni-Zr melts upon undercooling. In particular, the ratio  $D_{\rm Ni}/D_{\rm Zr}$  reaches about 3.3 for the model of  $Ni_{87.5}Zr_{12.5}$  melt at 1200 K. This is sufficient to overcome the damping effect of the mass ratio  $m_{\rm Ni}/m_{\rm Zr} \approx 0.64$  and to produce a sizable drop of  $S_0$  down to 0.92.

Thus, in contrast to the models of Ni-Al melts for which the contributions into S due to  $S_0$  and  $(1 + W_{12}/k_BT)$  are found to be fairly similar,<sup>[26]</sup> in the models of Ni-Zr melts the composition dependence of S basically follows the composition dependence of  $W_{12}/k_{\rm B}T$  (shifted up by one). The effect of  $S_0$  becomes notable only in the models of Ni-rich Ni-Zr melts upon undercooling. The main difference concerning behavior of  $W_{12}/k_{\rm B}T$ when comparing the models of Ni-Zr and Ni-Al melts, however, lies in the sign of  $W_{12}/k_{\rm B}T$  that becomes positive in the models of both Ni-rich and Zr-rich Ni-Zr melts upon undercooling. The strongest increase of  $W_{12}/k_{\rm B}T$  upon undercooling is observed in the models of Ni-rich Ni-Zr melts (see Figure 5c). In particular,  $W_{12}/k_{\rm B}T$  reaches 0.48 and 0.08, respectively, in the models of  $Ni_{87.5}Zr_{12.5}$  and  $Ni_{12.5}Zr_{87.5}$  melts at 1200 K just before the onset of their crystallization at 1150 K. Such behavior of  $W_{12}/k_{\rm B}T$ shows some correlation with the behavior of the ratio  $D_{\rm Ni}/D_{\rm Zr}$ , and is a manifestation of emerging heterogeneity in atomic dynamics of melt due to entering the energy landscape controlled regime upon undercooling.<sup>[10,49]</sup> However, a significant decoupling of the self-diffusion coefficients of Ni and Zr in the models of Ni-rich Ni-Zr melts upon undercooling results in a decrease of factor  $S_0$  which accounts for the contribution into S due to single-particle kinetic effects. Meanwhile, the contribution into S due to a collective energy generation-dissipation effect accounted by  $W_{12}/k_{\rm B}T$  is amplified upon transition to diffusion behavior approaching the energy landscape controlled regime. The variation of the latter contribution significantly dominates the variation of the former contribution resulting in considerable increase www.advancedsciencenews.com

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**Figure 5.** Composition dependence of a) the correction factor,  $S = \tilde{L}_{cc}/(c_{Zr}D_{Ni} + c_{Ni}D_{Zr})$ , as well as its parts due to b) single-particle kinetics,  $S_0 = [1 + c_{Ni}c_{Zr}(m_{Ni}D_{Ni} - m_{Zr}D_{Zr})^2/m^2D_{Ni}D_{Zr}]^{-1}$ , and c) a collective energy generation-dissipation effect,  $W_{12}/k_BT = (S - S_0)/S_0$ , (see main text for details) evaluated at temperatures 2200 K (open upward-facing triangles), 2000 K (open circles), 1700 K (open squares), 1400 K (open diamonds), and 1200 K (crossed downward-facing triangles) by making use of the Arrhenius parameters given in Table 2. The crossed diamond and the crossed downward-facing triangles indicate the data extrapolated down to 1400 and 1200 K, respectively. The grey-filled, downward-facing triangles show the actual calculated values of a) S, b)  $S_0$ , and c)  $W_{12}/k_BT$  at 1200 K. The lines serve as a guide for the eye.

in *S* above unity for the models of Ni-rich Ni–Zr melts upon undercooling.

In **Figure 7**, we show the composition dependence of the dimensionless factor  $\sigma_{12}$ , which defines the initial sign of  $P_{12}(t) = V\langle \mathbf{R}_{12}(t) \mathbf{J}_c(0) \rangle / 3 N c_1 c_2$  as the correlation between  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$  starts to develop with time (see Equations (17)–(23)), at the three different temperatures of 2200, 1700, and 1200 K (one point for  $c_{\text{Ni}} = 0.75$  is missed at 1200 K due to crystallization of the model of Ni<sub>75</sub>Zr<sub>25</sub> melt at 1650 K). As it can be expected for binary mixing melts exhibiting chemical ordering, the factor  $\sigma_{12}$  is found to be negative for the models of Ni–Zr melts in both normal and

undercooled liquid states over the whole composition range. As it can be seen in Figure 7, the composition dependence of  $\sigma_{12}$  is fairly similar to the composition dependence of  $W_{12}/k_{\rm B}T$  in the normal liquid state, also revealing the minimum value located in the range of  $0.5 \leq c_{\rm Ni} \leq 0.625$ . However, in contrast to the composition dependence of  $W_{12}/k_{\rm B}T$ , the composition dependence of  $\sigma_{12}$  changes only slightly upon melt undercooling, retaining negative values over the whole composition range.

Thus, the positive values of  $W_{12}/k_B T$  observed in the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> melts at 1200 K reflect changes in atomic dynamics of the models preceding the onset of their

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**Figure 6.** Enthalpy of mixing of the models of Ni–Zr melts evaluated as a function of Ni composition,  $h_m(c_{Ni})$ , at temperatures 2200 K (open upward-facing triangles), 2000 K (open squares), 1800 K (open diamonds), and 1600 K (open downward-facing triangles). The solid line drawn through the simulation data serves as a guide for the eye. The solid circles and dashed line show the assessment of enthalpy of mixing of Ni–Zr melts at 2200 K on the basis of experimental thermodynamic data.<sup>[53]</sup>



**Figure 7.** Composition dependence of the dimensionless factor  $\sigma_{12}$ , which defines the initial sign of  $P_{12}(t) = V \langle R_{12}(t) J_c(0) \rangle / 3 Nc_1 c_2$  as the correlation between  $R_{12}(t)$  and  $J_c(0)$  starts to develop with time (see Equations (17)–(23) and main text for details), evaluated at temperatures 2200 K (upward-facing triangles), 1700 K (squares), and 1200 K (downward-facing triangles). The lines serve as a guide for the eye.

crystallization at 1150 K. Therefore, an initial obtuse angle ( $\sigma_{12} < 0$ ) between  $R_{12}(t)$  and  $J_c(0)$  transforms to an acute angle to increase amplitude of fluctuations in atomic ordering in the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> melts toward more thermodynamically stable states, resulting in  $W_{12} > 0$ . It can be seen in Figure 5c that this effect is more pronounced for the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub> melt in comparison with the model of Ni<sub>12.5</sub>Zr<sub>87.5</sub> melt. Meanwhile,  $W_{12}/k_{\rm B}T$  remains negative for enriched alloy compositions upon melt undercooling. More specifically,  $W_{12}/k_{\rm B}T$  is practically independent of temperature in the composition range of  $0.25 \lesssim c_{\rm Ni} \lesssim 0.375$  while it starts to exhibit at 1200 K progressively larger rises toward zero as Ni content increases.

On the basis of the observed behavior of  $W_{12}/k_{\rm B}T$ , we suggest that in the composition range of 0.25  $\lesssim c_{\rm Ni} \lesssim 0.375$  the transition between normal and undercooled liquid states of Ni-Zr melts occurs in a smooth manner, without developing any significant changes in the collective diffusion dynamics. Furthermore, this observation is in accordance with the results for the ratio  $D_{\rm Ni}/D_{\rm Zr}$  presented in Figure 4. We recall that the ratio  $D_{\rm Ni}/D_{\rm Zr}$  is smallest in the composition range of 0.375  $\leq c_{\text{Ni}} \leq 0.5$  and also it is practically independent of temperature within this range. Overall, one can see in Figures 4 and 5c that both  $D_{\rm Ni}/D_{\rm Zr}$  and  $W_{12}/k_{\rm B}T$  change fairly slightly upon melt undercooling in the composition range of  $0.25 \leq c_{\text{Ni}} \leq 0.5$ . Thus, we may conclude that in this composition range both single-particle and collective diffusion dynamics in the models of Ni-Zr melts slow down homogeneously upon undercooling. Next, if we further suggest that such homogeneous dynamical slowdown is related to enhanced stability of undercooled melt against crystallization, then it follows that Ni-Zr alloys should reveal pronounced glass-forming ability in the composition range of  $0.25 \leq c_{\text{Ni}} \leq 0.5$ . In this context, one may also expect that Ni37.5 Zr62.5 alloy, located in the middle of the composition range, ought to be the best glass former in the binary Ni-Zr system.

In order to understand how the homogeneous dynamical slowdown is related to changes in the connectivity network of atomic clusters consisting of coordination polyhedrons of Ni and Zr atoms, a detailed analysis of evolution of disordered structure of the models of Ni-Zr melts upon undercooling is required in the composition range of  $0.25 \leq c_{\rm Ni} \leq 0.5$ . For instance, it was demonstrated previously that the connectivity network of icosahedra sharing common atoms percolates disordered structure as undercooled monatomic melt becomes glass.<sup>[54,55]</sup> Consequently, dynamical slowdown and peculiarities of crystal nucleation in undercooled monatomic melt were interpreted from this point of view.<sup>[56,57]</sup> Similar studies concerning the models of Ni–Zr melts will be the subject of our future work but lies beyond the scope of the present article. Furthermore, in a binary (or multicomponent) system surface-enhanced stabilization of atomic ordering in undercooled melt may play an important role and should be taken into account in the future studies as it was demonstrated in refs. [58,59].

Last, we may indicate that in multicomponent Zr-based BMGs the optimal ratio between larger "Zr-like" atoms (such as Zr, Ti, Hf, etc.) and smaller "Ni-like" atoms (such as Ni, Cu, Co, etc.) should be close to the "master" composition range of  $0.25 \lesssim c_{\rm Ni} \lesssim 0.5$  which is identified above for the binary Ni–Zr system. In particular, for Zr-based

multicomponent Zr<sub>46.75</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub>Be<sub>27.5</sub> glass-forming melt mentioned in this article, one can readily find that  $(c_{\rm Ni} + c_{\rm Cu})/(c_{\rm Ni} + c_{\rm Cu} + c_{\rm Zr} + c_{\rm Ti}) \approx 0.24$ .

## 5. Conclusions

We have presented a comprehensive, accurate, and selfconsistent database of diffusion properties of Ni–Zr melts generated within the framework of the molecular-dynamics method in conjunction with the state-of-the-art semi-empirical many-body interatomic potential developed in ref. [14]. We have carried out a careful comparison of our simulation results with the existing experimental data to assess the reliability of the model description of Ni–Zr melts. The high quality of the interatomic potential developed in ref. [14] for molecular dynamic simulation of Ni–Zr melts has been confirmed.

We have further elaborated theoretical insight into the interrelation between single-particle and collective diffusion in a binary melt developed in our recent article.<sup>[26]</sup> Specifically, the explicit expression for the cross-correlation function between the interdiffusion flux,  $I_{c}(0)$ , and the force caused by the difference in the average random accelerations of atoms of different species,  $R_{12}(t)$ , has been derived in the short time limit  $t \to 0$ , as  $P_{12}(t)/k_BT \approx \sigma_{12}\Omega_c^2 t$ . Hence, it has been demonstrated that the initial sign of  $P_{12}(t)$ , as the correlation between  $R_{12}(t)$  and  $J_{c}(0)$ starts to develop with time, is determined by the dimensionless factor,  $\sigma_{12} = (c_2 m_2 \Omega_1^2 + c_1 m_1 \Omega_2^2 - m \Omega_c^2) / m \Omega_c^2$ . This quantity depends on the composition, the ratio of the atomic masses, and the ratios between the so-called Einstein frequencies  $\Omega_{\alpha}$  ( $\alpha = 1, 2$ ) and  $\Omega_c$  associated with the atomic species and the interdiffusion flux, respectively. Furthermore, we have argued that for a binary mixing melt exhibiting chemical ordering in the normal liquid state (i.e., above its liquidus temperature), an initial ( $t \rightarrow 0$ ) obtuse angle ( $\sigma_{12} < 0$ ) between  $R_{12}(t)$  and  $J_c(0)$  should remain predominantly obtuse to ensure a negative value of the average amount of generated-dissipated energy,  $W_{12} < 0$ , over the whole correlation period between  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_{c}(0)$ . Accordingly, it appears that  $\sigma_{12} < 0$  and  $W_{12} < 0$  can be considered as necessary conditions for a binary mixing melt exhibiting chemical ordering to be in thermodynamic equilibrium. A relative change in  $W_{12}$ can be used to characterize the variation in dynamical stability of atomic ordering in a binary melt upon undercooling. Moreover, we have pointed out that an initial obtuse angle between  $R_{12}(t)$ and  $J_{c}(0)$  may principally transform to an acute angle leading to  $W_{12} > 0$  in an attempt to promote evolution of an undercooled binary mixing melt toward a more thermodynamically stable state.

We have employed the elaborated theoretical description of the interrelation between single-particle and collective diffusion in a binary melt to analyze our simulation data on diffusion properties of Ni–Zr melts. In particular, we have demonstrated that the positive values of  $W_{12}$  observed in the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> melts at 1200 K reflect changes in atomic dynamics preceding the onset of their crystallization at 1150 K. We have also found that the rise of  $W_{12}/k_BT$  toward positive values in the models of Ni-rich Ni–Zr melts upon undercooling is accompanied by a significant decoupling of the self-diffusion coefficients of Ni and Zr as characterized by their ratio  $D_{\rm Ni}/D_{\rm Zr}$ . Such joint behavior of  $W_{12}/k_BT$  and  $D_{\rm Ni}/D_{\rm Zr}$  upon undercooling has

been interpreted as a manifestation of emerging heterogeneities in atomic dynamics of melt due to entering the energy landscape controlled regime. We have observed that both  $D_{\rm Ni}/D_{\rm Zr}$ and  $W_{12}/k_{\rm B}T$  change fairly slightly upon melt undercooling in the composition range of  $0.25 \lesssim c_{\rm Ni} \lesssim 0.5$ . Hence, we have inferred that in this composition range both single-particle and collective diffusion dynamics slow down homogeneously upon the transition between the normal and undercooled liquid states of Ni–Zr melts. Finally, we have suggested that such homogeneous dynamical slowdown is related to the enhanced stability of undercooled melt against crystallization. This allows identifying Ni–Zr melts within the composition range of  $0.25 \lesssim c_{\rm Ni} \lesssim 0.5$  as systems exhibiting pronounced glass-forming ability.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

Green–Kubo formalism, mass transport, molecular dynamics, Mori– Zwanzig formalism, Ni–Zr melts

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# **Supporting Information**

# Diffusion in Ni-Zr Melts: Insights from Statistical Mechanics and Atomistic Modelling

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# Appendix A

We use calculations of the pair distribution function, g(r), to confirm the onset of crystallization in a model system. Physically,  $\frac{N}{V}g(r) = \frac{\Delta N(r)}{4\pi r^2 \Delta r}$  is the atomic density of particles at a distance r from a particle fixed at the centre, i.e., the number of particles  $\Delta N(r)$  inside the spherical shell between r and  $r + \Delta r$  divided by the volume  $4\pi r^2 \Delta r$  of the shell. In Figures SA1-SA5, we show g(r) calculated for the model Ni, Zr, Ni<sub>87.5</sub>Zr<sub>12.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, and Ni<sub>12.5</sub>Zr<sub>87.5</sub> systems at temperatures in the vicinity of the onset of crystallization.



