Complementary approaches to high T-high p crystal structure stability and melting

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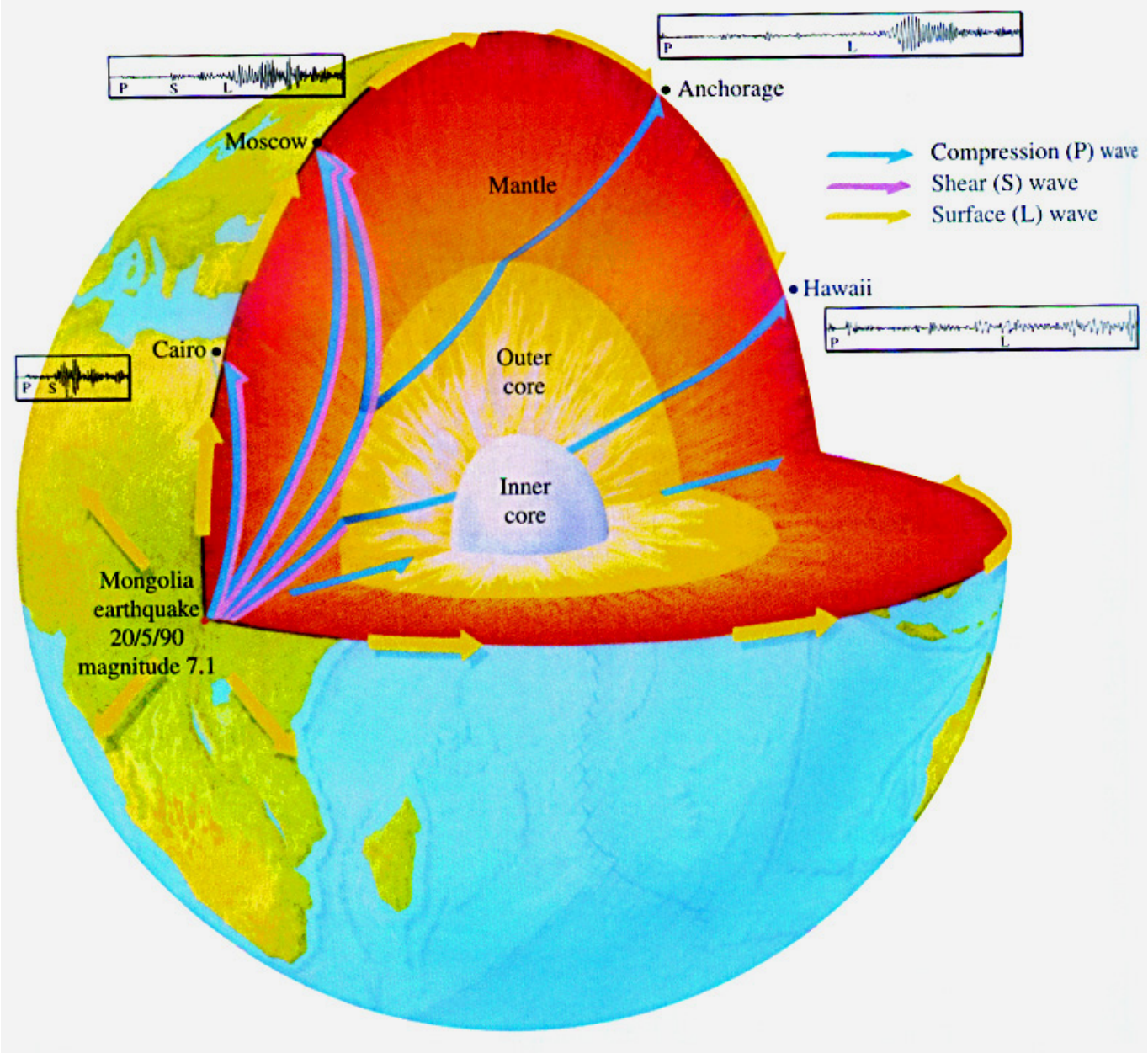
P
L
Anchorage
P
S
L
Moscow
Mantle
Compression (P) wave
Shear (S) wave
Surface (L) wave
Hawaii
P
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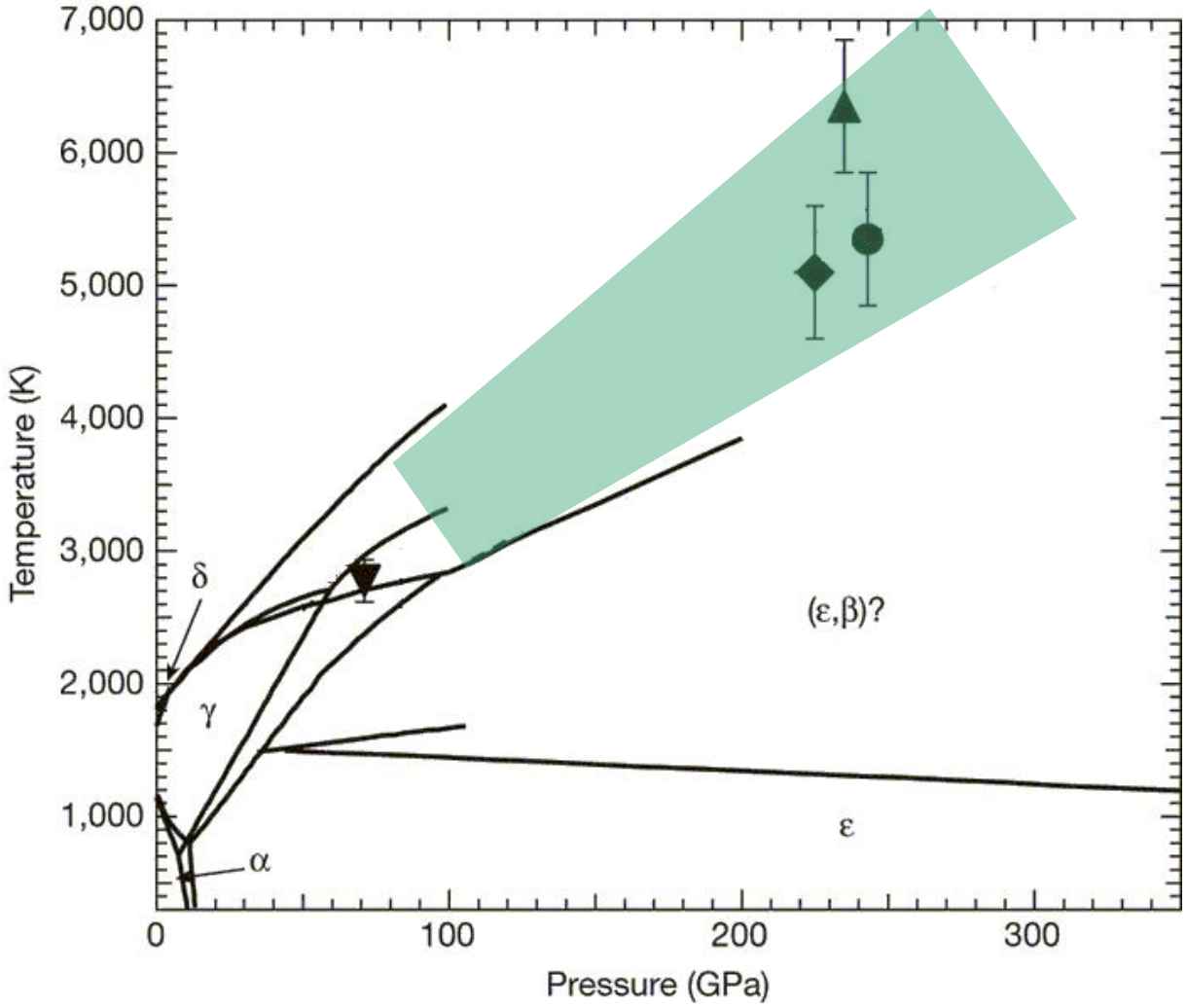
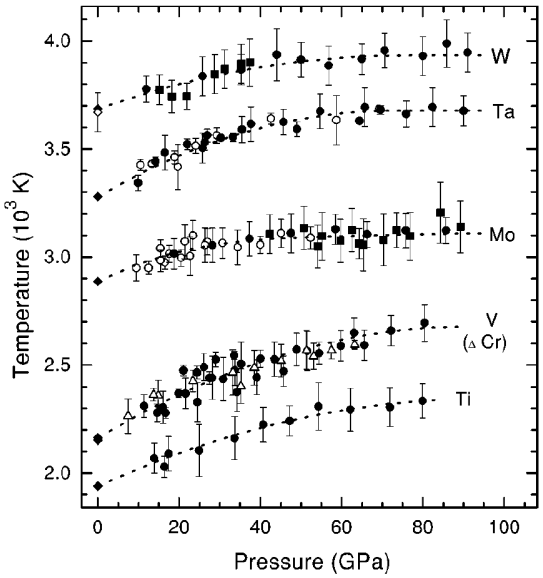
Cairo
P
S
Outer
core
Inner
core
Mongolia
earthquake
20/5/90
magnitude 7.1

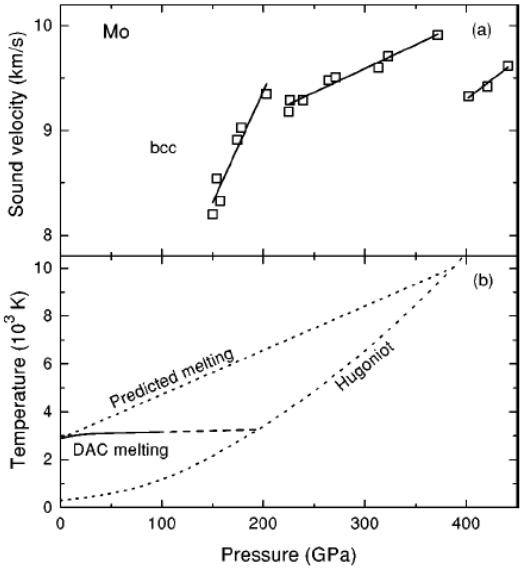
Phase diagram of Fe



Picture adapted from:
Nguyen and Holmes,
Nature, **427**, 339 (2004)

Transition metals





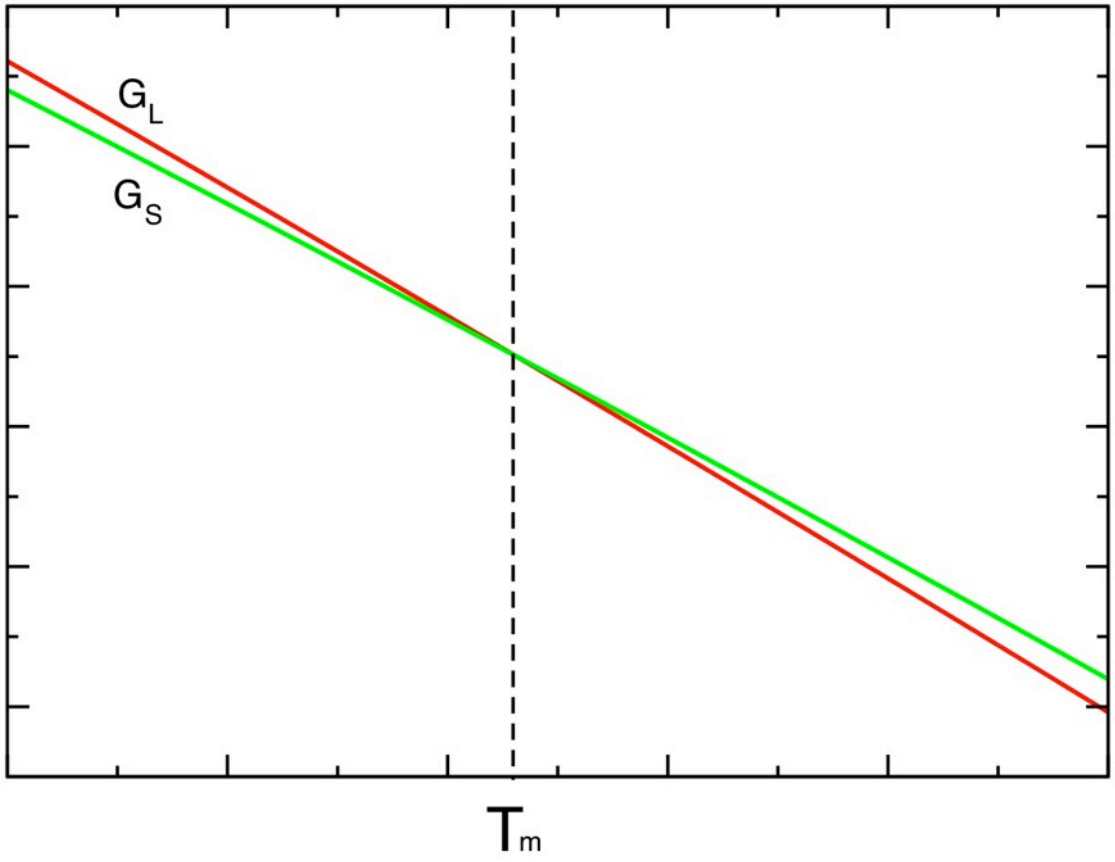
- Old DAC melting of transition metals appears to show "low" melting curves for W, Ta, Mo, V, Ti, which all flatten above 50-60 GPa (Errandonea et al., PRB **63**, 132104 (2001)).
- Shock data suggest "high" melting temperatures, with spectacular disagreement for example for Ta and Mo. New DAC data for Ta appear to resolve this disagreement (Dewaele et al. PRL **104**, 255701 (2010)).

