Diffusion Coefficients in Liquid Phase Predicted by *ab initio* Molecular Dynamics

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$$D = \lim_{t \to \infty} \frac{\left\langle R^2(t) \right\rangle}{6t}$$

Acknowledgments

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Benefits of NIST Workshops

- **2002 workshop on thermodynamics**
  - **Started our activity on CALPHAD automation in the NSF ITR project**
  - **Shang, Wang and Liu, "ESPEI: Extensible, Self-optimizing Phase Equilibrium Infrastructure for Magnesium Alloys,", *Magnesium Technology 2010, 617***
- **Diffusion workshop since 2003**
  - **Resulted in first-principles calculations of diffusion coefficients in crystals**
  - **Diffusion in liquid: this presentation**
- **Diffusion workshop at 2011 TMS annual meeting**

Objective: predict diffusion coefficients in liquid

- **Evaluate the *ab initio* molecular dynamics in calculating diffusion coefficients in liquid**
  - **Self diffusion coefficients of pure elements**
  - **Tracer diffusion coefficients of binary systems**
- ***Ultimate goal***
  - ***Diffusion coefficients in grain boundary: pure elements and binary systems***

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Previous work on diffusion coefficients

- Activities based on discussions at the NIST workshops
- Diffusion in crystals by first-principles
  - Self and tracer diffusion coefficients in fcc
  - Self and tracer diffusion coefficients in bcc/hcp
- Publications: Manjeera Mantina, presented and discussed at NIST workshops
  - fcc-Al: Phys. Rev. Lett., Vol.100 (2008) 215901
  - Impurity in fcc-Al: Acta Mater., Vol.57 (2009) 4102-4108.
  - 3d in fcc-Al: Phys. Rev. B, Vol.80 (2009) 184111
  - bcc and hcp: Defect Diffusion Forum, Vol. 294 (2009) pp 1-13

Prior work on *ab initio* Molecular Dynamics (AIMD)

- **Atomic structures of liquid as a function of temperature and compositions**
  - ***Comput. Mater. Sci.*, Vol.43 (2008) 1123-1129.**
  - ***Appl. Phys. Lett.*, Vol.94 (2009) 091904.**
  - ***Acta Mater.*, Vol.57 (2009) 376-391.**
- **Inspired by discussions at NIST workshop to extend the activities to evaluate diffusion coefficients.**

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AIMD

- **Molecular dynamics with atomic forces calculated on the fly using first-principles based on density functional theory**
- **Advantage: no need of fitted atomic potentials**
- **Disadvantage: limited number of atoms and time steps**

Diffusion coefficient and mean-square displacement (MSD)

$$D = \lim_{t\to\infty} \frac{\left\langle R^2(t)\right\rangle}{6t} = \lim_{t\to\infty} \frac{1}{6tN_i} \sum_{j=1}^{N_i} [R_j(t+t_0) - R_j(t_0)]^2$$

$\langle R_i^2(t)\rangle$: MSD of atom i

N_i: Total number of i atoms

R_j: Coordinates of j atom

t_0: Origin of time

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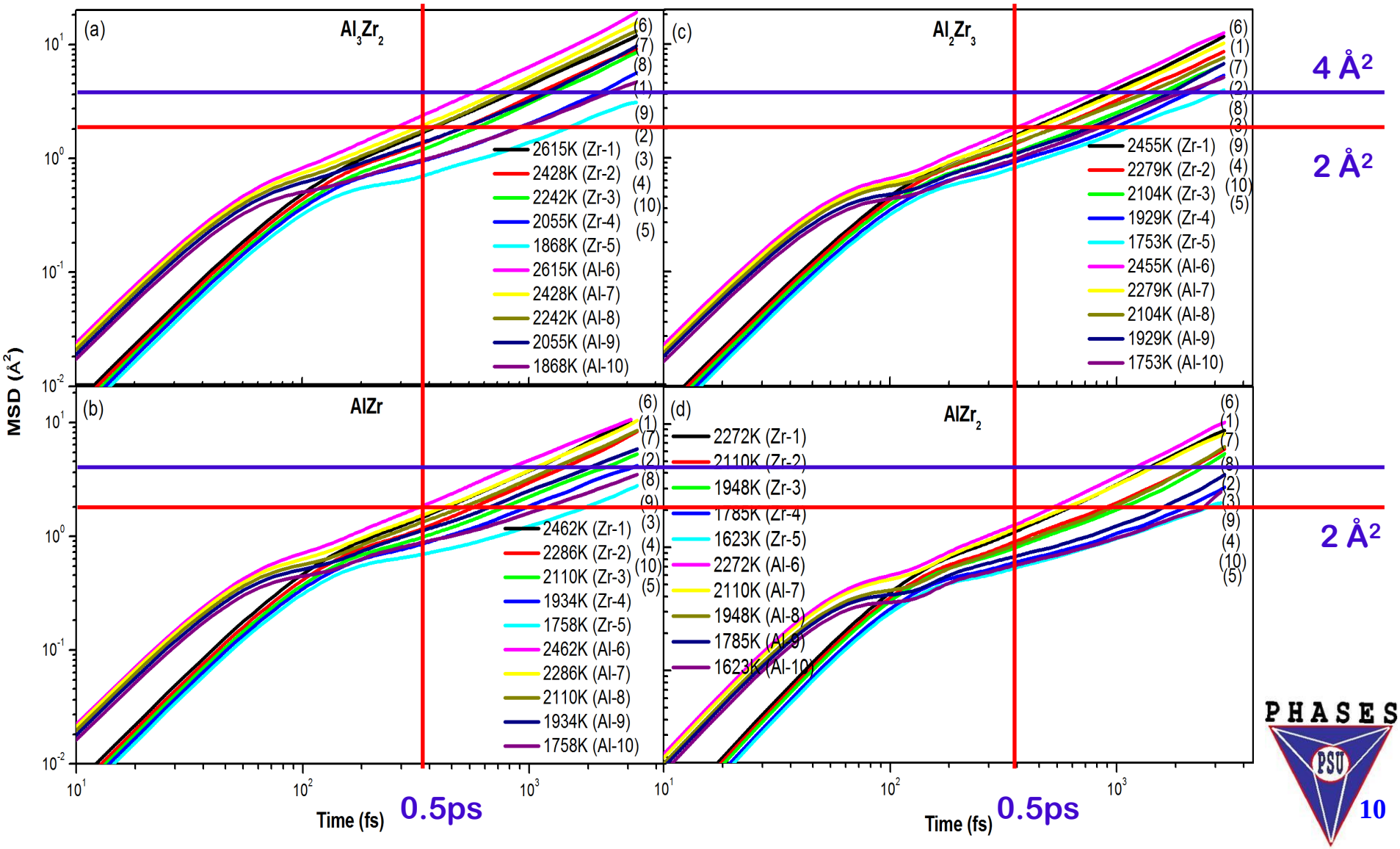
AIMD

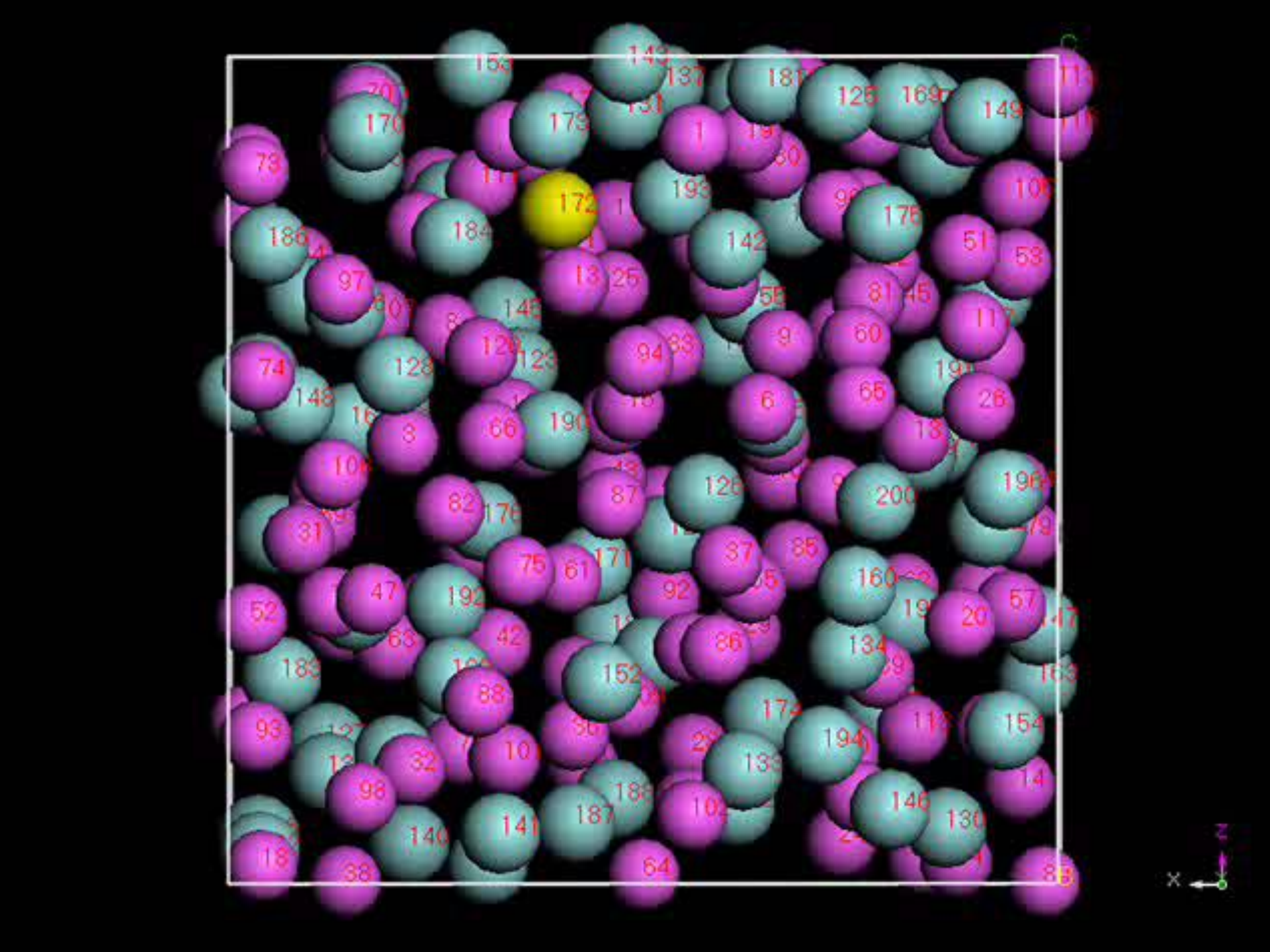
- **Software : VASP Version 4.6**
- **Supercell Size: 150/200 atoms**
- **Potential: GGA-PAW**
- **Time step: 3~5 fs**
- **Gamma point only k mesh and low accuracy**
- **Liquid configuration after running 10 ps above liquidus temperature (i.e. Al-Zr at 1.4Tm)**

