Ab-Initio Molecular Dynamics Modeling of Molten Superalloys

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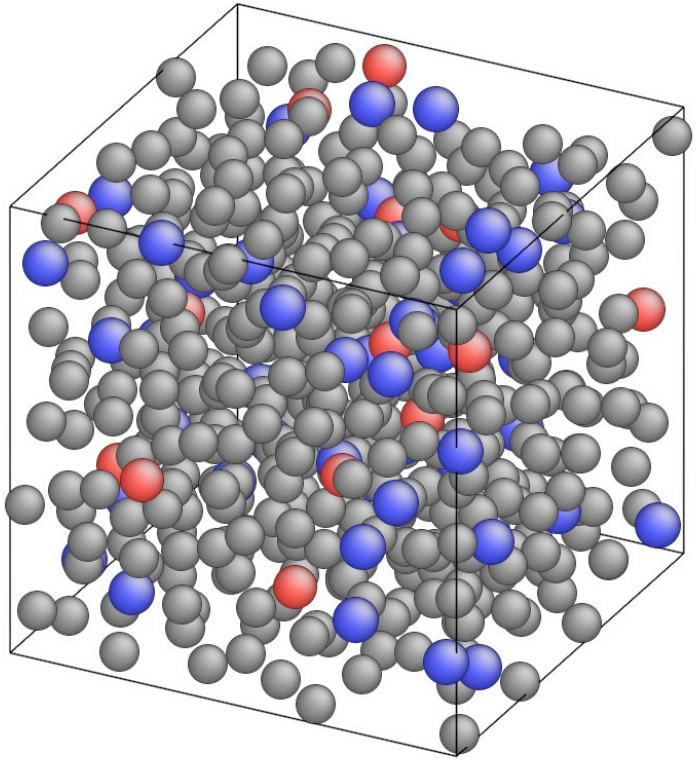

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Acknowledgements

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Research Support

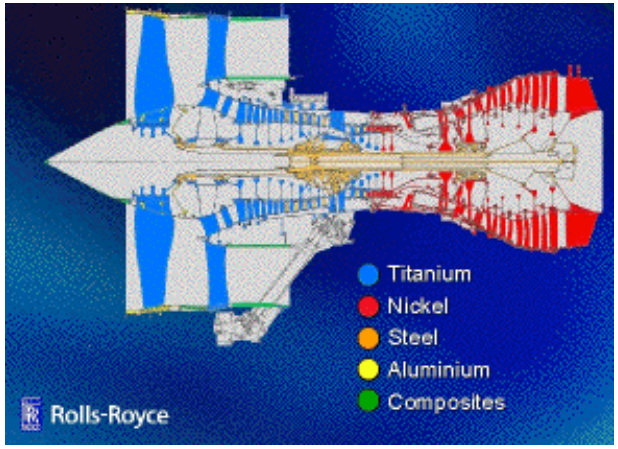
US DOE (Office of Basic Energy Sciences)

AFOSR (Materials Engineering for Affordable New Systems Program)

Supercomputing Resources

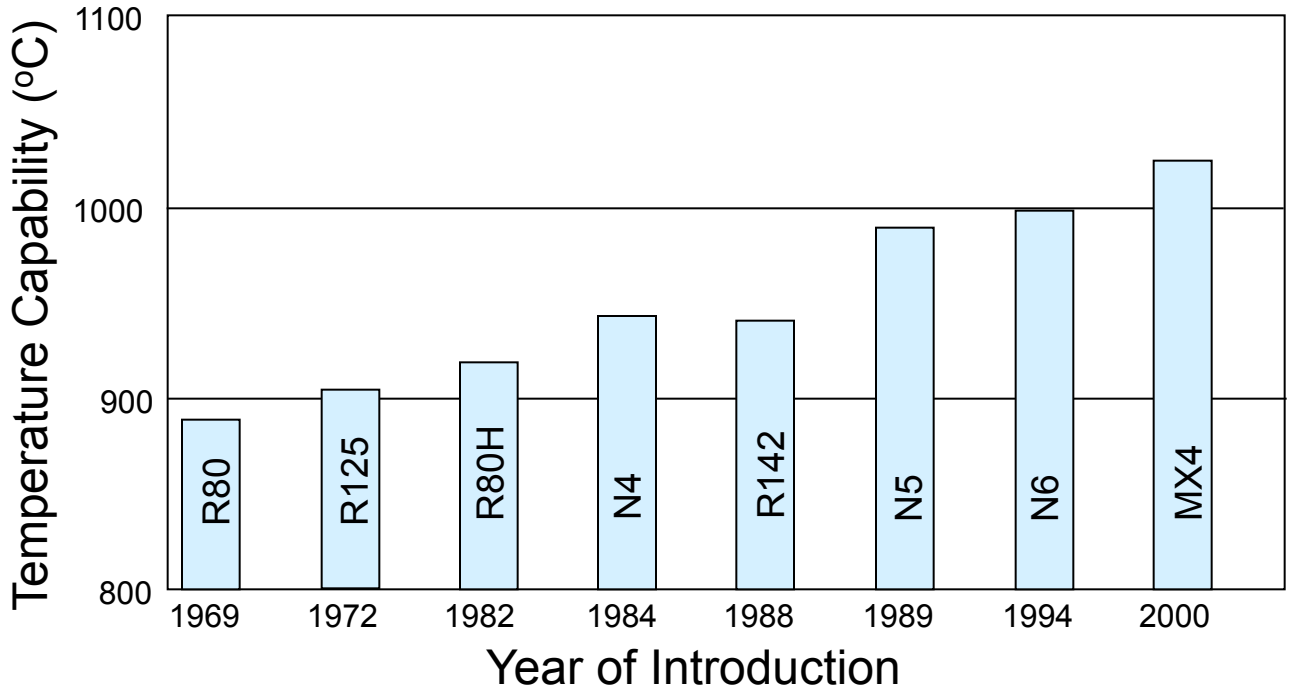
DoD ASC-MSRC Challenge Grant

Ni-Based Superalloys



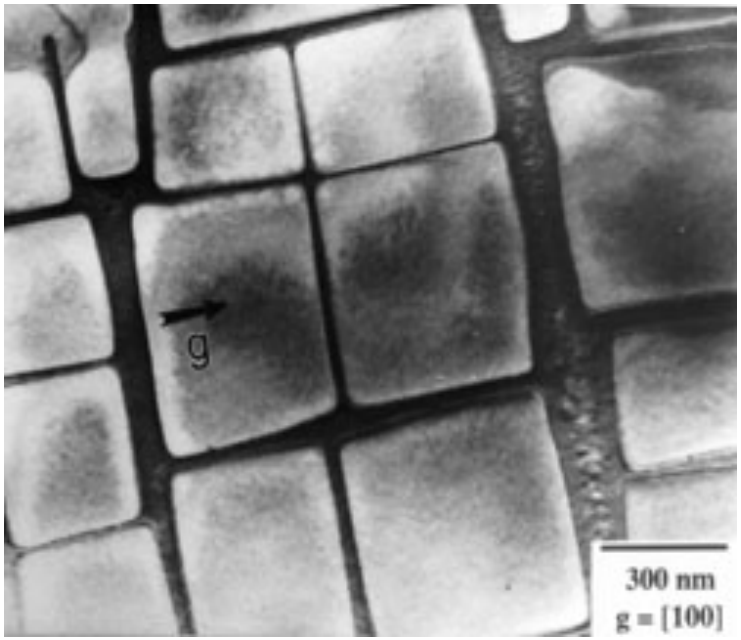
Higher-T Materials → Higher Efficiency

Evolution of Temperature Capability



1st-Principles Thermo & Kinetic Modeling

- **Design of High-Temperature Materials**
  - Requires Data for Bulk and Interfacial Free Energies, Diffusion Kinetics, Lattice Parameters, …
  - In Many Cases Data Difficult to Measure (e.g., Metastable Phases, High T)



