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Model Development for Molten State Al and Ti Metals

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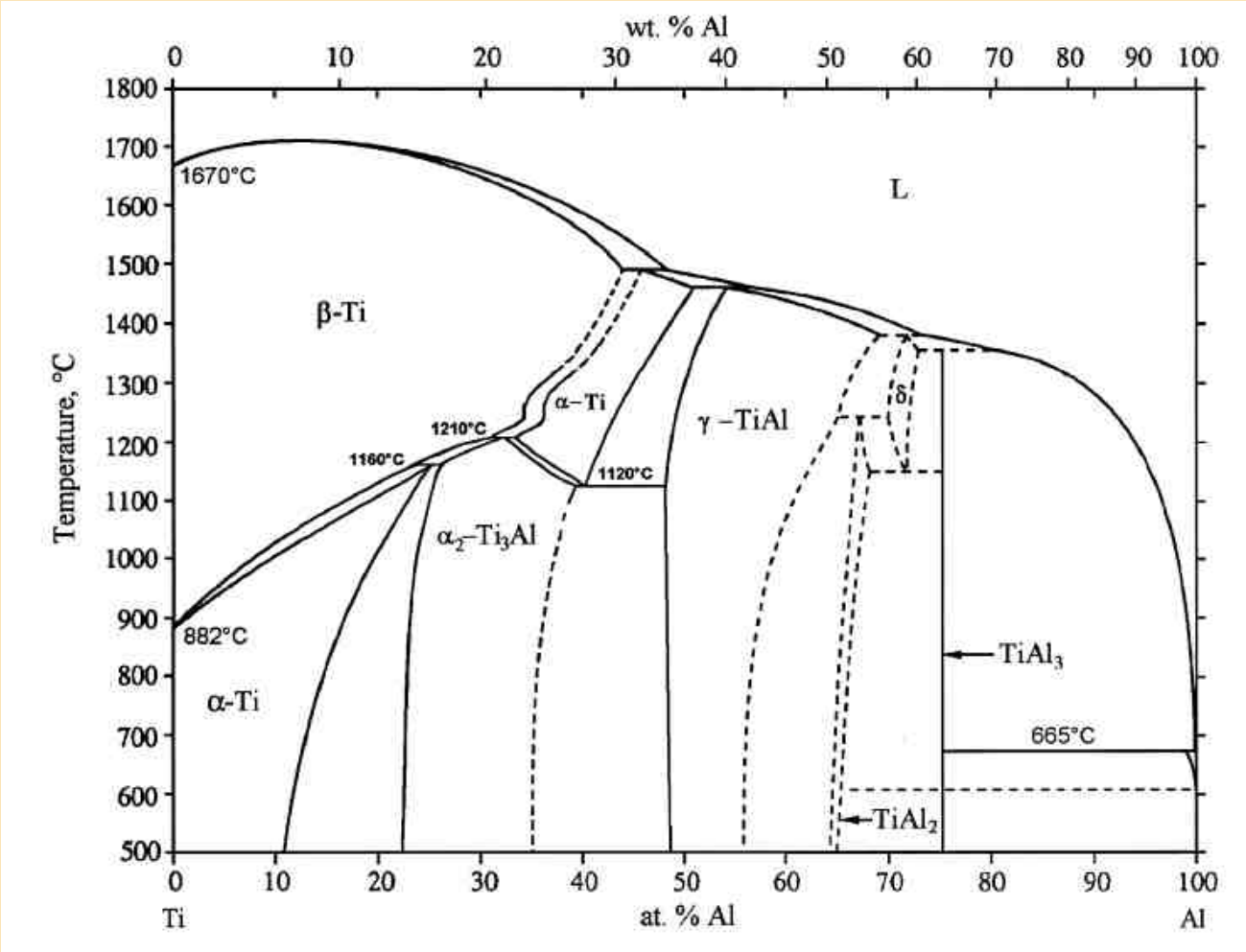
Ti-Al Production in DC Arc Furnace

- Pyrometallurgy Division of Mintek has Pilot scale DC Arc Furnaces up to 5.6MVA for smelting R&D
- Ti-Al alloys – useful properties, especially for Al casting industry
- 2 campaigns in 2006 to produce 35-40% Ti-Al alloys