Simulation steps

- **Establish the equilibrium liquid**
- **2000 converged configurations with simulation time no less than 10ps**
- **Using the last 1600 configurations for MSD**
- **Slop of the MSD curve ➔ 6 times of the self diffusion coefficient for six directions in the space.**
- **MSDs after 0.5ps and larger than 2 $Å^2$ used for diffusion analysis**

Simulation steps and MSD

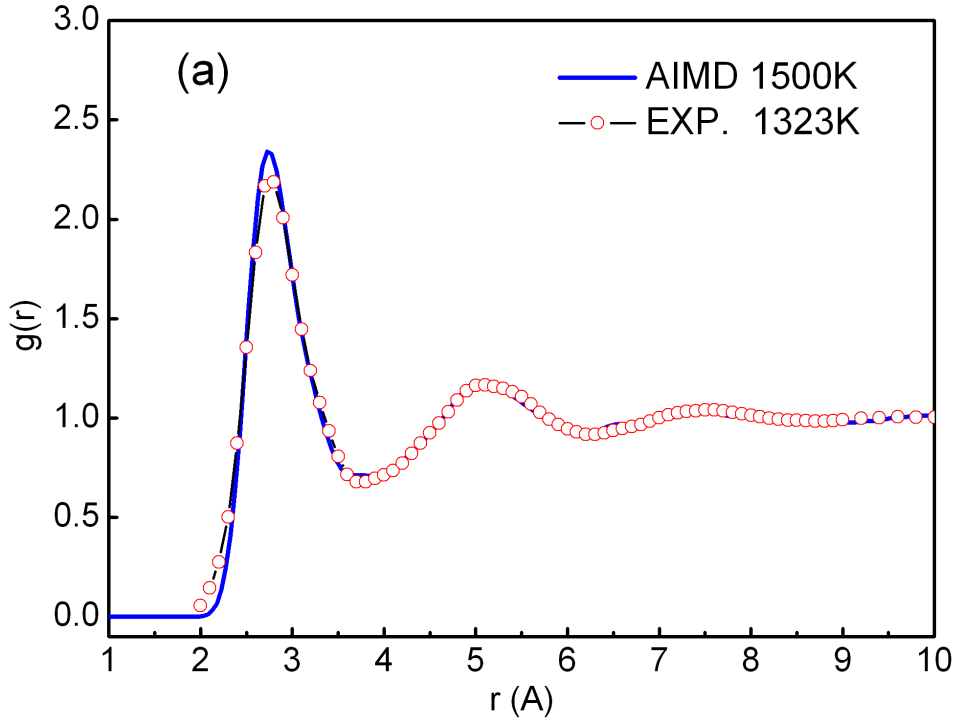


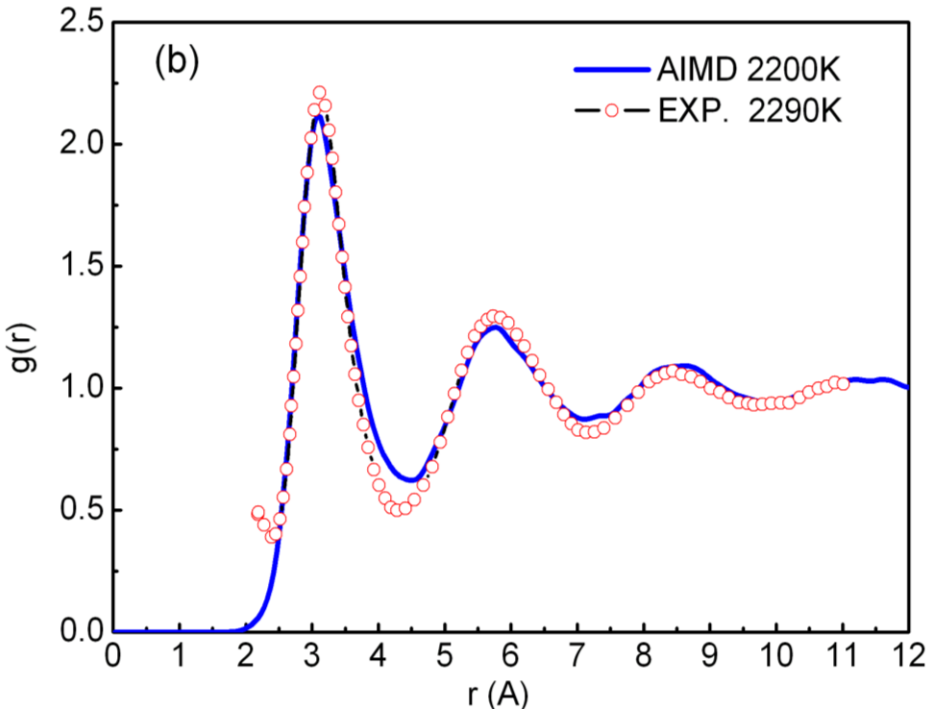

Z
X

Systems of interest

- **Studied**
  - **Pure elements: Al, Ni, Zr**
  - **Binary systems: Al-Ni, Al-Zr**
- **Under investigation**
  - **W, Ni-W**
  - **Mg, Mg-X**