CMSX-4 Superalloy
A.Dlouhy and G.Eggeler

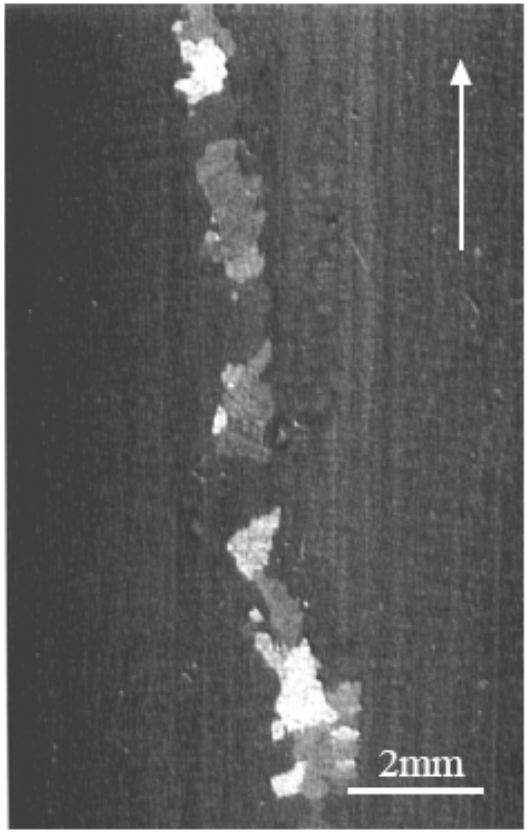
$Ni_{62.936}Cr_{7.5}Mo_{0.38}Al_{12.7}Co_{9.9}W_{2.1}Ti_{1.3}$
$Ta_{2.2}Re_{0.95}Hf_{0.034}$

- **Role of 1st-Principles Calculations**
  - Predictive Framework for Computing Structural, Thermodynamic and Kinetic Properties
  - Applicable to Both Stable and Metastable Phases, Bulk and Interfaces, High & Low T

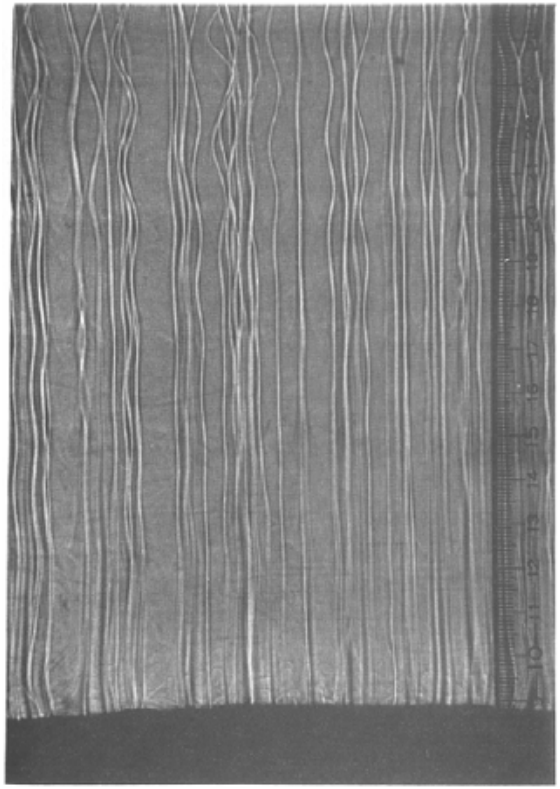
Defects in Directional Solidification

Directionally Solidified Superalloy Ingot
(A. F. Giamei, UTRC)

Freckle Chain in Superalloy
(Pollock and Murphy, 1996)



"Channels" in NH_4Cl
(Wooster, 1997)



Freckle-Formation Prediction

Convective Instabilities Expected When Critical Value of Ra_s Exceeded
(e.g., Beckermann et al., 2000)

High T

Temperature Gradient

$$Ra_S = \frac{(\Delta\rho / \rho_O) g K h}{\alpha \nu}$$

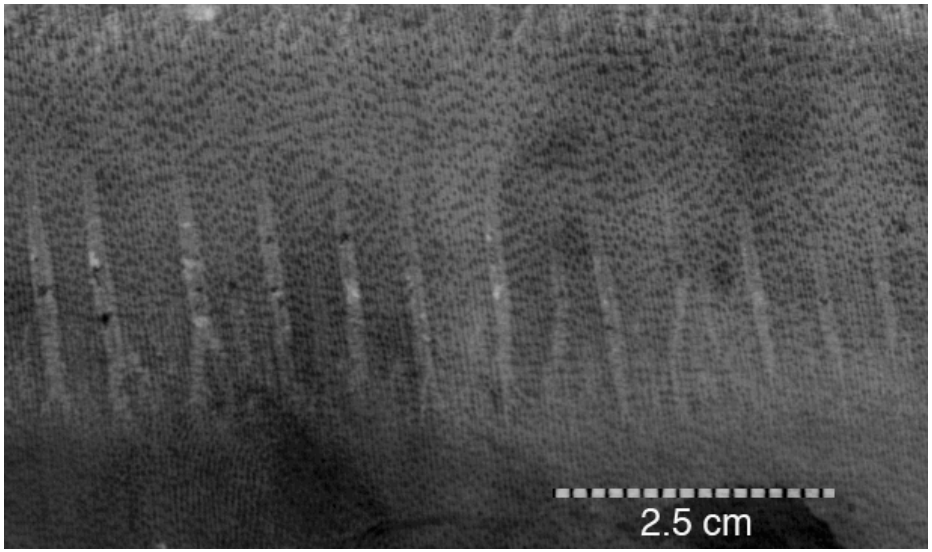
Low T

Ra_s ⟶ Ratio of Buoyancy to Retarding Frictional Forces

$\Delta\rho$ ⟶ Variation in Mass Density Across Mushy Zone

g ⟶ Gravity

K ⟶ Mushy Zone Permeability



Channels in a Superalloy
(Courtesy T. Pollock)

h ⟶ Mushy Zone Height

α, ν ⟶ Thermal Diffusivity and Viscosity

Mass Density

$$\rho(\{x_\alpha\},T) = \frac{1}{V(\{x_\alpha\},T)} \sum_\alpha x_\alpha M_\alpha$$

$x_\alpha \rightarrow$ Mole Fraction of Species α

$M_\alpha \rightarrow$ Molar Mass of Species α

$V(\{x_\alpha\},T) \rightarrow$ Molar Volume

*Accurate Parametrization of **Temperature and Composition Dependent Molar Volume** and **Solute Partitioning** Required to Predict Density Inversions Across Mushy Zone*

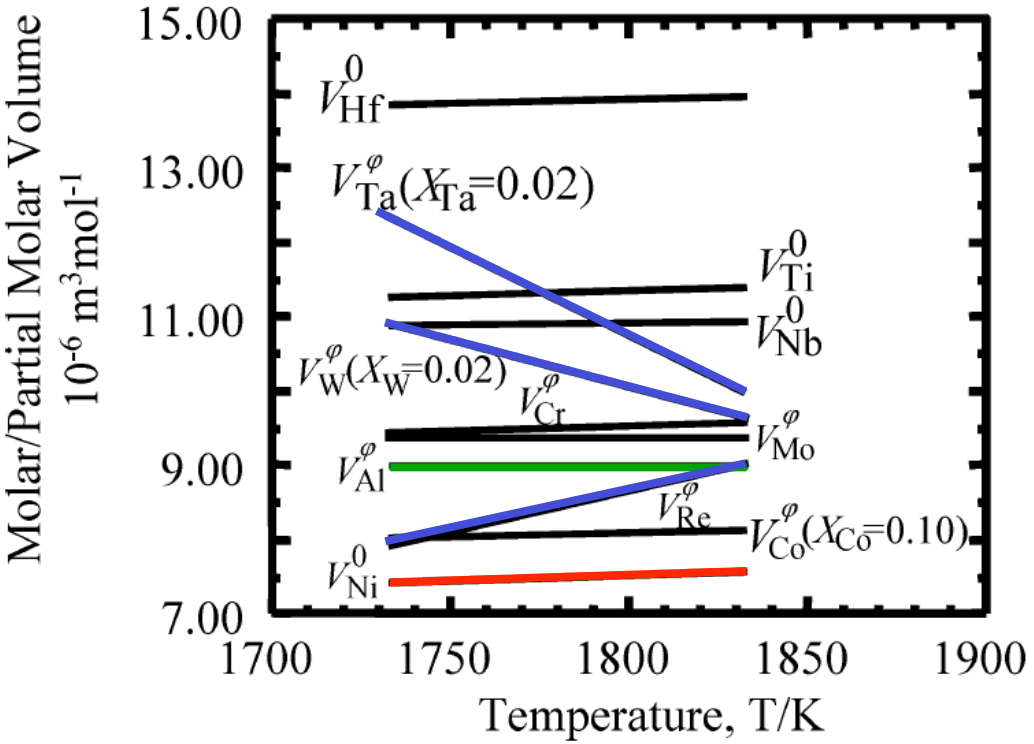
Molar-Volume Parametrization

K. Mukai, Z. Li and K. C. Mills, *Met. Trans. B*, vol. **36B**, 255 (2005)

$$V(\{x_\alpha\},T) \equiv \sum_\alpha x_\alpha \overline{V}_\alpha(x_\alpha,T)$$