Figure SA1. Pair distribution function, g(r), calculated at temperatures in the vicinity of the onset of crystallization of the model of Ni melt.

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Figure SA2. Pair distribution function, g(r), calculated at temperatures in the vicinity of the onset of crystallization of the model of Zr melt.



Figure SA3. Pair distribution function, g(r), calculated at temperatures in the vicinity of the onset of crystallization of the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub> melt.


Figure SA4. Pair distribution function, g(r), calculated at temperatures in the vicinity of the onset of crystallization of the model of Ni<sub>75</sub>Zr<sub>25</sub> melt.



Figure SA5. Pair distribution function, g(r), calculated at temperatures in the vicinity of the onset of crystallization of the model of Ni<sub>12.5</sub>Zr<sub>87.5</sub> melt.

As can be seen in Figure SA1, the crystalline FCC peaks appear in g(r) of the Ni model at 1150 K. Meanwhile, the second peak in g(r) of the model of Zr melt splits at 1550 K into two crystalline peaks located at  $r/r_1$  ( $r_1$  is the position of the first peak in g(r)) approximately equal to 1.6 and 1.9, respectively (see Figure SA2). These two peaks (strictly speaking the closest of them appears as a shoulder) are typical for both BCC and HCP (hexagonal close-packed) lattices. Since the first wide peak in g(r) of the Zr model at the beginning of the crystallization process can encompass the first and second ( $r/r_1 \approx 1.15$ ) nearest neighbour shells of BCC lattice, it is difficult to precisely identify nucleation of which of the two crystal lattices occurs primarily from the melt during our simulation. As it can be seen in Figures SA3-SA5, the transformations observed in g(r) at the beginning of the crystallization processes in the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub>, Ni<sub>75</sub>Zr<sub>25</sub>, and Ni<sub>12.5</sub>Zr<sub>87.5</sub> melts are similar to those which we discussed above for the model of Zr melt.

#### **Appendix B**

In the main text, we note that the calculation of the kinetic part of the interdiffusion coefficient,  $\tilde{L}_{cc}$ , is facilitated via the Green-Kubo formalism by making use of Eq. (9). As several examples, in Figures SB1-SB3 we show the normalised autocorrelation function of the interdiffusion flux  $J_c$ ,  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$ , as well as its time integral,

$$\xi_c(t) = \int_0^t \varepsilon_c(t') dt', \qquad (SB1)$$

calculated for the models of Ni<sub>62.5</sub>Zr<sub>37.5</sub>, Ni<sub>50</sub>Zr<sub>50</sub> and Ni<sub>37.5</sub>Zr<sub>62.55</sub> melts at 2000 an 1200 K. These Figures are designed to illustrate the evaluation of  $\tilde{L}_{cc}$ .



Figure SB1. (a) The normalised autocorrelation function of the interdiffusion flux  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b) its time integral  $\xi_c(t)$  calculated for the model of the Ni<sub>62.5</sub>Zr<sub>37.5</sub> melt at 2000 and 1200 K. The horizontal lines indicate the asymptotic values for: (a)  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b)  $\xi_c(t)$ .



Figure SB2. (a) The normalised autocorrelation function of the interdiffusion flux  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b) its time integral  $\xi_c(t)$  calculated for the model of the Ni<sub>50</sub>Zr<sub>50</sub> melt at 2000 and 1200 K. The horizontal lines indicate the asymptotic values for: (a)  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b)  $\xi_c(t)$ .



Figure SB3. (a) The normalised autocorrelation function of the interdiffusion flux  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b) its time integral  $\xi_c(t)$  calculated for the model of the Ni<sub>37.5</sub>Zr<sub>62.5</sub> melt at 2000 and 1200 K. The horizontal lines indicate the asymptotic values for: (a)  $\varepsilon_c(t) = C_{cc}(t)/C_{cc}(0)$  and (b)  $\xi_c(t)$ .

# **Chapter 4: Relevant Study of Different Type Binary Melts**

This chapter showcases further relevant molecular dynamics study on binary liquid alloys of Ni-Al and Cu-Ag melts and serves as a brief excursion beyond the Ni-Zr alloy melts to give insight into the research and treatment of the different model systems, which is later used to obtain further insight into diffusion dynamics, elaborated in Chapter 5. Here, the studies of the different systems are separated in two groups of melts with i) chemical ordering and ii) demixing tendency. The binary alloys of Ni-Al belong, like the Ni-Zr system, to the first type of melt, while the Cu-Ag system is grouped to the latter. Due to different type of atomic ordering behaviour, the alloys exhibit a significant change in diffusion characteristics. A thorough analysis and comparison of the different type of melts follows in Chapter 5, based on the discussed model systems.

#### 4.1 BINARY LIQUID ALLOY WITH MIXING TENDENCY

#### 4.1.1 The Ni-Al System

In one previous study [73], a new theoretical background for equilibrium molecular dynamics simulation is applied to a model of Ni<sub>50</sub>Al<sub>50</sub> to showcase the influence on thermotransport properties by the interatomic potential used for the simulation. By incorporation of the Green-Kubo formalism, thorough information about transport properties of the model system is gained. Driven by a temperature gradient, thermotransport behaviour is analysed. A different potential for the embedded-atom method is then used and results compared to other computational studies as well as experimental data. While the prediction of direct transport coefficients via both EAM potentials (EAM-2002 [74] and EAM-2009 [48]) consistently agree, a contrary behaviour of the cross-coupled heat and mass transport results arise, predicting opposite directions of the heat of thermotransport.

Simulations in molecular dynamics are performed for the model system Ni<sub>50</sub>Al<sub>50</sub> in a considered temperature range 4000 K to 1750 K [73]. For evaluation of the movement of atoms over time, the Verlet algorithm is used. Introducing time constants representing characteristic times of relaxation of the auto- and cross-correlation functions needed for evaluation of the total heat flux,  $J_q$ . Its reduced part,  $J'_q$ , contains enthalpic contributions, expressed through partial enthalpies carried by the interdiffusion flux,  $J_c$ . Further investigation of thermodynamic properties is then carried out and compared to experimental results and the EAM-2002 potential. Visualisation of partial enthalpies and autocorrelation functions are thoroughly explained by supporting in-depth explanation and derivation of theoretical background resulting in opposite signs of thermotransport for the different EAM potentials. For its calculation, the sign of  $L'_{cq}$  is dependent on the two variables of  $C_{cq}(0)$  and  $\overline{H}_c$  (the characteristic enthalpy per atom), both of which are dependent on each potential of the embedded-atom method. Therefore it is established, that under the presence of a temperature gradient, component 1 will diffuse from the cold to the hot end if  $\frac{C'_{cq}(0)}{C_{cc}(0)} =$ 

 $\frac{c_{cq}(0)}{c_{cc}(0)} - \overline{H}_c > 0.$  Vice versa, component 1 will diffuse from the hot to the cold end if  $\frac{C'_{cq}(0)}{c_{cc}(0)} = \frac{c_{cq}(0)}{c_{cc}(0)} - \overline{H}_c < 0.$  This method is very useful for fitting interatomic potential for reproduction of the sign of thermotransport obtained from experiments in a very time efficient manner.

The work provides detailed understanding of phenomenological coefficients of thermotransport and thermodynamic properties in the melt and their dependence on the potential used. Introducing a novel methodology for quick analysis for fitting interatomic potential, while also elaborating on a quantitative prediction of complete thermotransport processes, by making use of the reduced heat of transport parameter,  $J'_q$ , associated with the interdiffusion flux,  $J_c$ . Consequently, this content helps for a better understanding of peculiarities of transport properties of the model system by decomposing transport coefficients into the product of equal-time correlation of fluxes and the time constant that characterises decay in their correlation. Knowledge gained on the thermotransport and thermodynamic properties in alloys is crucial for the choice and the design of materials, particularly in the wide field of materials science and its broad range of engineering applications.

Further research is undertaken on binary melts of the Ni-Al system, considering a wide composition and temperature range, creating an extensive database on diffusion and thermotransport properties in [14]. This work [14] provides elaborated insights into theoretical background with simulation results of high accuracy and careful comparison with existing experimental data. Here, a model describing the behaviour of enthalpy of mixing in the melt is developed, which can be used for the evaluation of partial enthalpies. This is a great method for a detailed description of thermotransport properties. Calculations on  $Q_C^{*'}$ , the reduced heat of transport, are used to describe pure heat conduction in isothermal conditions. The evaluation allows for the prediction of the direction of atoms of different species as a result of their migration under a temperature gradient, concluding that Ni atoms migrate to the cold end; whilst the Al atoms migrate toward the hot end [14]. The simulation results are collected in an extensive set of data which is then further used in [11] (follows in Chapter 5) to establish theoretical relations in diffusion and thermotransport properties for melts of different types.

#### 4.2 BINARY LIQUID ALLOY WITH DEMIXING TENDENCY

#### 4.2.1 The Cu-Ag System

Previous work [16] investigates mass transport properties of liquid Cu-Ag alloys using molecular dynamics. The simulation is performed by applying the Green-Kubo formalism to obtain results over a wider temperature and composition range. The benefit of this method over other theoretical approaches used in the field is, the minimisation of errors that occur otherwise in approaches based on the correctness of physical assumptions on structure and type of diffusive motion. The molecular dynamics method is a reliable approach to obtain diffusion coefficients in the melt and interaction of atoms with each other calculated with interatomic potentials. Statistical mechanics are applied to solve the time evolution of the system, resulting in tracer coefficients and various measurable transport properties of the liquid melt. Simulation results are validated by comparison to existing experimental data. The large number of calculations creates a vast set of mass transport coefficients, temperature- and composition dependent, which can be used to predict the outcome of real life experiments on Cu-Ag melts [16].

The calculations in [16] elaborate on theoretical relations of the interdiffusion flux,  $J_c$ , and its relation involving microscopic fluxes of matter of atoms of different species in the melt. Using statistical mechanics to calculate phenomenological coefficients that are then evaluated with the Green-Kubo formalism via integration of correlation functions over time. Additionally, calculating the tracer- and collective diffusion coefficients in the melt as well as the well-known Manning factor. These are then used to obtain the mean-squared displacement of atoms of different species. The phenomenological coefficients evaluated in [16] characterise kinetics of tracer and collective diffusion in the melt of Cu-Ag models. Diffusion processes that arise in the melt of a system typically follow the Arrhenius law and are well described by the equation:  $D = D_0 exp(-E_A/k_BT)$ . As a result of thorough treatment of simulation data and establishing theoretical relations with help of statistical mechanics, a set of Arrhenius-parameters is presented, liquidus temperatures of pure Ag and Cu, in addition to several alloys shown and finally compared to existing experimental results. Visualisation of tracer diffusion coefficients including Arrhenius fits and experimental data showcase the high accuracy of the applied simulation method and used interatomic potential [16].

This work [16] offers a detailed insight into mass transport properties of liquid Cu-Ag melts. Via comparison of simulation and experiments, the accuracy of this study is confirmed and can therefore be used to predict kinetics that arise in the solidification process of Cu-Ag melts [16]. The created overview gives a broad picture of temperature- and composition dependencies of diffusion properties, describing self-diffusion, tracer diffusion and the kinetic part of interdiffusion as well as the Manning factor. Increasing commercial demand for copper materials and its alloys operating at high temperatures, makes a better understanding of solidification processes that arise in the melt a crucial requirement and amplifies the importance of the chosen system [75,76]. Theoretical relations elaborated become a significant help for designing new materials with critical material-properties requirements for applications in the field of engineering. Finally, outcomes of this study are used for a comparison of melts of different types in the following Chapter 5.

# Chapter 5: Diffusion Kinetics in Binary Liquid Alloys with Ordering and Demixing Tendencies

# 5.1 INTRODUCTION

This chapter explores theoretical relation of diffusion coefficients in terms of tracer and collective diffusion dynamics and addresses the objectives stated in section 2.7. The presented work has already been published as a book chapter as part of the Springer series in materials science. Its manuscript has been reproduced in its entirety to contextualise the achieved methodology and results in the framework of this thesis. The thorough examination of theoretical background exploits generalised Langevin equations for velocities, using differential calculations for the velocity autocorrelation functions and discusses their properties in the equilibrium state of the system. Also, with tracer memory kernels and random forces of the atoms of different species, it presents an alternative expression for the interdiffusion flux,  $J_c$ . By taking into consideration the dependence of frequency of diffusion coefficients, correlations between the random forces and the interdiffusion flux are elaborated. The correction factor, S, which characterises cross-correlation effects in the collective part of diffusion kinetics, is decomposed. By making use of the energy fluctuation-dissipation theorem and its application to different types of melts with chemical ordering (Ni-Zr and Ni-Al) and demixing tendency (Cu-Ag) case study systems, contrary behaviour of the different type systems is derived.

The decomposed properties of the correction factor, S, namely  $S_0$  and  $W_{12}/k_BT$ , are calculated and shown as composition dependent figures, clearly displaying the different trends of systems with chemical ordering and demixing tendency. As predicted by previously established theoretical treatment, in case of chemical ordering, i.e. Ni-Al and Ni-Zr, the correction factor is not exceeding unity over the whole composition range, in contrast to the case study of Cu-Ag which shows the correction factor greater than unity. A closer look into the decomposed factor  $S_0$  shows differences within melts of systems with chemical ordering as a result of their ratio of atomic masses and diffusion coefficients, creating a damping effect of single-particle kinetics in the Ni-Zr system while magnifying said effect in the Ni-Al system. Further investigations of the properties display and clarify alterations in the behaviour of the different type systems, additionally applying gained knowledge and understanding of theoretical background for validation to experimental work.

This work dives deep into the background and derivation of theoretical treatment of thermotransport properties in binary melts, reflecting significant results dependent on atomic ordering properties of the melt. A clear distinction between melts with mixing- and demixing tendency is established via behaviour of the correction factor and its decomposed properties. For binary liquid random alloy, introducing a novel concept, stating that the correction factor  $S = S_0$  when  $W_{12} = 0$ . Further investigation determines  $S < S_0$  ( $W_{12} < 0$ ) for binary mixing melts with chemical ordering and opposite behaviour for melts with demixing tendency  $S > S_0$  ( $W_{12} > 0$ ). Thus, demonstrated theory can be used to interpret experimental results obtained related to the Darken equation and to study the correction factor more detailed. The outcomes of this chapter deliver fundamental understanding of atomic behaviour of the simulated alloy systems. This is used to predict diffusion dynamics of melts upon solidification and its resulting microstructure. Hence, improving the controllability of designing advanced materials, like metallic glass.