- Here present *ab initio* methods to compute melting curves and solid-solid phase transitions, and show applications for Fe, Ta and Mo.

Theory

- Statistical mechanics
  - Free energies
  - Coexistence of phases
  - Z method
- Interatomic interactions
  - Empirical potentials
  - Density functional theory
  - Quantum Monte Carlo

Phase stability



The Helmholtz free energy

Solids: Low T

$$F(V,T) = F_{perf}(V,T) + F_{harm}(V,T) + \cancel{F_{anharm}(V,T)}$$

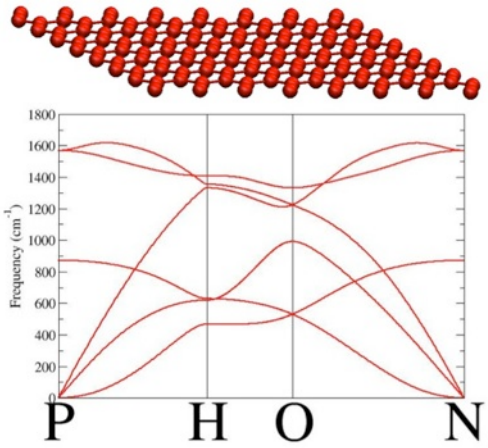
$$F_{harm}(V,T) = 3k_BT \frac{1}{N_{\mathbf{q},s}} \sum_{\mathbf{q},s} \ln\left[2\sinh\left(\frac{\hbar\omega_{\mathbf{q},s}(V,T)}{2k_BT}\right)\right]$$

Dynamical matrix: $$\mathrm{D}(\mathbf{q}) = \frac{1}{\mathrm{M}} \sum_{\mathbf{R}} \Phi(\mathbf{R})\, e^{i\mathbf{q}\cdot\mathbf{R}}$$

Force constant matrix: $$F_\alpha(\mathbf{R}) = -\sum_{\mathbf{R}',\beta} \Phi_{\alpha\beta}(\mathbf{R}-\mathbf{R}')\, \mathrm{u}_\beta(\mathbf{R}')$$

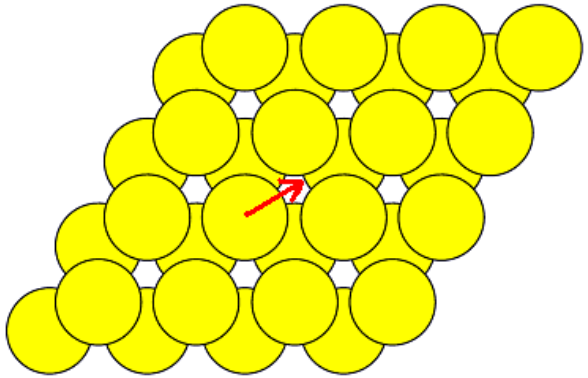
Phonons

Small displacement method:

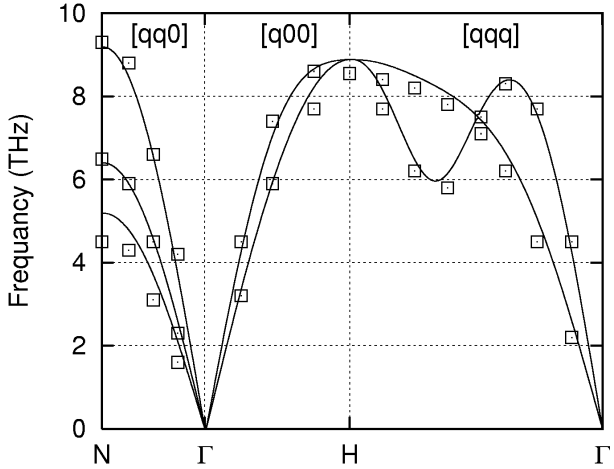


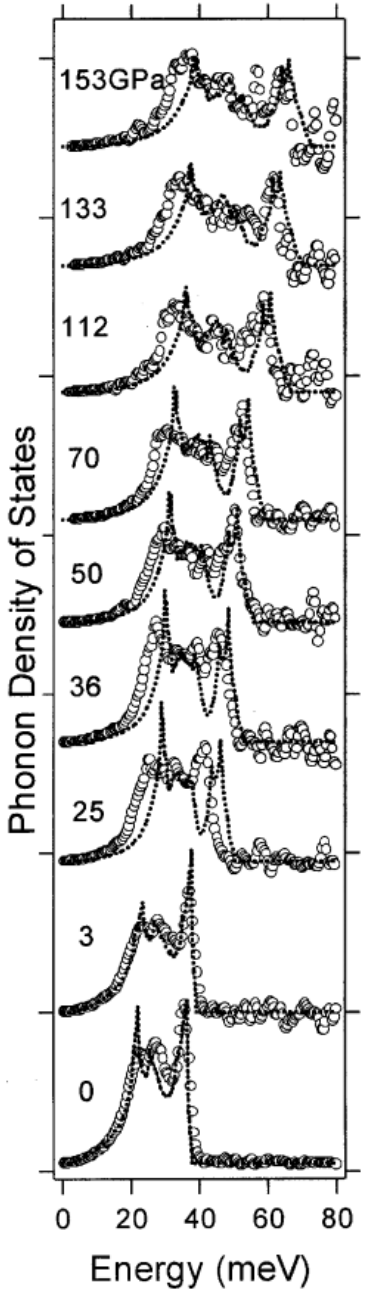
freely available at:
http://chianti.geol.ucl.ac.uk/~phon

D. Alfè Comp. Phys. Comm. ***180*** *2622 (2009)*



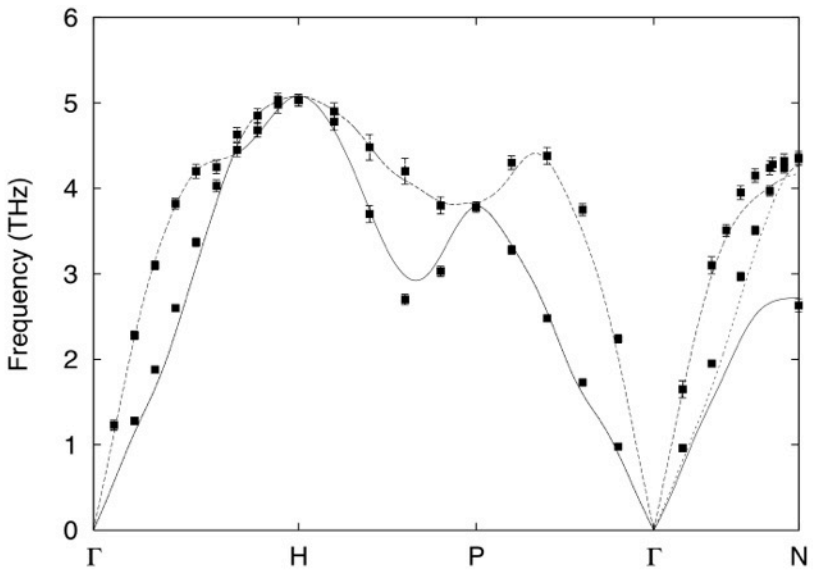
Iron:



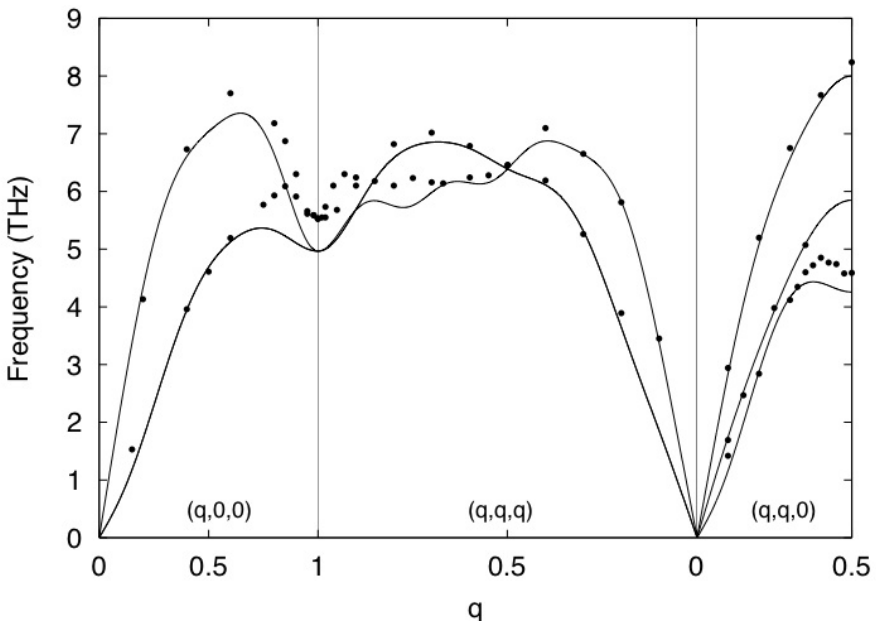


Phonon dispersions of Ta and Mo at p=0

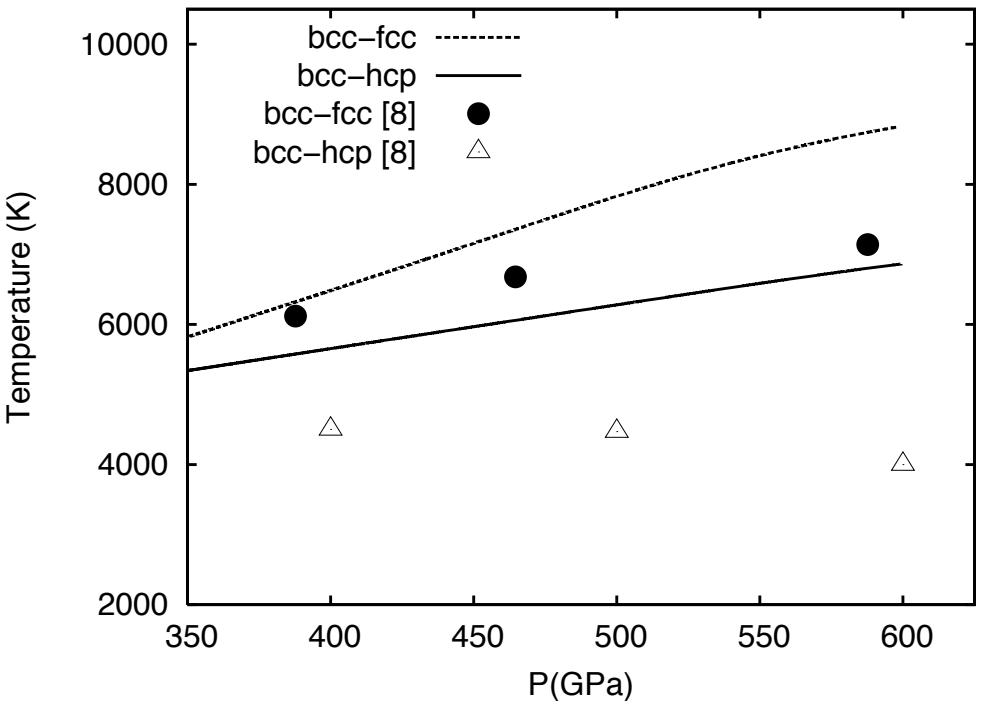
Tantalum



Molybdenum

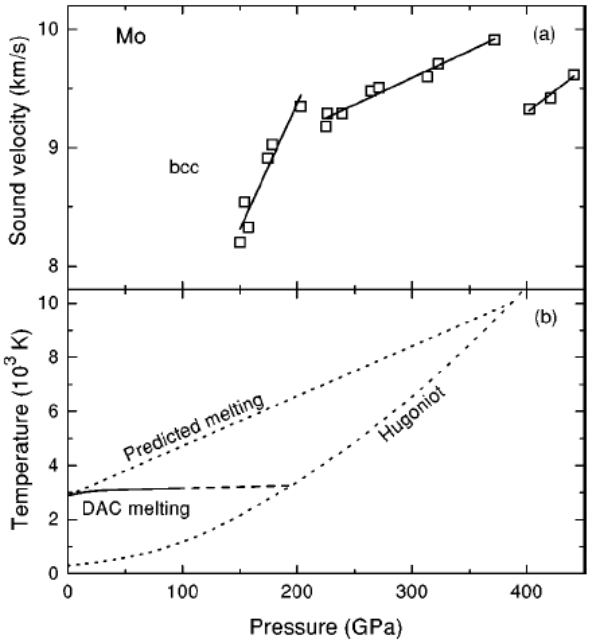


Stability of Mo with the harmonic approximation



[8] *Belonoshko et al., Phys. Rev. Lett.* ***100****, 135701 (2008)*

FCC is the stable high temperature phase at high pressure. Possible explanation of the Hixson's data:



What about anharmonicity ?