$\overline{V}_\alpha(\{x_\alpha\},T) \rightarrow$ Partial Molar Volume of Species α

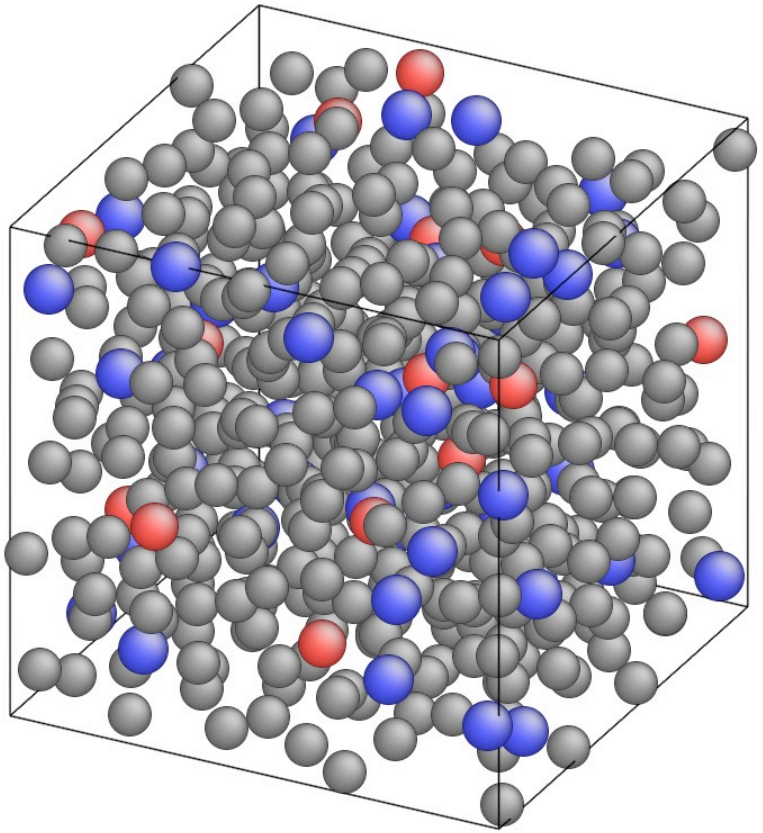
- **Assume $\overline{V}_\alpha$ Depends Only on x_α and T**
  - *Neglects Multicomponent Interactions*
- **Molar Volumes Fit to Experimentally Measured Binary Alloy Data**
  - *Large Variations of Partial Molar Volumes w/ Temperature & Composition Obtained from Fits*