#### 5.2 PUBLICATION

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The statement of co-authorship can be found in Appendix A.

Abstract. Theoretical relationship between collective and tracer diffusion coefficients has been derived and tested for different types of binary melts: (i) with an ordering tendency (case study on Ni-Al and Ni-Zr melts) and (ii) with a demixing tendency (case study on Cu-Ag melts). The obtained relationship explicitly demonstrates microscopic cross-correlation effects in the kinetics of collective diffusion. Our approach incorporates molecular dynamics calculations, modelling and statistical mechanical analysis based on fundamental concepts of the fluctuation-dissipation theorem, generalized Langevin equation and Mori-Zwanzig formalism. We also applied the developed theory to interpret recent available experimental data as well as our molecular dynamics data of diffusion kinetics in different types of binary melts: with chemical ordering and contrarily with demixing tendency.

#### 5.2.1 Introduction

The alloys of the studied systems (Ni-Al, Ni-Zr, Cu-Ag) attracted attention thanks to their unique physical, chemical and electrical properties [1-8]. Since the studied alloys have significant engineering importance, it is necessary to have an excellent understanding of mass transport properties of these alloys within the liquid state. In particular, the knowledge of diffusion coefficients in liquid alloys is essential for controlling of the crystalline microstructure during solidification process in experiment [9] as well as for essential parameters input in phase field modelling [9,10]. However, the current capacity of existing experimental diffusion database of liquid alloys is very limited [11-18] because of the diffusion properties in the melts. Hence, establishing theoretical relation between different mass transport coefficients is important for a quantitative prediction of materials properties as some of the unknown coefficients can be expressed via others, which are reliably measurable in the experiment [19].

Dynamical and transport properties of many-body system can be expressed in terms of the time-correlation functions of appropriate physical variables. For example, the frequency-dependent thermal conductivity and diffusion coefficient of a manybody system are the one-sided Fourier transforms of the time-correlation functions of the heat and mass currents, respectively. Therefore, for understanding, predicting, controlling dynamical, and transport properties of many-body systems, it is important to develop methods of calculation, modelling and analysis of this time-correlation functions. Our group developed an innovative approach based on fundamental concepts of the Brownian motion [20,21], the fluctuation-dissipation theorem [20,21], generalized Langevin equation [20,21] and Mori-Zwanzig formalism [22-25]. These concepts state a general relationship between response of a given system to an external disturbance and the internal fluctuations of the system in the absence of the disturbance. In this chapter, we will focus on mass transport properties in different types of binary melts: with chemical ordering (case study on Ni-Al and Ni-Zr melts) and with phase separation tendency (case study on Cu-Ag melts).

In 1948 Darken [26] introduced an equation for a binary system, which expressed the interdiffusion coefficient,  $D_c$ , via two self-diffusion coefficients,  $D_1$  and  $D_2$ :

$$D_c = \Phi(c_2 D_1 + c_1 D_2), \tag{1}$$

where  $c_1$  and  $c_2$  are the atomic fractions of species 1 and 2,  $\Phi$  is the thermodynamic factor. Note  $c_1 = \frac{N_1}{N}$ ,  $c_2 = \frac{N_2}{N}$ , where  $N_1$  is number of atoms of species 1,  $N_2$  is number of atoms of species 2, N is the total number of atoms in the system, i.e.  $N = N_1 + N_2$ .

Equation (1) is known as Darken equation. Both  $D_c$  and  $\Phi$  are in principal accessible in experiment. The thermodynamic factor  $\Phi$  is the normalized second derivative of the molar Gibbs free energy G/N with respect to the composition  $c_1$  ( $c_2$ ) at constant temperature T and pressure P:

$$\Phi = \frac{c_1 c_2}{k_{\rm B} T} \left( \frac{\partial^2 (G/N)}{\partial c_1^2} \right)_{T,P} = \frac{c_1 c_2}{k_{\rm B} T} \left( \frac{\partial^2 (G/N)}{\partial c_2^2} \right)_{T,P},\tag{2}$$

where  $k_{\rm B}$  is the Boltzmann constant.

In 1961 Manning [27] included a certain correction factor of the microscopic kinetic origin, *S*, into the (1):

$$D_c = \Phi S(c_2 D_1 + c_1 D_2), \tag{3}$$

Equation (3) is known as the Darken-Manning equation [28].

On the other hand, the Onsager phenomenological transport equation can be written as [29,30]

$$\boldsymbol{J_c} = \boldsymbol{L_{cc}}\boldsymbol{X_c'}.$$

where  $J_c$  is the interdiffusion flux,  $L_{cc}$  is Onsager phenomenological coefficient for mass transport and  $X'_c$  conjugated thermodynamic force related to interdiffusion flux. Interdiffusion flux  $J_c$  links with interdiffusion coefficients  $D_c$  by Fick's law:

$$\boldsymbol{J}_{c} = c_{2}\boldsymbol{J}_{1} - c_{1}\boldsymbol{J}_{2} = -\frac{N}{V}D_{c}\nabla c_{1} = \frac{N}{V}D_{c}\nabla c_{2} = -\frac{N}{V}D_{c}(c_{2}\nabla c_{1} - c_{1}\nabla c_{2}), \quad (5)$$

where *V* is the volume of the system.

Furthermore, according to the Onsager formalism of the thermodynamics of irreversible processes for an isotropic binary melt [21,22], the ratio  $D_c/\Phi$  is equal to the renormalized phenomenological Onsager coefficient  $\tilde{L}_{cc}$  [23]:

$$\frac{D_c}{\Phi} = \frac{Vk_{\rm B}T}{Nc_1c_2}L_{cc} = \tilde{L}_{cc}.$$
(6)

Now for correction factor we have:

$$S = \frac{D_c}{\Phi(c_2 D_1 + c_1 D_2)} = \frac{V k_{\rm B} T L_{cc}}{N c_1 c_2 (c_2 D_1 + c_1 D_2)} = \frac{\tilde{L}_{cc}}{c_2 D_1 + c_1 D_2}$$
(7)

Hence, the correction factor *S* characterises cross-correlation effects in collective diffusion process. Available experimental [17] and simulation data [12,19,31] for the correction factor suggested that it should be approximately less than unity for alloys

with ordering tendency. However, a detailed formula for the correction factor S involving a cross correlation term has not been obtained until now.

In this chapter, we will derive an expression relating collective and tracer diffusion coefficients. We are aiming to reveal explicitly the cross-correlation effects in collective diffusion. We will analyse the obtained relation for different types of binary melts: with chemical ordering (case study on Ni-Al and Ni-Zr melts) and with phase separation tendency (case study on Cu-Ag melts). Finally, we apply our theoretical findings for interpretation of recent available experimental data and our molecular dynamics (MD) data of diffusion kinetics.

#### 5.2.2 Theoretical Treatment

## Generalized Langevin Equations for the Velocities and Integral-Differential Equations for the Velocity Autocorrelation Functions

The generalised Langevin equation plays a key role in the theoretical development through use of the projection-operator formalism of statistical mechanics introduced by Zwanzig and Mori [22-25,32]. First, consider an isotropic binary liquid alloy consisting of  $N_1$  atoms with mass  $m_1$  and  $N_2$  atoms having mass  $m_2$  in a fixed volume V at thermal equilibrium.

By the Mori-Zwanzig formalism [22-25,32] the total force  $f_{\alpha i}(t)$  acting on the tagged particle can be decomposed on the sum of systematic and random terms, the first and the second summands on the RHS of Equation (8) respectively:

$$m_{\alpha} \frac{d\boldsymbol{v}_{\alpha i}(t)}{dt} = \boldsymbol{f}_{\alpha i}(t) = -m_{\alpha} \int_{0}^{t} K_{\alpha}(t-t')\boldsymbol{v}_{\alpha i}(t')dt' + \boldsymbol{R}_{\alpha i}(t).$$
(8)

This is a generalized Langevin equation for the velocities  $v_{\alpha i}(t)$  for a binary system, where  $\alpha = 1, 2$  ( $\alpha = 1: i \in [1, ..., N_1], \alpha = 2: i \in [1, ..., N_2]$ ) are tagged atoms of species 1 and 2;  $K_{\alpha}(t)$  is the memory kernel for the evolution of the systematic/ frictional forces acting on the tagged atom  $\alpha$  at time t. The memory kernel is proportional but opposite to the velocities of the tagged atoms at times prior to time  $t, 0 \le t' \le t$ .

 $R_{\alpha i}(t)$  is the random force. A random force possesses three properties [22-25,32]:

- (1) It vanishes in the mean  $\langle \mathbf{R}_{\alpha i}(t) \rangle = 0$  (notation  $\langle \cdots \rangle$  means the statistical time average at thermal equilibrium),
- (2)  $f_{\alpha i}(0) = R_{\alpha i}(0)$ , i. e. initially, the total and random forces are the same (see Equation (8)).
- (3) Total and random forces evolve differently with time and relation  $\langle \mathbf{R}_{\alpha i}(t) \mathbf{v}_{\alpha i}(0) \rangle = 0$  is preserved for all times t. In other words: random force is not correlated with the initial velocity  $\mathbf{v}_{\alpha i}(0)$ .

Hence, if we multiply Equation (8) by  $v_{\alpha i}(0)$  and take the thermal average, using the above mentioned third property of random force we will get the integraldifferential equation for the velocity autocorrelation functions, which often called a satellite equation for Langevin generalised Equation (8):

$$\frac{d\varepsilon_{\alpha}(t)}{dt} = -\int_{0}^{t} K_{\alpha}(t-t')\varepsilon_{\alpha}(t')dt', \qquad (9)$$

where  $\varepsilon_{\alpha}(t) = \langle \boldsymbol{v}_{\alpha i}(t) \boldsymbol{v}_{\alpha i}(0) \rangle / \langle \boldsymbol{v}_{\alpha i}^2 \rangle = m_{\alpha} \langle \boldsymbol{v}_{\alpha i}(t) \boldsymbol{v}_{\alpha i}(0) \rangle / 3k_B T$  are the normalized velocity autocorrelation functions. The squared static velocities, also called thermal velocities, are equal to  $\langle \boldsymbol{v}_{\alpha i}^2 \rangle = 3k_B T / m_{\alpha}$ , so that  $\varepsilon_{\alpha}(0) = 1$ .

# Properties of the Correlation Functions of Dynamical Variables in Equilibrium

We should note, that throughout the chapter, above and below, we implicitly employ useful properties of the correlation functions of dynamical variables in equilibrium. Namely, in equilibrium the derivative of the time correlation function of dynamical variables Z(t) and Y(t) with respect to the initial time  $t_0$  must be zero, namely:  $\frac{d}{dt_0} \langle Z(t + t_0) Y(t_0) \rangle = 0$ . So, applying the product rule the LHS of the above expression we get:

$$\langle \frac{d}{dt_0} \left( Z(t+t_0) \right) Y(t_0) \rangle + \langle Z(t+t_0) \frac{d}{dt_0} \left( Y(t_0) \right) \rangle$$
$$= \langle \dot{Z}(t+t_0) Y(t_0) \rangle + \langle Z(t+t_0) \dot{Y}(t_0) \rangle = 0.$$
(10)

And in case of autocorrelation function, i.e. Z(t) = Y(t), in we get  $\langle \dot{Z}(t)Z(0) \rangle = -\langle Z(t)\dot{Z}(0) \rangle$ ,  $\langle \dot{Z}(t)Z(t) \rangle = \langle \dot{Z}(0)Z(0) \rangle = \langle \dot{Z}Z \rangle = 0$ , and for the second derivative  $\langle \ddot{Z}(t)Z(0) \rangle = -\langle \dot{Z}(t)\dot{Z}(0) \rangle$ , where  $\dot{Z} = \frac{dZ}{dt}$  and  $\ddot{Z} = \frac{d^2Z}{dt^2}$ .

Using these properties and random force properties, we can now express the memory kernels as autocorrelation of the random forces [22-25,32]. Indeed, multiplying Equation (8) by  $\mathbf{R}_{\alpha i}(0)$ , or by  $\mathbf{f}_{\alpha i}(0)$ , which is the same by the above mentioned second property of the random force, and taking the thermal average and using Equation (9), we will get:

$$K_{\alpha}(t) = \langle \boldsymbol{R}_{\alpha i}(t) \boldsymbol{R}_{\alpha i}(0) \rangle / m_{\alpha}^2 \langle \boldsymbol{v}_{\alpha i}^2 \rangle$$
(11)

or

$$K_{\alpha}(t) = \langle \boldsymbol{R}_{\alpha i}(t) \boldsymbol{R}_{\alpha i}(0) \rangle / 3m_{\alpha} k_{B} T, \qquad (12)$$

using expression for squared static velocities  $\langle v_{\alpha i}^2 \rangle = 3k_B T/m_{\alpha}$ .

In addition, it can be seen from Equation (9) that functions  $\varepsilon_{\alpha}(t)$  and  $K_{\alpha}(t)$  are even. It is interesting to highlight that at zero time, the memory kernels represent a square of Einstein frequency,  $K_{\alpha}(0) = \Omega_{\alpha}^2$ , a frequency, at which a tagged atom of species  $\alpha$  would vibrate on average if they were experiencing small oscillations in the potential wells generated by the neighbouring atoms when retained at their mean equilibrium positions around the tagged atom. Indeed,  $K_{\alpha}(0) = \frac{\langle \mathbf{R}_{\alpha i}^2 \rangle}{3m_{\alpha}k_{\mathrm{B}}T} = \frac{m_{\alpha}\langle \mathbf{v}_{\alpha i}^2 \rangle}{3k_{\mathrm{B}}T}$ , where  $\dot{\mathbf{v}}_{\alpha i} = \frac{d\mathbf{v}_{\alpha i}(t)}{dt} = -m_{\alpha}^{-1}\nabla_{\alpha i}U$  is acceleration and U is potential energy.

#### **Total Force Decomposition**

Total force decomposition involves two steps [24]:

- (1) The total force is represented of the sum:  $f_{\alpha i}(t) = f_{\alpha i}^{(I)}(v_{\alpha i}(t')) + f_{\alpha i}^{(II)}(t)$ , where the first summand  $f_{\alpha i}^{(I)}(v_{\alpha i}(t'))$  depends on the past history of velocity  $v_{\alpha i}$  since  $0 \le t' \le t$  while the second summand  $f_{\alpha i}^{(II)}(t)$  describes contribution which depends explicitly on dynamics of the other atoms at time t.
- (2) The functional  $f_{\alpha i}^{(l)}(v_{\alpha i}(t'))$  can be further decomposed into linear and nonlinear terms:  $f_{\alpha i}^{(l)}(v_{\alpha i}(t')) = f_{\alpha i}^{(l,\text{linear})}(v_{\alpha i}(t')) + f_{\alpha i}^{(l,\text{non-linear})}(v_{\alpha i}(t'))$ . The linear term of the expansion is the systematic force of the generalized Langevin equation, i.e. the first summand in the Equation (8) (integral term of Equation (8)). While the sum of the non-linear term together with  $f_{\alpha i}^{(\text{II})}(t)$  uniquely defines the random force of the generalized Langevin equation, namely the random force is equal to  $\mathbf{R}_{\alpha i}(t) = f_{\alpha i}^{(l,\text{non-linear})}(v_{\alpha i}(t'), 0 \le t' \le t) + f_{\alpha i}^{(\text{II})}(t)$ .