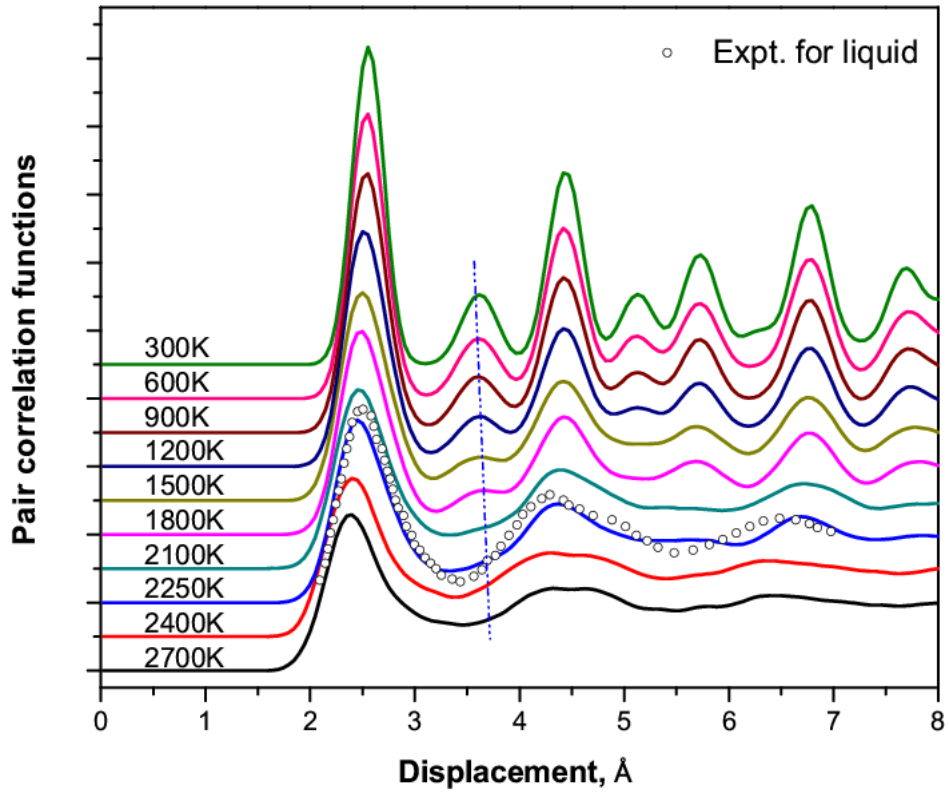
Pure Al: pair correlation function

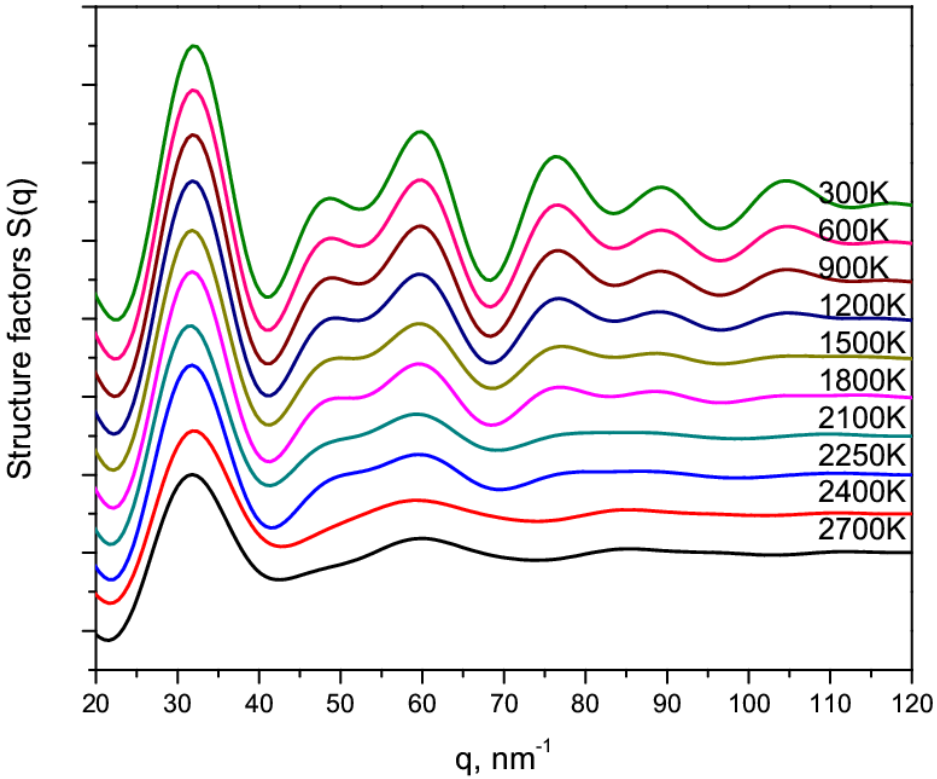




Waseda, The structure of non-crystalline materials. New York: McGraw-Hill, 1980

Pure Ni: pair correlation function and structure factor





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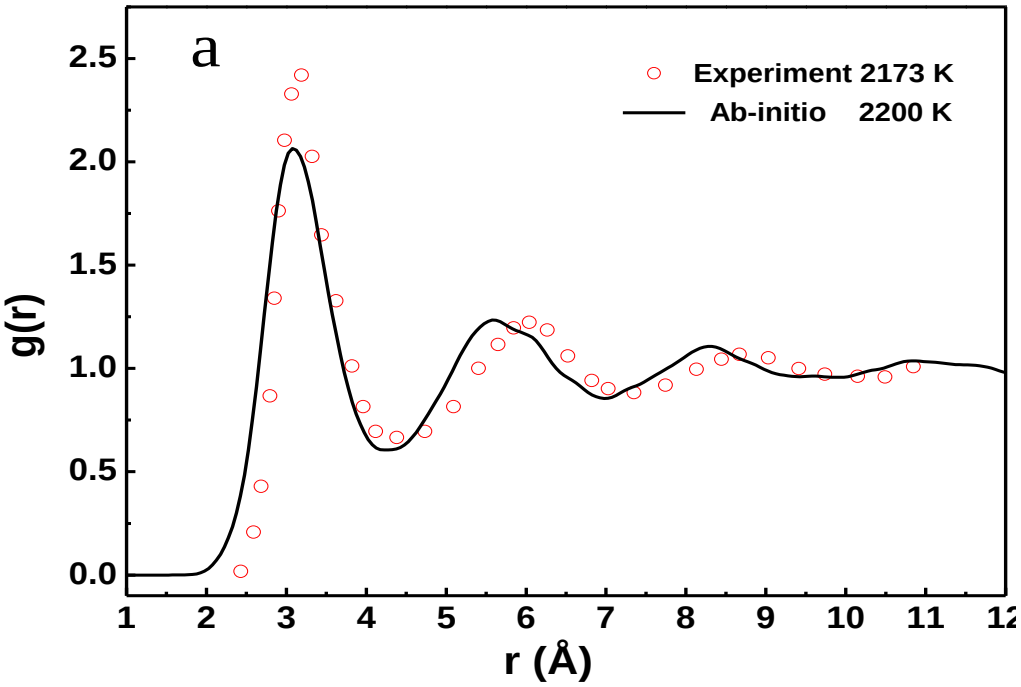
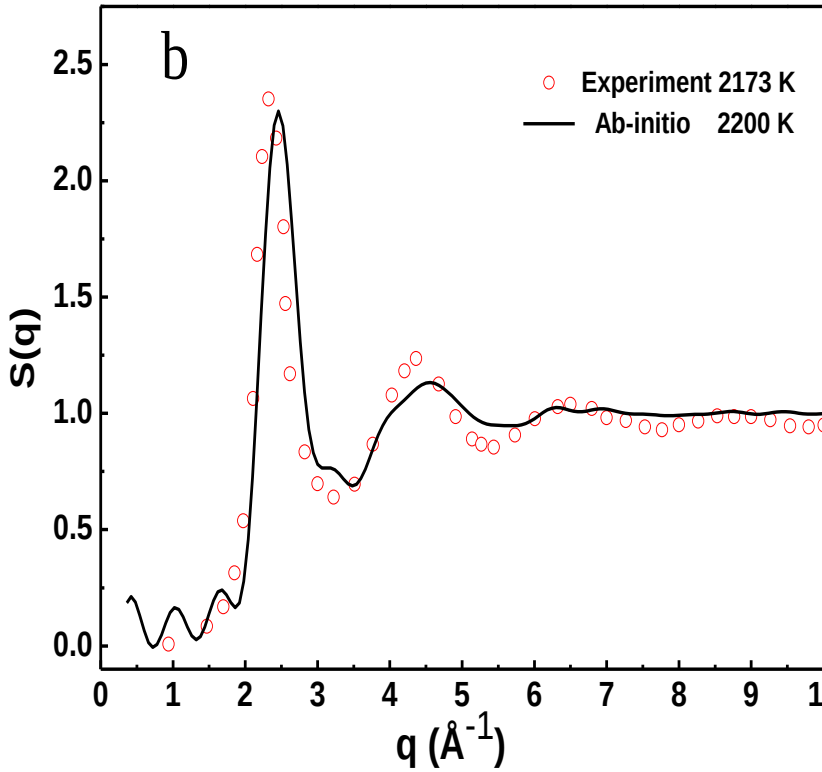
Pure Zr: pair correlation function and structure factor





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Fang, *Comput. Mater. Sci., Vol.43, 2008, 1123*