Ti-Al Production in DC Arc Furnace: Phase Diagram



- The Ti-Al phase diagram is rather complicated - many phases
- So smelting behaviour not well understood
- Seek a better understanding

Ti-Al Production in DC Arc Furnace

- Aluminothermic reduction of Titanium Dioxide (TiO_2 or rutile, etc)
- Products include metals/alloys such as Ti, Ti_3Al, TiAl, $TiAl_3$ and Al
- Campaigns partially successful: large amount of slag and buildup of high melting compounds found in the digout
- Understanding - Improvement in Efficiency, Reducing of Slag and Environmental Impact
- Computational Modelling yields Understanding – Atomistic Simulations

Embedded Atom Method (EAM)

- Suited to metals & alloys - atoms in sea of electrons
- Interaction Energy: Embedding + Pair Potential:

Energy for whole system: $E_{total} = \Sigma E_i$

Energy for each atom: $E_i = F_i(\rho_i) + \Sigma\Phi_{ij}(r_{ij})$

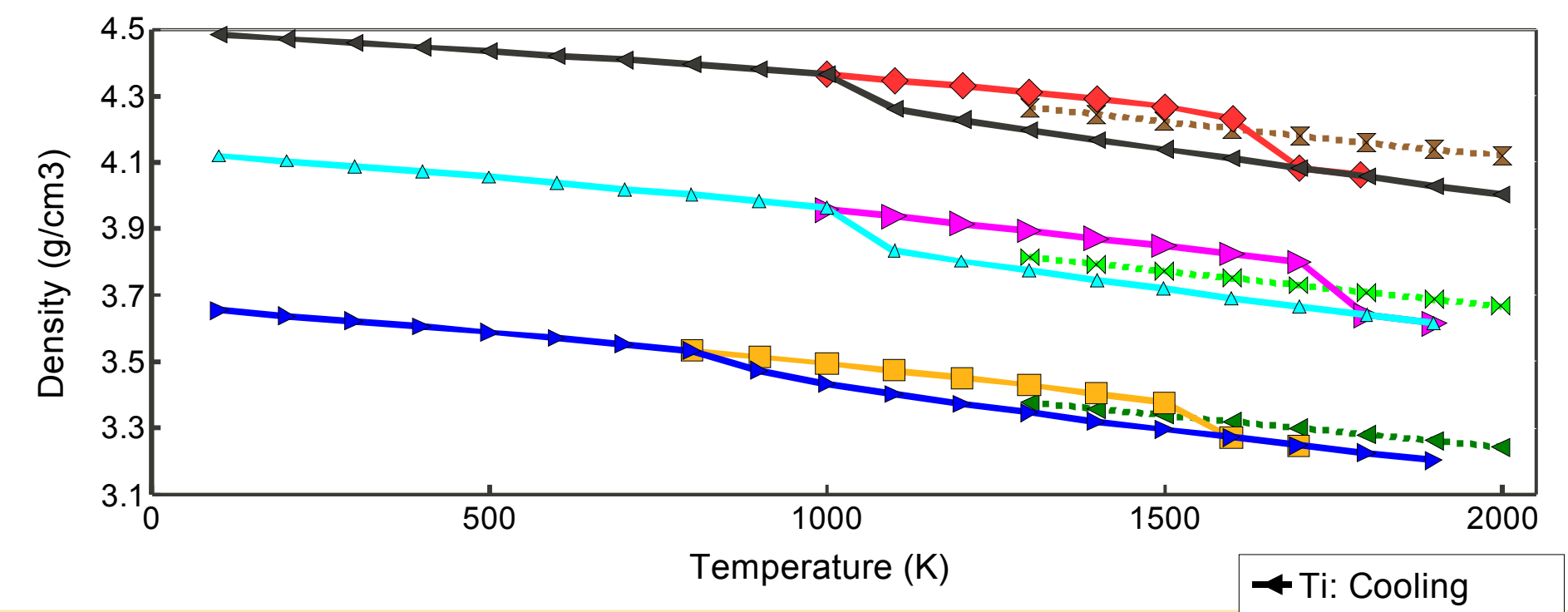
Electron density of each atom: $\rho_i = \Sigma f_j(r_{ij})$

$F_i(\rho_i)$: Embedding Function – energy to embed atom i in electron density ρ_i.

$\Phi_{ij}(r_{ij})$: Non-bonded interaction between atoms i & j at distance r_{ij}.