Consequently, the total force can be decomposed as:

$$\boldsymbol{f}_{\alpha i}(t) = -m_{\alpha} \int_{0}^{t} K_{\alpha}(t-t') \boldsymbol{v}_{\alpha i}(t') dt' +$$
$$+ \boldsymbol{f}_{\alpha i}^{(I,\text{non-linear})} (\boldsymbol{v}_{\alpha i}(t')) + \boldsymbol{f}_{\alpha i}^{(\text{II})}(t)$$
(13)

### Generalized Langevin Equations and Its Satellite Equations for the Interdiffusion Flux

As stated by the Mori-Zwanzig formalism [22-25,32], we can write equations analogous to Equations (8) and (9) for any arbitrary chosen dynamical variable and its autocorrelation function, as we did for velocity. Our choice for further theoretical treatment in this chapter will be the interdiffusion flux  $J_c(t)$ , due to its invariance to the choice of reference frame [31, 33, 34] as we will demonstrate below. Therefore, the microscopic expression for the interdiffusion flux  $J_c(t)$  of a binary liquid alloy at thermal equilibrium in fixed volume V is equal to [31, 33, 34]:

$$\boldsymbol{J}_{c}(t) = \frac{N}{V} c_{1} c_{2} \bar{\boldsymbol{v}}_{c}(t) = \frac{N}{V} c_{1} c_{2} [\bar{\boldsymbol{v}}_{1}(t) - \bar{\boldsymbol{v}}_{2}(t)] = c_{2} \boldsymbol{J}_{1}(t) - c_{1} \boldsymbol{J}_{2}(t) , \qquad (14)$$

where  $J_1(t)$  and  $J_2(t)$  are the fluxes of species 1 and 2 and  $\bar{\mathbf{v}}_1(t)$  and  $\bar{\mathbf{v}}_2(t)$  are the mean velocities of species 1 and 2,  $\bar{\mathbf{v}}_c(t) \equiv \bar{\mathbf{v}}_{12}(t)$ .

Now from Equation (14) we can see that the interdiffusion flux  $J_c(t)$  is indeed does not depend on the choice of reference frame because it defines the fluxes of components  $J_1(t)$  and  $J_2(t)$  relative to each other. In the zero-momentum reference frame, we have  $c_1m_1\bar{\mathbf{v}}_1(t) + c_2m_2\bar{\mathbf{v}}_2(t) = 0$  or  $m_1J_1(t) + m_2J_2(t) = 0$ , so that:

$$\boldsymbol{J}_{c}(t) = \frac{N}{V}c_{1}c_{2}\bar{\boldsymbol{v}}_{c}(t) = \frac{m}{m_{2}}\boldsymbol{J}_{1}(t) = -\frac{m}{m_{1}}\boldsymbol{J}_{2}(t) = \frac{m}{m_{2}V}\sum_{i=1}^{N_{1}}\boldsymbol{v}_{1i}(t) = -\frac{m}{m_{1}V}\sum_{i=1}^{N_{2}}\boldsymbol{v}_{2i}(t), \quad (15)$$

where  $m = c_1m_1 + c_2m_2$  is the total system mass per atom. Here, mass per atom carried by flux  $J_1$  is  $m_1$  and mass per atom carried by flux  $J_2$  is  $m_2$ . Then, it follows from Equation (15) that the effective mass per atom carried by interdiffusion flux  $J_c$  is equal to  $m_c = m_1m_2/m$ . In other words, at thermal equilibrium the interdiffusion flux is produced by an effective system element containing  $Nc_1c_2$  identical particles of mass  $m_c$  in the given volume V with the mean velocity equal to zero and the thermal velocity  $(3k_BT/m_c)^{1/2}$  from the Maxwell–Boltzmann distribution. Furthermore, on a basis of Equation (15) we can obtain  $3Nc_1c_2k_BT/m_c = V^2\langle J_c^2\rangle$  [31]. Hence, we can readily derive from an explicit analytical expression of the form  $V^2\langle J_c^2\rangle =$  $3Nc_1c_2k_BT/m_c$ . This is analogous to the expression for the squared static velocities  $\langle v_{\alpha i}^2 \rangle$  derived in Section 2.1 above and confirmed by our MD simulations [31].

Therefore, the generalized Langevin equation for the interdiffusion flux  $J_c(t)$ and the equation for its normalized autocorrelation function  $\varepsilon_c(t) = m_c V^2 \langle J_c(t) J_c(0) \rangle / 3N c_1 c_2 k_B T$  ( $\varepsilon_c(0) = 1$ ) can be presented as:

$$m_{c}V\frac{dJ_{c}(t)}{dt} = F_{c}(t) = -m_{c}V\int_{0}^{t}K_{c}(t-t')J_{c}(t')dt' + R_{c}(t),$$
(16)

$$\frac{d\varepsilon_c(t)}{dt} = -\int_0^t K_c(t-t')\varepsilon_c(t')dt'.$$
(17)

In these equations,  $F_c(t)$  and  $R_c(t)$  are the total and random forces, respectively, acting on the mass  $m_c$ . Consequently,  $R_c(t)$  has random force properties listed in Section 2.1 and similar to the properties of  $R_{\alpha i}(t)$ , namely:

(i)  $\langle \boldsymbol{R}_{c}(t) \rangle = 0,$ 

(ii) 
$$F_c(0) = R_c(0)$$

(iii) 
$$\langle \boldsymbol{R}_c(t)\boldsymbol{J}_c(0)\rangle = 0$$
, and

(iv) 
$$K_c(t) = \langle \mathbf{R}_c(t) \mathbf{R}_c(0) \rangle / m_c^2 V^2 \langle \mathbf{J}_c^2 \rangle = \langle \mathbf{R}_c(t) \mathbf{R}_c(0) \rangle / 3Nc_1 c_2 m_c k_B T$$
).

The memory kernel  $K_c(t)$  describes the evolution of the systematic force acting on the mass  $m_c$ . As we can see from Equation (17) both autocorrelation functions  $\varepsilon_c(t)$ and  $K_c(t)$  are even functions of time. Furthermore, at initial time the memory kernel can be expressed via corresponding effective Einstein frequency  $\Omega_c$ :  $K_c(0) = \Omega_c^2 = \frac{\langle \mathbf{R}_c^2 \rangle}{3m_c k_B T} = \frac{m_c V^2 \langle \mathbf{j}_c^2 \rangle}{3Nc_1 c_2 k_B T}$ , where  $\mathbf{j}_c = \frac{dJ_c(t)}{dt} = (-1)^{\alpha} m_c^{-1} \sum_{i=1}^{N_{\alpha}} \nabla_{\alpha i} U$ .

### Alternative Expression for Interdiffusion Flux via Single-Particle Memory Kernels and Random Forces

Alternatively combining Langevin equation for velocity Equation (8) and interdiffusion flux definition Equations (14) and (15) we will arrive to more significant expression for  $J_c(t)$ , because it includes the single-particle memory kernels,  $K_1(t)$  and  $K_2(t)$ , and random forces,  $R_{1i}(t)$  and  $R_{2j}(t)$ :

$$m_{c}V\frac{d\boldsymbol{J}_{c}(t)}{dt} = \boldsymbol{F}_{c}(t) =$$
$$= -m_{c}V\int_{0}^{t} \left[c_{2}\frac{m_{2}}{m}K_{1}(t-t') + c_{1}\frac{m_{1}}{m}K_{2}(t-t')\right]\boldsymbol{J}_{c}(t')dt' + \boldsymbol{R}_{12}(t). (18)$$

where force  $\mathbf{R}_{12}(t)$  represents the contribution to the total force associated with interdiffusion flux  $\mathbf{F}_c(t)$  due to the difference in the average random accelerations of atoms of species 1 and 2,  $\frac{\overline{\mathbf{R}}_1(t)}{m_1}$  and  $\frac{\overline{\mathbf{R}}_2(t)}{m_2}$  respectively Equation (19), so that:

$$\boldsymbol{R}_{12}(t) = Nc_1 c_2 m_c \left( \frac{\overline{\boldsymbol{R}}_1(t)}{m_1} - \frac{\overline{\boldsymbol{R}}_2(t)}{m_2} \right), \tag{19}$$

where

$$\overline{R}_{1}(t) = \frac{1}{N_{1}} \sum_{i=1}^{N_{1}} R_{1i}(t), \qquad \overline{R}_{2}(t) = \frac{1}{N_{2}} \sum_{j=1}^{N_{2}} R_{2j}(t)$$
(20)

are the average random forces acting on atoms of species 1 and 2 at time t, respectively. It follows from Equation (18) that  $F_c(0) = R_{12}(0) = R_c(0)$  and  $\langle R_{12}(t) \rangle = 0$ . It should be highlighted that  $R_{12}(t)$  is not truly a random force by definition, but the difference between the random forces.

Since Equations (16) and (18) both describe the total force acting on the mass carried by the interdiffusion flux  $J_c$  we can equate them and divide by the effective mass  $m_c$ :

$$V\int_{0}^{t} \left[ c_2 \frac{m_2}{m} K_1(t-t') + c_1 \frac{m_1}{m} K_2(t-t') - K_c(t-t') \right] J_c(t') dt' = \frac{R_{12}(t) - R_c(t)}{m_c}.$$
 (21)

Now, after multiplying both sides of Equation (21) by  $J_c(0)$  and taking the thermal average, we arrive to:

$$\int_{0}^{t} \left[ c_2 \frac{m_2}{m} K_1(t-t') + c_1 \frac{m_1}{m} K_2(t-t') - K_c(t-t') \right] \varepsilon_c(t') dt' = \frac{P_{12}(t)}{k_{\rm B}T}, \quad (22)$$

where

$$P_{12}(t) = \frac{V}{3Nc_1c_2} \langle \boldsymbol{R}_{12}(t) \boldsymbol{J}_c(0) \rangle.$$
(23)

corresponds to the correlations between fluctuations of  $R_{12}(t)$  and  $J_c(0)$  at t > 0.

# Frequency-Dependent Diffusion Coefficients in a Binary Liquid Alloy

Now, taking the one-sided Fourier transforms of Equations (9), (17) and (22) and combining them, in frequency domain we will get:

$$\tilde{L}_{cc}(\omega) = \frac{m^2 D_1(\omega) D_2(\omega)}{c_1 m_1^2 D_1(\omega) + c_2 m_2^2 D_2(\omega)} \left[ 1 + \frac{W_{12}(\omega)}{k_{\rm B} T} \right].$$
(24)

where

$$D_1(\omega) = \frac{k_{\rm B}T}{m_1} \int_0^\infty \varepsilon_1(t) e^{-i\omega t} dt, \qquad (25)$$

$$D_2(\omega) = \frac{k_{\rm B}T}{m_2} \int_0^\infty \varepsilon_2(t) e^{-i\omega t} dt, \qquad (26)$$

$$\tilde{L}_{cc}(\omega) = \frac{k_{\rm B}T}{m_c} \int_0^\infty \varepsilon_c(t) e^{-i\omega t} dt, \qquad (27)$$

are the frequency-dependent diffusion coefficients in a binary liquid alloy represented via related velocity autocorrelation functions consistent with the basic theorem for linear responses [21-25,32,35].

$$W_{12}(\omega) = \int_{0}^{\infty} P_{12}(t) e^{-i\omega t} dt = \frac{V}{3Nc_1 c_2} \int_{0}^{\infty} \langle \mathbf{R}_{12}(t) \mathbf{J}_c(0) \rangle e^{-i\omega t} dt.$$
(28)

# Correlations Between Fluctuations of $R_{12}(t)$ and $J_c(0)$

In short time limit  $t \to 0$  the value of  $P_{12}(t)$  can be approximated via the first derivative of  $P_{12}(t)$  evaluated t = 0 [36], as

$$\frac{\dot{P}_{12}(0)}{k_B T} = \frac{1}{k_B T} \frac{dP_{12}(t)}{dt} \bigg|_{t=0} = c_2 \frac{m_2}{m} \Omega_1^2 + c_1 \frac{m_1}{m} \Omega_2^2 - \Omega_c^2, \quad (29)$$

Due to common MD simulation configurations of interatomic interactions, in the short time limit  $t \rightarrow 0$ ,  $P_{12}(t)$  can be estimated as [36]

$$\frac{P_{12}(t)}{k_{\rm B}T} \approx \sigma_{12} \Omega_c^2 t, \tag{30}$$

where

$$\sigma_{12} = \frac{c_2 m_2 \Omega_1^2 + c_1 m_1 \Omega_2^2}{m \Omega_c^2} - 1 \tag{31}$$

is the dimensionless factor which defines the initial sign of  $P_{12}(t)$  as the correlation between  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$  starts to develop with time. As a result,  $\sigma_{12} < 0$  and  $\sigma_{12} > 0$  indicate that  $\mathbf{R}_{12}(t)$  tends to initially create with  $\mathbf{J}_c(0)$  obtuse and acute angles, respectively as it is shown in Figure 1 representing the initial instant of time defined by  $\sigma_{12}$ .

The behaviour  $\sigma_{12} < 0$  and  $W_{12} < 0$  is expected for a binary melt exhibiting chemical ordering in the normal liquid state. Therefore an the initial angle in short time limit  $t \to 0$  for  $\sigma_{12} < 0$  (obtuse angle) between  $R_{12}(t)$  and  $J_c(0)$  should remain obtuse, ensuring a negative value of  $W_{12}$  which is expected for these type of melts accounting for their mixing tendency [36]. However, during the transition between the normal liquid state and the undercooled liquid state the angle between  $R_{12}(t)$  and  $J_c(0)$  may principally transform from and obtuse angle into an acute angle. This can be caused by the short-range atomic ordering which becomes unfavourable in the undercooled liquid state of the binary melt. This change advocates behaviour of the undercooled binary mixing melt towards a more thermodynamically stable state. Consequently, we can observe  $W_{12} > 0$  in the undercooled liquid state of a binary mixing melt exhibiting chemical ordering. Therefore, we may conclude that  $\sigma_{12} < 0$ and  $W_{12} < 0$  can be considered as necessary conditions for a binary mixing melt exhibiting chemical ordering to be in thermodynamic equilibrium. In addition, a relative change in  $W_{12}$  can be used to characterize variation in dynamical stability of atomic ordering in a binary mixing melt upon undercooling.