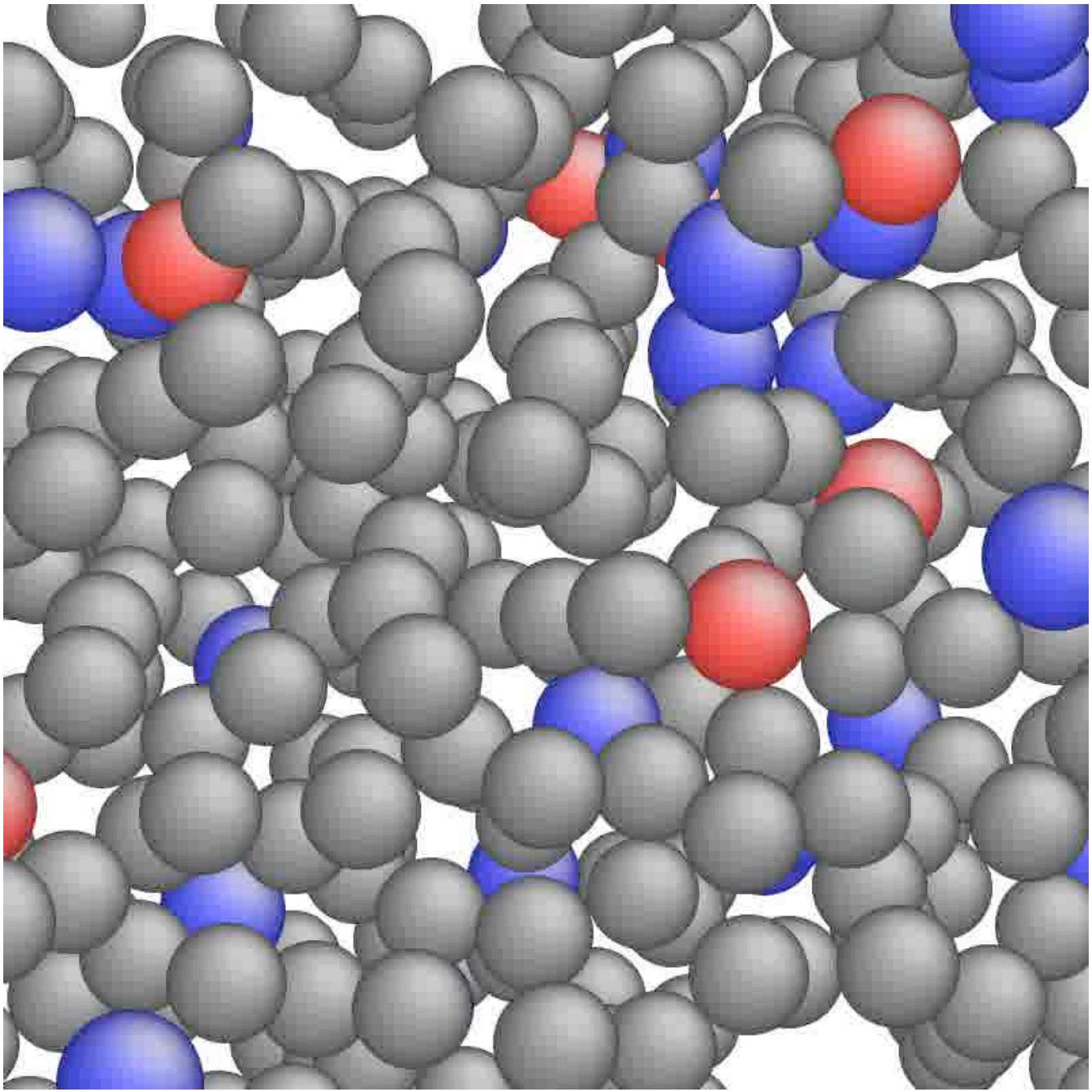


Quantum MD for Molten Ni-Based Alloys

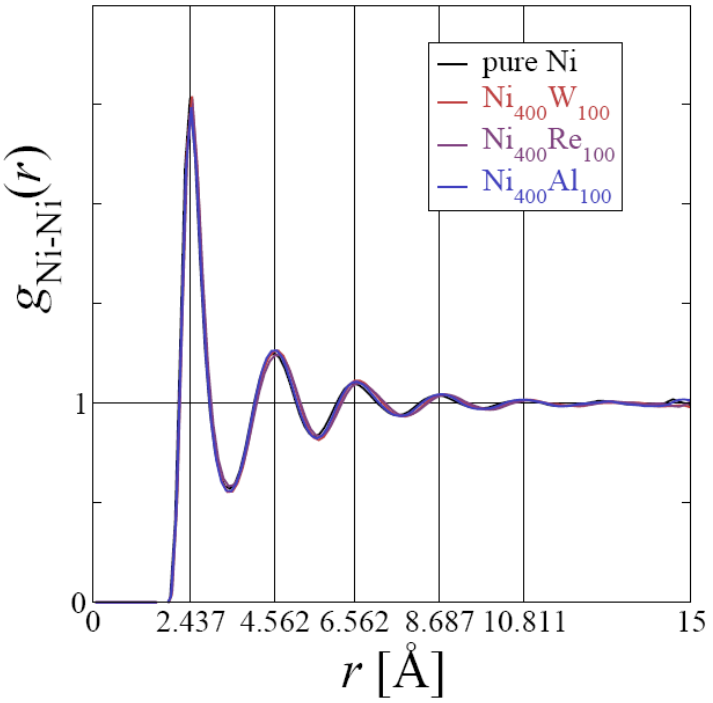
- **Simulation Details**
  - (NVT) Dynamics at T=1750 & 1830 K
  - Time Step: 0.002 or 0.003 ps
  - ~5-10 ps Simulation Time
  - 500 Atom System Size
  - VASP Code on 64 Processors
  - Ultrasoft Pseudopotentials and PAW
- **Volumes**
  - 3 or 4 Volumes: 0.95 V_{ref} – 1.05 V_{ref}
  - Equations of State and Equilibrium Volume
- **Systems**
  - Elemental Ni and Al
  - Binary Ni-Al, Ni-W, Ni-Re, Ni-Ta
  - Ternary Ni-Al-W, Ni-Al-Re, Ni-Al-Ta

Snapshot of Simulation for $Ni_{436}Al_{50}W_{14}$





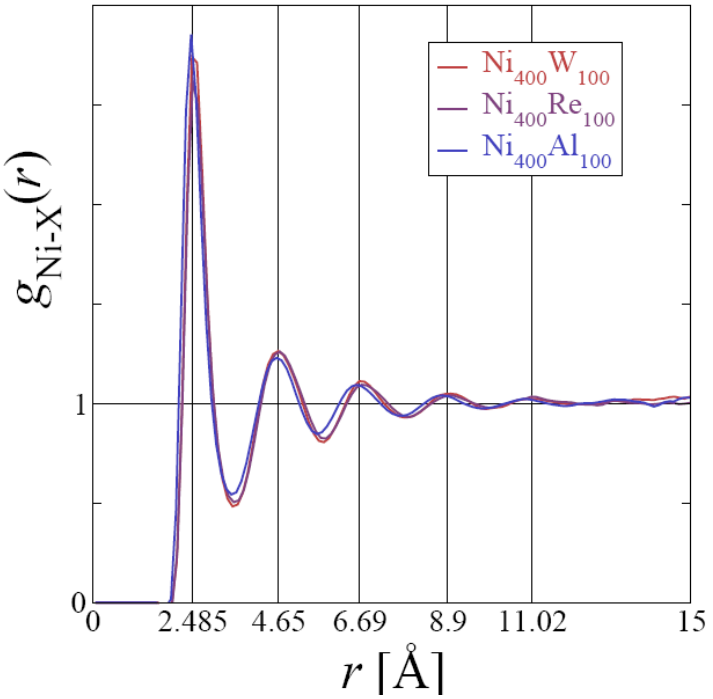
Radial Distribution Functions

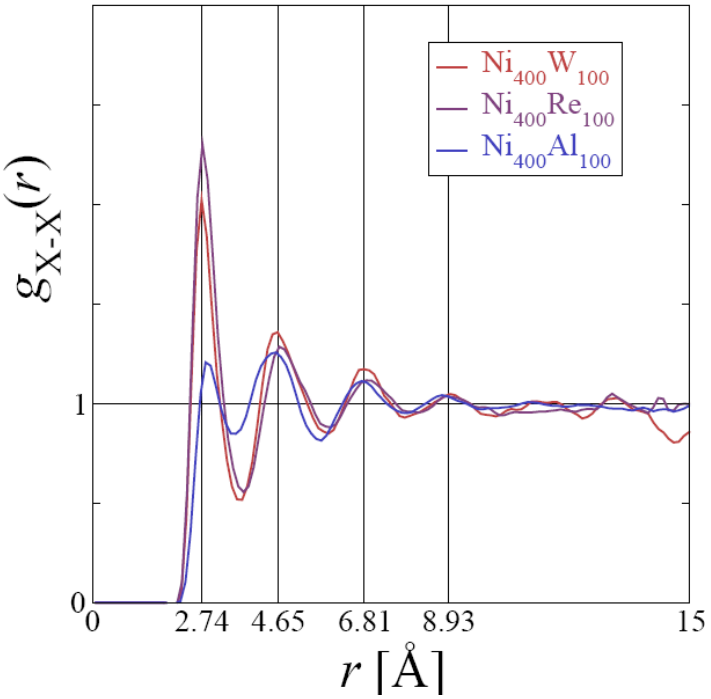


- Results Indicate Tendency for Chemical Short-Range Ordering
- Nearest-Neighbor Bond Lengths