The Helmholtz free energy

Solids: Low T High T

$$F(V,T) = F_{perf}(V,T) + F_{harm}(V,T) + F_{anharm}(V,T)$$

$$F_{harm}(V,T) = 3k_BT \frac{1}{N_{\mathbf{q},s}} \sum_{\mathbf{q},s} \ln\left[2\sinh\left(\frac{\hbar\omega_{\mathbf{q},s}(V,T)}{2k_BT}\right)\right]$$

Liquids:

$$F(V,T) = -k_BT \ln \frac{1}{N!\Lambda^{3N}} \int_V dR\, e^{-U(R)/k_BT}$$

Thermodynamic integration

$$U_{ref}, F_{ref} \qquad\qquad U_\lambda = (1-\lambda)U_{ref} + \lambda U$$

$$F_\lambda = -k_B T \ln \frac{1}{N!\Lambda^{3N}} \int_V dR\, e^{-U_\lambda(R)/k_B T}$$

$$F - F_{ref} = \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

$$\frac{dF_\lambda}{d\lambda} = \frac{\int_V dR \frac{\partial U_\lambda}{\partial \lambda} e^{-U_\lambda(R)/k_B T}}{\int_V dR\, e^{-U_\lambda(R)/k_B T}} = \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda = \left\langle U - U_{ref} \right\rangle_\lambda$$

$$\boxed{F = F_{ref} + \int_0^1 d\lambda \left\langle U - U_{ref} \right\rangle_\lambda}$$

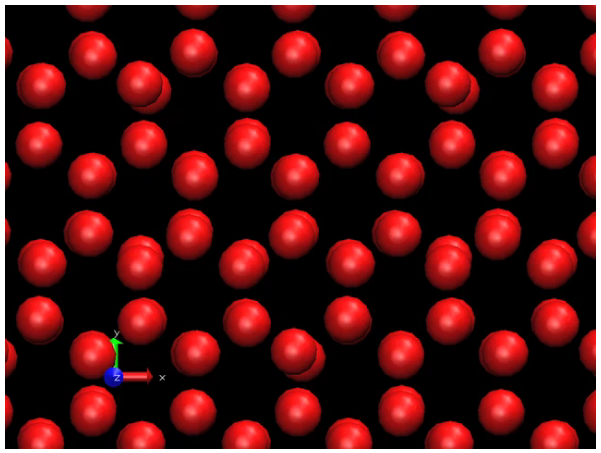
Thermodynamic integration

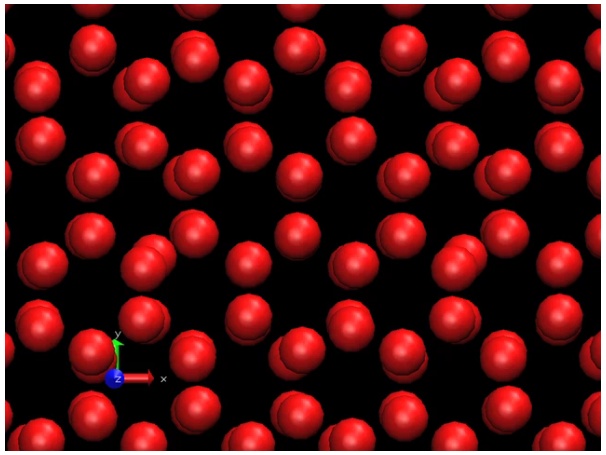
$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda$$

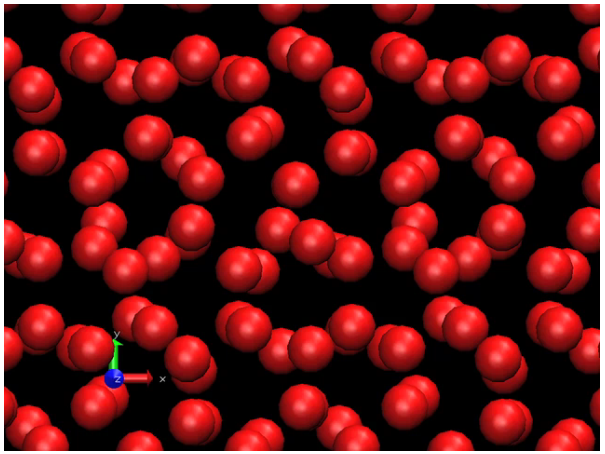
$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda = F_{ref} + \int_0^T dt \frac{d\lambda}{dt} \left(U - U_{ref} \right)_\lambda$$

M. Watanabe and W. P. Reinhardt, Phys. Rev. Lett. **65**, 3301 (1990)

Example: anharmonic free energy of solid Fe at ~350 GPa



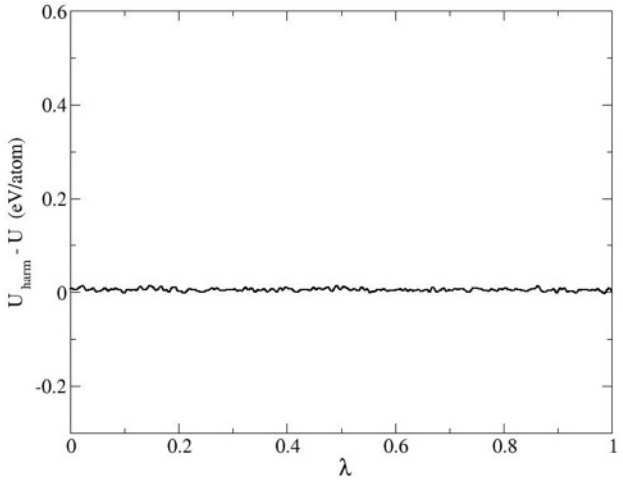


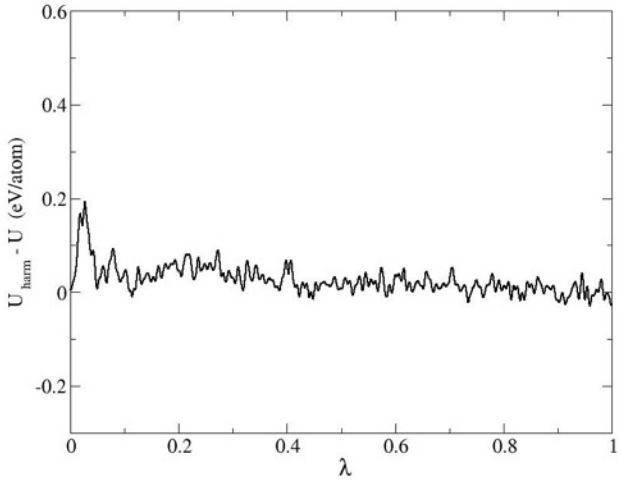


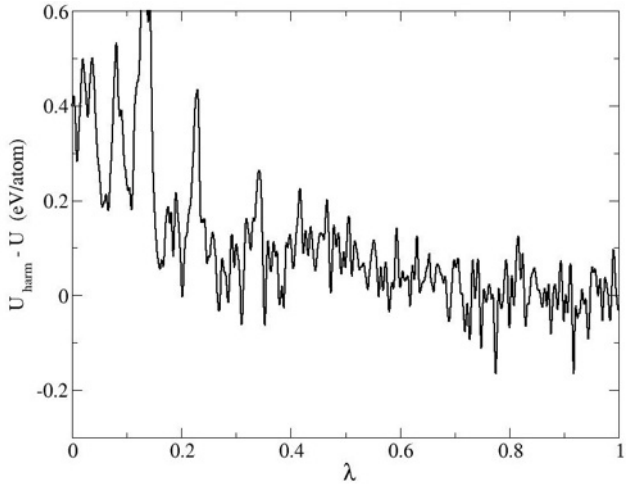
T=1000 K

T=3000 K

T=6500 K

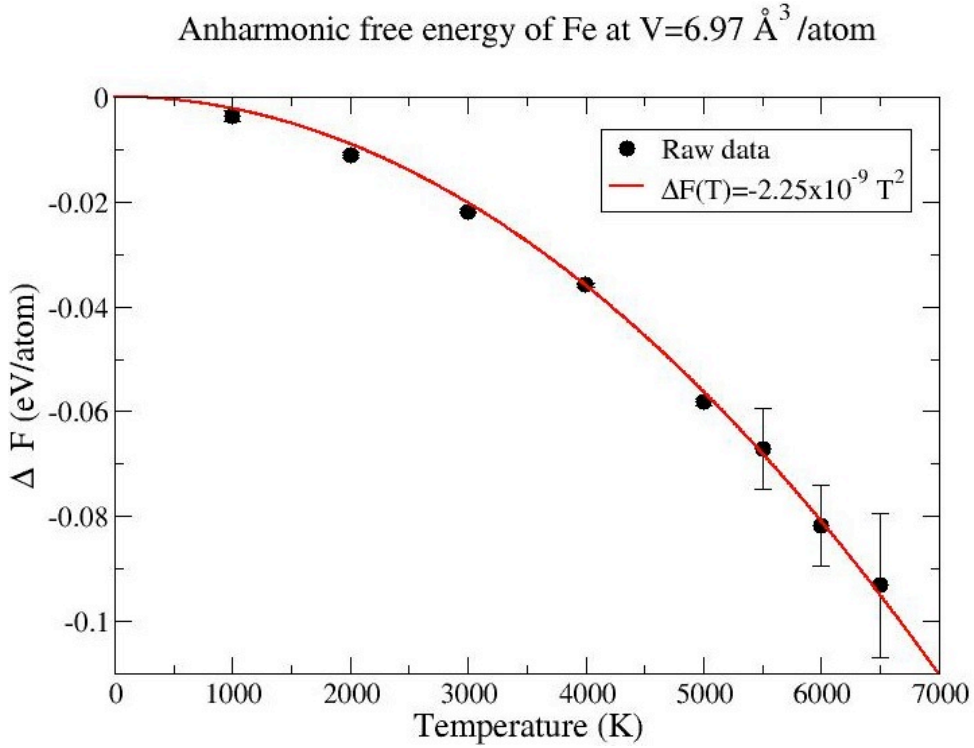






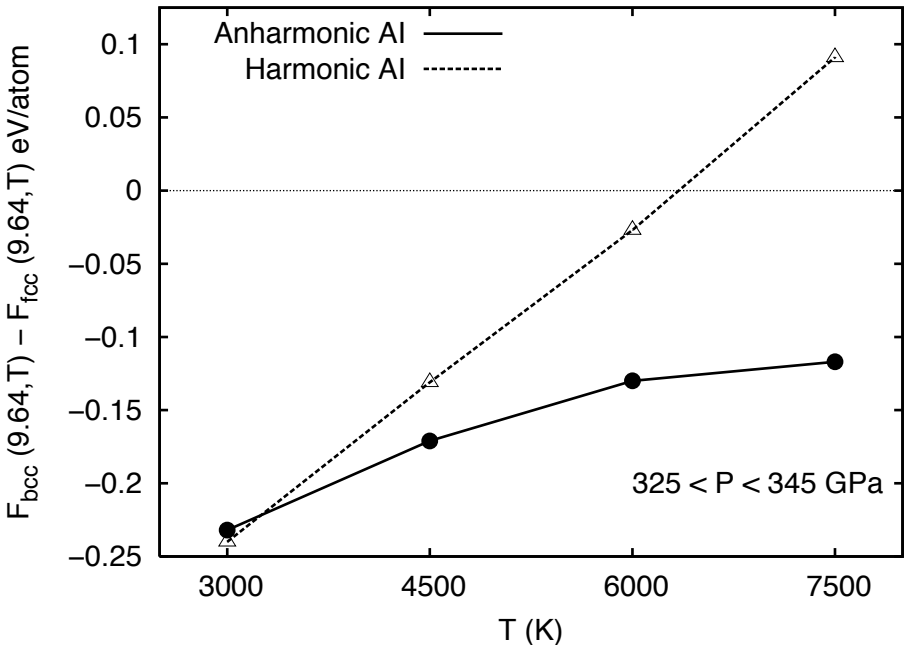
Example: anharmonic free energy of solid Fe at ~350 GPa