Figure 1: Evaluation of correlation between fluctuations of  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$  as a) the time average over correlation length  $W_{12}$  and b) in short time limit  $t \to 0$  for  $P_{12}$  (develops over time) and its initial instant  $\sigma_{12}$ 

#### 5.2.3 Results and Discussion

#### Frequency-Dependent Mass Transport Coefficients in the Hydrodynamic Limit

The most practical case for frequency-dependent mass transport coefficients is when  $\omega \to 0$ , i.e.  $t \to \infty$ , so called case of the hydrodynamic limit. In other words, we consequently leave out the frequency dependence in the notation. In this case Equation (24) for the Onsager coefficient  $\tilde{L}_{cc}$  becomes

$$\tilde{L}_{cc} = \frac{m^2 D_1 D_2}{c_1 m_1^2 D_1 + c_2 m_2^2 D_2} \left[ 1 + \frac{W_{12}}{k_{\rm B} T} \right]$$
(32)

and can be written with a sequence of three nested equations:

$$\tilde{L}_{cc} = S(c_2 D_1 + c_1 D_2), \tag{33}$$

where

$$S = S_0 \left( 1 + \frac{W_{12}}{k_{\rm B}T} \right) \tag{34}$$

with

$$S_0 = \frac{m^2 D_1 D_2}{m^2 D_1 D_2 + c_1 c_2 (m_1 D_1 - m_2 D_2)^2}.$$
(35)

From the obtained equations for pure components, i.e. for  $c_1 = 0$  or  $c_2 = 0$ , we get  $S_0 = 1$  as follows from Equation (35) and  $W_{12} = 0$  and S = 1, since  $R_{12} = 0$ , as

follows from Equations (15), (19), (23) and (28). Also from Equation (33) on the limit when  $c_1 \rightarrow 0$ , then  $\tilde{L}_{cc} \rightarrow D_1$  and if  $c_2 \rightarrow 0$ , then  $\tilde{L}_{cc} \rightarrow D_2$ . Moreover, in these cases the interdiffusion coefficient  $D_c \rightarrow \tilde{L}_{cc}$ , because  $\Phi \rightarrow 1$  (Equation (6)). Hence, within mentioned limits the coefficient of interdiffusion is approaching the coefficient of selfdiffusion of the minority species, so that  $D_c \rightarrow \tilde{L}_{cc} \rightarrow D_1$  when  $c_1 \rightarrow 0$  and  $D_c \rightarrow \tilde{L}_{cc} \rightarrow$  $D_2$  when  $c_2 \rightarrow 0$ .

#### **Decomposition of the Correction Factor**

In addition, further investigation of Equations (32)-(35) provides new insight into a relation of self and collective diffusion in binary melts. It follows from Equation (28) that  $W_{12} \equiv W_{12}(0)$  is associated to the average amount of generated-dissipated energy owed to the correspondences between fluctuations of  $R_{12}$  and  $J_c$ . Therefore in thermal equilibrium, the absolute value of  $W_{12}$  cannot surpass the characteristic thermal energy,  $k_{\rm B}T$ , by equipartition law [36], namely:  $|W_{12}| \leq k_{\rm B}T$ .

Next, it follows from Equation (35) that for all binary alloys:  $0 < S_0 \le 1$ . This means that for the correction factor S:  $0 \le S \le 2S_0$  or simply,  $0 \le S \le 2$ . Consequently, the correction factor S appears to break down into the product of two factors, see Equation (34). In binary melts for which a greater tracer diffusion coefficient is carried by the species with greater mass, it can become significant, i.e. substantially less than unity.

The first factor in Equation (34)  $S_0$  can be also be written in form of the ratio of the self-diffusion coefficients  $D_1/D_2$ , the ratio of the atomic masses  $m_1/m_2$ , and the composition  $c_1$  (or  $c_2$ ). Indeed, if we divide numerator and denominator of Equation (35) by  $m^2D_1D_2$  and rearrange we will get:

$$S_{0} = \frac{1}{1 + \frac{c_{1}c_{2}}{m^{2}D_{1}D_{2}}(m_{1}D_{1} - m_{2}D_{2})^{2}} = \frac{1}{1 + \frac{c_{1}c_{2}}{m^{2}D_{1}D_{2}}(m_{1}^{2}D_{1}^{2} - 2m_{1}D_{1}m_{2}D_{2} + m_{2}^{2}D_{2}^{2})} = \frac{1}{1 + c_{1}c_{2}\left(\frac{m_{1}^{2}D_{1}}{m^{2}D_{2}} - \frac{2m_{1}m_{2}}{m^{2}} + \frac{m_{2}^{2}D_{2}}{m^{2}D_{1}}\right)}$$
(36)

where  $m = m_1 c_1 + m_2 c_2$ .

Meanwhile, the second factor in the Equation (34),  $(1 + W_{12}/k_BT)$  is responsible for a collective energy generation-dissipation effect as a result of the correlations between fluctuations of the interdiffusion flux  $J_c$  and the force  $R_{12}$ , introduced by the average random accelerations  $\overline{R}_{\alpha}$  as stated by Equations (19-20).

For binary mixing melts showing tendency of ordering (Ni-Al, Ni-Zr) the angle between vectors  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$  should be obtuse as predicted in Section 2.7. In other words, during fluctuations the force  $\mathbf{R}_{12}$  effectively supresses the interdiffusion flux's deviation from equilibrium. Accordingly, in this case  $W_{12}$  is negative as well as the enthalpy of formation. According to Equation (34), when  $W_{12} < 0$ , we get S < 1.

On the other hand, for binary melts with demixing tendency (Cu-Ag), it is predicted that the angle between  $\mathbf{R}_{12}(t)$  and  $\mathbf{J}_c(0)$ , should be acute. In this case during fluctuations  $\mathbf{R}_{12}$  effectively stimulates interdiffusion flux deviation from equilibrium. Consequently, in this case we can predict that  $W_{12}$  is positive. For  $W_{12} > 0$ , S > 1according to Equation (34).

Hence, in general we can conclude  $W_{12}$  is connected with the free energy of formation of binary melts. Furthermore,  $W_{12}$  can be used to introduce the concept of random of a binary liquid random alloy, where  $W_{12} = 0$ , hence  $S = S_0 \le 1$ .

# Composition Dependence of S, $S_0$ and $W_{12}/k_BT$ for Ni-Al, Ni-Zr and Cu-Ag Systems: Molecular Dynamics, Theoretical Predictions and Experimental Data

For illustration, we show in Figures 2-4 the composition dependencies of S,  $S_0$  and  $W_{12}/k_BT$  for the different types of systems, namely: with an ordering tendency (a) Ni-Al and (b) Ni-Zr and with a demixing tendency (c) Cu-Ag, respectively.

The melts are MD models of their corresponding systems, calculated at various compositions and temperatures range from 1000 – 2200 K using the embedded-atom method (EAM) potential developed in [37]. For calculation of *S* and *S*<sub>0</sub> based on Equations (33) and (35), respectively, we made use of our MD data for  $\tilde{L}_{cc}$ ,  $D_1$  and  $D_2$ . Meanwhile,  $W_{12}/k_{\rm B}T$  was calculated based on Equation (34) using the results for *S* and *S*<sub>0</sub>, i.e.:  $\frac{W_{12}}{k_{\rm B}T} = \frac{S}{S_0} - 1$ .

The Onsager coefficient  $\tilde{L}_{cc}$  was evaluated within the framework of the Green-Kubo formalism [21,32,35,38] by means of the time integral of  $\varepsilon_c(t)$  (see Equation (27) at  $\omega = 0$ ), namely  $\tilde{L}_{cc} = \frac{k_{\rm B}T}{m_c} \lim_{t \to \infty} \int_0^t \frac{\langle J_c(t')J_c(0) \rangle}{\langle J_c^2 \rangle} dt'$ .

The self-diffusion coefficients of Ni and Al atoms [39], Ni and Zr atoms in [36] and Cu and Ag atoms [43] were calculated, according to the well-known Einstein relation [21,32,35], as:  $D_{\alpha} = \lim_{t \to \infty} \frac{\langle \frac{1}{N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \Delta r_{\alpha i}^{2}(t) \rangle}{6t}$ , where  $\Delta r_{\alpha i}(t) = r_{\alpha i}(t) - r_{\alpha i}(0)$  represent the time-displacements of single atoms of species 1 ( $i = 1 \dots N_{1}$ ) and 2 ( $j = 1 \dots N_{2}$ ), respectively (we assume here that Ni, Cu  $\equiv 1$  and Al, Zr, Ag  $\equiv 2$ ).

We took into consideration seven alloy compositions in Ni-Al system for example: Nis7.5Al12.5, Ni75Al25, Ni62.5Al37.5, Ni50Al50, Ni37.5Al62.5, Ni25Al75 and Ni12.5Al87.5. We also considered seven alloy compositions across the Ni-Zr and Cu-Ag systems correspondingly in the similar manner. Calculations were performed in 3D simulation cells with periodic boundary conditions in all three directions using microcanonical ensemble dynamics at zero pressure. The simulation cells consist of about 4000 atoms (for different models the number of atoms varied slightly within the range 4000 – 4394). For numerical integration of the equations of motion we apply the Verlet algorithm in the velocity form [40] with a time step  $\Delta t$ =1.5 fs. To ensure the zero-momentum reference frame, we conserved the total momentum of the model systems at a zero value. To obtain the statistical time average at thermal equilibrium of the autocorrelation function of the interdiffusion flux and the mean-squared displacements of atoms, we use about  $1.8 \times 10^7$  time origins.



**Figure 2**: Composition dependence of the correction factor  $S = \frac{\tilde{L}_{cc}}{c_2 D_1 + c_1 D_2}$  for (a) Ni-Al melts, (b) Ni-Zr melts and (c) Cu-Ag melts at various temperatures

As it is proposed by theoretical treatment above for a binary mixing melt with tendency of ordering, the correction factor *S* is found to be less than unity ( $W_{12} < 0$ ) across the whole composition range of the MD models of Ni-Al binary melts (see Fig.

2a). The correction factor S of Ni-Zr binary melts (see Fig. 2b) shows analogous trends to those of Ni-Al melts at high temperatures i.e. the normal liquid state. In agreement with the approach that, upon increasing concentration of the minority species toward the equi-atomic composition, the kinetics of collective diffusion in mixing binary liquid alloys slow down, minima of S in the composition dependence of Ni-Al and Ni-Zr melts are found to be of similar position and depth.

Confirming our theoretical analysis, the composition dependence of the correction factor *S* of Cu-Ag binary melts (see Fig. 2c), serving as an example for a binary system with demixing tendency, clearly shows a reversed behaviour of the graph, compared to Figs. 2a and 2b. The value of  $S \ge 1$  over the whole composition range, reaching its maximum of 1.91 for the composition Cu<sub>50</sub>Ag<sub>50</sub> at a temperature of 1000 K. The maximum sort of plateaus towards the Ag-rich side of the Cu-Ag alloys ranging from Cu<sub>50</sub>Ag<sub>50</sub> to Cu<sub>12.5</sub>Ag<sub>87.5</sub>.

The composition dependence of  $S_0$  of Ni-Zr melts (see Fig. 3b), despite also showcasing a system with mixing tendency, looks inarguably different to the Ni-Al melt (see Fig. 3a). In the case of Ni and Zr, the larger self-diffusion coefficient is carried by the lighter Ni species  $(m_{\rm Ni}/m_{\rm Zr} \approx 58.69/91.22 \approx 0.64)$ . This is in contrast to the situation of the Ni-Al melt, where the larger self-diffusion coefficient is also carried by the Ni species, which in this configuration is the heavier  $(m_{\rm Ni}/m_{\rm Al} \approx$  $58.69/26.98 \approx 2.18$ ). The ratio of the masses of Ni and Zr  $(m_{\rm Ni}/m_{\rm Zr} \approx 0.64)$ effectively damp the single-particle kinetic effect due to the ratio  $D_{\rm Ni}/D_{\rm Zr}$  above unity (varying between 1.2 and 1.8 at high temperatures [36]) resulting in  $S_0 \approx 1$  covering the whole composition range. In the case of the configuration of Ni-Al melts, the mass ratio  $m_{\rm Ni}/m_{\rm Al} \approx 2.18$  magnifies the single-particle kinetic effects due to an increase of the ratio  $D_{\rm Ni}/D_{\rm Al}$  above unity even further, resulting in a reduction of  $S_0$  below unity at all compositions (see Fig. 3a). The minimum of  $S_0$  is reached with a value of 0.85 for the models of Ni-Al melts in the normal liquid state in the vicinity of equiatomic composition. For the Ni-rich models in Ni-Zr melts (see Fig. 3b) a considerable drop of  $S_0$  can be seen upon undercooling. This observation is the result of the increasing value of the ratio of the self-diffusion coefficients  $(D_{\rm Ni}/D_{\rm Zr})$  for the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub> melt at 1200 K [36]. This increase overcomes the damping effect of the mass ratio  $m_{\rm Ni}/m_{\rm Zr} \approx 0.64$  and therefore producing a sizable drop of  $S_0$  as can be seen on Figure 3b.



**Figure 3**: Composition dependence of  $S_0 = \frac{m^2 D_1 D_2}{m^2 D_1 D_2 + c_1 c_2 (m_1 D_1 - m_2 D_2)^2}$  for (a) Ni-Al melts, (b) Ni-Zr melts and (c) Cu-Ag melts at various temperatures

According to Fig. 4a it can be seen that for Al-rich alloy compositions with  $c_{\text{Ni}} \leq$  0.125, the term  $|W_{12}|/k_{\text{B}}T \leq 0.03$ , meaning that the correction factor *S* is less than 3% smaller than  $S_0$  (see Figs. 2a and 3a respectively). Thus, an Al-rich liquid alloy (with  $c_{\text{Ni}} \leq 0.125$ ) of the model system can be considered as a good approximation for the suggested concept of a binary liquid random alloy. Consequently, by assuming that a comparable condition  $S \approx S_0$  is satisfied for real Al-rich liquid alloys of Ni-Al binary system, recent experimental data on the correction factor in Al-rich Ni-Al melts [17] can be analysed by making use of Equations (33) and (35).

In the models of Ni-Zr melts the trend of the composition dependence of *S* follows, shifted up by one, the trend of the composition dependence of  $W_{12}/k_BT$ . This is in contrast to the models of Ni-Al melts, for which the composition dependence of  $S_0$  and  $(1 + W_{12}/k_BT)$  as contribution of *S* are found to be similar. During undercooling of the Ni-Zr melts the effect of  $S_0$  becomes notable. The main difference however, upon undercooling the sign of  $W_{12}/k_BT$  becomes positive for the Ni-rich and Zr-rich Ni-Zr melts (see Fig. 4b). The strongest increase of  $W_{12}/k_BT$  upon undercooling is observed in the models of Ni-rich Ni-Zr melts (see Fig. 4b), where  $W_{12}/k_BT$  reaches 0.48 and 0.08, respectively, in the models of Nis7.5Zr12.5 and Ni12.5Zr87.5 melts at 1200 K just before the onset of their crystallization at 1150 K. This behaviour is interpreted as an expression of emerging heterogeneity in atomic dynamics of melt due to entering the energy landscape controlled regime upon undercooling derived from a correlated behaviour of  $W_{12}/k_BT$  and the ratio  $D_{Ni}/D_{Zr}$ .