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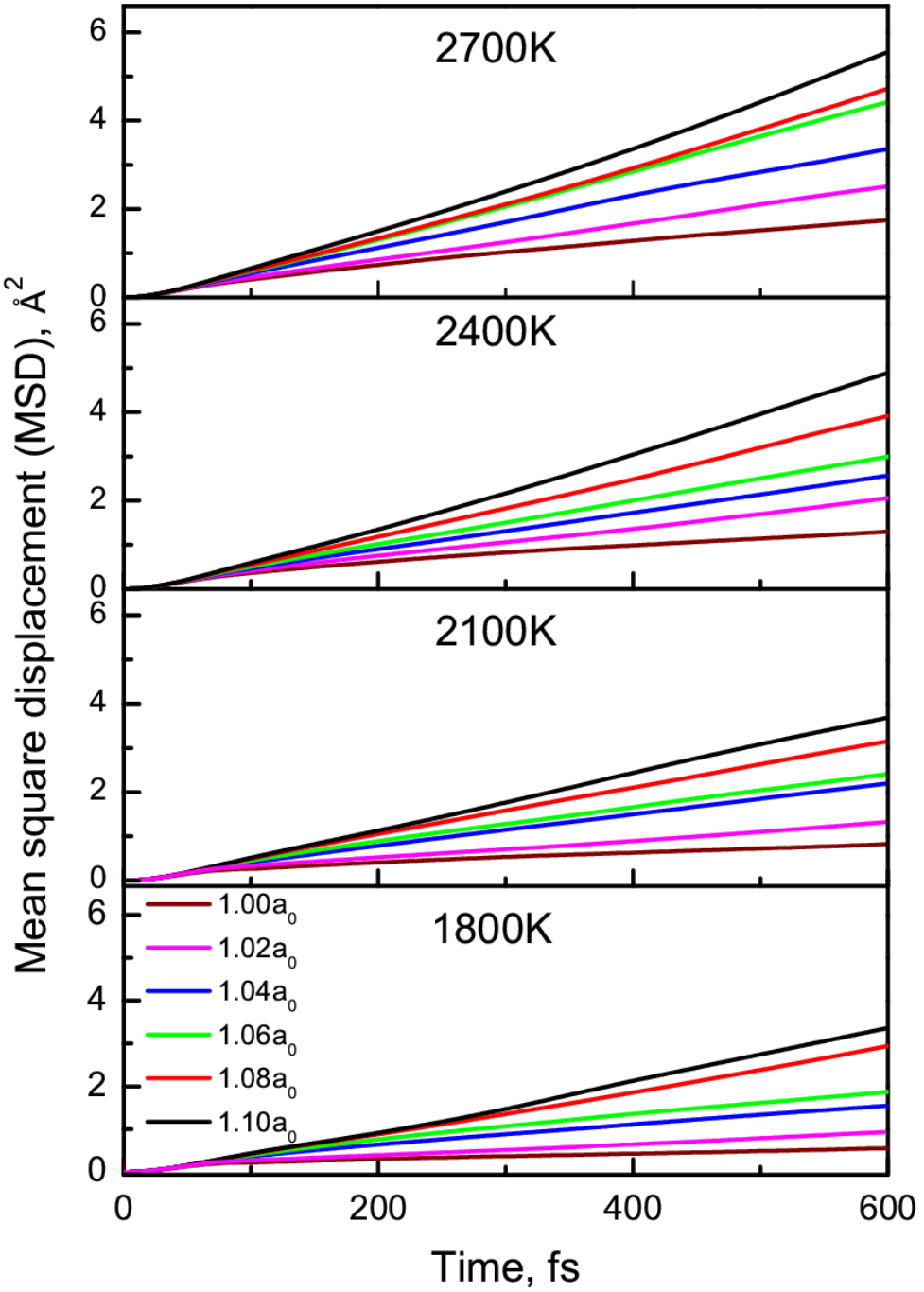
Ni: MSD at different temperatures and volumes



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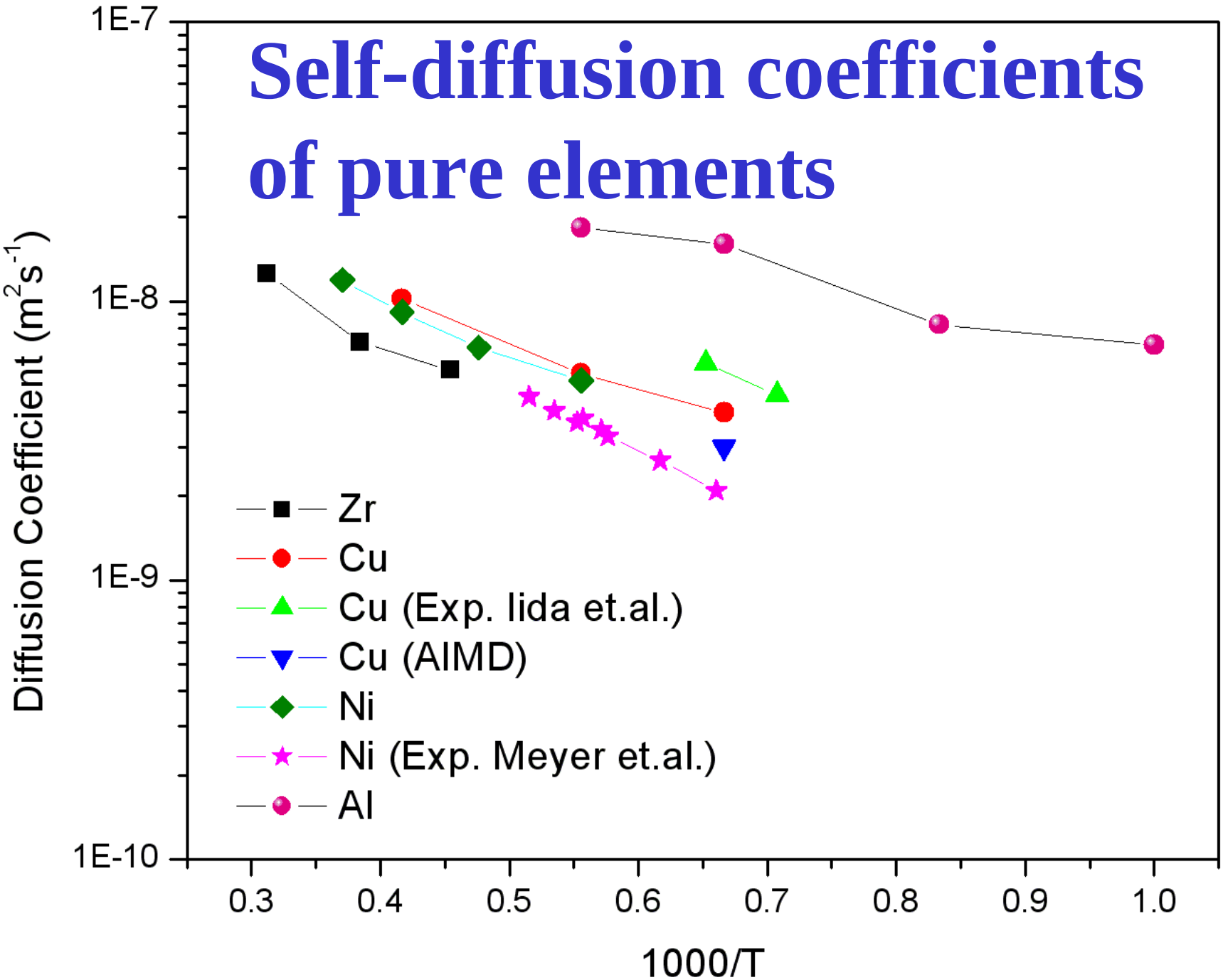
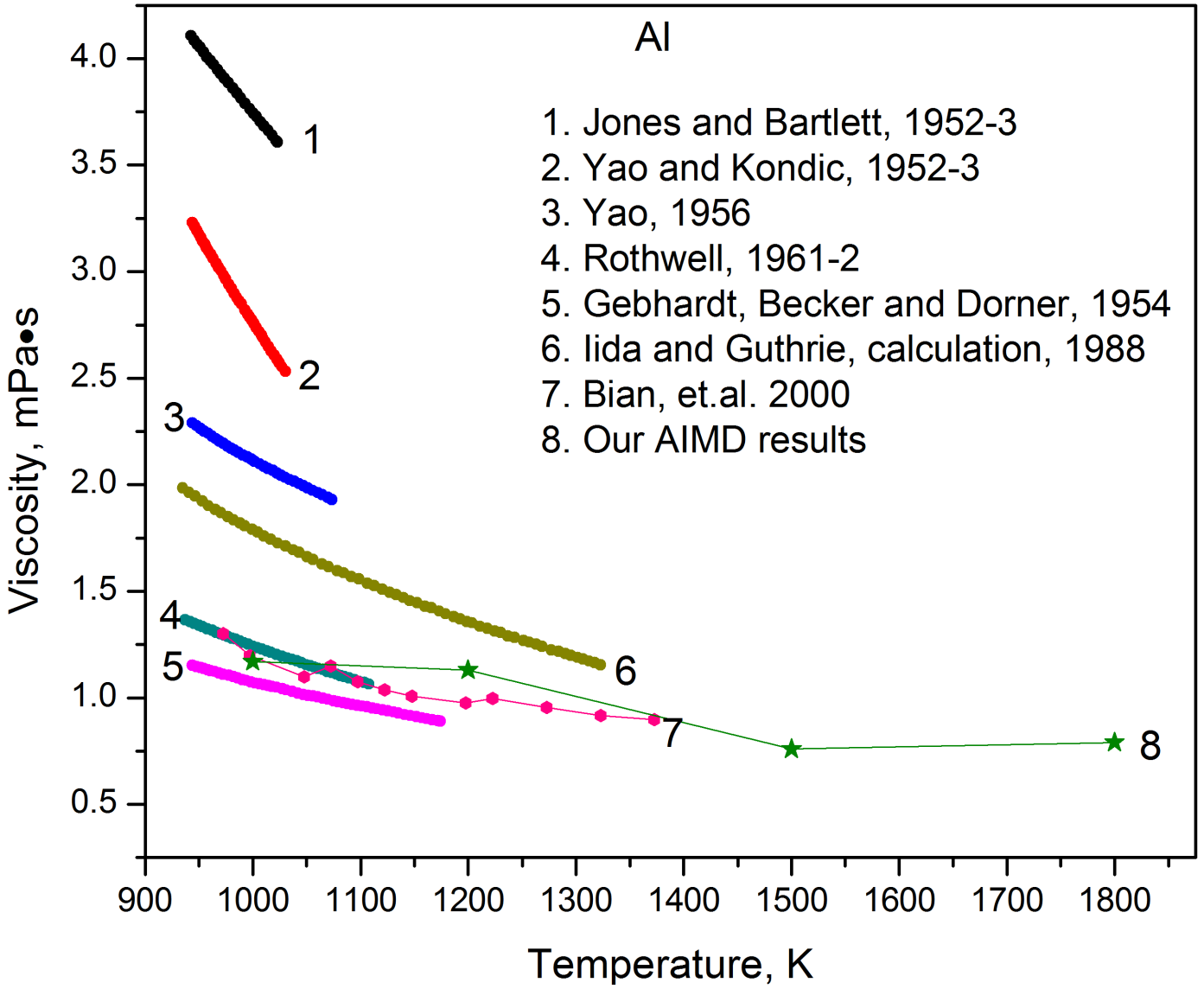
Self-diffusion coefficients of pure elements