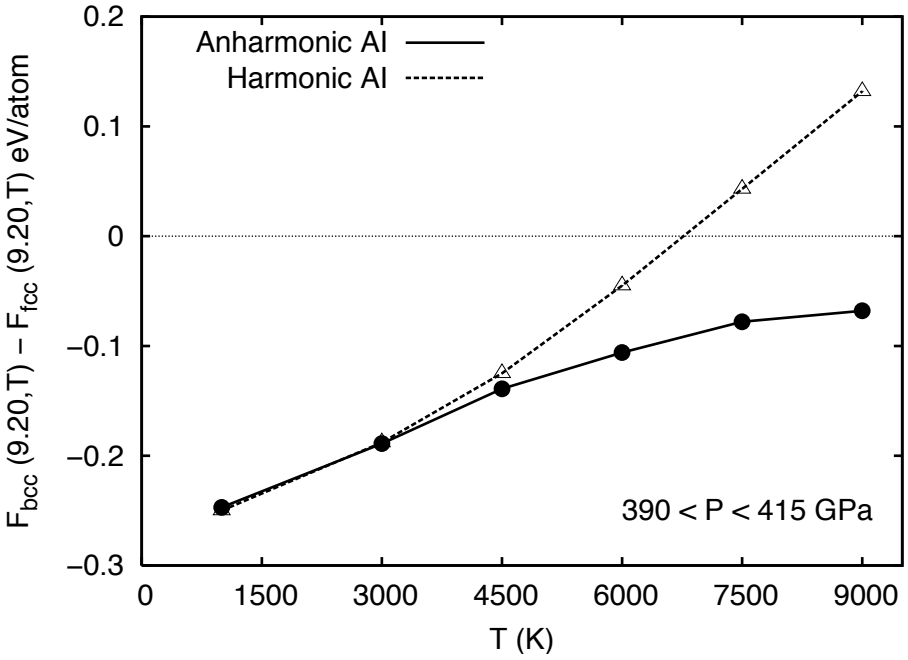
$$F = F_{harm} + \int_0^T dt \frac{d\lambda}{dt}\left(U - U_{harm}\right)_\lambda \qquad U_{harm} = \frac{1}{2}\sum_{i\alpha,j\beta} u_{i\alpha}\Phi_{i\alpha,j\beta}u_{j\beta}$$



Anharmonic contribution to the free energy is important at high T

Stability of Mo including anharmonicity

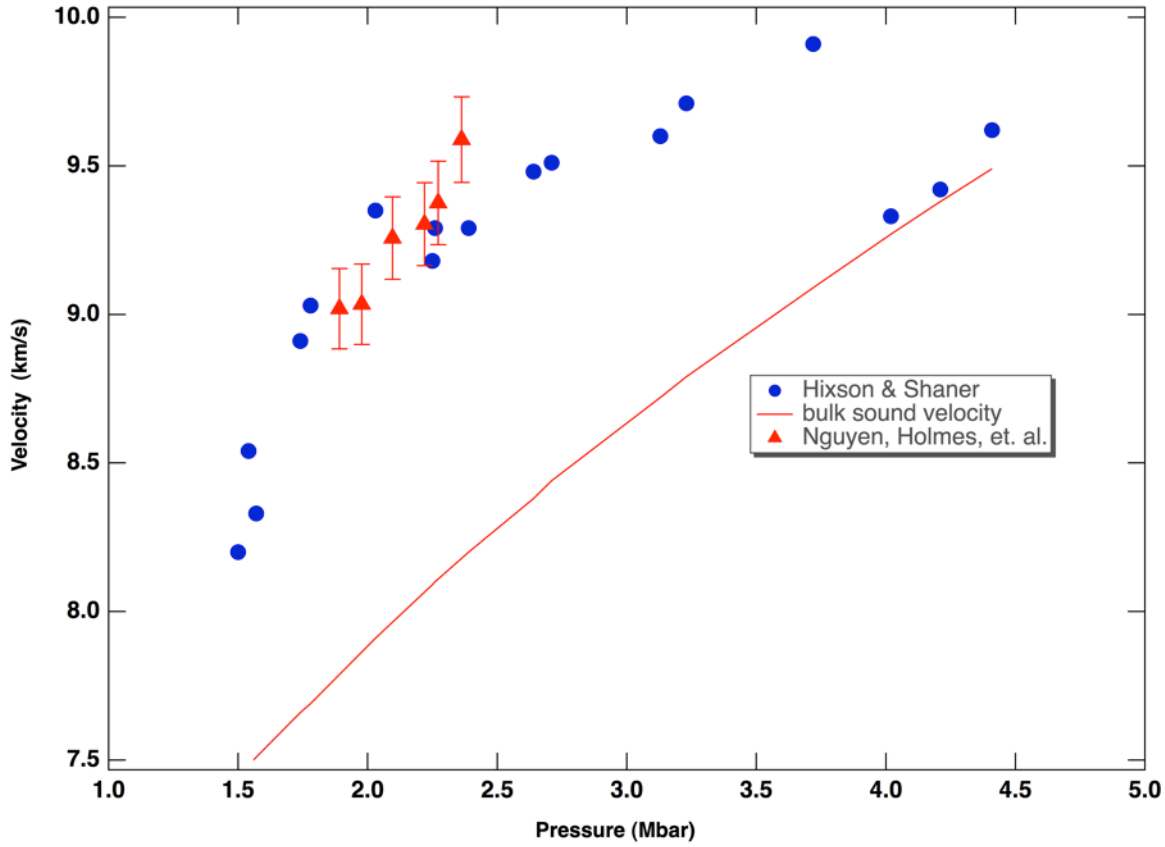




BCC is more stable than fcc at high temperature

*C. Cazorla, D. Alfè and M. J. Gillan, PRB **85**, 064113*

New shock data (courtesy of Neil Holmes, Nguyen, Chao, Asimow, LLNL)



Maybe there is no discontinuity after all…

Improving the efficiency of TI

$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda$$

F is independent on the choice of U_{ref}, but for efficiency choose U_{ref} such that:

$$\langle (U - U_{ref} - \langle U - U_{ref} \rangle)^2 \rangle$$

is minimum. For solid iron at Earth's core conditions a good U_{ref} is:

$$U_{ref} = c_1 U_{harm} + c_2 U_{IP}$$

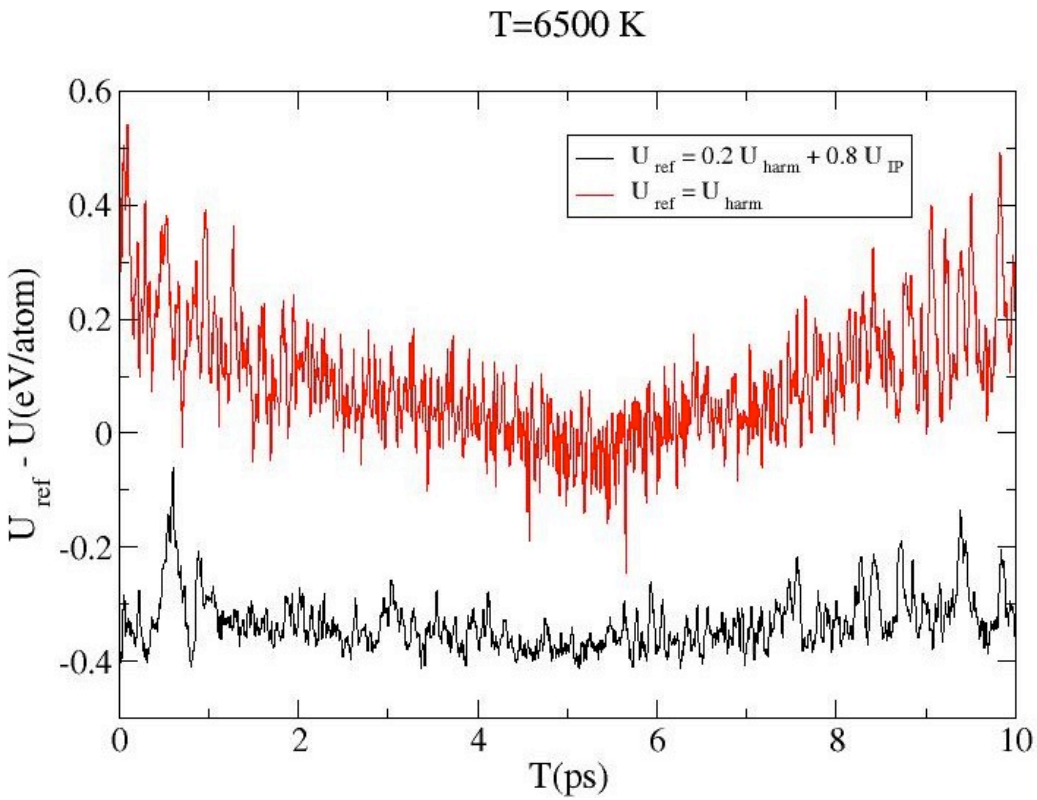
$$U_{harm} = \frac{1}{2} \sum_{i\alpha, j\beta} u_{i\alpha} \Phi_{i\alpha, j\beta} u_{j\beta}$$

$$U_{IP} = \frac{1}{2} \sum_{i \neq j} \frac{A}{\left| r_i - r_j \right|^B}; \quad B = 5.86$$

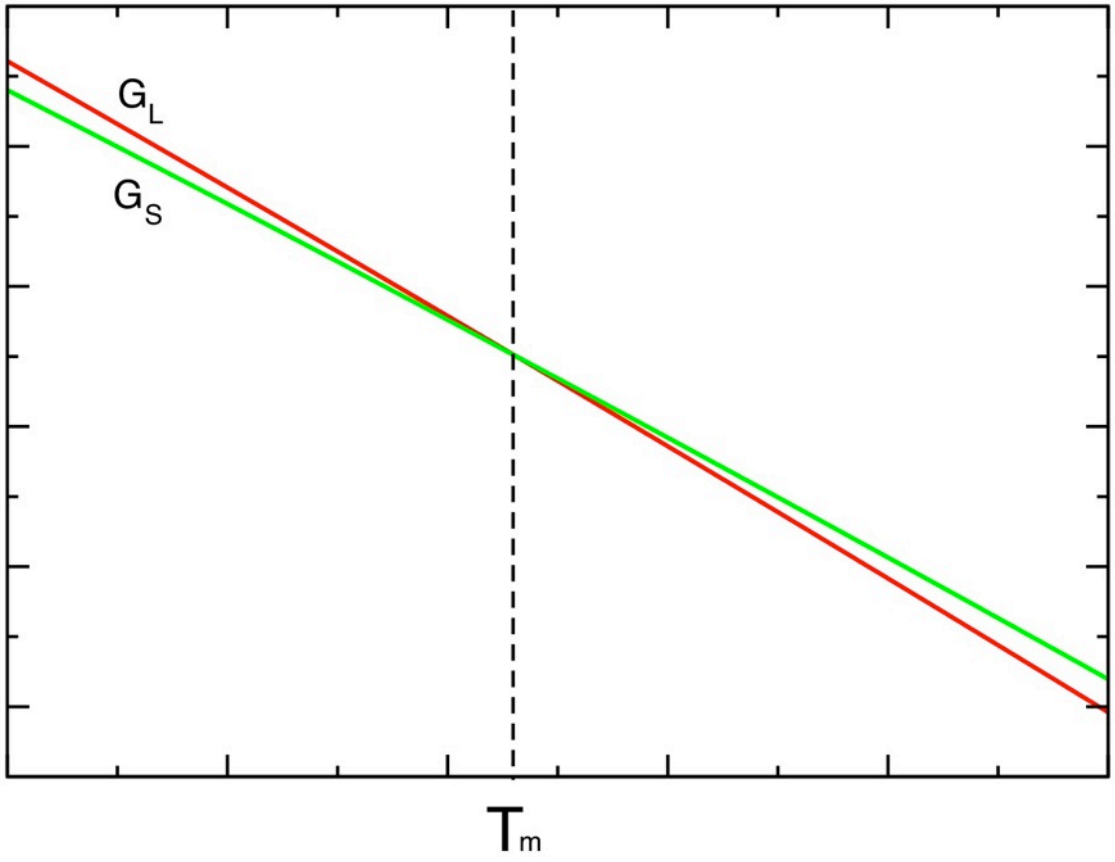
Improving the efficiency of TI (2)