Though, a noteworthy decoupling of the self-diffusion coefficients of Ni and Zr in the models of Ni-rich Ni-Zr melts upon undercooling marks in a decrease of factor  $S_0$  (see Fig. 3b) that accounts for the contribution into the correction factor S due to single-particle kinetic effects. At the same time, the contribution into S due to a collective energy generation-dissipation effect accounted by  $W_{12}/k_BT$  is amplified upon transition to diffusion behaviour approaching the energy landscape controlled regime. The variation of the latter contribution significantly controls the variation of the former contribution causing substantial increase in the correction factor S above unity for the models of Ni-rich Ni-Zr melts upon undercooling.

As for a binary system with de-mixing tendency, according to the results of our MD simulations of Cu-Ag melts [43] with the EAM potential developed in [41], the behaviour of  $W_{12} > 0$  over the whole composition range (see Fig. 4c) as in contrast to  $W_{12} < 0$  for systems with mixing tendency like the melts of Ni-Al and Ni-Zr, Figs. 1a and 1b. Moreover, the value of  $W_{12}/k_{\rm B}T$  nears practically unity in the vicinity of the eutectic point of the model system with demixing tendency. Consequently, the correction factor S in the vicinity of the eutectic point is expected to be slightly less than two in real Cu-Ag melts with a reasonable approximation that  $D_{\rm Cu}/D_{\rm Ag} \sim 1$  (recall that  $m_{\rm Cu}/m_{\rm Ag} \approx 63.55/107.87 \approx 0.59$ ).







**Figure 4**: Composition dependence of  $\frac{W_{12}}{k_BT} = \frac{s}{s_0} - 1$  for (a) Ni-Al melts, (b) Ni-Zr melts and (c) Cu-Ag melts at various temperatures

To the best of our knowledge, the shown experimental data are the only available data on the correction factor in binary melts available in literature at the present time. The self-diffusion coefficients of Al,  $D_{Al}$  in Ni-Al cannot be measured [12,13,17] because of the very low coherent scattering cross section of Al, as well as lack of suitable isotopes. Therefore it was first assumed in [17] that  $D_{Al} \approx D_{Ni}$ . Next, with this assumption a quantity  $S_1 = \tilde{L}_{cc}/D_1$  (we use our notation) was assessed on account of experimental measurements [17]. In fact, as it can be seen from Equation (33),  $S_1 = S$ 

if  $D_1 = D_2$ . Though, Equations (33) and (35) propose (assuming  $S \approx S_0$ ) that both  $S_1 = S(c_2 + c_1 D_2/D_1)$  and *S* may differ noticeably when the ratio  $D_1/D_2$  reaches a value above unity (note that for Ni-Al system:  $m_1/m_2 \approx 58.71/26.98 \approx 2.18$ ), even already for sufficiently small values of  $c_1$  (Al-rich alloy compositions). In Fig. 5, alongside experimental data for  $S_1$  (at 1173 K) [17], we present the predicted composition dependence based on Equations (33) and (35) in Al-rich Ni-Al melts for: (i) *S* at fixed  $D_1/D_2 = 1$ , and (ii) *S* and  $S_1$  at fixed  $D_1/D_2 = 2$ . One can clearly see in Fig. 5, a good agreement of the predicted results and the experimental results for the composition dependence of  $S_1$  predicted based on our theoretical consideration at fixed  $D_1/D_2 = 2$ . Now also taking into account our main supposition  $S \approx S_0$  for Al-rich Ni-Al melts, on the basis of the results of MD simulations of Ni-Al melts, we should indicate that  $D_1/D_2 \sim 2$ , the ratio of the tracer diffusion coefficients in real Al-rich Ni-Al melts.



**Figure 5**: Composition dependence of the correction factor in Al-rich Ni-Al liquid alloy. The symbols and the dashed line represent, respectively, experimental (at 1173 K) [17] and theoretical (at fixed  $D_1/D_2 = 2$ ) data for  $S_1 = \tilde{L}_{cc}/D_1$ . The thin and thick solid lines represent the theoretical data for S at fixed  $D_1/D_2 = 1$  and  $D_1/D_2 = 2$ , respectively.

We can see from Fig. 4c that at 50% of Ag concentration  $W_{12}$  reaches its theoretical upper limit, namely it can not exceed  $k_BT$ . In other words, at about eutectic composition  $W_{12}$  pushes system to decomposition. Indeed, on Fig. 6 we can see the phase separation at both EAM calculations and experimental data for Cu-Ag melt [41].



**Figure 6**: Phase diagram of the Cu-Ag system. Filled symbols representing calculations using a thermodynamic model; open symbols where attained from the solid-melt interface simulations [41]

Comprehensively, the presented theoretical treatment is a significant step to help analysing the relationship between the kinetic part of single-particle and collective diffusion dynamics in a binary melt which is not far from its equilibrium state. However, we remind that the term  $W_{12}/k_BT$  is expected to deviate from its equilibrium range in the vicinity of a phase transition in the liquid state, as in cases of liquid-liquid demixing in addition to upon undercooling below equilibrium melting temperature. Additionally, the self-diffusion coefficients contributing to  $S_0$  may give a temperature dependence to  $\tilde{L}_{cc}$  that is even more complex in the undercooled liquid state. The selfdiffusion coefficients in this state are rapidly reduced compared to higher temperatures. For future work it would therefore be compelling to study the temperature dependence of relative magnitude of these two contributions,  $W_{12}/k_BT$ and  $S_0$ , into  $\tilde{L}_{cc}$  in the undercooled liquid states of different binary alloys.

#### Analogy with the Kirkwood-Buff Solution Theory

Finally, we recall that the Kirkwood-Buff solution theory [42] gives a significant link between the thermodynamic factor  $\Phi$  and the partial pair distribution functions  $g_{\alpha\beta}(r)$  of species  $\alpha$  and  $\beta$  ( $\alpha, \beta = 1, 2$ ) in a binary melt, as:

$$\Phi = \frac{c_1 c_2}{k_{\rm B} T} \left( \frac{\partial^2 (G/N)}{\partial c_{\alpha}^2} \right)_{T,P} = \frac{c_{\alpha}}{k_{\rm B} T} \left( \frac{\partial \mu_{\alpha}}{\partial c_{\alpha}} \right)_{T,P} = \frac{1}{1 + c_1 c_2 (l_{11} + l_{22} - 2l_{12})}, \quad (37)$$

where  $\mu_{\alpha}$  denotes the chemical potential of species  $\alpha$ , and

$$I_{\alpha\beta} = 4\pi \frac{N}{V} \int_{0}^{\infty} \left[ g_{\alpha\beta}(r) - 1 \right] r^2 dr$$
(38)

denotes the so-called Kirkwood-Buff integrals. Physically,  $\frac{N}{V}c_{\beta}g_{\alpha\beta}(r)$  is the average number density of atoms of species  $\beta$  at a distance r from an atom of species  $\alpha$  fixed at the centre. Now, by taking Equations (6), (33)–(35) and (37) into consideration, then in a binary melt the interdiffusion coefficient,  $D_c$ , can now be expressed as:

$$D_{c} = \Phi \tilde{L}_{cc} = \frac{\left(1 + \frac{W_{12}}{k_{\rm B}T}\right) (c_{2}D_{1} + c_{1}D_{2})}{\left[1 + c_{1}c_{2}(I_{11} + I_{22} - 2I_{12})\right] \left[1 + c_{1}c_{2}\frac{m_{1}^{2}D_{1}^{2} + m_{2}^{2}D_{2}^{2} - 2m_{1}D_{1}m_{2}D_{2}}{m^{2}D_{1}D_{2}}\right]}.$$
(39)

By comparing the algebraic structures of the Kirkwood-Buff expression for the thermodynamic factor  $\Phi$  and our expression for  $S_0$  a close affinity between them can be seen. Actually, the Kirkwood-Buff expression for the thermodynamic factor  $\Phi$  gives quantification of the thermodynamic effect caused by deviation from random mixing on collective diffusion in terms of local structuring or rather chemical ordering

as  $I_{11} + I_{22} - 2I_{12}$  (see Equation (38)). Where local structuring describes the relative preference of a species to be surrounded by another species. The decay of the excess or deficiency of atoms of species  $\beta$  around atoms of species  $\alpha$ , where the distance is expressed through space integrals of the partial pair correlation functions  $g_{\alpha\beta}(r) - 1$ are relevant in regards to the thermodynamic factor  $\Phi$ . In a similar manner quantifies our expression for  $S_0$  the kinetic effect on collective diffusion in terms of the relative difference in the decay of single-particle dynamics of different species with time phrased via the time integrals of the velocity autocorrelation functions of different species, as  $\frac{m_1^2 D_1^2 + m_2^2 D_2^2 - 2m_1 D_1 m_2 D_2}{m^2 D_1 D_2}$  (see Equations (25) and (26)). Consequently,  $S_0 =$  $\left[1 + c_1 c_2 \frac{m_1^2 D_1^2 + m_2^2 D_2^2 - 2m_1 D_1 m_2 D_2}{m^2 D_1 D_2}\right]^{-1}$  expresses the kinetic factor of the interdiffusion coefficient given by Equation (39). Eventually, in binary melts,  $\frac{W_{12}}{k_BT}$  accounts for crosscoupling between thermodynamic and collective kinetic effects in the interdiffusion processes. Indeed, it captures, according to Equation (28), the decay peculiarities of both space and time dependent correlations in dynamics of species in a binary melt. Nevertheless, further and extensive study of the properties of the factor  $\frac{W_{12}}{k_{\rm P}T}$  are needed to propose any more quantitative claims.

#### 5.2.4 Conclusion

Analysis of diffusion kinetics in binary melts with mixing tendency as well as demixing tendency were carried out in the framework of the Mori-Zwanzig formalism. For the first time, the Onsager coefficient for mass transport has been related to the two self-diffusion coefficients of species in binary melt through an analytical expression. The expression serves as an exceptional alternative option to the well-known Darken equation. We presented the derived expression that includes the correction factor S to the Darken equation.

Additionally, the correction factor S appears to break down into the product of two other factors as:  $S = S_0(1 + W_{12}/k_BT)$ . The first factor  $S_0 \le 1$  is expressed in terms of the ratio of the tracer diffusion coefficients  $D_1/D_2$ , the ratio of the atomic masses  $m_1/m_2$ , and the alloy composition. The second factor  $(1 + W_{12}/k_BT)$  is related to a collective energy generation-dissipation effect (term  $W_{12}/k_BT$ ) due to the
correlations between fluctuations of the interdiffusion flux and the force caused by the difference in the average random accelerations of atoms of different species. Evaluation of the recognizable different behaviour of the correction factor *S* for melts in regards to their tendency of mixing shows that for binary mixing melts exhibiting mixing tendency (i.e. Ni-Al and Ni-Zr melts) the correction factor should typically be  $S < S_0$  ( $W_{12} < 0$ ), while for binary melts where precursors of liquid–liquid demixing are important (such as Cu-Ag melts) the correction factor should be  $S > S_0$  ( $W_{12} > 0$ ). In the case of thermal equilibrium it was pointed out that for the correction factor  $0 \le S \le 2S_0$ , due to a constraining effect of the energy of thermal fluctuations ( $|W_{12}| \le k_BT$ ).

In addition, the extensive results of this study can be utilized to establish a concept of a binary liquid random alloy for which  $W_{12} = 0$ , so that the correction factor  $S = S_0$ . A systematic comparison of results of binary systems with mixing tendency i.e. Ni-Al melts and Ni-Zr melts, as well as demixing tendency i.e. Cu-Ag, which has shown opposite behaviour of the correction factor S and its contributions of  $S_0$  and  $W_{12}/k_BT$ . Concluded with  $S < S_0$  ( $W_{12} < 0$ ) for binary mixing melts with chemical ordering and  $S > S_0$  ( $W_{12} > 0$ ) for binary demixing melts.

Lastly, this study and the related theory significantly supports analysis for better, more in-depth interpretation of recent experimental data [17] on the correction factor to the Darken equation in Al-rich Ni-Al melts.

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This chapter addresses the implications (Section 2.6) and objectives (Section 2.7) of this research and discusses first, the main findings focussing on the Ni-Zr system, followed by a thorough insight into novel theoretical relations for the previously discussed different types of melts. The studied systems are selected due to their high technological interest and material properties, as it has been elaborated earlier in Chapter 2. The premise for the creation of databases for different systems is a result of their significance for the progress in research in this field. These databases build the foundation for development and verification of predictive measurements for coupled heat and mass transport in binary liquid alloys based on theoretical models that result in a better understanding of occurring phenomena. Finally, this helps to improve the design of new advanced materials, due to the profound insights into the diffusion dynamics at atomic scale.

# 6.1 THE NI-ZR SYSTEM

The main focus of this study is the binary system of simulated Ni-Zr melts. A detailed introduction on its importance and applicability relating to glass forming multicomponent systems is given in Chapter 3.

For evaluation of diffusion, thermotransport and thermodynamic properties, the liquid binary melt is studied. Hence, the melting temperatures are of high interest. The simulation gives accurate results for the pure materials of Nickel and Zirconium, as well as the seven studied compositions. With help of the composition dependence of melting temperatures,  $T_{mel}$ , and their validation with experimental results, the temperature range for further relevant calculations of diffusion properties including  $D_{Ni}$ ,  $D_{Zr}$  and  $\tilde{L}_{cc}$  is selected between 2200 K – 1200 K. To further confirm the onset of crystallisation, calculations of the pair distribution function, g(r), are used and visualised. Based on the distribution of peaks of the graphs of different temperatures, the transformation shows a change of atomic ordering and when taking the ratio of the peaks, confirming crystallisation patterns. One example of the applied pair distribution function on the model melts of pure Ni is shown in Figure 4. The evolution of peaks

is distinct between the different temperatures and can clearly be seen in the highlighted section of the graph.



Figure 4 Pair distribution function applied to the model melt of pure Ni

# 6.1.1 Tracer- and Collective Diffusion

Diffusion processes generally follow the Arrhenius law. This is important for the calculation of the activation energy,  $E_A$ , of the diffusion process, and a temperature independent pre-factor,  $D_0$ . During treatment of the simulation data, fits according to the Arrhenius law are performed in the temperature range determined for diffusion processes between 2200 K – 1200 K, however notable deviations are found. For further calculations to obtain values for the parameters of  $E_A$  and  $D_0$ , it is found that the best fit is possible for the temperature range between 2200 K – 1400 K. Here, for the models of pure Zr and Ni<sub>75</sub>Zr<sub>25</sub> and their crystallisation at 1550 K and 1650 K respectively, data is extrapolated.

