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

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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

I hereby certify that this thesis is in the form of a series of papers. I have included as part of the thesis a written declaration from each co-author, endorsed in writing by the Faculty Assistant Dean (Research Training) attesting to my contribution to any jointly authored papers.

Andreas Kromik

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 semi-empirical 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 $0.25 \lesssim c_{Ni} \lesssim 0.5$ 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 $t \to 0$ 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:

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:10.1002/adts.201800109

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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_i	Mole fraction of *i*
D	Diffusion coefficient
μ_i	Chemical potential of *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 *t*
$\widetilde{D}$	Interdiffusion coefficient
H	Enthalpy
U	Internal energy
p	Pressure
V	Volume
N	Number of atoms
E	Total energy
T	Temperature
e_i	Total energy of *i*-th atom
m	Mass
v	Velocity
$F_{\mu i}$	Embedding energy of atom
$\bar{\rho}_i$	Host electron density

$V_{\mu_i\mu_j}$	Pair interaction potential
k	Thermal conductivity
k_B	Boltzmann constant
J	Heat current vector
$\mathcal{L}$	Lagrangian function
PS	Phase space
T_g	Glass transition temperature
J_C	Interdiffusion flux
Q_C^*	Heat of transport
$Q_C^{*\prime}$	Reduced heat of transport
S	Correction factor
S_0	Kinetic factor of the correction factor
W_{12}	Collective energy generation-dissipation effect
P_{12}	Resulting force of fluctuations between J_C and R_{12}
R	Random force acting on atoms
σ_{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