$$U_{ref} = c_1 U_{harm} + c_2 U_{IP}$$

At high temperature we find c_1 = 0.2, c_2 = 0.8



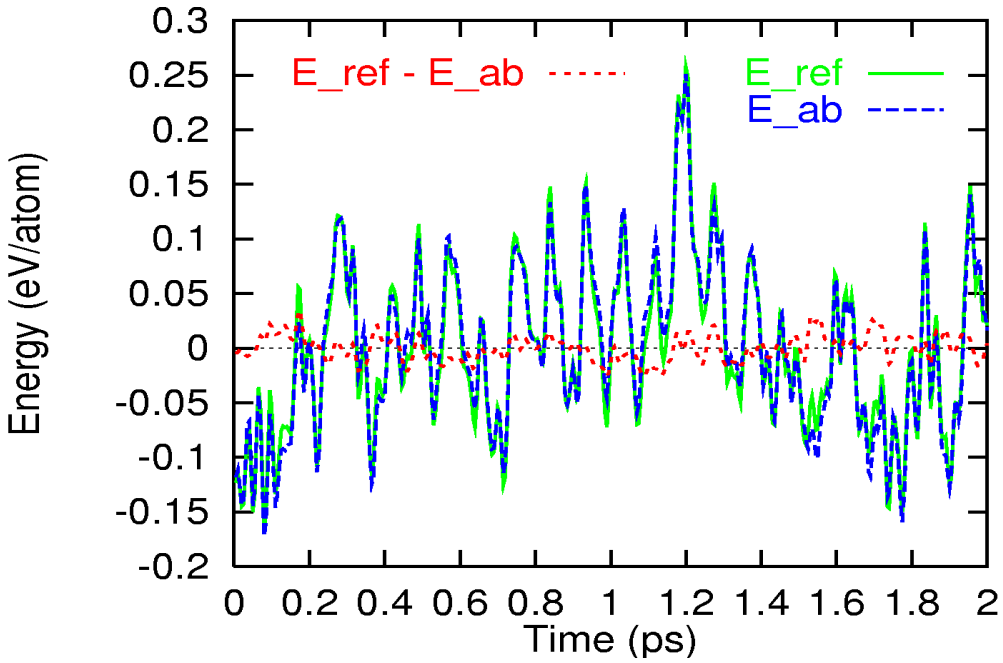
Melting

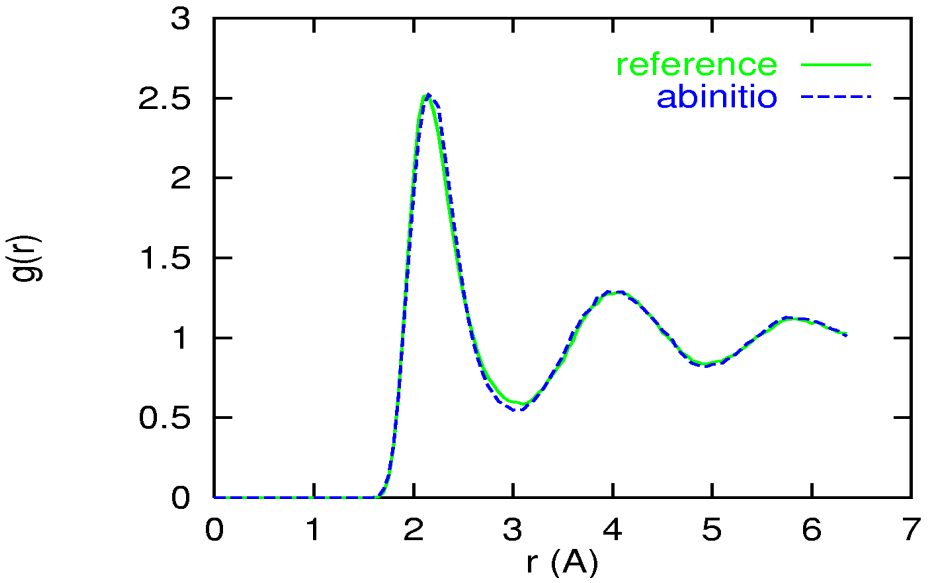


Liquid Fe

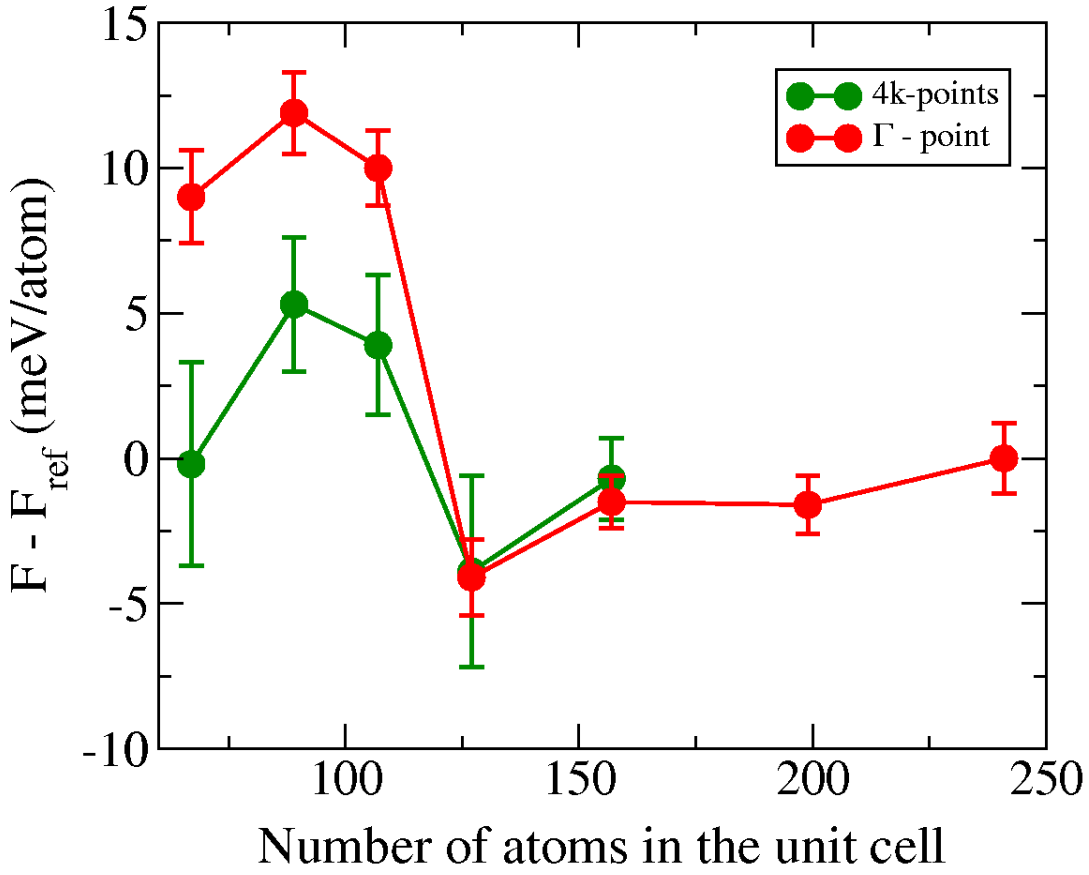
$$U_{ref} = \frac{1}{2}\sum_{i \neq j} \frac{A}{\left|r_i - r_j\right|^B}$$