  $R_{NiX} < (R_{NiNi}+R_{XX})/2$
- Nearest-Neighbor Coordinations

  $g_{NiX}(R_{NiX})>g_{NiNi}(R_{NiNi})>g_{XX}(R_{XX})$

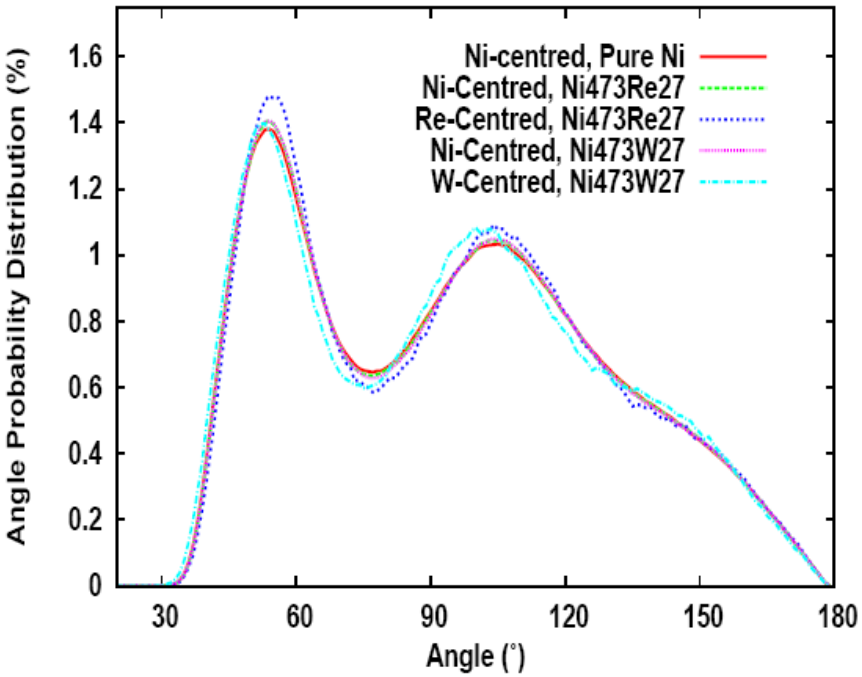




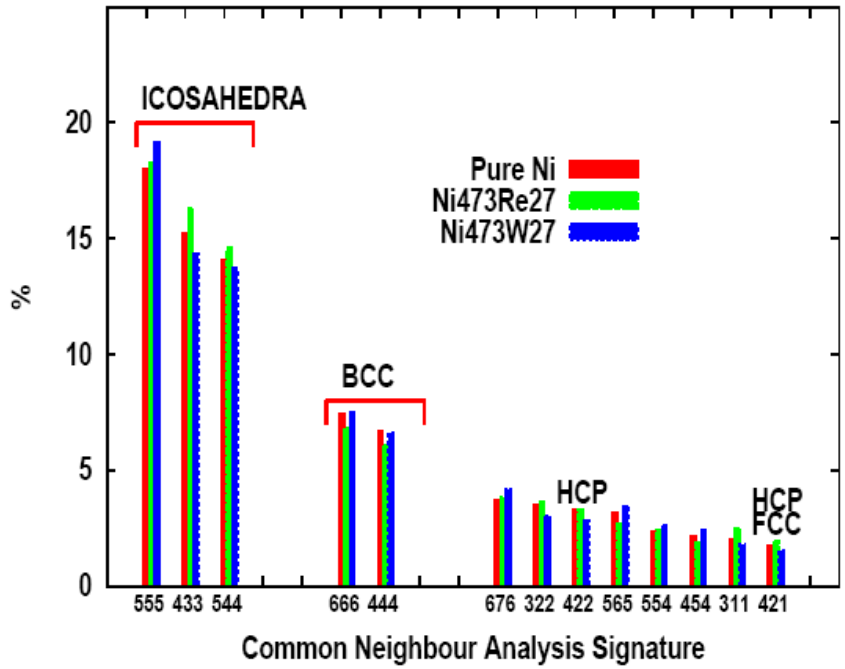
Liquid Structure

Ni, $Ni_{473}W_{27}$ and $Ni_{473}Re_{27}$ at 1830 K

Bond Angle Distributions

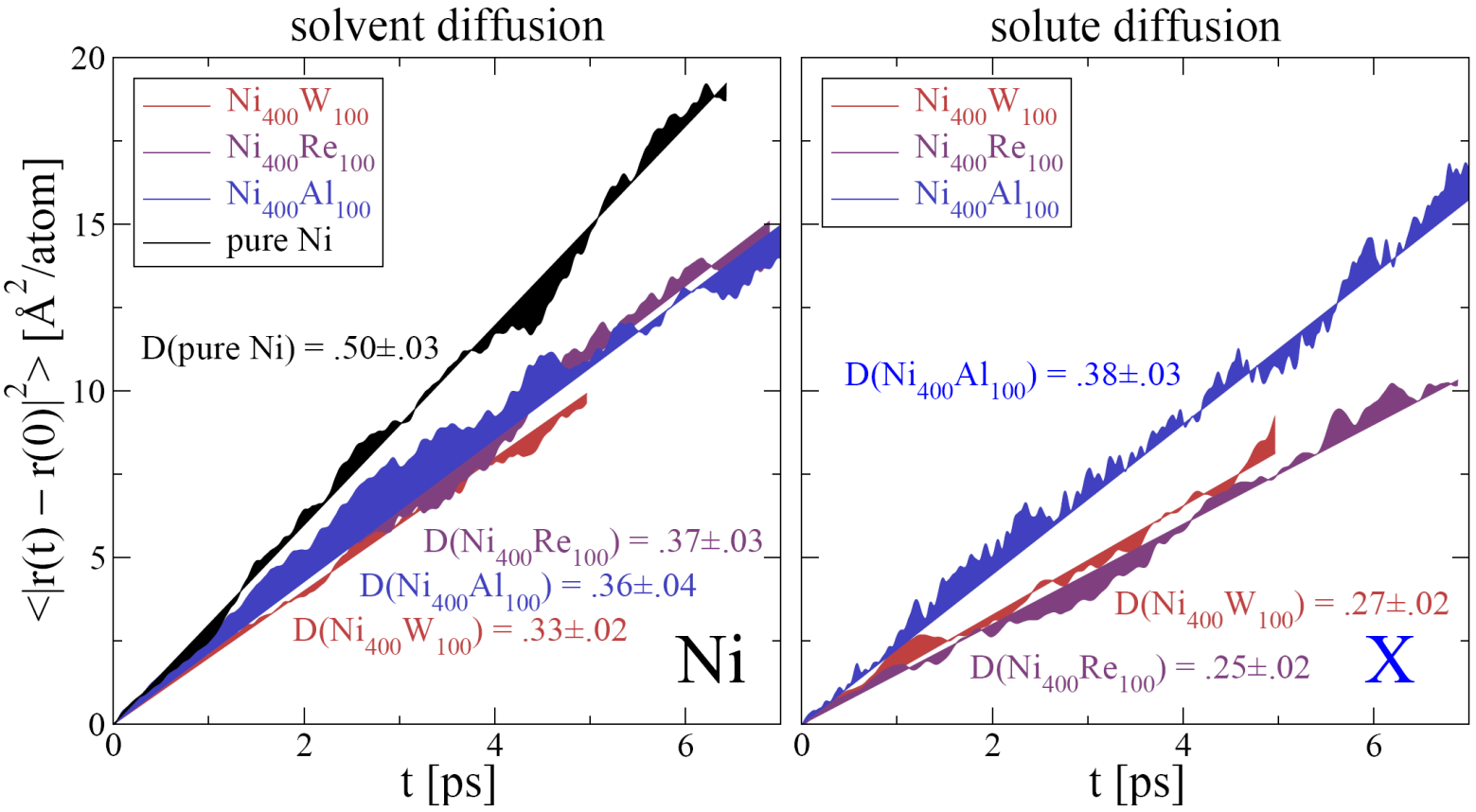


Common-Neighbor Analysis



Liquid Structures Display Short Range Order
Featuring Predominantly Icosahedral and BCC Local Structures

Diffusion Constants



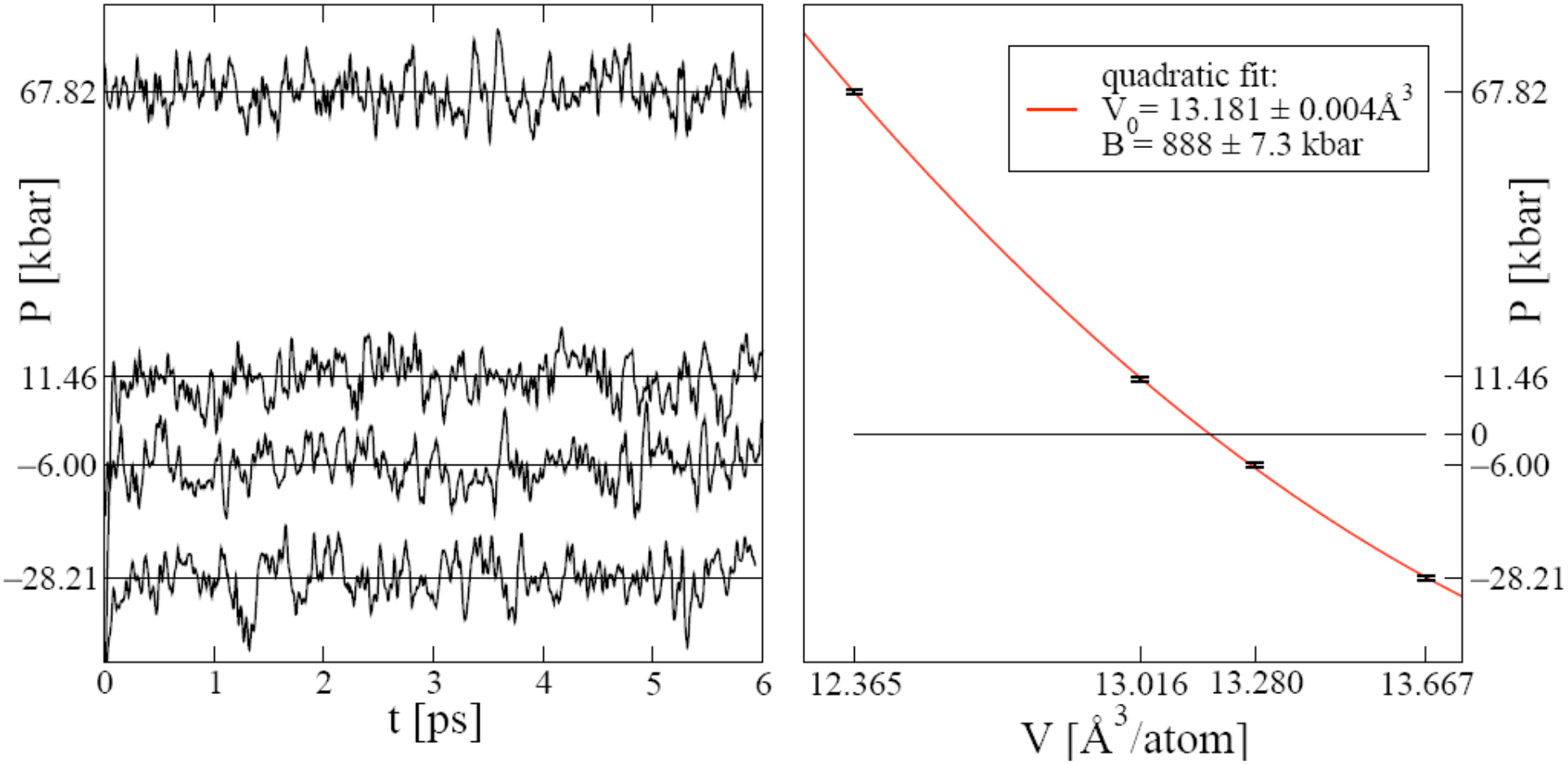
W Tracer Diffusion Constants

$(2.4 \pm 0.2) \times 10^{-5}\,cm^2/s$ Ni-0.52 at.%W,1755-2022 K
Leonard et al. (2004)