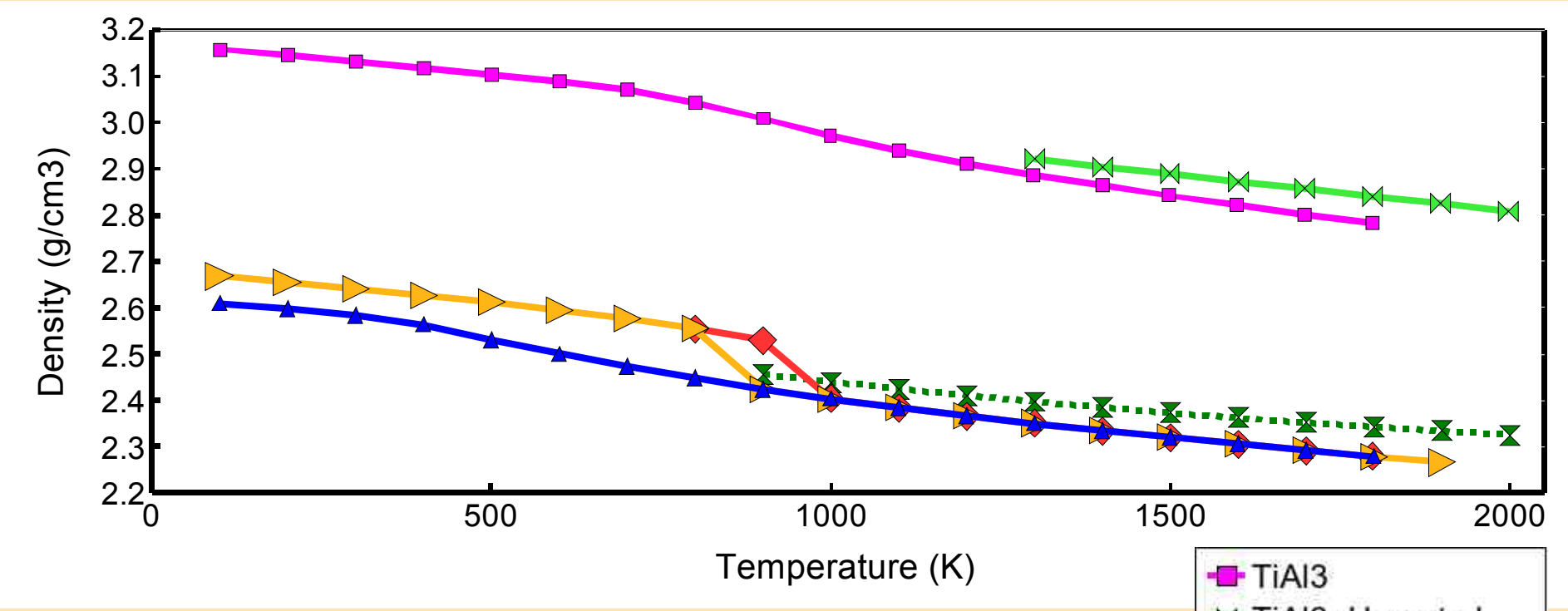
- EAM generates **forces/interactions** for **MD** (molecular dynamics). Hence similar procedures & properties
- Computational platform: DL-POLY-2
- Literature models: Shimono-Onodera and Mishin et al
- Literature results of Han-Chen use Mishin model

Titanium-Rich Systems: Density



- Simulated Annealing performed
- Results consistent with the lit of Han et al (as required)
- Supercooling & heating cycles (glass transition & melting points)
- Slopes yield Thermal Expansion Coefficient