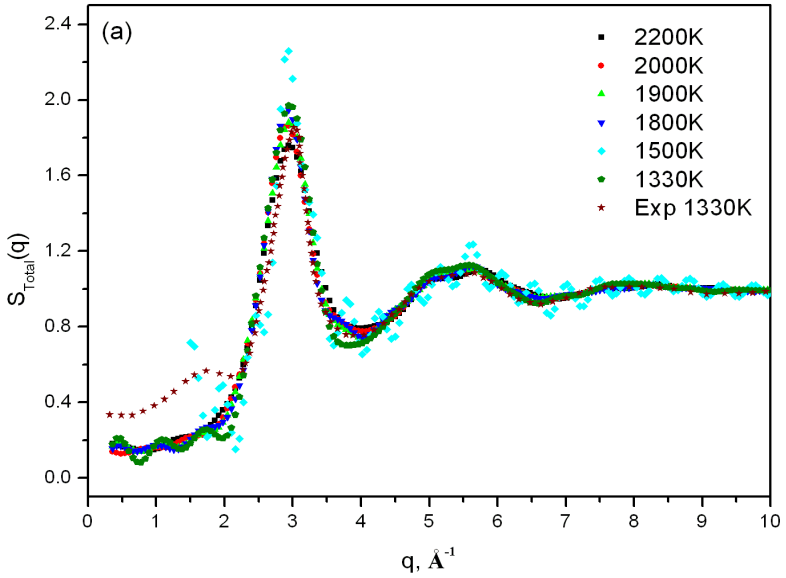


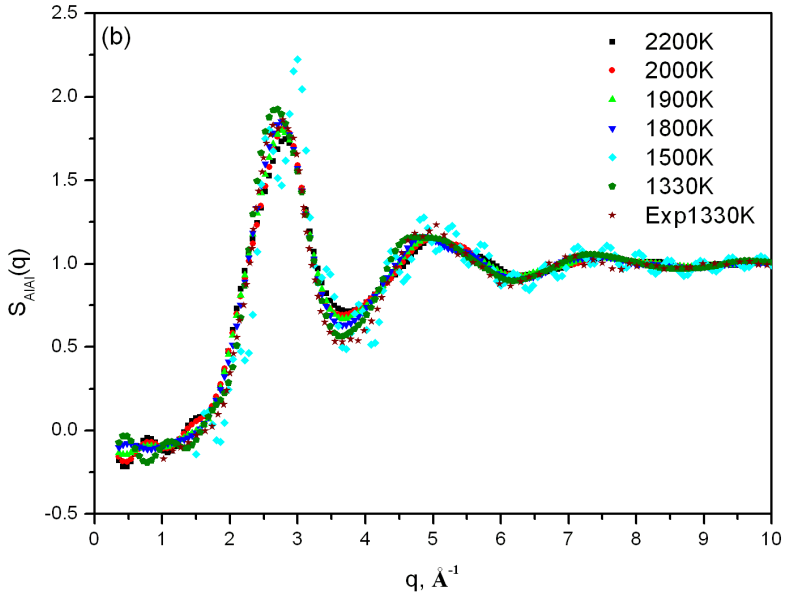
Viscosity of pure Al

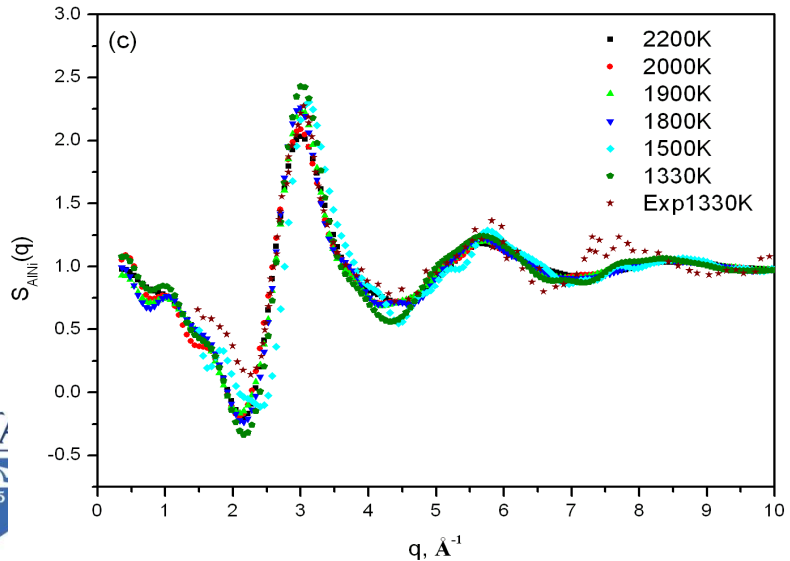
$$\eta = \frac{k_B T}{2\pi a D}$$

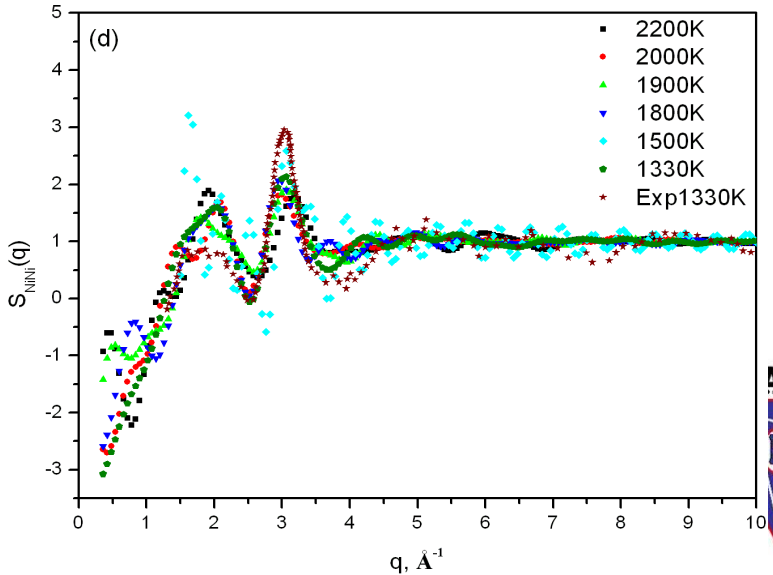


Al-20Ni: structure factor