$(2.7 \pm 0.2) \times 10^{-5}\,cm^2/s$ Ni_4W, 1830 K
Current Work

Pressure-Volume Relations

$Ni_{400}Al_{100}$ at T=1830 K



Molar Volumes for Molten Ni-Based Alloys

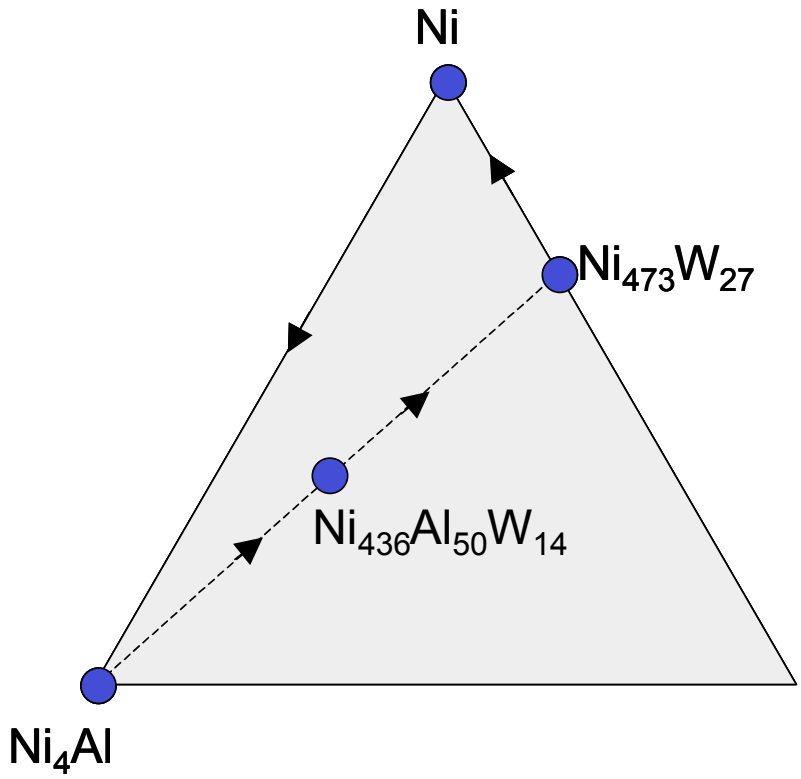
MD Calculations, Mukai Model and Experiment

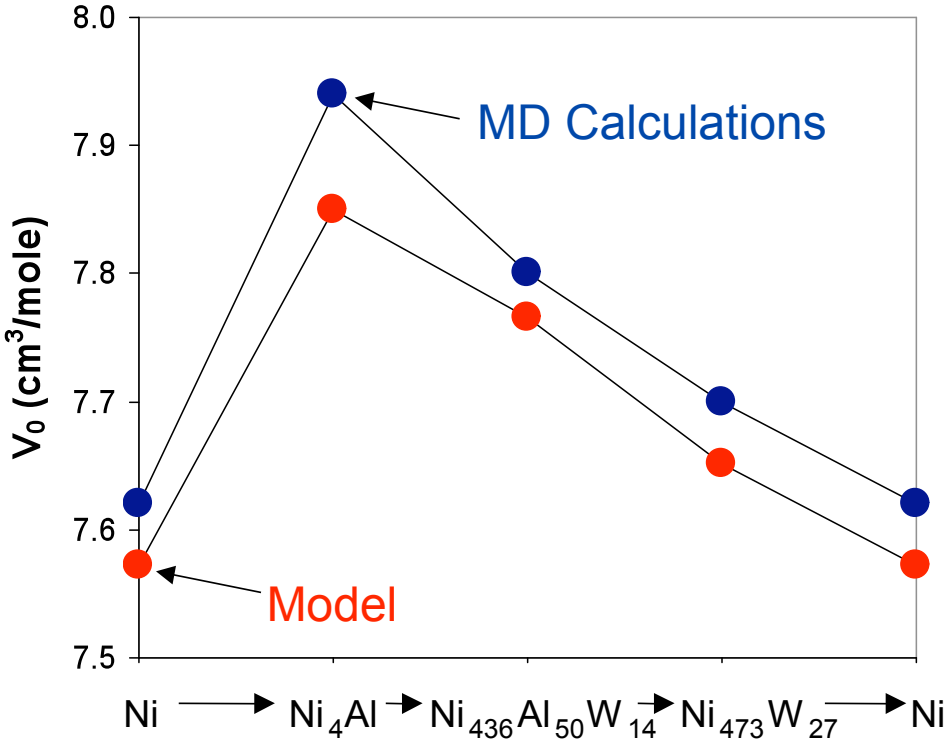
All Volumes in Units of cm^3/mole

	T=1750 K			T=1830 K		
Composition	Mukai	AIMD	V_{AIMD}/V_{EXPT}	Mukai	AIMD	V_{AIMD}/V_{EXPT}
Ni_{500}	7.4597	7.57(1)	1.015	7.5724	7.62(1)	1.006
$Ni_{400}Al_{100}$	7.7628	7.88(1)	1.015	7.8492	7.94(1)	1.012
$Ni_{473}W_{27}$	7.5534	7.66(1)	1.014	7.6520	7.70(1)	1.006
$Ni_{400}W_{100}$	6.5192	7.94(1)		7.3294	7.98(1)	
$Ni_{473}Re_{27}$	7.4940	7.65(1)		7.6499	7.69(1)	
$Ni_{400}Re_{100}$	7.5869	7.91(1)		7.8593	7.93(1)	
$Ni_{473}Ta_{27}$	7.3310	7.70(1)		7.5053	7.75(1)	
$Ni_{400}Ta_{100}$	1.1043	8.14(1)		4.1440	8.18(1)	
$Ni_{436}Al_{50}W_{14}$	7.6920	7.77(1)		7.7655	7.80(1)	
$Ni_{436}Al_{50}Re_{14}$	7.6921			7.7510	7.80(1)	
$Ni_{436}Al_{50}Ta_{14}$	7.6911	7.79(1)		7.7553	7.84(1)	