$$B = 5.86$$





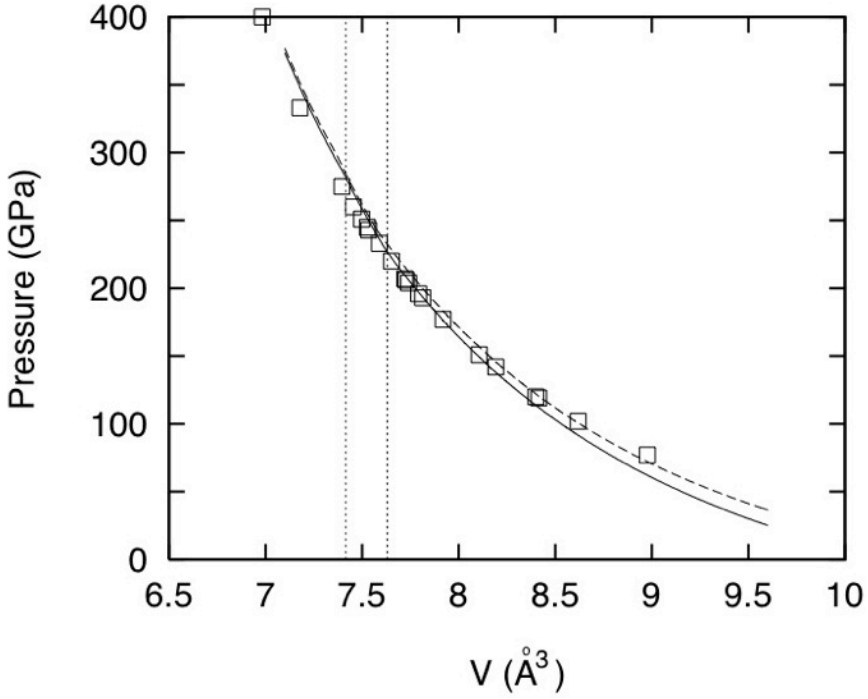
Size tests

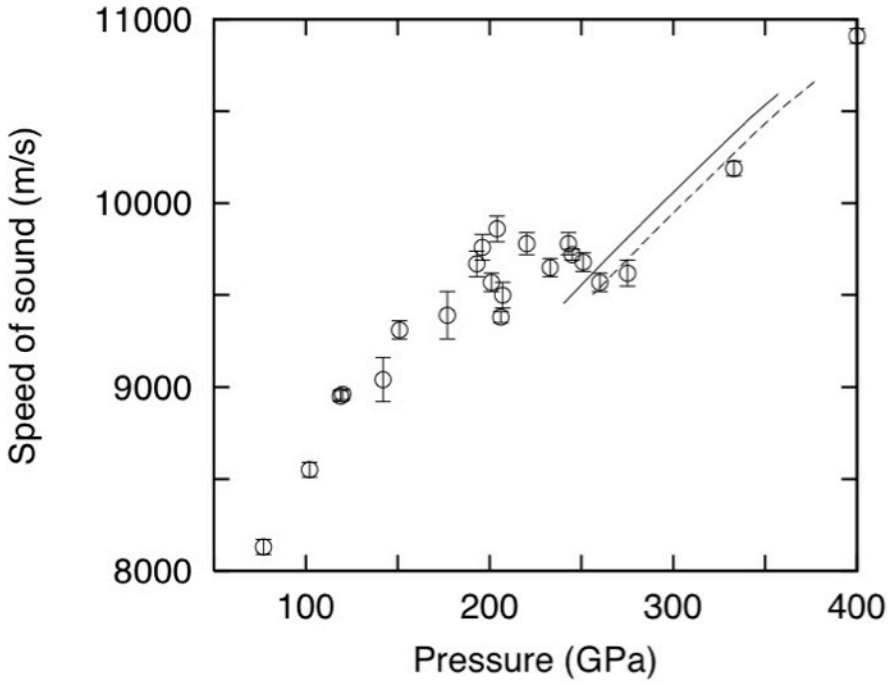


$$\Delta T \approx 100\ K \ \rightarrow\ \Delta G \approx 10\ meV\ /\ atom$$

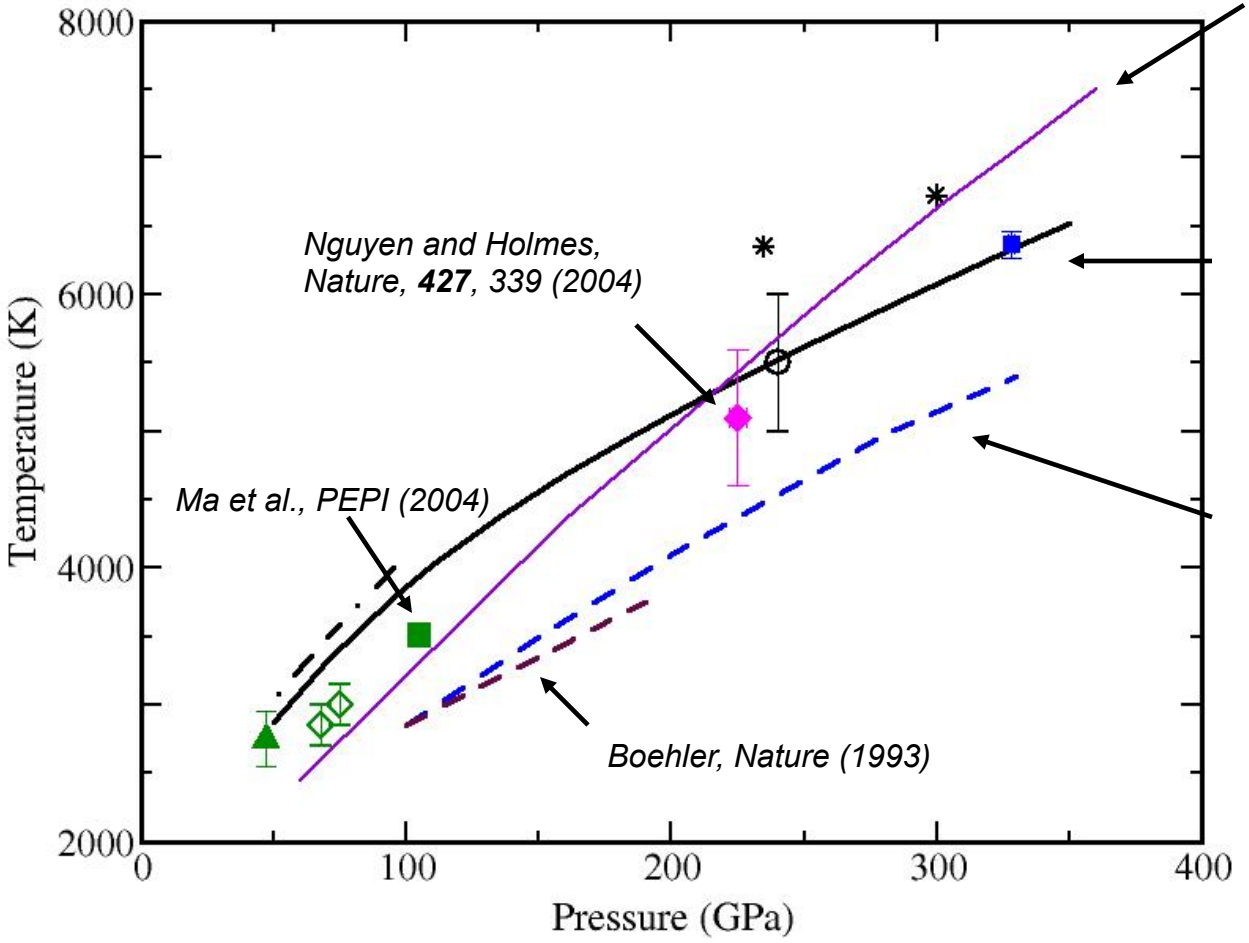
Hugoniot of Fe

$$\frac{1}{2} p_H (V_0 - V_H) = E_H - E_0$$





The melting curve of Fe

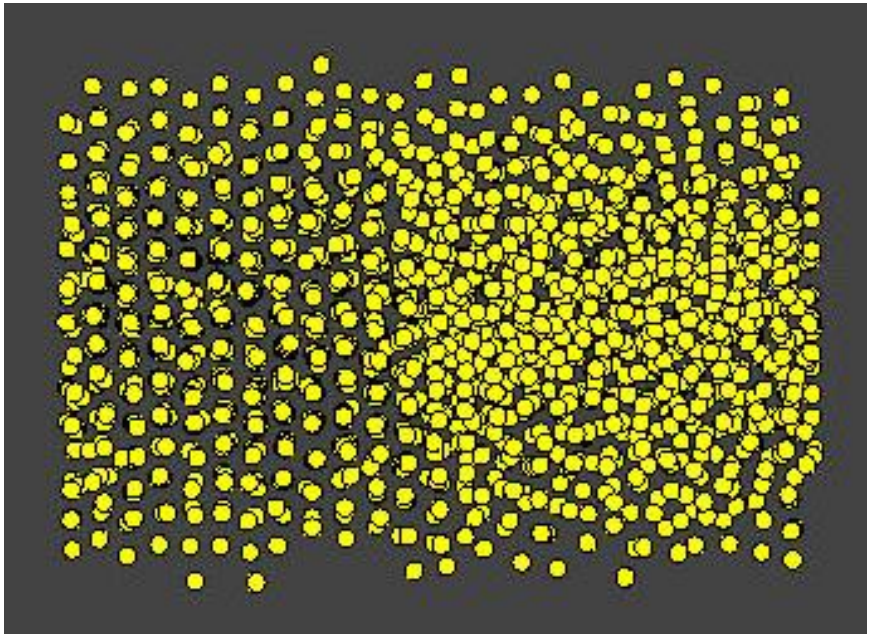


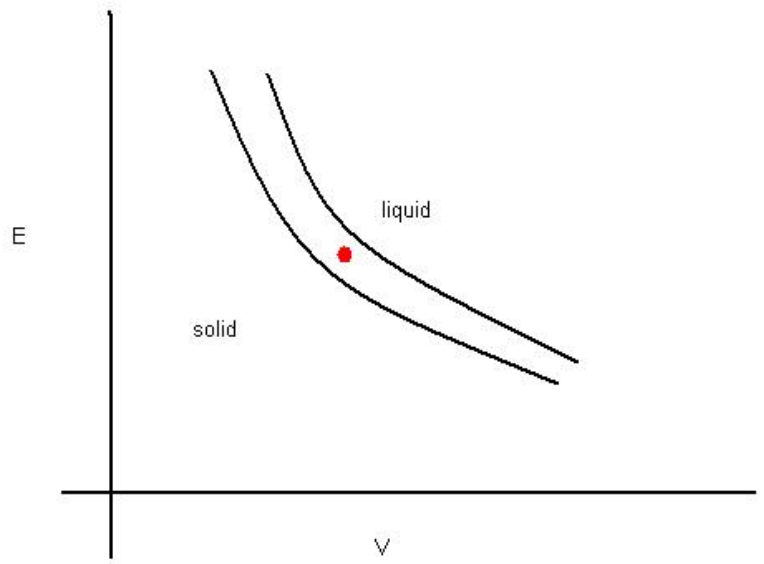
*Belonoshko et al., PRL, **84**, 3638 (2000)*

*Alfè, Price,Gillan, Nature, **401**, 462 (1999); PRB, **64**, 045123 (2001); PRB, **65**, 165118 (2002);*
*Alfè, PRB **79**, 060601(R) (2009)*

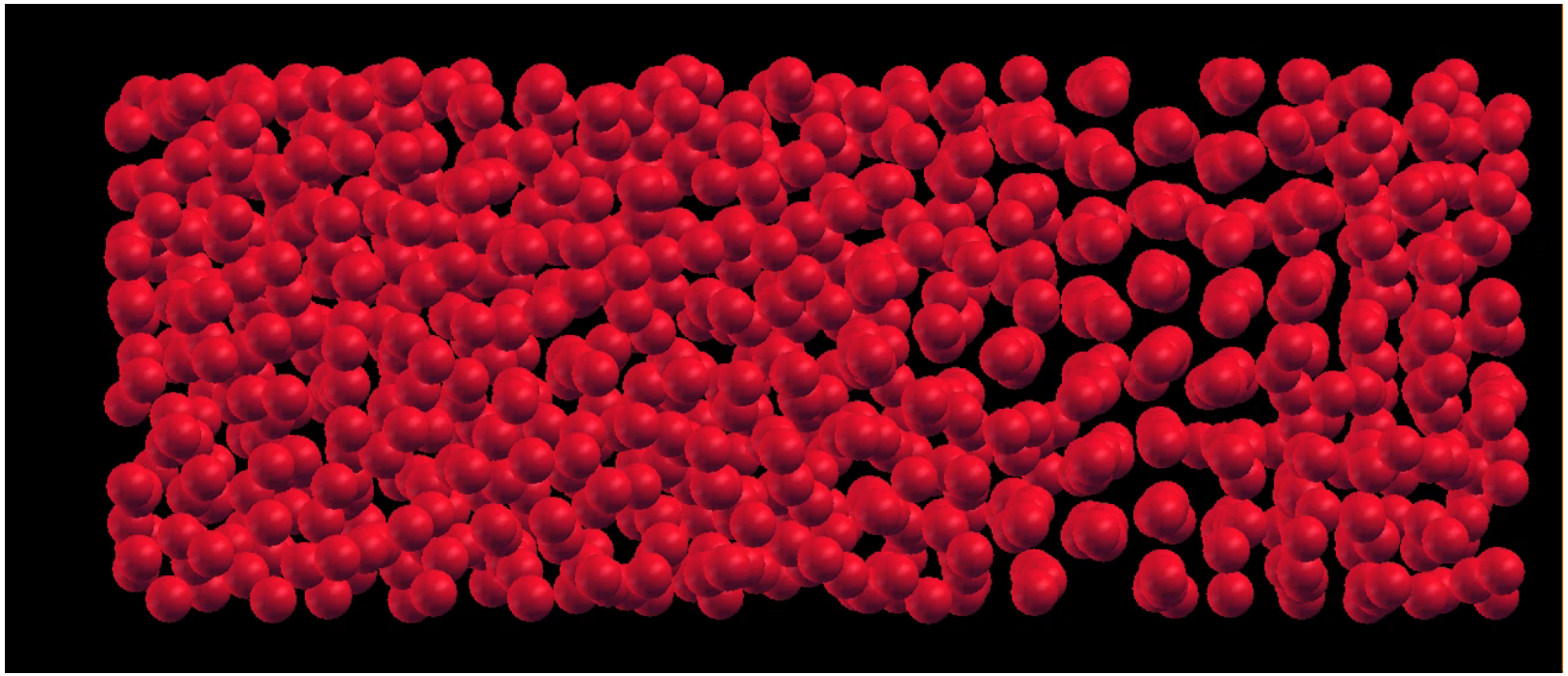
*Laio et al., Science, **287**, 1027 (2000)*

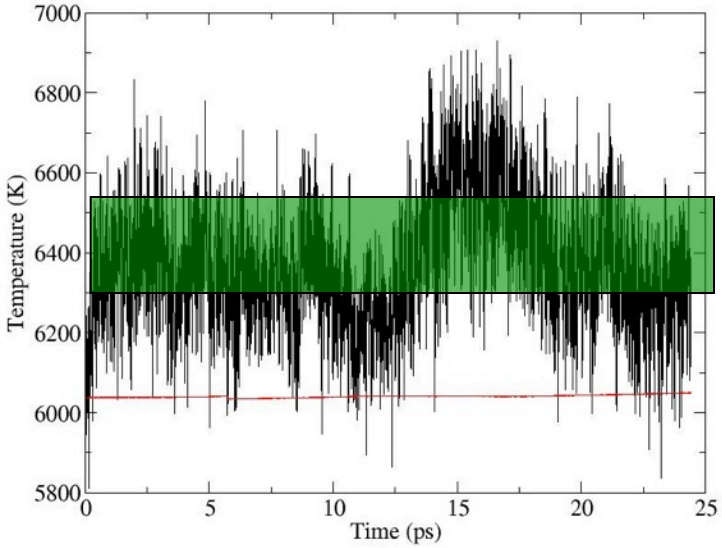
Melting: coexistence of phases

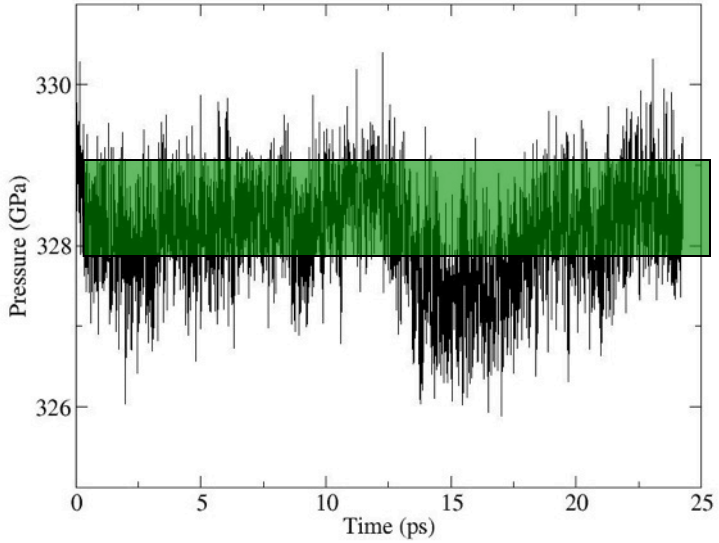




NVE ensemble: for fixed V, if E is between solid and liquid values, simulation will give coexisting solid and liquid