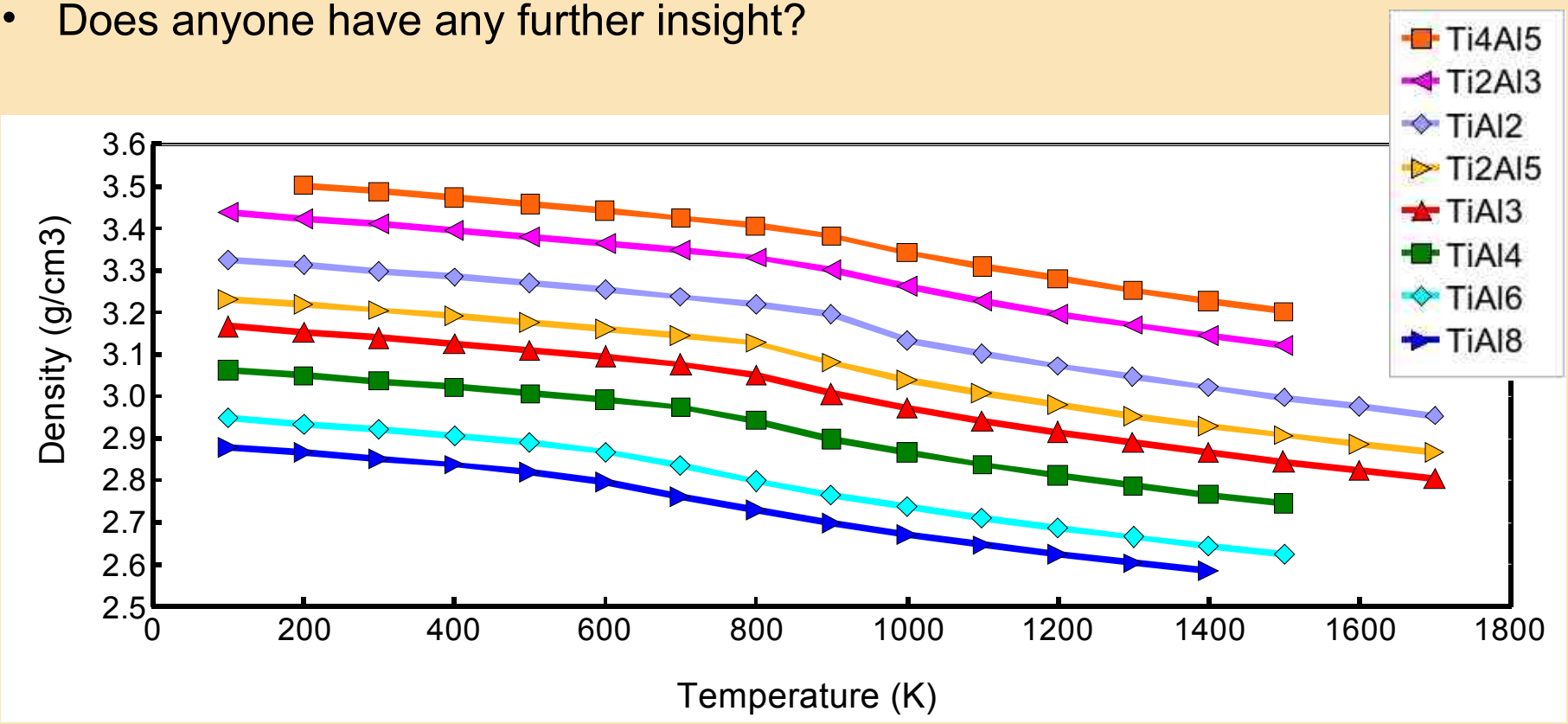
Aluminium-Rich Systems: Density



- Results consistent with literature of Han et al (as required)
- Supercooling & heating cycles (glass transition & melting points) for Al
- $TiAl_3$ shows only one phase transition – occurs with **only change in slope**
- Slopes yield Thermal Expansion Coefficient

Amorphous: Second Order Phase Transitions

- Most 18-59% Ti-Al alloys show phase transitions occurring with only a change in slope (no latent heat)
- Such are Second Order Phase Transitions such as glass transitions
- Cooling rates for simulations are always extremely rapid (simulation artifact?)
- These alloys do show a stronger amorphous propensity than other Ti-Al alloys
- Does anyone have any further insight?



Predicted Physical Properties at Room Temperature

Metal/Alloy	Model	Density ρ (g/cm³)	Linear Thermal Expansion Coefficient α (10^{-6} /K)	Heat Capacity CP (J/K mol)
Al	Shimono	2.62	30.2	26.4
	Mishin	2.58	17.9	27.8
	Literature	2.702	22.8	24.3
$TiAl_3$	Shimono	2.97	23.1	26.0
	Mishin	3.13	15.0	25.8
TiAl	Shimono	3.36	19.2	26.0
	Mishin	3.62	15.8	25.8
	Literature	3.7-3.9	-	-
Ti_3Al	Shimono	3.82	18.6	25.4
	Mishin	4.08	14.3	25.6
	Literature	4.1-4.7	-	-
Ti	Shimono	4.28	17.8	25.7
	Mishin	4.46	9.6	25.4
	Literature	4.54	8.41	25.00