First, temperature dependence graphs are created for the visualisation of the calculated data of self-diffusion coefficients of Ni and Zr in models of their pure melts respectively, alongside available experimental data for Ni [77,78]. The results reveal a very good agreement in the case of Ni, as can be seen in Figure 5. Due to limitations that arise during experiments and therefore a lack of available measurements in case of Zr, no experimental values are found. According to further experimental results of  $D_{Zr}$  in binary Ni-Zr melts and its very good agreement of presented simulation data, one can assume, that the accuracy of the self-diffusion coefficient relating to the pure Zr melt model to be of high quality. These graphs are Arrhenius type plots and include the Arrhenius fits based on the calculated Arrhenius parameters for the activation energy and pre-exponential factor, to give a detailed overview for each considered composition. Available experimental data is included within the graphs next to the simulation data and carefully compared. Here, for both self-diffusion coefficients, the results are in good agreement for the different model systems. The model system of Ni<sub>62.5</sub>Zr<sub>37.5</sub> displaying the best agreement with experimental data [7,8], and is shown in Figure 5. While for the systems of Ni<sub>50</sub>Zr<sub>50</sub> and Ni<sub>37.5</sub>Zr<sub>62.5</sub> the results for  $D_{Ni}$  are also in good agreement, the simulation slightly overestimates experimental results. The values of the self-diffusion coefficient of Zr,  $D_{Zr}$ , from experiments inarguably harder to obtain, lie as a consequence of error of experimental measurements, tightly spread around the simulation data of the model system Ni<sub>37.5</sub>Zr<sub>62.5</sub>.



Figure 5 Self-diffusion coefficients

Second, the kinetic part of the interdiffusion coefficient,  $\tilde{L}_{cc}$ , is identified. By making use of the Green-Kubo formalism, this value is obtained through the normalised autocorrelation function of the interdiffusion flux and its time integral. After extensive literature review, no experimental data on the kinetic part of interdiffusion could be found. This showcases the importance of creating a complete database on the Ni-Zr system, with the ability to make valid predictions for diffusion properties. The detailed explanation of evaluation of  $\tilde{L}_{cc}$  can be found in Chapter 3.

Results for the diffusion coefficients and Arrhenius parameters for binary Ni-Zr melts are gathered in Table 1 and Table 2 respectively in Section 3.2. Due to formatting reasons, the temperature step presented equals  $\Delta 100 K$ , while all calculations were performed and data therefore also available for the temperature step of  $\Delta 50 K$  in the given temperature range. Thus, allowing a more precise evaluation of the diffusion behaviours.

For further insights into theoretical relations, the composition dependencies of diffusion coefficients ( $D_{Ni}$ ,  $D_{Zr}$ , and  $\tilde{L}_{cc}$ ) are studied and trends, minima, and maxima evaluated. The results show minima of similar shape in the composition region between 0.625  $< c_{Ni} < 0.75$  for all diffusion coefficients. The data, based on a set of Arrhenius parameters, allow to encode a diffusion coefficient and its temperature dependence. In addition, after extrapolation using the Arrhenius parameters to visualise lower temperatures, the greatest dynamical slowdown of diffusion dynamics in the melts is observed for the model system of Ni<sub>62.5</sub>Zr<sub>37.5</sub>.

## 6.1.2 Decoupling of Self-Diffusion Coefficients

Next, for evaluation of decoupling behaviour of the diffusion coefficients of Ni and Zr,  $D_{Ni}$  and  $D_{Zr}$  respectively, their ratio is inspected. By calculation of  $D_{Ni}/D_{Zr}$ , a considerable decoupling towards the Ni-rich side of the system models is found and shown in Figure 6, alongside experimental data [8,63]. The greatest decoupling of the self-diffusion coefficients for the model system of Ni<sub>87.5</sub>Zr<sub>12.5</sub> occurred at a value of 3.3 at a temperature of 1200 K. This is one temperature step before its simulated crystallisation at 1150 K. More extrapolated data is also taken into consideration showing values that exceed the original set of data. Here, for the model system Ni<sub>75</sub>Zr<sub>25</sub> the extrapolation shows the behaviour for undercooling of the melt down to 1200 K

while avoiding crystallisation, with the strongest decoupling of self-diffusion coefficients. Existing experimental data [8,63] is taken into consideration for validation of the simulation results and shows good agreement.

The Ni-Zr system is a type of melt with mixing tendency, showcasing pronounced chemical short-range order of atoms. This means that in theory, it should supress such decoupling of diffusion. Further insights into the origin of the occurring decoupling was argued in [8,63] relating to the interaction of Ni and Zr atoms with each other. Due to a saturation effect of available Ni-Zr pairs that interact very strong to one another towards the Ni-rich side, the number of Zr decreases, while the remaining Ni atoms now only find other residual Ni atoms to pair with, creating Ni-Ni pairs. As a consequence, the fraction of Ni-Zr pairs beyond saturation is followed by an increase of the weaker couple Ni-Ni pairs. Finally, this adds to the diffusion mobility in melts of Ni-rich compositions.

Now taking into consideration the overview of the ratio of the self-diffusion coefficients, a value greater than one is dominant over the studied temperature and composition range. This again indicates stronger bonds of Zr atoms to next-near neighbours compared to Ni atoms, as was previously discussed in [8]. This implies that a greater amount of thermal energy is required for breaking the bonds of Zr atoms. Now, with decreasing temperature, the available amount of thermal energy decreases also. As a result, the motion of Zr atoms slows down in a more rapid manner than of Ni atoms, due to the energy landscape. In conclusion, the observed decoupling for lower temperatures is related to a change of diffusion behaviour transitioning from a liquid-like motion towards the energy landscape controlled regime [8,79].

The gained insights into binary melts of Ni-Zr can be translated, to a certain extent, towards Zr-based multicomponent systems and used for further interpretation. *Vitreloy 4* for instance, is the name of a commercialised amorphous alloy developed by the California Institute of Technology, Caltech. This glass-forming alloy consists of Zr<sub>46.75</sub>Be<sub>27.5</sub>Ti<sub>8.25</sub>Cu<sub>7.5</sub>Ni<sub>10</sub> exhibiting a strong decoupling of components, with a ratio of  $D_{Ni}/D_{Zr} \approx 4$  close to its liquidus temperature 1050 K [80]. After extrapolation of the data above 1200 K, the ratio further decreases to a factor of less than two for the self-diffusion coefficients of Ni and Zr according to [8], which again relates to the previously discussed influence of the energy landscape. Observation of the extrapolated results of the ratio of the multicomponent system are in close agreement with the presented simulation data of the binary Ni-Zr melts at 1200 K.

Returning to the results for the binary system, a ratio between  $1.2 \leq D_{Ni}/D_{Zr} \leq$ 1.3 the decoupling of the self-diffusion coefficients is the smallest for the composition range of  $0.375 \leq c_{Ni} \leq 0.5$ . It is also shown that for this composition range, the ratio  $D_{Ni}/D_{Zr}$  stays the same, regardless of the temperature. This temperature independence leads to the conclusion, that in this composition range, the influence related to the decoupling of both self-diffusion coefficients due to the energy landscape, is the least affected. Hence, diffusion dynamics in this composition range slow down, independent of temperature.



Figure 6 Decoupling of self-diffusion coefficients

# 6.1.3 Correction Factor S

To elaborate microscopic cross-correlation effects in terms of the kinetic part of collective diffusion, the correction factor, S, is studied carefully. The factor relates to the concentrations of Ni and Zr, the kinetic part of interdiffusion and self-diffusion coefficients. Additional decomposition of the correction factor into its kinetic factor  $S_0$  and the collective energy generation-dissipation theorem allows for further in-depth understanding of diffusion dynamics occurring in the melts.

The composition dependence of  $S = \tilde{L}_{cc}/(c_{Zr}D_{Ni} + c_{Ni}D_{Zr})$  is evaluated for the temperature range between 2200 K and 1200 K, as can be seen in Figure 7. It shows typical behaviour for a binary melt with mixing tendency i.e. S < 1 over the whole composition range in the normal liquid state of the melt. This type of behaviour is expected and was previously studied for binary Ni-Al melts [14,15,67,81-83] and confirms the discussed theory of previous sections. Hence, for this type of melt, collective diffusion dynamics are expected to slow down with an increase of its minority species concentration towards equi-atomic composition [14,15,67,82,83]. The observed values of S with its minimum between  $0.5 \leq c_{Ni} \leq 0.625$  support the elaborated insight. The absolute minimum can be estimated at approximately  $S_{min} \approx$ 0.67 and is practically independent of temperature.



Figure 7 Correction factor

Further study of the decomposed contributions towards the correction factor are divided into terms of  $S_0$  and  $W_{12}/k_BT$ . Taking into account single-particle kinetic effects, as well as the collective energy generation-dissipation effect into the correction factor,  $S_0$  gives interesting insight into its factorisation with  $S_0 = [1 + c_{Ni}c_{Zr}(m_{Ni}D_{Ni} - m_{Zr}D_{Zr})^2/m^2D_{Ni}D_{Zr}]^{-1}$ . Now this part of the contribution gets particularly interesting for the models of the Ni-Zr system, due to its mass ratio between the components and the ratio of self-diffusion coefficients. Looking at the mass ratio  $(m_{Ni}/m_{Zr} \approx 58.69/91.22 \approx 0.64)$ , the heavier Zr species also hold the

smaller diffusion coefficient. The observed value  $S_0 \approx 1$  over the composition range in the normal liquid state is a result of the mass ratio damping the effect on the increase of the ratio of diffusion coefficients  $D_{Ni}/D_{Zr}$  above unity (ranges between 1.2 and 1.8 at high temperatures).

However, upon undercooling a significant drop of  $S_0$  below unity down to 0.92 is simulated for the model of Ni<sub>87.5</sub>Zr<sub>12.5</sub>. To understand the origin for this type of behaviour, one needs to look at the ratio of diffusion coefficients again (see Figure 6). It is shown that a strong decoupling of self-diffusion for different species occurred for this model system at a temperature of 1200 K, reaching about  $D_{Ni}/D_{Zr} \approx 3.3$ , hence outweighing the damping effect resulting in this considerable reduction of  $S_0$ .

Now looking into the term of  $W_{12}/k_BT$ , its composition dependence is shown in Figure 8. This term is closely related to the previously discussed collective energy generation-dissipation effect resulting of fluctuations of the interdiffusion flux,  $J_c$ , and the force,  $R_{12}(t)$ . Its composition dependence for the binary Ni-Zr model melts is found to closely follow the behaviour of *S*, shifted up by one. Upon undercooling of the melts, its sign becomes positive towards both ends, the Ni-rich and the Zr-rich side reaching up to 0.48 and 0.08 for the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> respectively at a temperature of 1200 K, which is one temperature step away from their crystallisations at 1150 K. This behaviour correlates to the composition dependence of the ratio of self-diffusion coefficients in binary Ni-Zr melts (see Figure 6) and demonstrates, upon undercooling, heterogeneous behaviour of atomic dynamics in the melt as a consequence of entering the energy landscape controlled regime [8,79].

In conclusion, the decoupling of  $D_{Ni}$  and  $D_{Zr}$  in the models towards the Ni-rich side upon undercooling decrease  $S_0$ , accounting for single-particle kinetic effects and their contribution into the correction factor, S. On the other hand,  $W_{12}/k_BT$ , accounting for a collective energy generation-dissipation effect and its contribution into S, is enlarged further by a transition to diffusion behaviour that approaches the energy landscape controlled regime. Finally this results in a considerable increase of the correction factor, S, above unity on the Ni-rich side.



Figure 8 Collective energy generation-dissipation effect

## 6.1.4 Enthalpy

In addition, the previously discussed correction factor and its composition dependence, follow a similar shape compared to the composition dependence of the enthalpy of mixing calculated per atom,  $h_m = h - c_{Ni}h_{Ni}^* - c_{Zr}h_{Zr}^*$ . Here, the total enthalpy of the model systems of Ni-Zr melts are described as h, where  $h_{Ni}^*$  and  $h_{Zr}^*$  describe the enthalpies of the models of pure Ni and Zr melts respectively. Figure 9 shows the calculated composition dependence of the enthalpy of mixing values. Due to crystallisation occurring in the simulated Zr melt at 1550 K, the evaluated temperature range of  $h_m$  based on the simulation was limited to a temperature range of 2200 K to 1600 K and is compared to existing experimental data on thermodynamic properties [84]. Simulated data shows good agreement towards the Ni-rich side, however some error towards the Zr-rich side plus some sort of shift of the minimum in the simulation results from equi-atomic towards the Ni-rich side are evident.



Figure 9 Enthalpy of mixing

# 6.1.5 Fluctuations between $R_{12}(t)$ and $J_{C}(0)$

It was previously shown in Section 3.2, that the novel, dimensionless factor  $\sigma_{12}$  is used for evaluation of the initial sign of the correlation between the interdiffusion flux,  $J_c$ , and its fluctuations with the force,  $R_{12}(t)$ , as a result of different average random accelerations of Ni- and Zr atoms. The simulated composition dependence shows only weak temperature dependence (see Figure 10), hence for normal and undercooled liquid states of the model systems the behaviour of  $\sigma_{12}$  is typical for binary melts with chemical ordering, displaying negative values of the whole composition range. Its trend is very similar compared to the behaviour of the graph of  $W_{12}/k_BT$  (see Figure 8). Looking into the normal liquid state, the minimum of  $\sigma_{12}$  is between  $0.5 \leq c_{Ni} \leq 0.625$ . Although it is important to note that it remains negative across the composition range and changes only slightly upon undercooling, contrary to the composition dependence of  $W_{12}/k_BT$ .



Figure 10 Dimensionless factor  $\sigma_{12}$ 

Conclusively, the insights of  $\sigma_{12}$  in combination with gained relations of  $W_{12}/k_BT$  lead to the understanding, that the positive values of the latter, which are shown for the models of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> at 1200 K, depict a change of atomic dynamics of the melt that occur ahead of onset of their crystallisation at 1150 K. In other words, the early obtuse angle between  $R_{12}(t)$  and  $J_C(0)$  which is described by a value greater than zero for  $\sigma_{12}$ , converts into an acute angle to further act on fluctuations of atomic ordering towards a thermodynamically more stable state for the model systems of Ni<sub>87.5</sub>Zr<sub>12.5</sub> and Ni<sub>12.5</sub>Zr<sub>87.5</sub> and increase their amplitude and hence,  $W_{12} > 0$ .

The first of the two alloy systems is stronger affected than the latter. This agrees with the observation of a negative value for  $W_{12}/k_BT$  for enriched model systems upon undercooling. Here, the behaviour in the range of  $0.25 \leq c_{Ni} \leq 0.375$  is hardly affected by temperature; meanwhile at a temperature of 1200 K, with increasing Ni content of the alloys, starting to rise toward zero more progressively. Finally suggesting that, within this composition range the occurring transitioning of normal states as well as undercooled liquid states of the model systems for the binary Ni-Zr melts happen very smooth. Therefore, preventing any significant changes of collective diffusion dynamics of the melts.

#### 6.1.6 Glass Forming Ability

The glass-forming ability of an alloy is strongly related to its stability against crystallisation upon undercooling, hence a thorough understanding of its diffusion dynamics and atomic ordering is crucial [85-88]. Firstly, recalling the earlier discussion of single-particle diffusion dynamics of the melts (see Section 6.1.2) in terms of decoupling of the diffusion coefficients. After evaluation of occurring dynamics of the melt it is discussed that the composition range with the smallest decoupling is also practically independent of temperature (composition range 0.375  $\leq c_{Ni} \leq 0.5$ ).