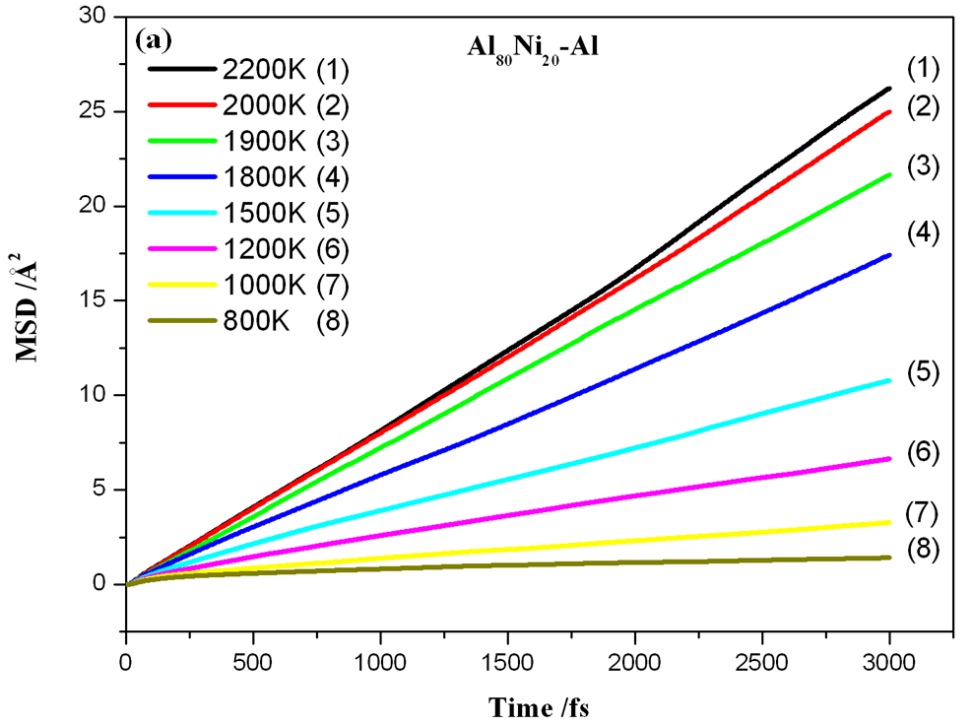


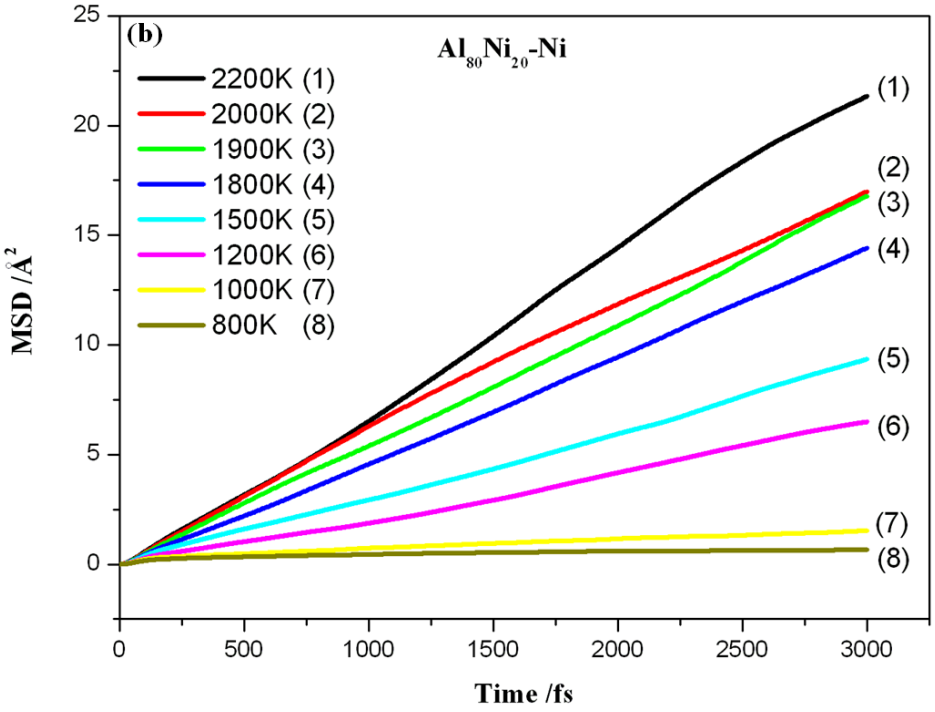






Al-20Ni: MSD





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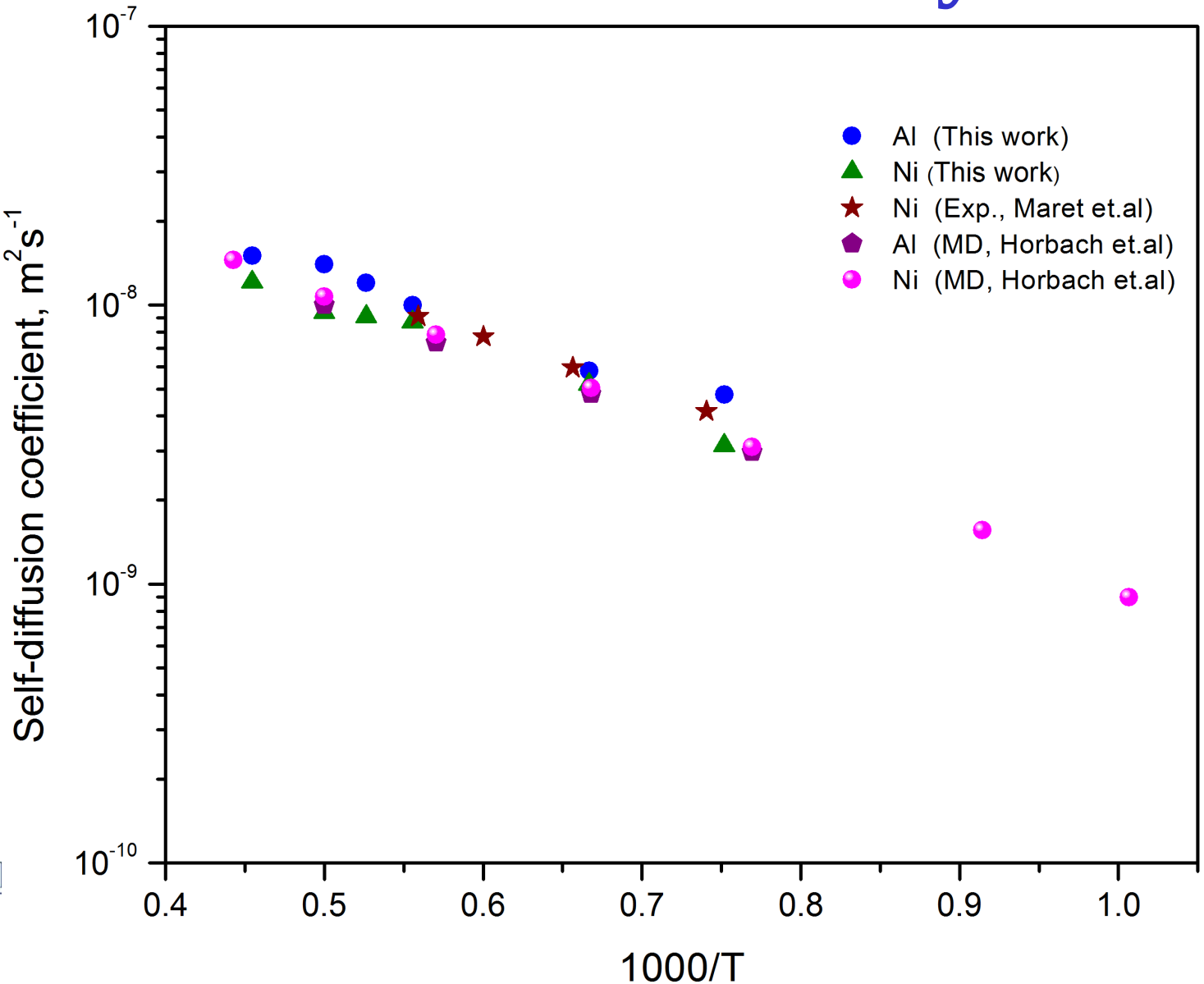
Al-20Ni: tracer diffusivity