Properties: Furnace Operating Temperature

	Al	$TiAl_3$	TiAl	Ti_3Al	Ti
MP (K)	800-900	-	1500-1600	1700-1800	1600-1700
GT (K)	-	800-900	800-900	1000-1100	1000-1100
Density at 1600K (g cm^{-3})	2.31	2.82	3.27	3.82	4.20
Enthalpy at 1600K (kJ mol^{-1})	-269	-328	-370	-409	-419
Density at 1800K (g cm^{-3})	2.28	2.78	3.23	3.64	4.06
Enthalpy at 1800K (kJ mol^{-1})	-264	-322	-364	-390	-402

- Trend with increase Ti content: increase MP, GT and Density,
  decrease Enthalpy – increase stability
- **Ti-rich** are **most stable** with **higher MP and densities**
- In line with **Buildup of High Melting Compounds** observed in DC arc furnace

Need for New Models

- Ti metal with small amounts of C,O and N impurity are of interest in terms of aerospace applications
- Most existing EAM potential for the Ti, Al and other metals are solid state models and our interest is molten metallic systems
- Hence our goal is model development (parameterisation) using QM (planewave) data
- Model types: General (transferable) – works reasonably everywhere
  Tailored – works well specific region, eg liquid phase
- The PotFit program which uses the Force Matching Method is ideal

PotFit: Force Matching

- Force Matching (Ercolessi & Adams): Planewave QM Data – cohesive Energy, Forces, Stresses for set of representative configurations
- Initial EAM (pair, dens, embed): spline **Data Pts** or **Analytic Potential**
- Model predicts energy, forces (& stresses): compare to QM data
- Optimise the model & generate additional better configurations

- **PotFit:** Powerful program – EAM as well as **Pair Potentials**
- Powell optimisation & Simulated Annealing in parameter space
- Data Variety: Populations for regions of Pair, Dens & Embed
- Energy weighting: 10-100 times forces
- Data and independent Test Configurations: Overfitting/Transferability

Details of Quantum Data Fitting: Al

- Generated a number (25) small configurations (63 atoms) using DLPOLY at various temps
- Hence much shorter CPU time in Quantum Espresso (QE) & sufficient data
- Planewave calculations were performed in QE using either of these methodologies

Method	Exchange Correl Fn/Pseudopot
LDA	PZ-VBC: Perdew-Zunger & Von Barth-Car
GGA	PBE-RRKJ: Perdew-Becke-Erzenhof & Rabe-Rapp-Kaxiras-Joannopoulos

Cohesive Energy = [QM Energy for Crystal] – [QM Energy for Free Atom]

- Previously - last CHPC Meeting - models generated using QM & PotFit poor
- The Lennard-Jones Pair Potentials had minima at short distances – high density
- The reasons were not understood at this stage
- Subsequent tests revealed L-J unstable while Morse potentials behaved well

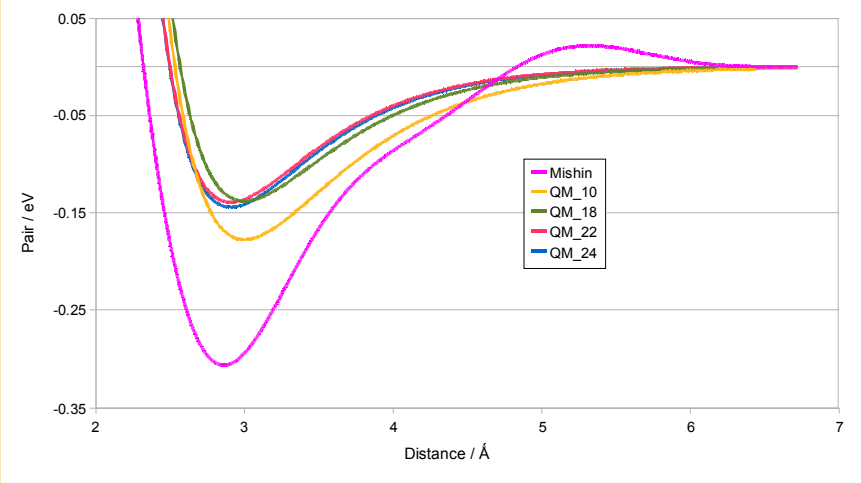
Selected Al Models obtained from Quantum Data