Further investigation of the decoupling of self-diffusion coefficients (see Section 6.1.2) and also changes of the collective diffusion dynamics based on fluctuations of  $R_{12}(t)$  and  $J_c(0)$  (see Section 6.1.5) show, that the composition range between  $0.25 \leq c_{Ni} \leq 0.5$  demonstrates a slowdown of i) single- particle and ii) collective diffusion dynamics of the melt upon undercooling. This homogeneous dynamical type of behaviour relates to increased stability of the model melts against their crystallisation, thus exhibiting pronounced glass-forming ability in this composition range.

# 6.2 DIFFUSION KINETICS – A SUMMARY FOR DIFFERENT TYPES OF MELT

This section discusses the insights and novel understanding of diffusion kinetics of melts for different types i) with chemical ordering and ii) with phase separation tendencies. Based on previous work and their resulting molecular dynamics data [10,14,16,73], theoretical relations are applied and for further investigation compared in [11]. The main focus of the mass transport properties in this section are related to microscopic cross-correlation effects that arise in the melt upon undercooling and influence atomic stability of the melt against crystallisation. For the main system of this study, the models of binary Ni-Zr, this discussion was previously covered in Section 6.1. The additional model systems of Ni-Al and Cu-Ag are ideal candidates for further insight due to their importance in the field of engineering [80,89-94]. Additionally, they represent melts with different types of tendencies, with Ni-Al representing chemical ordering, and Cu-Ag representing clustering, recalling that the Ni-Zr system belongs to the first group, of chemical ordering. Hence an interesting

comparison of two model systems with similar tendencies reveal an even more thorough insight on the impact of different factors (Ni-Zr and Ni-Al), meanwhile the Cu-Ag system is used to predict contrary behaviours. For this matter, the properties of S,  $S_0$ , and  $W_{12}/k_BT$  are analysed and compared in conjunction with gained understandings of the correlations between fluctuations of  $R_{12}(t)$  and  $J_C(0)$ .

#### 6.2.1 Binary Liquid Alloys with Mixing Tendency

Firstly, decomposition of the correction factor, *S*, reveals its dependence on selfand collective diffusion of a binary melt. According to novel theoretical relations established in Section 5.2 for types of melt with chemical ordering, it is expected that  $S < S_0$  ( $W_{12} < 0$ ). Investigation of the model systems of Ni-Al reveals a value for the correction factor, *S*, across the composition range of less than unity, and similar behaviour in the normal liquid state compared to the models of Ni-Zr. The minima located in the range between  $0.5 \leq c_{Ni} \leq 0.625$  for the Ni-Al model systems resembles the composition dependence of Ni-Zr model systems, but shows even less temperature dependence. The behaviour of the correction factor depicts the slowdown of collective diffusion kinetics upon an increase of the minority species toward the equi-atomic composition concentration.

Now, further investigation of the first factor,  $S_0$ , after decomposing the correction factor (see Sections 3.2 and 5.2 for methodological approach), illustrates a significant different trend than the composition dependence of Ni-Zr melts. This factor depends on the ratio of mass,  $m_1/m_2$ , as well as self-diffusion coefficients of atoms of different species,  $D_1/D_2$ . For instance, the Ni-Al system holds a mass ratio of  $m_{Ni}/m_{Al} \approx 58.69/26.98 \approx 2.18$ , where the heavier species also possesses the greater self-diffusion coefficient (further discussion on the diffusion coefficient of Al in Ni-Al follows later in this section). As a consequence,  $S_0$  is reduced below unity across the composition range with its minimum for normal liquid states of 0.85 located in the vicinity of the equi-atomic composition. The composition wide reduction is a result that is amplified by the mass ratio in conjunction with an increase of the ratio of self-diffusion coefficients above unity. Here it is important to note, that compared to the model systems of Ni-Zr melts, also exhibiting chemical ordering tendency, this effect is remarkably damped by its mass ratio ( $m_{Ni}/m_{Zr} \approx 58.69/91.22 \approx 0.64$ ),

demonstrated by the behaviour of  $S_0 \approx 1$  across different compositions in normal liquid states.

Lastly, the composition dependence of  $W_{12}/k_BT$  shown in Chapter 5, identifies for composition on the Al-rich side with  $c_{Ni} \leq 0.125$  a behaviour of  $|W_{12}|/k_BT \leq$ 0.3. The sign of the graph is negative in the normal liquid state and remains so upon undercooling, which is in contrast to the model systems of studied Ni-Zr melts. It concludes, the impact on the correction factor, *S*, which as a result is 3% smaller than its first factor,  $S_0$ . Therefore, the suggested concept of a binary liquid random alloy is applicable for discussed Al-rich liquid alloys of the binary model system Ni-Al. Finally, one can assume that  $S \approx S_0$  for real Al-rich compositions of binary Ni-Al melts. The obtained results support further investigation of recent experimental data [83], by making use of this novel insight.

In addition to the previously discussed self-diffusion coefficients of Al, one needs to know that, due to limitations of measuring capabilities in experiments that arise due to i) lack of isotopes and ii) a low coherent cross section for scattering of Al, the ratio of diffusion coefficients in binary melts of Ni-Al were considered to be roughly equal with  $D_{Ni} \approx D_{Al}$  [83]. Application of the developed theoretical relations  $S_1 = \tilde{L}_{CC}/D_1$  (see Section 3.2 and 5.2), that in case of the assumed [83]  $D_{Ni} = D_{Al}$  then  $S_1 = S$ . However, the influence of the ratio of diffusion coefficients,  $D_1/D_2$ , if reached a value above unity on the correction factor is significant, since for binary melts exhibiting chemical ordering  $S \approx S_0$ , for instance the Ni-Al system. This was taken into account when the correction factor, S, was calculated and compared to existing experimental data from [83] with assumed ratio of self-diffusion coefficients  $D_{Ni} \approx D_{Al}$ . Ultimately it is concluded, that a much better agreement with experimental data is obtained, when assumed ratio shifts toward a value of two is used (see Section 5.2). Hence expressing that  $D_1/D_2 \sim 2$  in real Al-rich Ni-Al melts.

#### 6.2.2 Binary Liquid Alloys with Demixing Tendency

Analogous to the discussion of binary liquid alloys with mixing tendency, now follows further insight into binary liquid alloys with clustering tendency based on previous molecular dynamics simulation results of the Cu-Ag system [16]. Given the newly established theoretical relations in Section 5.2 for types of melt with demixing tendency, it is expected that  $S > S_0$  ( $W_{12} > 0$ ). Upon first inspection of the correction factor, S, of the model systems of Cu-Ag [16], the novel theory could be confirmed. The behaviour of its composition dependence shows clear contrary behaviour compared to the model systems of Ni-Zr and Ni-Al. Its value is greater than unity across the composition range with a maximum of 1.91 for the equi-atomic alloy Cu<sub>50</sub>Ag<sub>50</sub> at 1000 K (see graph in Chapter 5). The form of the maximum plateaus toward the Ag-rich side with a concentration of  $0.5 \leq c_{Ag} \leq 0.875$ . Occurring microscopic cross-correlation effects of the kinetic part of collective diffusion in terms of the correction factor, are amplified for the Cu-Ag models with a decrease of temperature.

Next, the inspection of  $W_{12}$  reveals insight into the systems behaviour of phase transitioning of atoms of different species. According to the established theoretical approach, one can see  $W_{12} > 0$  across the whole composition range. Simulation results [16] evaluated with the EAM potential developed in [95] depict the term  $W_{12}/k_BT$ , reaching a close approximation of unity at 1000 K for the vicinity of its eutectic point.

As a result, it is expected that  $S \leq 2$  in real Cu-Ag melts, when the self-diffusion coefficients are approximated to be roughly equal with  $D_{Cu}/D_{Ag} \sim 1$ . This is reasonable, when also taking their atomic mass into consideration,  $m_{Cu}/m_{Ag} \approx$  $63.55/107.87 \approx 0.59$ . The behaviour of the graph of  $W_{12}/k_BT$  is found to approach its theoretical upper limit for the equi-atomic melt since it cannot exceed  $k_BT$ , demonstrating the model melts promotion to decompose.

# 7.1 CONCLUSIONS

Novel insights into diffusion, thermotransport and thermodynamic properties of binary liquid melts of model systems of Ni-Zr have successfully been revealed, established and applied by the author within the scope of the PhD program. To showcase applicability and reach of gained understandings, further studies of different types of melt based on previous work conducted [14,16,73], have been analysed and concluded in different type of behaviour for melts of different types in terms of atomic ordering and their tendency of mixing or clustering. The content presented tackles the lack of understanding in the complex field of diffusion and thermodynamic properties of melts. Processes in the melt on atomic scale that affect their microstructure and material properties have been studied and theoretical relations established. Thorough investigation on the topics of self-diffusion coefficient, interdiffusion, decoupling behaviours, correction factor, enthalpy, collective energy generation-dissipation effect, and time correlation functions helps bridging the gap, which slows down the profound understanding, production, and development of advanced materials. These insights are addressed separately in the previous discussion chapter (Chapter 6). The following section gives information, summarising the previously focused insights relating to the objectives of this thesis.

The molecular dynamics method was used with a semi-empirical many-body interatomic potential to create an extensive database on the discussed material properties for the binary system of Ni-Zr melts. Simulation results were carefully compared to existing experimental data to ensure their quality and reliability. The approach using mechanical statistics and atomistic modelling, demonstrates crosscorrelation effects between single-particle and collective diffusion dynamics in the melt. Further investigation into the stability of the melt in short time limit  $t \rightarrow 0$  upon undercooling determining the composition range  $0.25 \leq c_{Ni} \leq 0.5$  as viable glass formers due to the manifestation of a homogeneous slowdown of diffusion dynamics, which indicates enhanced stability of the undercooled melt against its crystallisation.

In addition, the correction factor, S, was decomposed for advanced investigation of atomic ordering behaviour of the melt upon undercooling. Here, using the gained novel understandings of fluctuations between  $R_{12}(t)$  and  $J_c(0)$ , to establish conditions to describe dynamical stability of the melt and the transition toward a more thermodynamically stable state. It was found that for the model systems of binary liquid Ni-Zr melts the obtuse angle  $(\sigma_{12}(0))$  between  $R_{12}(t)$  and  $J_{C}(0)$  in hydrodynamic limit  $t \rightarrow 0$  remains as it is related to its negative value of  $W_{12} < 0$ describing the average amount of generated-dissipated energy. Furthermore,  $W_{12}$  and its behaviour in terms of a relative change, can be utilised to show a variation of stability of atomic ordering upon undercooling and as a result the above mentioned obtuse angle can transform to an acute angle (now  $W_{12} > 0$ ) for promotion of the binary mixing melt toward a more thermodynamically stable state. The extensive work on binary melts of the Ni-Zr system has been concluded in an accurate and comprehensive database on its diffusion, thermotransport and thermodynamic properties based on molecular dynamics simulation with state-of-the-art semiempirical many-body interatomic potential and acts as immense support for the decision making process of future experiments, processing routes and compositions.

New innovative theoretical relations were established for the treatment of thermotransport properties in different types of binary melts. By making use of Langevin equations, velocity auto-correlation functions, tracer memory kernels and random forces that act on atoms of different species, an improved understanding of an alternative expression for the interdiffusion flux was derived. Next, the frequency dependency of tracer diffusion coefficients was taken into account to comment on the correlation between  $R_{12}(t)$  and  $J_c(0)$  in order to reveal the different types of behaviour of melts with i) chemical ordering and ii) demixing tendency in terms of stability of the melt against crystallisation. The previous study into the systems of Ni-Al and Cu-Ag showcased dissimilar behaviour for the different melt types, but also for melts within one group (Ni-Al and Ni-Zr both belong to the chemical ordering type of melt).

Finally, a clear distinction of conditions was found to describe atomic ordering properties of the different types of melt. This novel insight determines, that for the correction factor  $S = S_0$  when  $W_{12} = 0$ . In terms of the different melts it has been derived that for binary mixing melts exhibiting chemical ordering,  $S < S_0$  ( $W_{12} < 0$ ); meanwhile melts with demixing tendency indicate opposite behaviour terms of S >

 $S_0$  ( $W_{12} > 0$ ). This approach and its established theory is very useful for the interpretation of experimental data related to the Darken Equation and also for advanced investigation of the correction factor.

# 7.2 OUTLOOK

In the field of research, any type of study is always considered a work in progress. Hence, there is always more options, different perspectives and further advancement possible in countless ways. Following are some recommendations that should be considered pursuing for future research:

- For the Ni-Zr system further study of the identified viable glass forming range of  $0.25 \leq c_{Ni} \leq 0.5$  in terms of its evolution of disordered structure upon undercooling i.e. connectivity network of icosahedra sharing common atoms percolates disordered structure as undercooled monoatomic melts forms glass.
- Advanced insights into the topic of enthalpy for the model system for Ni-Zr melts, for instance the more detailed use of partial enthalpies in order to describe thermotransport properties.
- The applied theoretical approach can be used for investigation of other binary model systems of high technological interest to create databases on their respective material properties. Then, extensive investigation of cross-links between different systems and their behaviours can be used to increase quality and efficiency of both, the simulation and experimental side for the development of viable glass formers and their production.

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# Appendix A

# **Co-Author Statements**

Enclosed in the following section are the author-contribution statements for the publications entitled:

**A. Kromik**, E. V. Levchenko, C. Massobrio, A. V. Evteev, "Diffusion in Ni-Zr Melts: Insights from Statistical Mechanics and Atomistic Modeling", *Adv. Theory Simul.*, **1**: 1800109. doi:<u>10.1002/adts.201800109</u>

**Kromik A.**, Levchenko E.V., Evteev A.V. (2020) Diffusion Kinetics in Binary Liquid Alloys with Ordering and Demixing Tendencies. In: Levchenko E., Dappe Y., Ori G. (eds) *Theory and Simulation in Physics for Materials Applications*. Springer Series in Materials Science, vol **296**. Springer, Cham.

# Statement of Co-authorship

By signing below I confirm that research higher degree candidate Andreas Kromik is the lead author of, and contributed conceptualization, the preparation and interpretation of data and results, visualization, formal analysis as well as writing (draft and editing) to the publication entitled:

Diffusion in Ni-Zr Melts: Insights from Statistical Mechanics and Atomistic Modeling.

Authors: A. Kromik, E. V. Levchenko, C. Massobrio & A. V. Evteev Accepted by *Advanced Theory and Simulations*, on 11 September 2018.

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Carlo Massobrio (Apr 17, 2020)	Apr 17, 2020
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Dr. Alexander V. Evteev	Date
Georgios Kouretzis (Apr 17, 2020)	Apr 17, 2020
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By signing below I confirm that research higher degree candidate Andreas Kromik is the lead author of, and contributed conceptualization, the preparation and interpretation of data and results, visualization, formal analysis as well as writing (draft and editing) to the publication entitled:

#### Diffusion Kinetics in Binary Liquid Alloys with Ordering and Demixing Tendencies.

Authors: A. Kromik, E. V. Levchenko & A. V. Evteev

Accepted by *Theory and Simulation in Physics for Materials Applications*, on 14 February 2020.

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