Molar Volume Predictions

Results for Ternary Ni-Al-W Alloys at T=1830 K



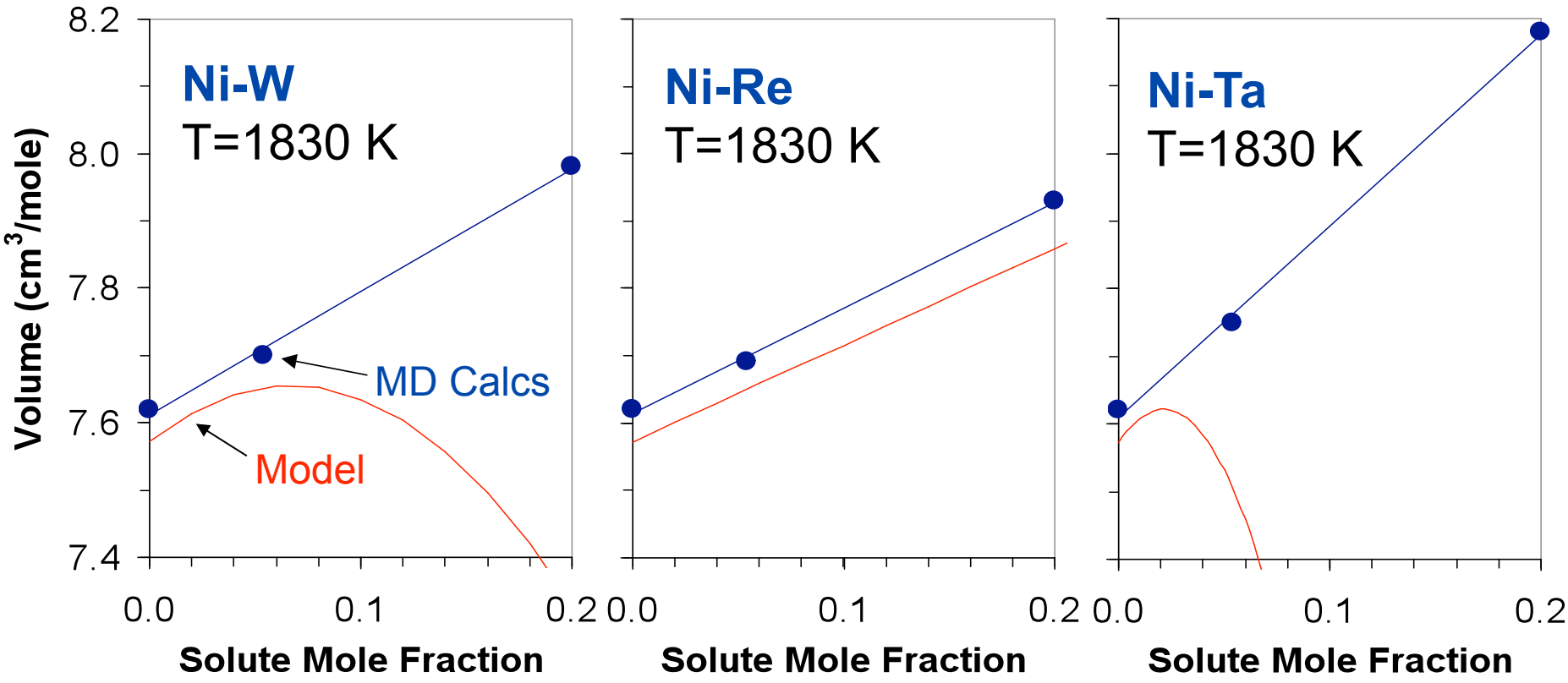


Similar results obtained for Ni-Al-Re and Ni-Al-Ta

Results suggest high accuracy of published parameterization for compositions bounded by experimental measurements

Molar Volume Predictions

Results for Binary Alloys



MD results demonstrate limitations in accuracy of published parameterizations when extrapolated beyond bounds of experimental measurements

Partial Molar Volumes

Results for Infinite Dilution

T=1830 K

	Ni-W	Ni-Re	Ni-Ta
MD Calcs	$\overline{V}_W^{\infty} / \overline{V}_{Ni}^{0} = 1.24$	$\overline{V}_{\mathrm{Re}}^{\infty} / \overline{V}_{Ni}^{0} = 1.20$	$\overline{V}_{Ta}^{\infty} / \overline{V}_{Ni}^{0} = 1.37$
Model	$\overline{V}_W^{\infty} / \overline{V}_{Ni}^{0} = 1.33$	$\overline{V}_{\mathrm{Re}}^{\infty} / \overline{V}_{Ni}^{0} = 1.19$	$\overline{V}_{Ta}^{\infty} / \overline{V}_{Ni}^{0} = 1.61$

T=1750 K

	Ni-W	Ni-Re	Ni-Ta
MD Calcs	$\overline{V}_W^{\infty} / \overline{V}_{Ni}^{0} = 1.25$	$\overline{V}_{\mathrm{Re}}^{\infty} / \overline{V}_{Ni}^{0} = 1.22$	$\overline{V}_{Ta}^{\infty} / \overline{V}_{Ni}^{0} = 1.38$
Model	$\overline{V}_W^{\infty} / \overline{V}_{Ni}^{0} = 1.55$	$\overline{V}_{\mathrm{Re}}^{\infty} / \overline{V}_{Ni}^{0} = 1.08$	$\overline{V}_{Ta}^{\infty} / \overline{V}_{Ni}^{0} = 2.13$

MD results suggest relatively weak temperature dependencies for partial molar volumes

Ab-Initio Calculations of Solid-Liquid Phase Equilibria

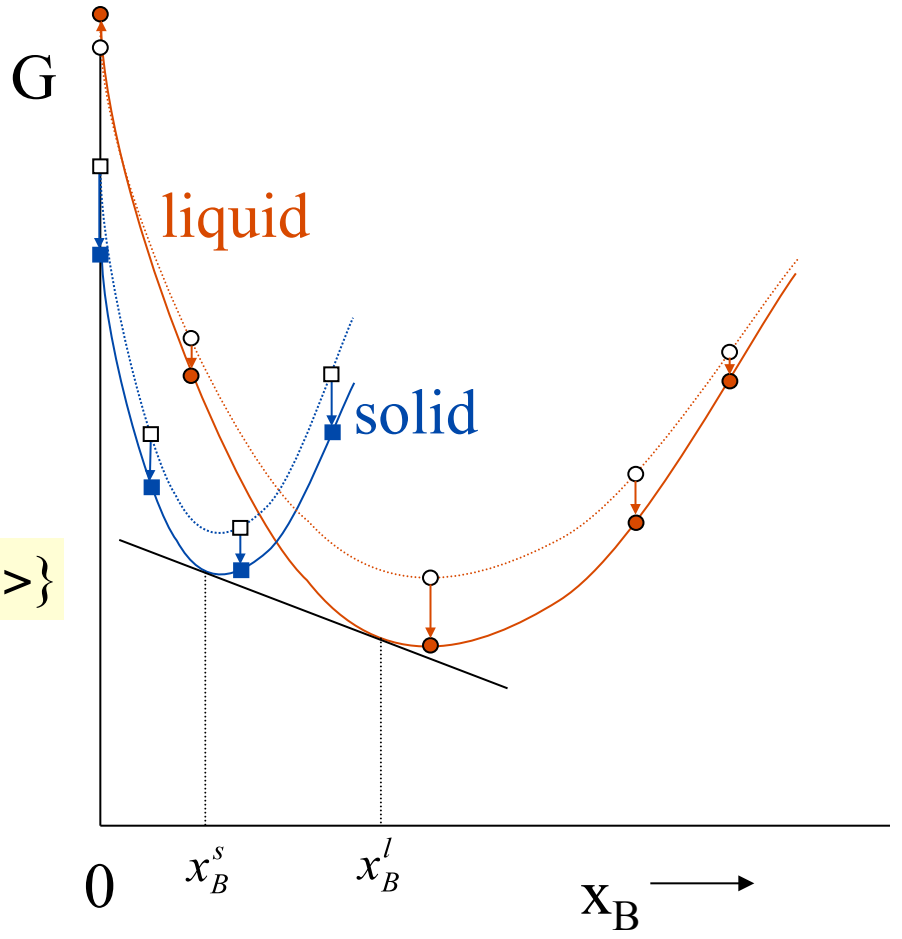
Free Energies from "Perturbation" Approach

- **Free Energies Readily Derived for Classical Interatomic Potentials**
  - *Thermodynamic Integration Employing MD and Monte-Carlo Methods*
- **"Corrections" to Classical Free Energies to Achieve DFT Accuracy**

$$F_B - F_A = -k_B T \ln\{< \exp[-(U_B - U_A)/k_B T] >\}$$

<…> Ensemble Average over States of Reference System A

U_B-U_A Energy Difference Between System B and A for Given State of System A



S. Angioletti-Uberti, M. Asta, M. W. Finnis and P. D. Lee, *Phys. Rev. B* (2008)
Closely related: C. W. Greeff, *J. Chem. Phys.* (2008)