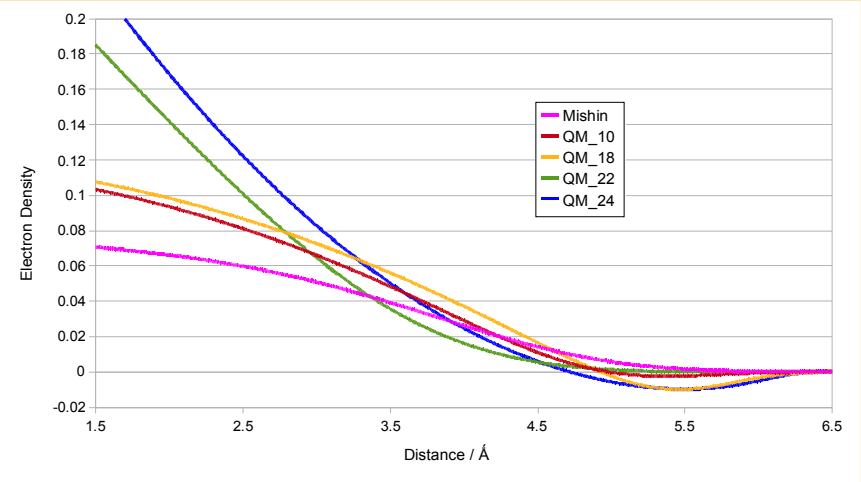
- Fitting functions: Pair: Morse
  Electron Density: Smoothed Parabola
  Embedding Function: Concave Parabola (smoothed for QM_24)
- QM_10 & QM_18: Al.pbe-rrkj pseudopotential & PotFit Annealing (QM_10 incomplete opt)
- QM_22 & QM_24: Al.pz-vbc pseudopotential & PotFit Annealing+Powell opt

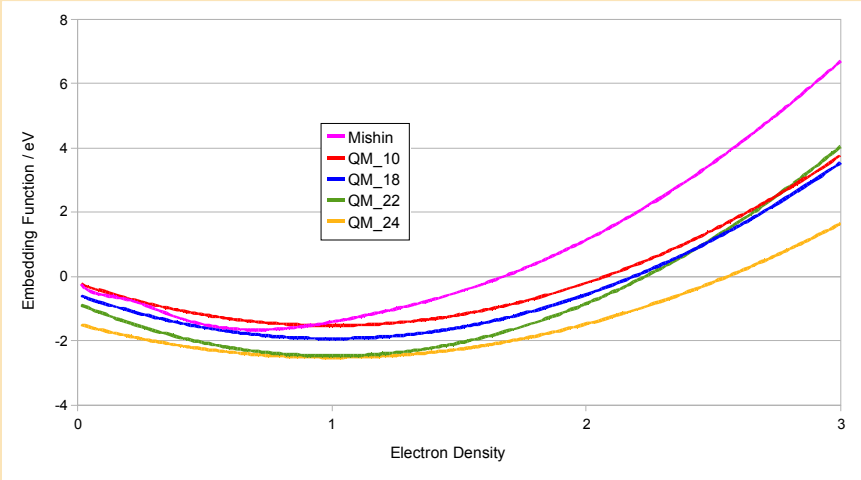
- Similar curves: QM_10/QM_18 or QM_22/QM_24
- Pair: QM_22/QM_24 shorter minimum
- Elec Density: Convex vs Concave

  Negative undesirable: QM_18 & QM_24
- Embedding Fn: Gauge constraint - zero slope at unity

  affects flexibility of parabolic fitting fn







Predictions of these Models for Al

- Density: QM_10 & QM_18 reasonable (within 1% & 4%); QM_22 & QM_24 perfect
- Enthalpy: QM_10 & QM_18 poor (14%); QM_22 & QM_24 reasonable (within 2%)
- Melting point predictions are out – our implementation using Simulated Annealing unreliable
- We find PotFit fitting quality criteria (not shown) are not fully consistent in general
- PotFit criteria can discern a poor model from a reasonable one – not between high quality
- Physical predictions are thus main criteria