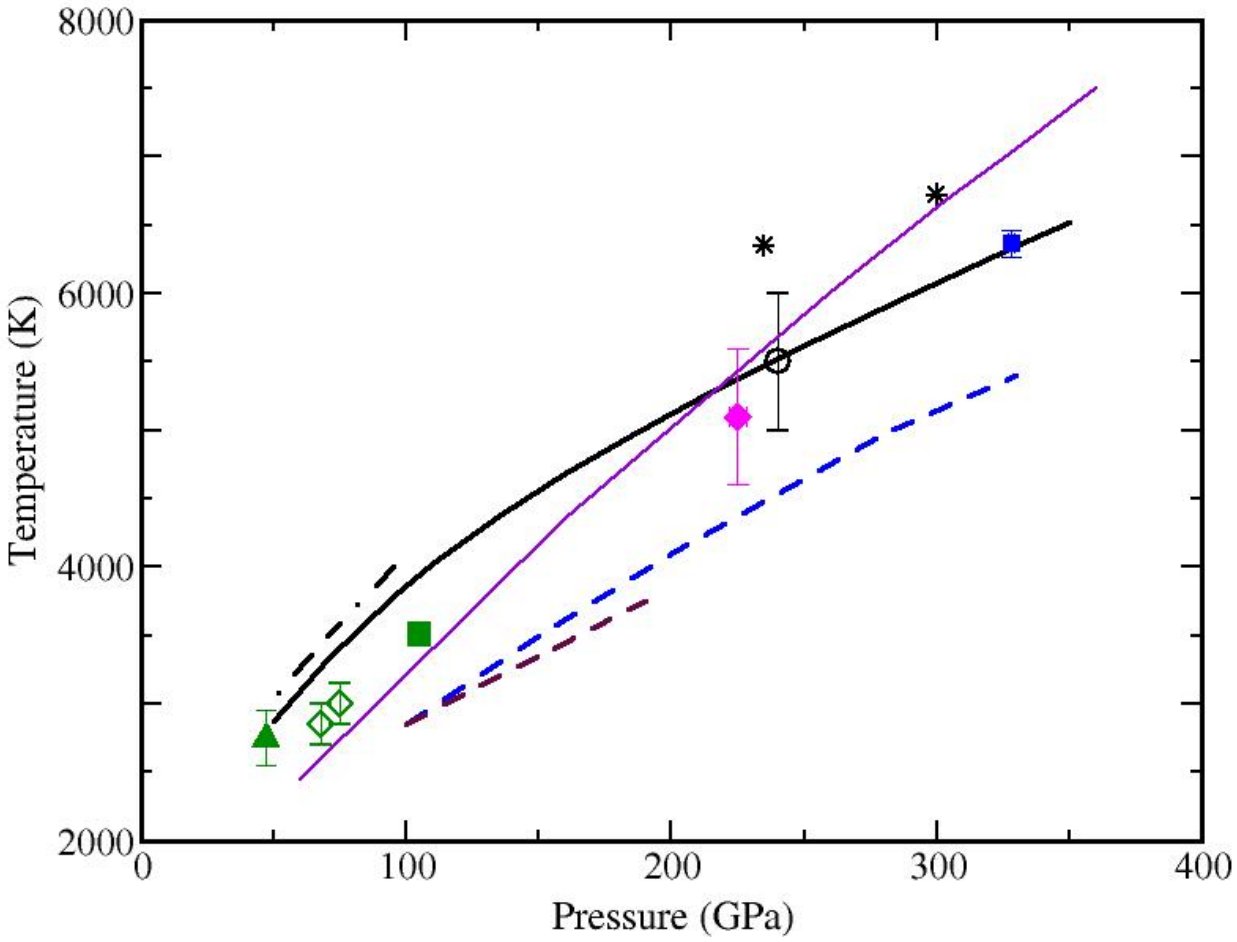




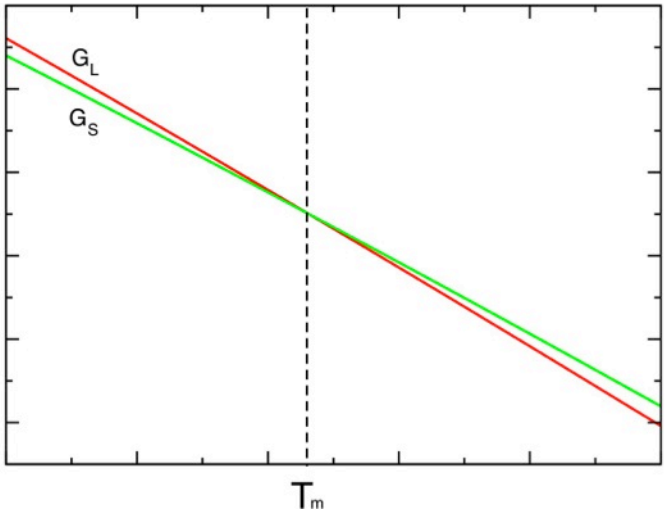


*D. Alfè, Phys. Rev. B, **79**, 060601(R) (2009)*

The melting curve of Fe



Melting of Fe from QMC:



Free energy corrections from DFT to QMC:

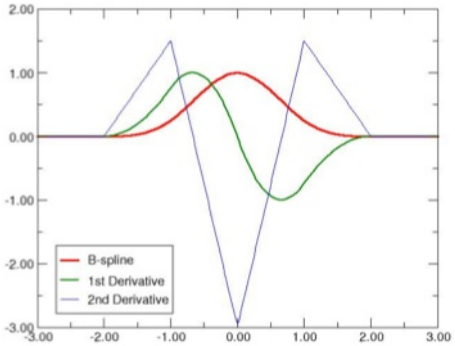
$$\delta T_m = \frac{\Delta G^{ls}(T_m^{ref})}{S_{ref}^{ls}}$$

QMC on Fe, technical details

- CASINO code: R. J. Needs, M. D. Towler, N. D. Drummond, P. Lopez-Rios, CASINO user manual, version 2.1, University of Cambridge, 2007.
- DFT pseudopotential, $3s^2 3p^6 4s^1 3d^7$ (16 electrons in valence)
- Single particle orbitals from PWSCF (plane waves), 150 Ry PW cutoff. Then expanded in B-splines.

$$\Psi_T(\mathbf{R}) = \exp[J(\mathbf{R})] D^{\uparrow}\{\phi_i(\mathbf{r}_j)\} D^{\downarrow}\{\phi_i(\mathbf{r}_j)\}$$

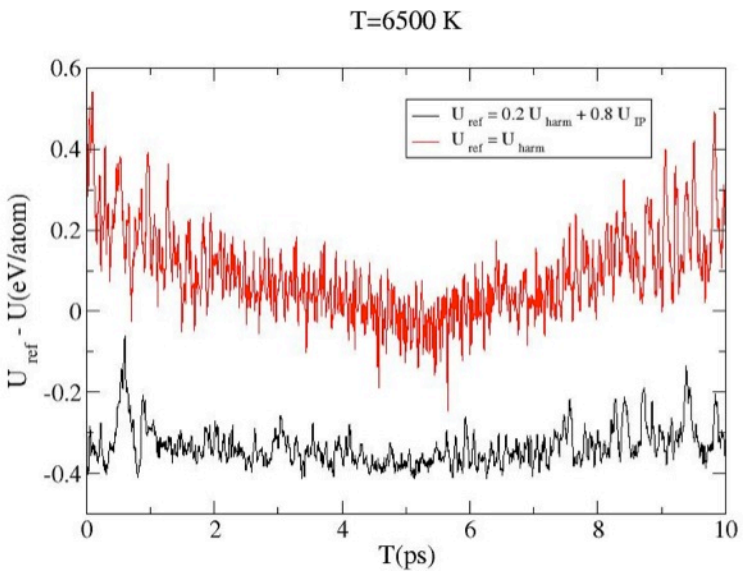
*(D. Alfè and M. J. Gillan, Phys. Rev. B, **70**, 161101(R), (2004))*



Thermodynamic integration, a perturbative approach:

$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda$$

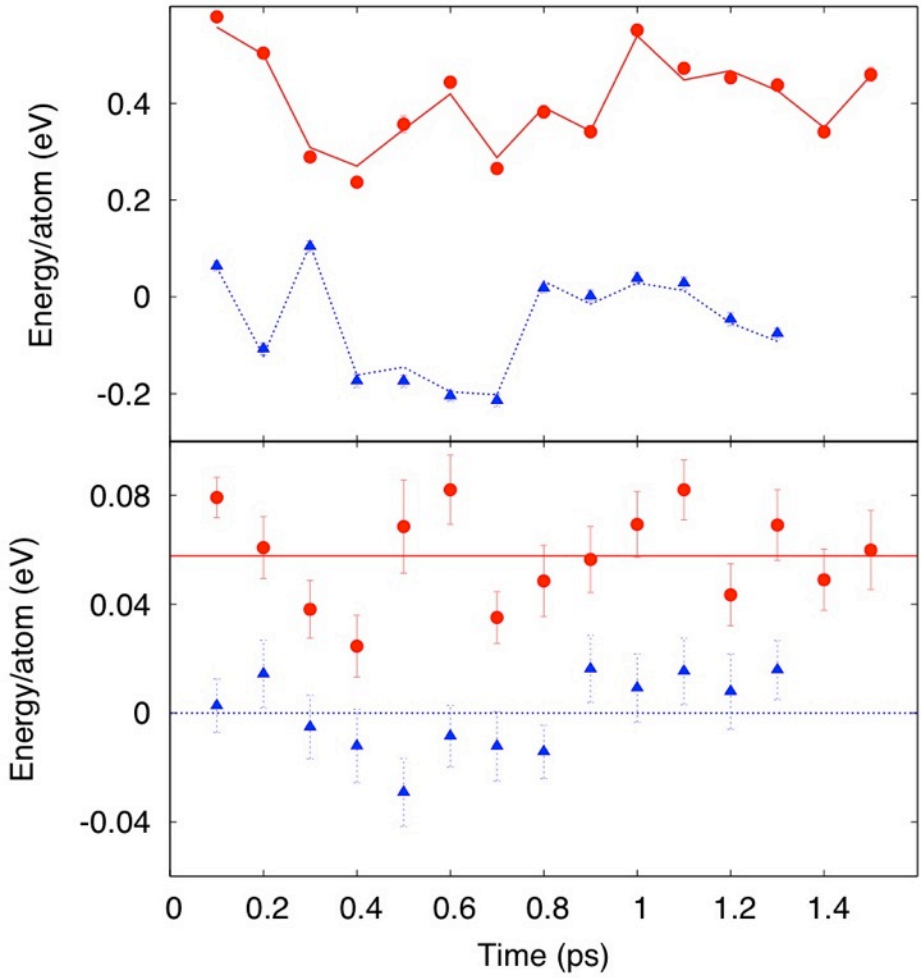
$$\left\langle U - U_{ref} \right\rangle_\lambda = \left\langle U - U_{ref} \right\rangle_{\lambda=0} + \lambda \left. \frac{\partial \left\langle U - U_{ref} \right\rangle_\lambda}{\partial \lambda} \right|_{\lambda=0} + o(\lambda^2)$$



$$\int_0^1 d\lambda \left\langle U - U_{ref} \right\rangle_\lambda \simeq \left\langle U - U_{ref} \right\rangle_{\lambda=0} - \frac{1}{2k_B T} \left\langle \delta\Delta U_0^2 \right\rangle_{\lambda=0}$$

$$\delta\Delta U_\lambda = U - U_{ref} - \left\langle U - U_{ref} \right\rangle_\lambda$$

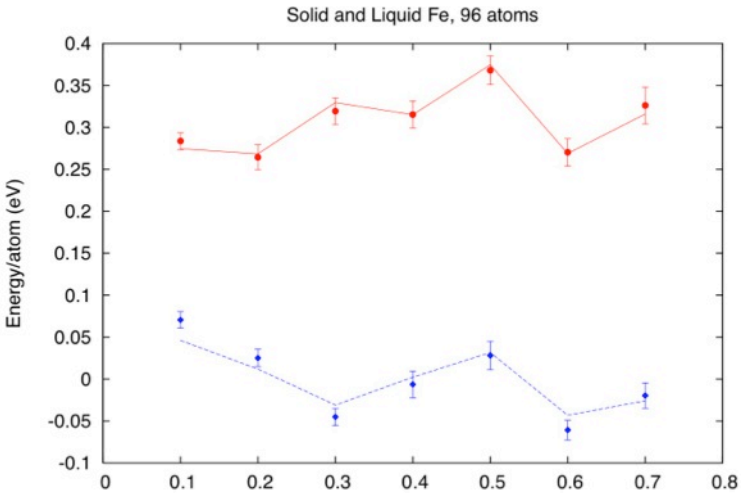
QMC correction to the DFT Fe melting curve