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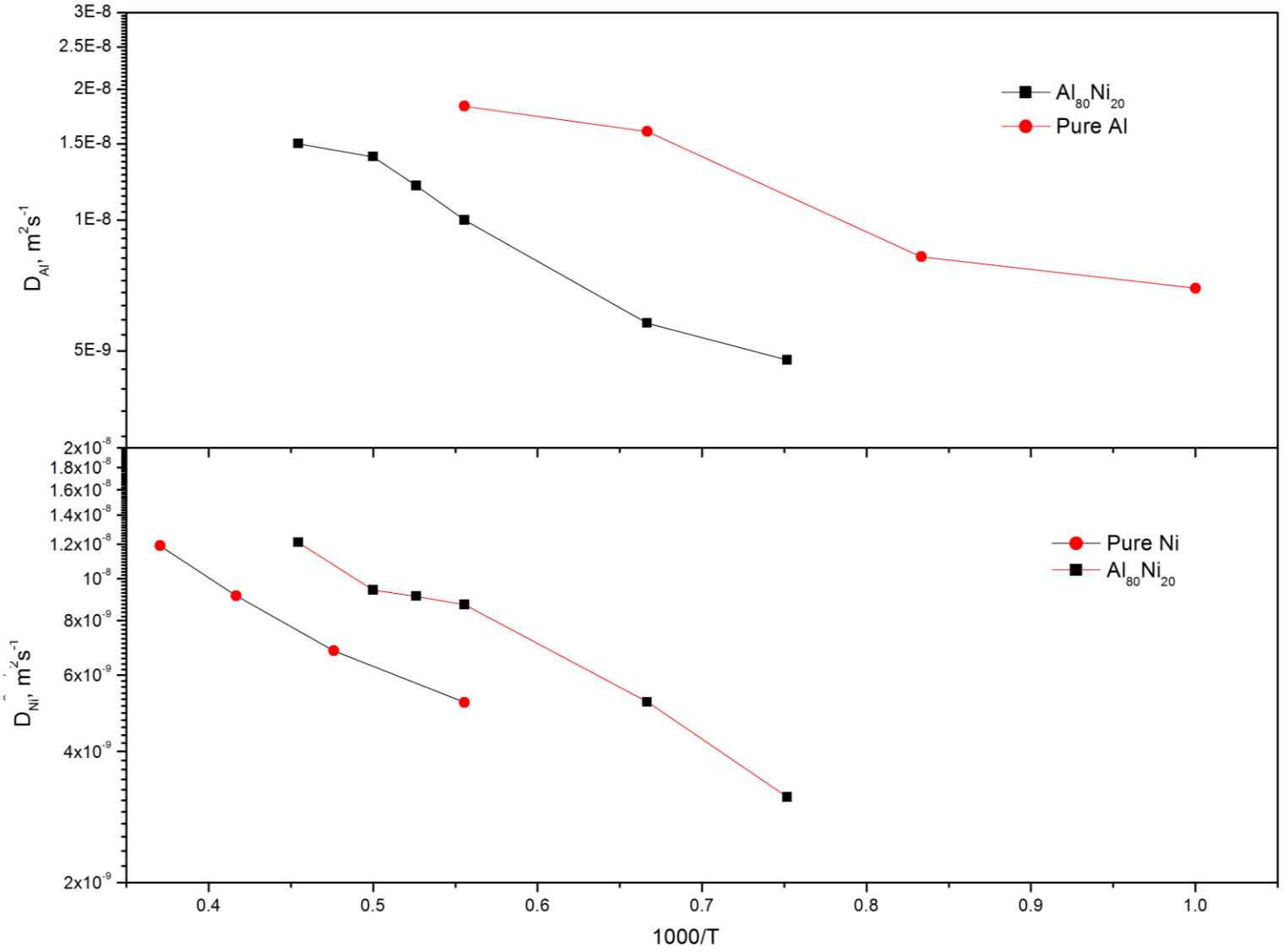
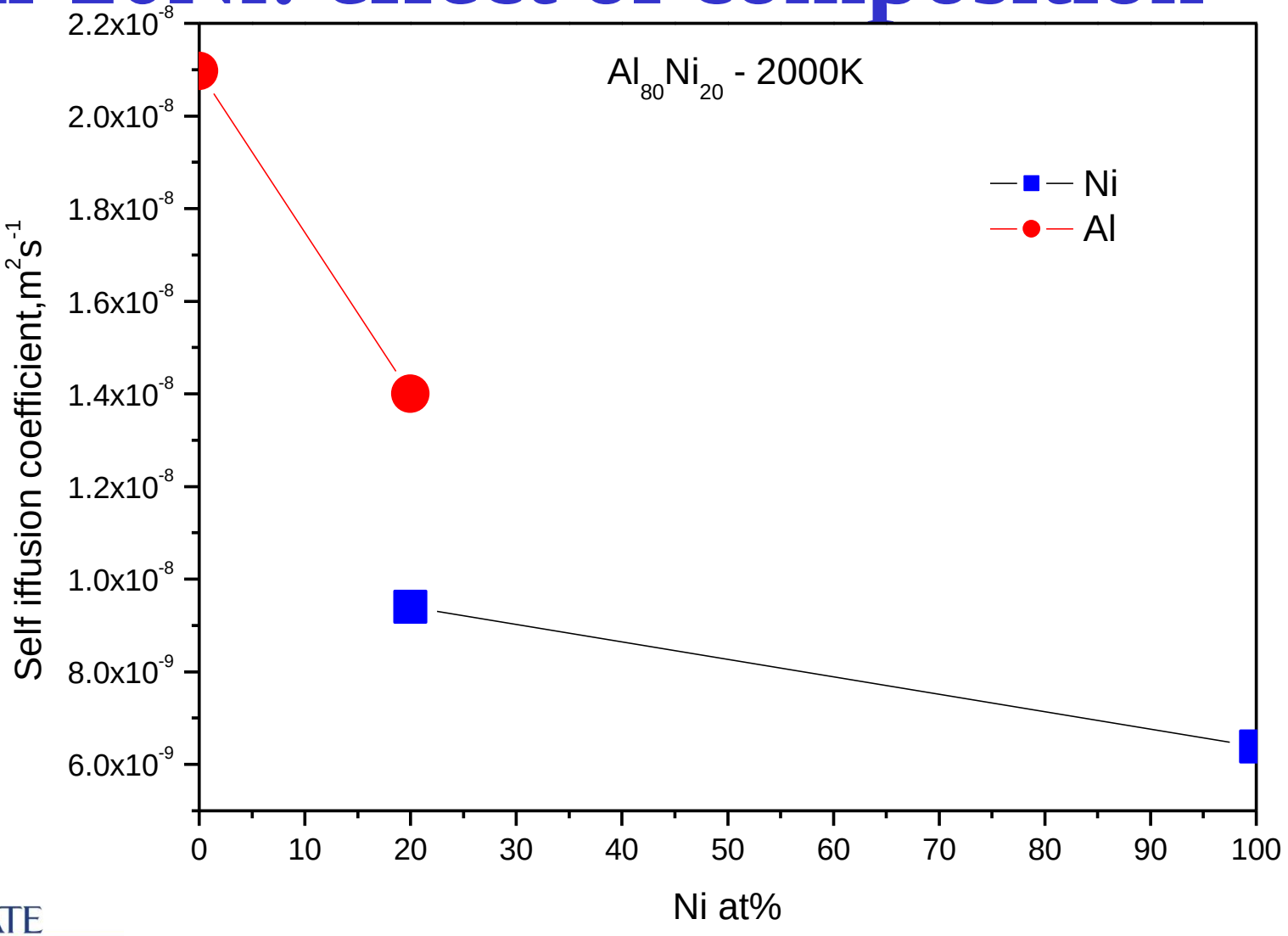
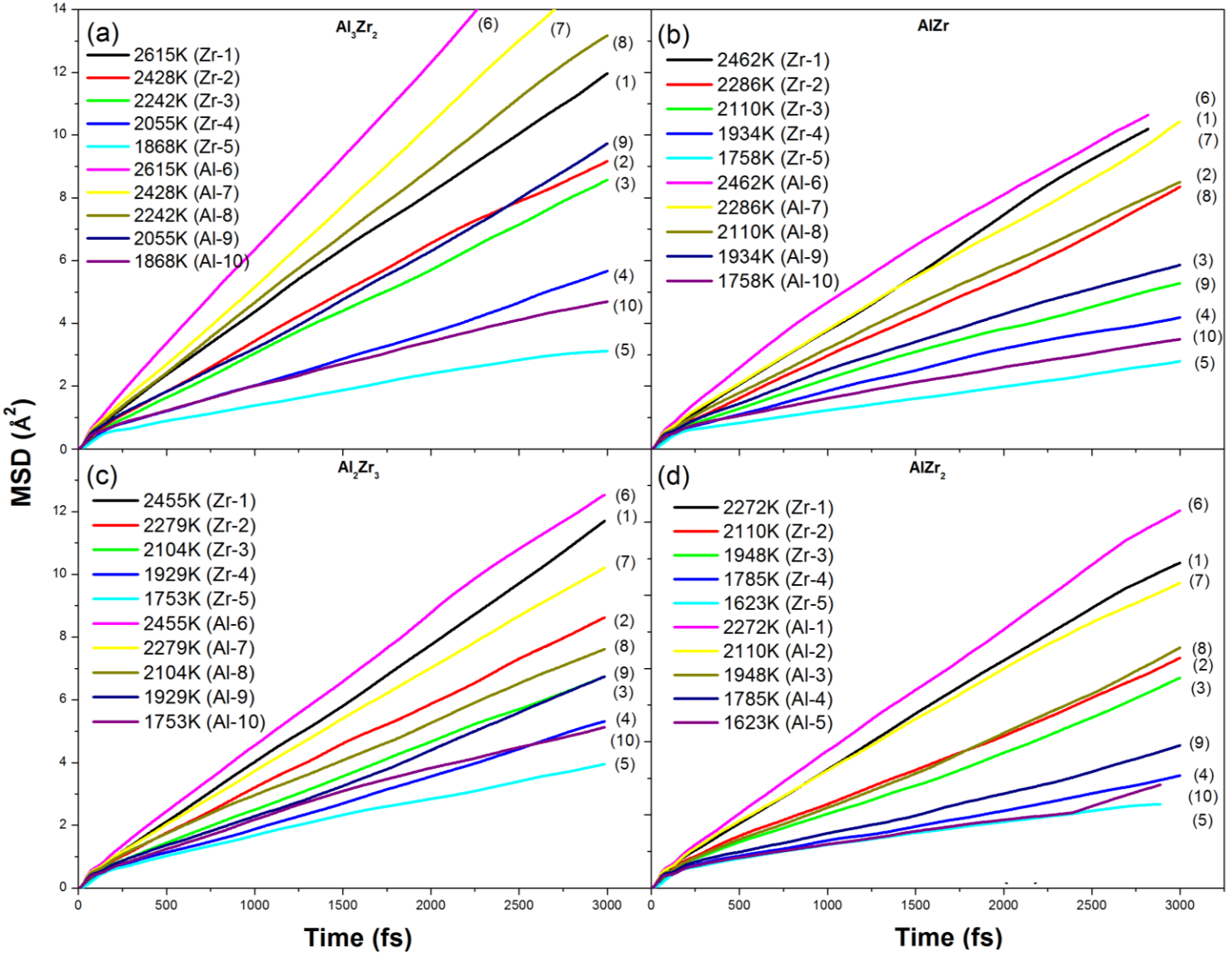
Al-20Ni: compared to pure