Model	**Param. Scheme**	**Density** (g/cm^3)	**Enthalpy** (kJ/mol)	**Melting Point** (K)
Literature	-	2.702	-322.2	933.4
Mishin	-	2.583	-311.0	600-700
QM_10	Al.pbe-rrkj + Incomplete PotFit Opt	2.679	-277.3	-
QM_18	Al.pbe-rrkj	2.606	-277.3	-
QM_22	Al.pz-vbc	2.698	-328.4	1100-1200
QM_24	Al.pz-vbc Smoothed Morse	2.704	-328.5	1100-1200

Details of Quantum Data Fitting: Ti

- Preliminary validation tests with CASTEP and QE
- 27 configurations (of 63 Ti) at various temperatures from DLPOLY
- QE planewave calculations using Ti.pz-sp-van_ak pseudopotential
- No convergence for SCF (Self Consistent Field) – QE settings need adjustment
- Reducing *degauss* and *mixing_beta* ensured convergence
- However – found at later stage *degauss* alters results: mainly energy & stresses, while forces are only slightly affected
- Only *mixing_beta* should be altered
- Our QM data obtained with Ti.pz-sp-van_ak has this defficiency

Method	**Exchange Correl Fn/Pseudopot**
LDA	Ti.pz-sp-van_ak: Perdew-Zunger, Vanderbilt Ultrasoft
GGA	Ti.pbe-sp-van_ak: Perdew-Burke-Erzenhof, Vanderbilt Ultrasoft

Selected Ti Models obtained from Quantum Data

- QM_20 is based on Ti.pbe-sp-van_ak, while Ti.pz-sp-van_ak for other QM models
- QM_7*: Fitted with Parabola similar to Al models; Range 6.72Ą; Nopunish in PotFit (no gauge limits)
- QM_13 to QM_20: Exp Decay & Pohlong fitting fns for Elec Dens & Embedding Fns; Range 5.19Ą