Convergence Properties

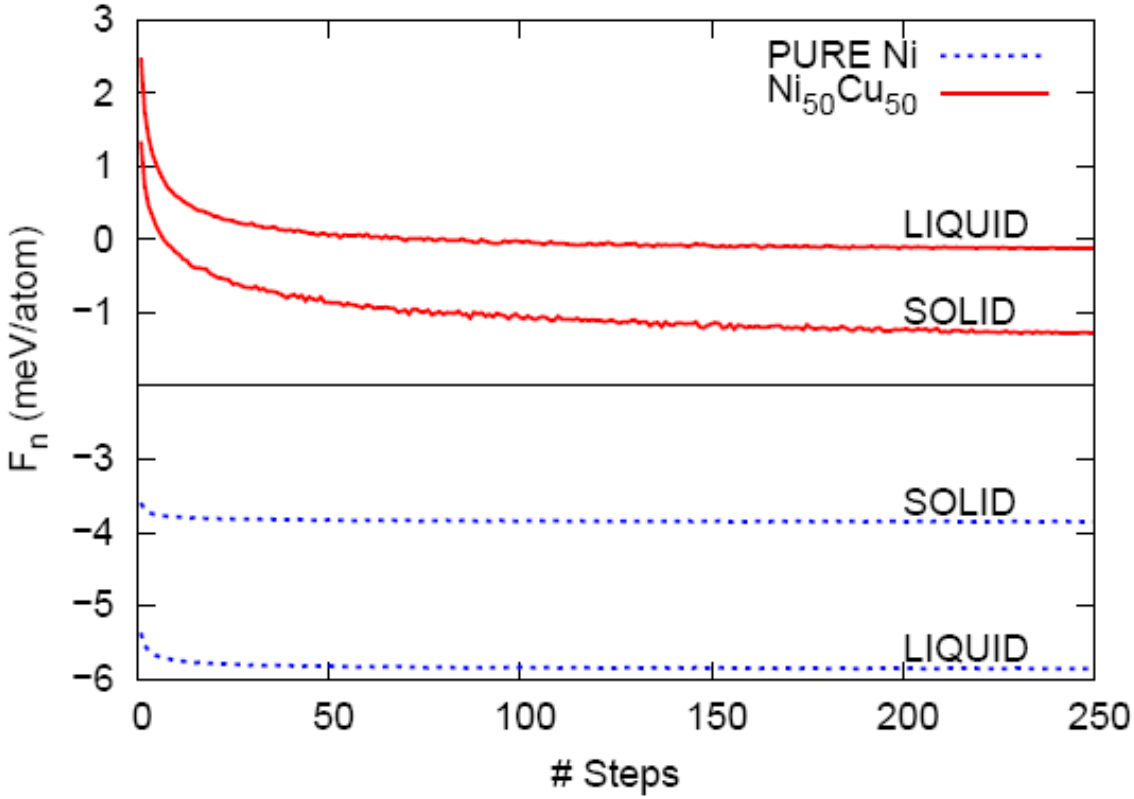
Description of Test System

- Two classical Embedded Atom potentials for Ni-Cu
  - **Reference**: "smf7" potential due to Foiles (1985)
  - **Target**: "u3" potential due to Foiles, Baskes & Daw (1984)
- Melting temperature and solidus/liquidus boundaries
  - Known to be approximately 100 K higher for smf7 than u3 from previous thermodynamic integration calculations
- Compositions and trajectories
  - **Solid and Liquid Pure Ni**: Reference trajectory from NVT MD
  - **Solid and Liquid NiCu Equiatomic Alloy**: Reference trajectory from NVT Monte-Carlo
- Calculated quantities
  - Free Energy Differences
  - Differences in Pure-Ni Melting Temperatures

Convergence Properties

Results for Test System

$$F_B - F_A \approx F_n \equiv -k_B T \ln\left[\frac{1}{n}\sum_{i=1}^{n}\exp\left(-\left[U_B(\sigma_i^A) - U_A(\sigma_i^A)\right]/k_B T\right)\right]$$



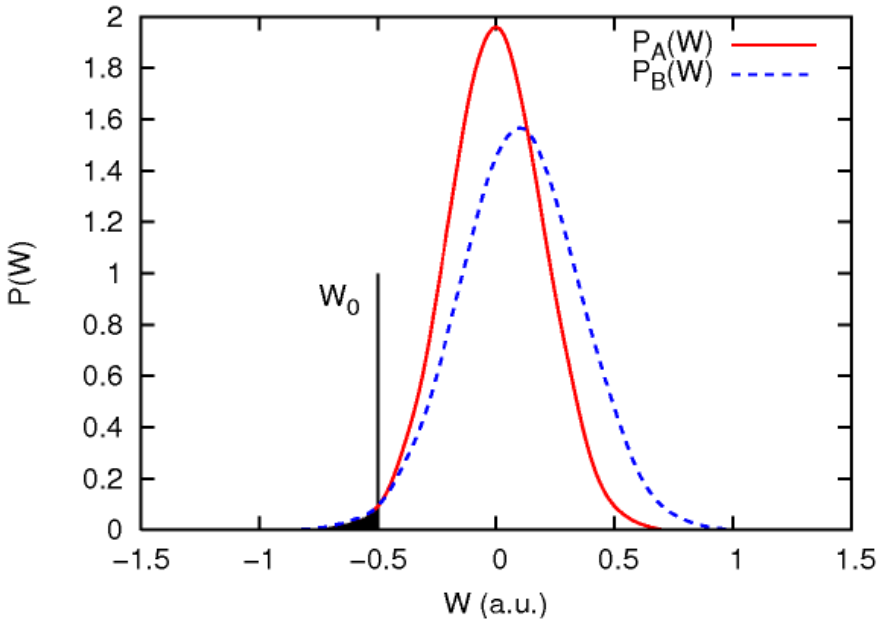
Convergence to within 1 meV/atom
~20 Steps for Pure Element
~100 Steps for Alloy

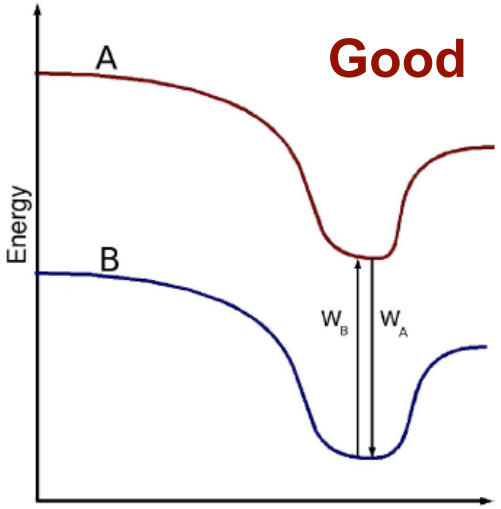
Convergence Properties

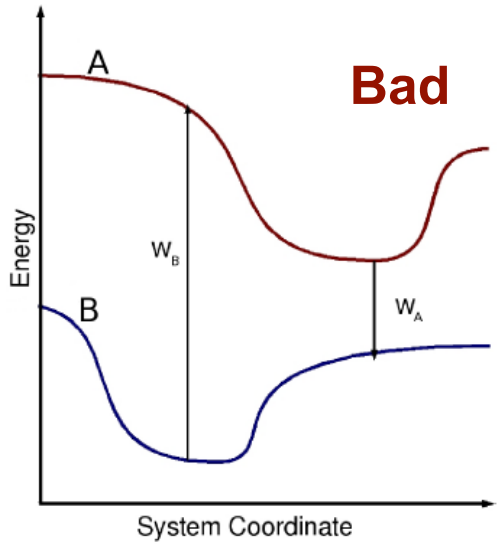
Some Theoretical Considerations

Lu and Kofke (2001)

$$\frac{\exp(-\beta\Delta F_{true}) - \exp(-\beta\Delta F_{calc,B})}{\exp(-\beta\Delta F_{true})} = \int_{-\infty}^{W_0} P_A(W)\,dW$$







Summary

- Quantum molecular dynamics simulations of molten superalloys
  - Good accuracy demonstrated for molar volumes, diffusivities (and mixing enthalpies)
  - Results provide data to refine molar-volume parametrizations for higher length-scale models in materials design
- Towards first-principles calculations of alloy solid-liquid phase equilibria and thermodynamic properties
  - Free-energy perturbation approach as framework for coupling classical and first-principles simulations for calculation of free energies with DFT accuracy
  - Promising convergence demonstrated for classical model system
  - Approach requires reasonably accurate classical-potential models