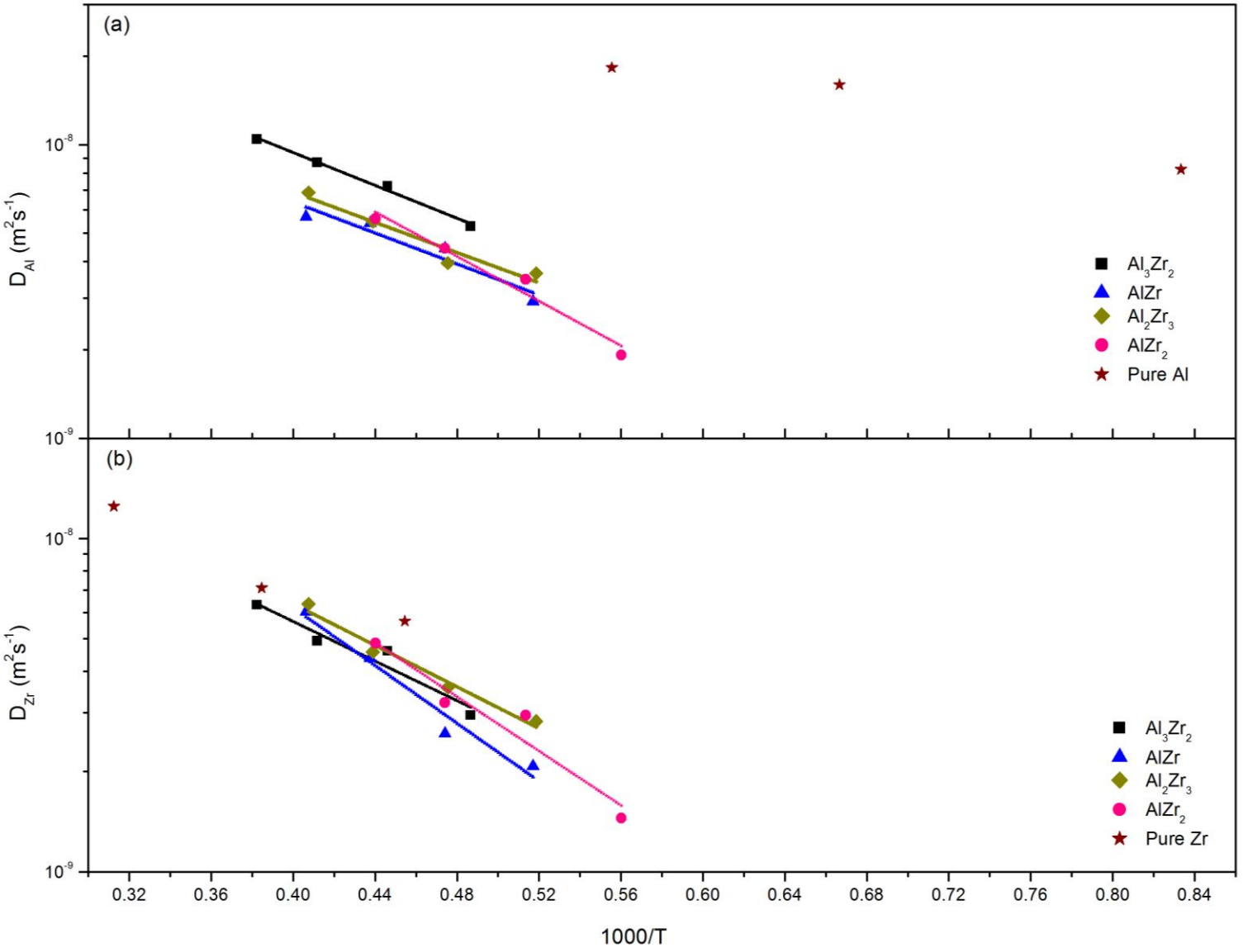
Al-20Ni: effect of composition



Al-Zr: MSD


(a)
Al_3Zr_2
2615K (Zr-1)
2428K (Zr-2)
2242K (Zr-3)
2055K (Zr-4)
1868K (Zr-5)
2615K (Al-6)
2428K (Al-7)
2242K (Al-8)
2055K (Al-9)
1868K (Al-10)
(b)
AlZr
2462K (Zr-1)
2286K (Zr-2)
2110K (Zr-3)
1934K (Zr-4)
1758K (Zr-5)
2462K (Al-6)
2286K (Al-7)
2110K (Al-8)
1934K (Al-9)
1758K (Al-10)
(c)
Al_2Zr_3
2455K (Zr-1)
2279K (Zr-2)
2104K (Zr-3)
1929K (Zr-4)
1753K (Zr-5)
2455K (Al-6)
2279K (Al-7)
2104K (Al-8)
1929K (Al-9)
1753K (Al-10)
(d)
$AlZr_2$
2272K (Zr-1)
2110K (Zr-2)
1948K (Zr-3)
1785K (Zr-4)
1623K (Zr-5)
2272K (Al-1)
2110K (Al-2)
1948K (Al-3)
1785K (Al-4)
1623K (Al-5)
MSD (Å^2)
Time (fs)
Time (fs)

Al-Zr: diffusion coefficients



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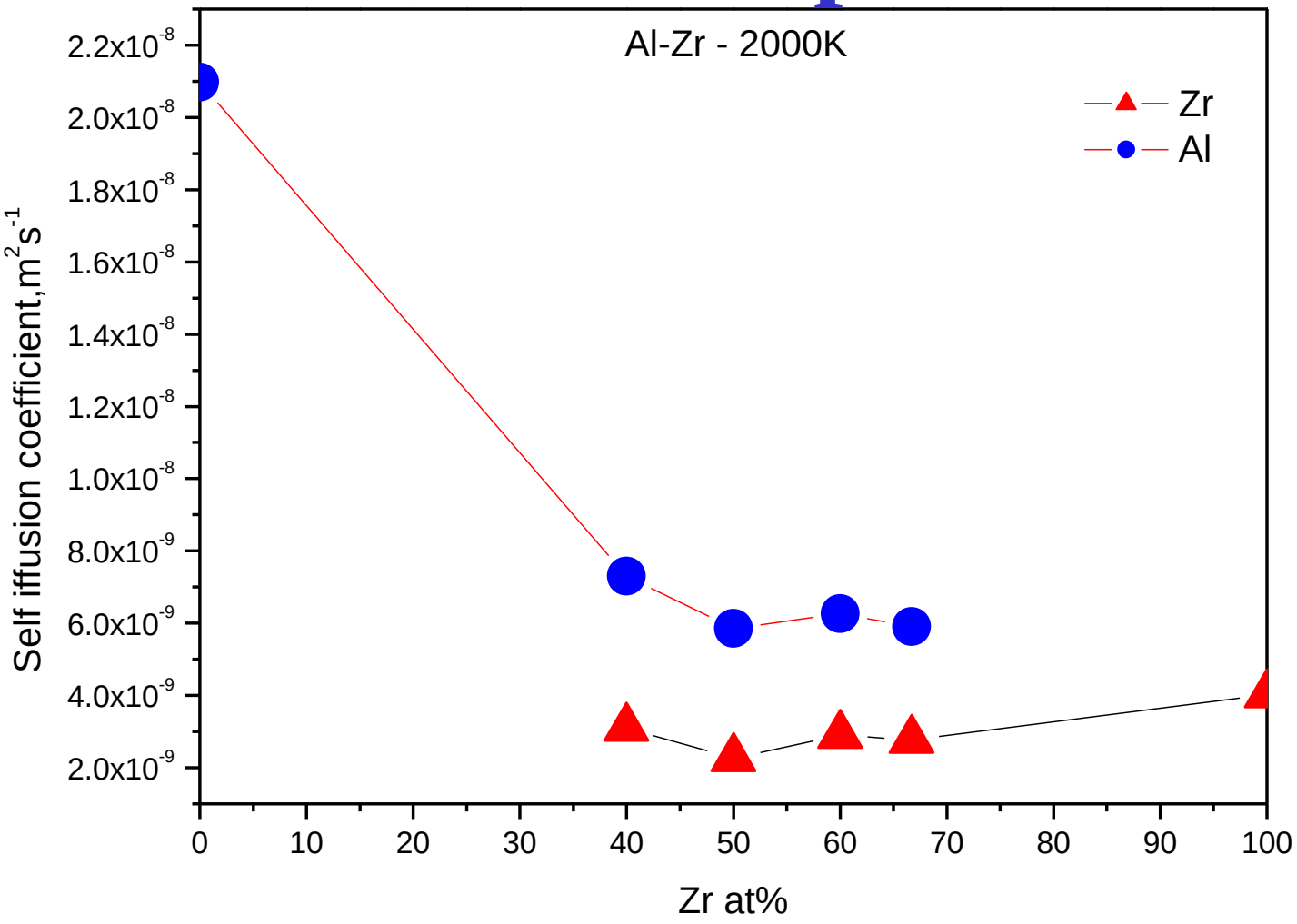
Al-Zr: effect of composition



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Summary

- **Self-diffusion coefficients of pure elements and some binary alloys in the liquid state are predicted from the AIMD, showing good agreement with the experimental data.**