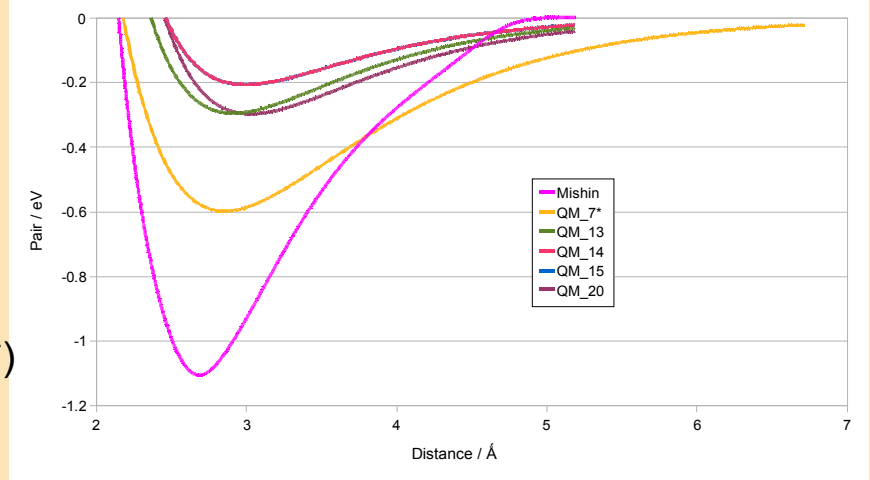
Exponential Decay

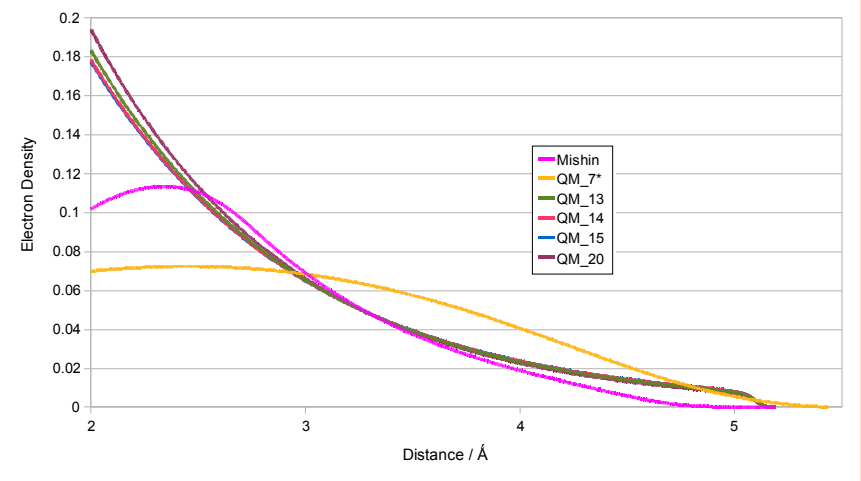
$$\rho(r) = \alpha \exp(-\beta r)$$

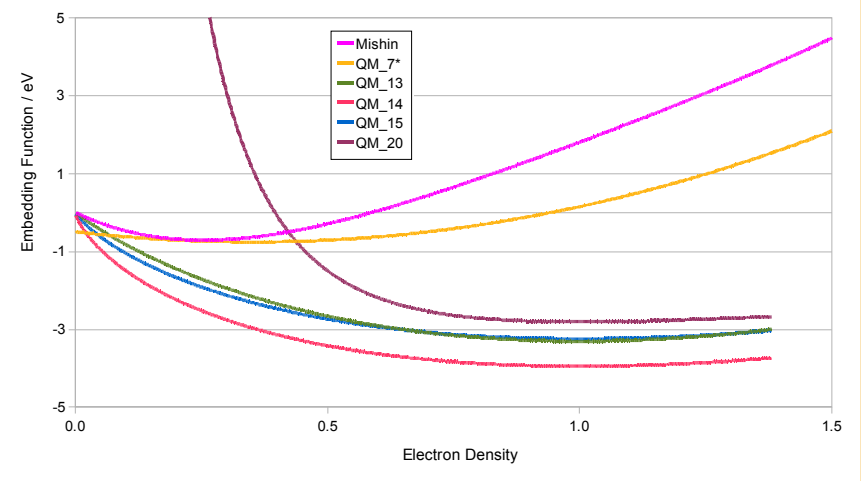
Pohlong

$$F(\rho) = F_0[1 - \gamma \ln \rho]\, \rho^{\gamma} + F_1 \rho$$

- QM_15: Fitting energy manually adjusted
- QM_14 and QM_15: Identical Pair & E. Dens curves
- E. Dens curves: Concave - new models (except QM_7*)







Predictions of these Models for Ti

- Density: All models reasonable (within 4%) except QM_7* (over 6%); QM_14 & QM_15 excellent
- Enthalpy: All models poor except Mishin and manually adjusted QM_15
- Melting point prediction poor – even when considering our unreliable simulated annealing method
- Would including stress tensor QM fitting information improve melting point predictions for models?

Model	**Main Difference in Fitting**	**Density** (g/cm^3)	**Enthalpy** (kJ/mol)	**Melting Point** (K)
Literature	-	4.506	-468.6	1941
Mishin	-	4.460	-458.4	1600-1700
QM_7*	Parabolic fit fn, range 6.72, nopunish	4.783	-553.6	-
QM_13	Exp Decay+Pohlong	4.675	-545.6	1000-1100
QM_14	Energy weighting 1 (reduced from 10)	4.498	-535.5	900-1000
QM_15	Fitting Energy Manually Adjusted	4.497	-467.9	900-1000
QM_20	Ti.pbe-sp-van_ak pseudopotential	4.605	-511.2	1200-1300

Conclusions

- EAM modelling approach: Physical Properties and Behaviour
- Understanding of behaviour of Ti-Al systems in DC arc furnace
- The unknown high melting material is likely to be Ti-rich
- 18-59% Ti-Al alloys have higher amorphous propensities

- A need for models parameterised for the molten phase
- PotFit/Force Matching approach using QM data is invaluable
- Generated good quality models for Al and Ti
- Models deficient in terms of melting point prediction – perhaps stress tensor QM data should be included

- Both LDA and GGA data have produced reasonable models
- Quantum Espresso calcs require adjustment of *mixing_beta* for convergence

- PotFit criteria not fully consistent: final criterion physical predictions
- Choice fitting functions important: Morse, Exp Decay & Pohlong
- Manual adjustment/shifting of fitting energies – curves maintain shape

- Currently modelling Fe-Ni-Cu-S systems related to Mintek's Consmelt process for obtaining Platinum Group Metals – literature models & developing our own

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Thank you

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