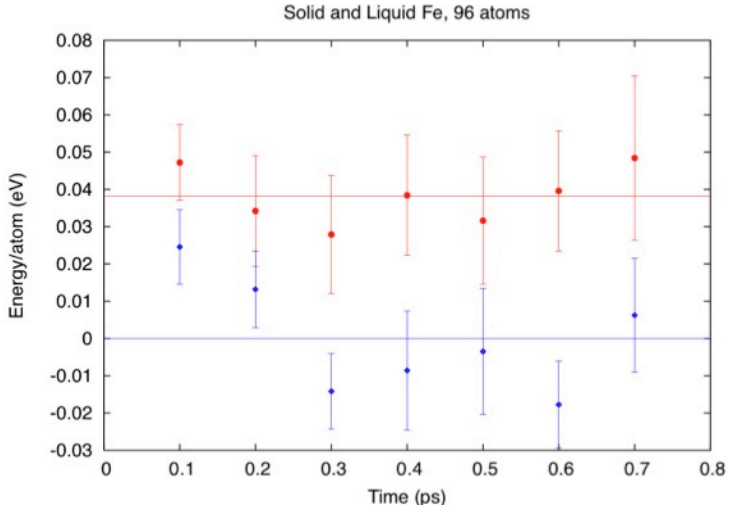


$$\Delta G^{ls}(T_m^{ref}) = 0.05 \pm 0.02 \text{ eV/atom}$$

$$\delta T_m = \frac{\Delta G^{ls}(T_m^{ref})}{S_{ref}^{ls}} = 550 \pm 250$$

QMC correction to the DFT Fe melting curve

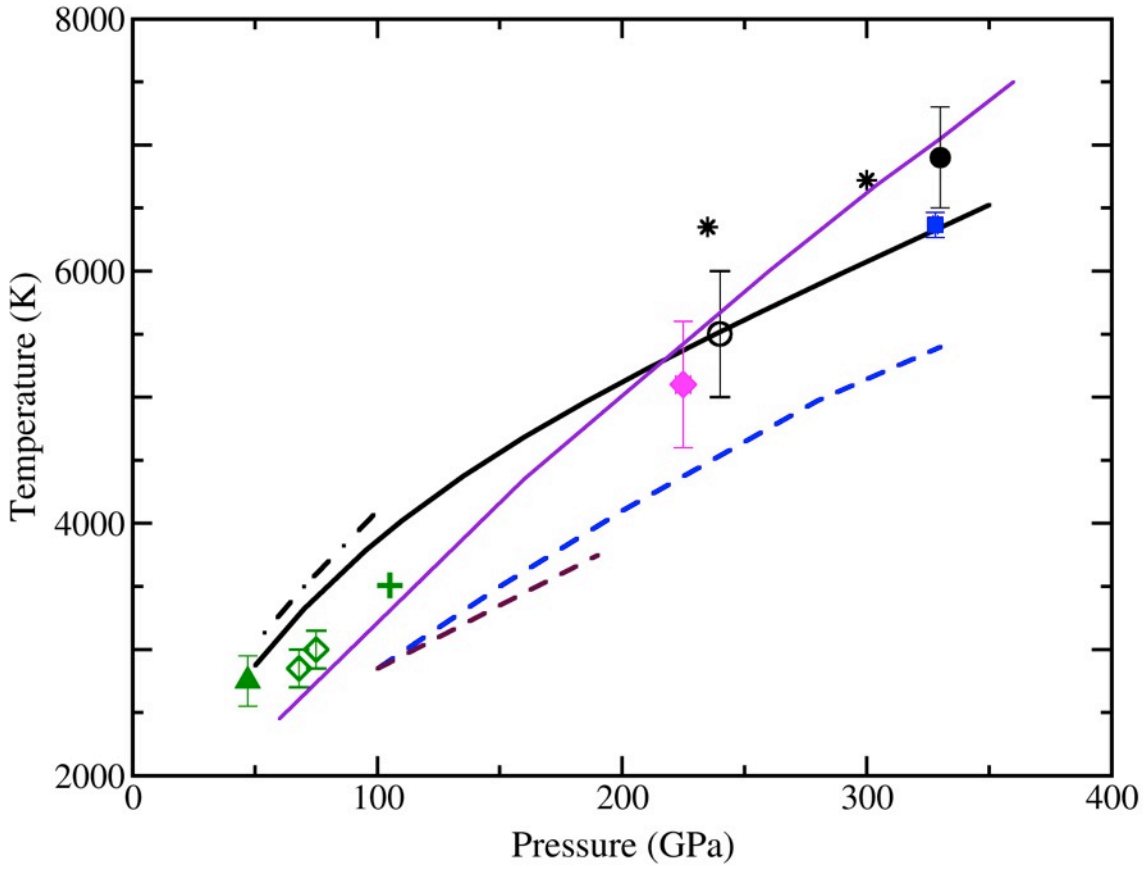




$$\Delta G^{ls}(T_m^{ref}) = 0.05 \pm 0.025 \text{ eV/atom}$$

$$\delta T_m = \frac{\Delta G^{ls}(T_m^{ref})}{S_{ref}^{ls}} = 550 \pm 300$$

Melting curve of Fe



E. Sola and D. Alfè, Phys. Rev. Lett, ***103****, 078501 (2009)*

Strategy for melting of Ta and Mo:

Coexistence of phases with classical potential:

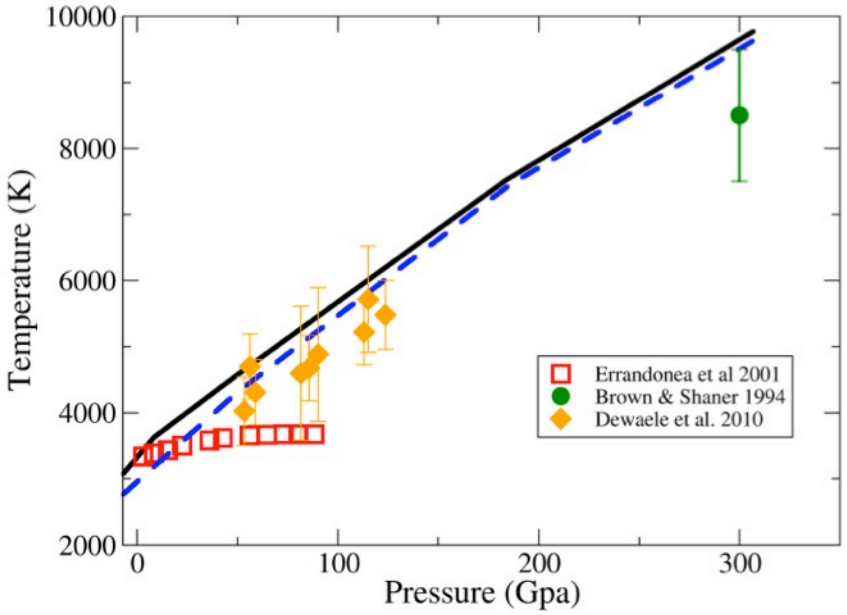
$$U_{\mathrm{ref}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{\mathrm{N}}) = \frac{1}{2}\varepsilon\sum_{i\neq j}\left(\frac{a}{r_{ij}}\right)^n - C\varepsilon\sum_i\left[\sum_{j(\neq i)}\left(\frac{a}{r_{ij}}\right)^m\right]^{1/2}$$

Free energy corrections:

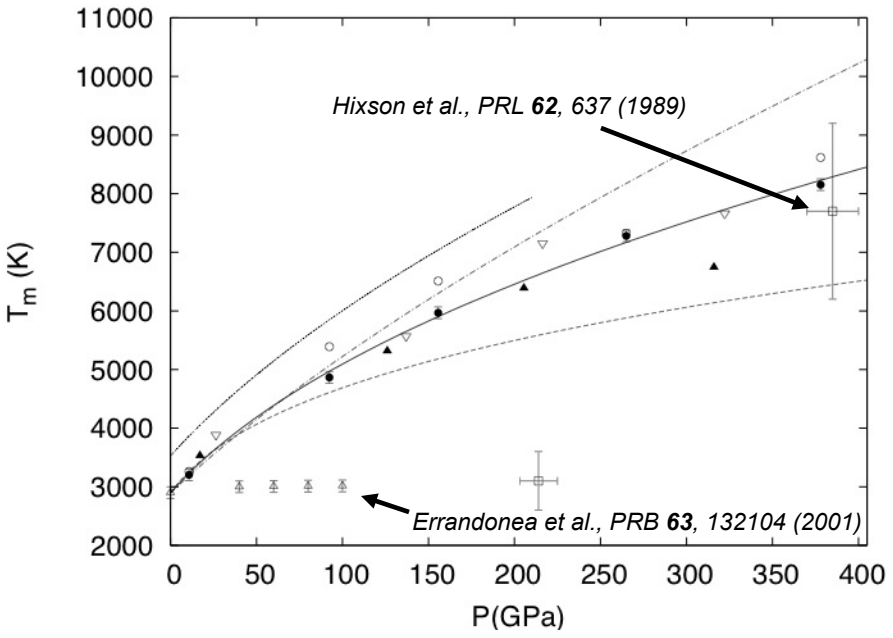
$$\delta T_m = \frac{\Delta G^{ls}(T_m^{ref})}{S_{ref}^{ls}}$$

Melting curves of Ta and Mo

Tantalum

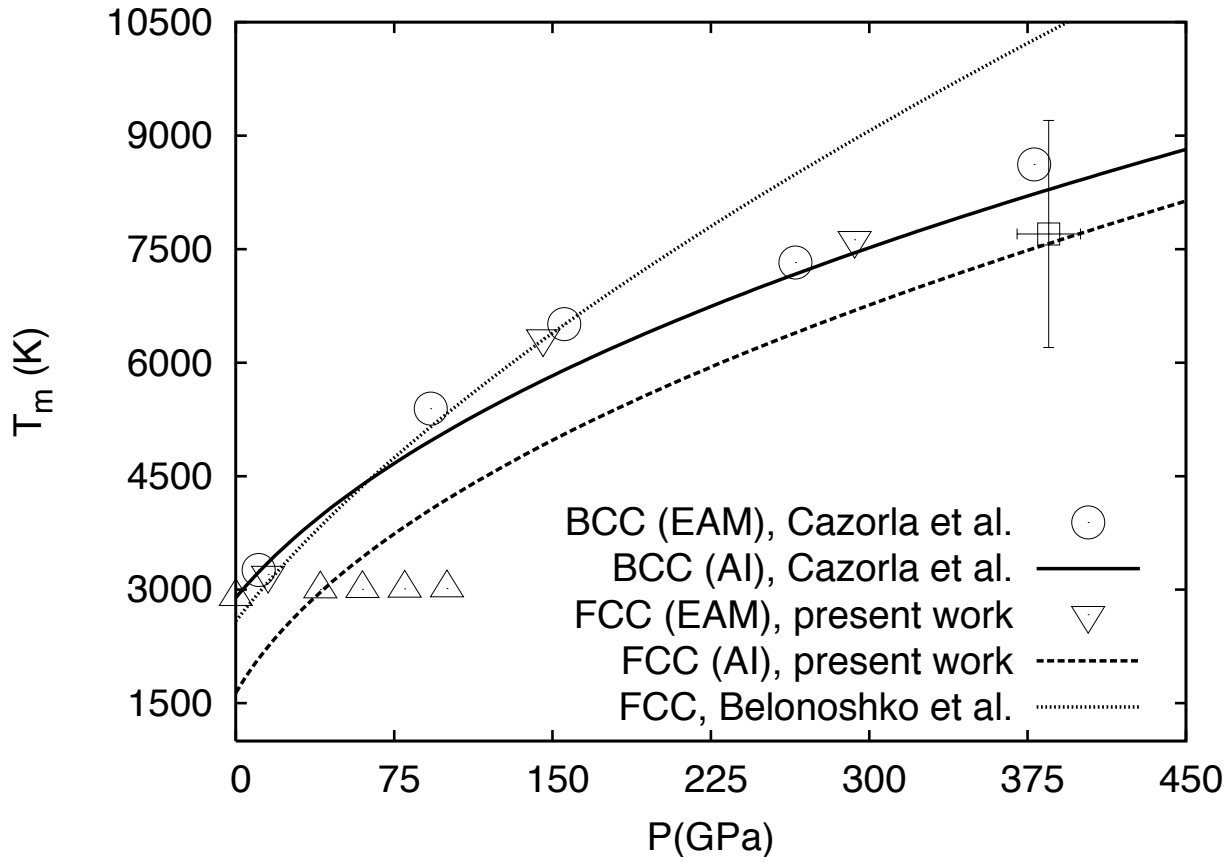


Molybdenum



*S. Taioli, C. Cazorla, M. J. Gillan, and D. Alfè, Phys. Rev B **75**, 214103 (2007), J. Chem. Phys. **126**, 194502 (2007)*

Phase stability of Mo from highest melting curve



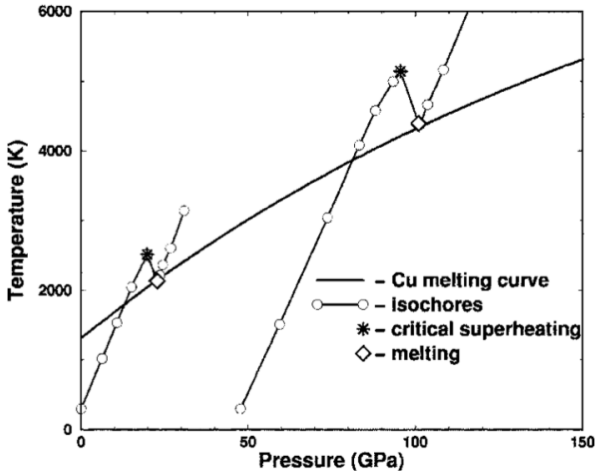
*C. Cazorla, D. Alfè and M. J. Gillan, PRB **85**, 064113*

Theory

- Statistical mechanics
  - Free energies
  - Coexistence of phases
  - Z method
- Interatomic interactions
  - Empirical potentials
  - Density functional theory
  - Quantum Monte Carlo

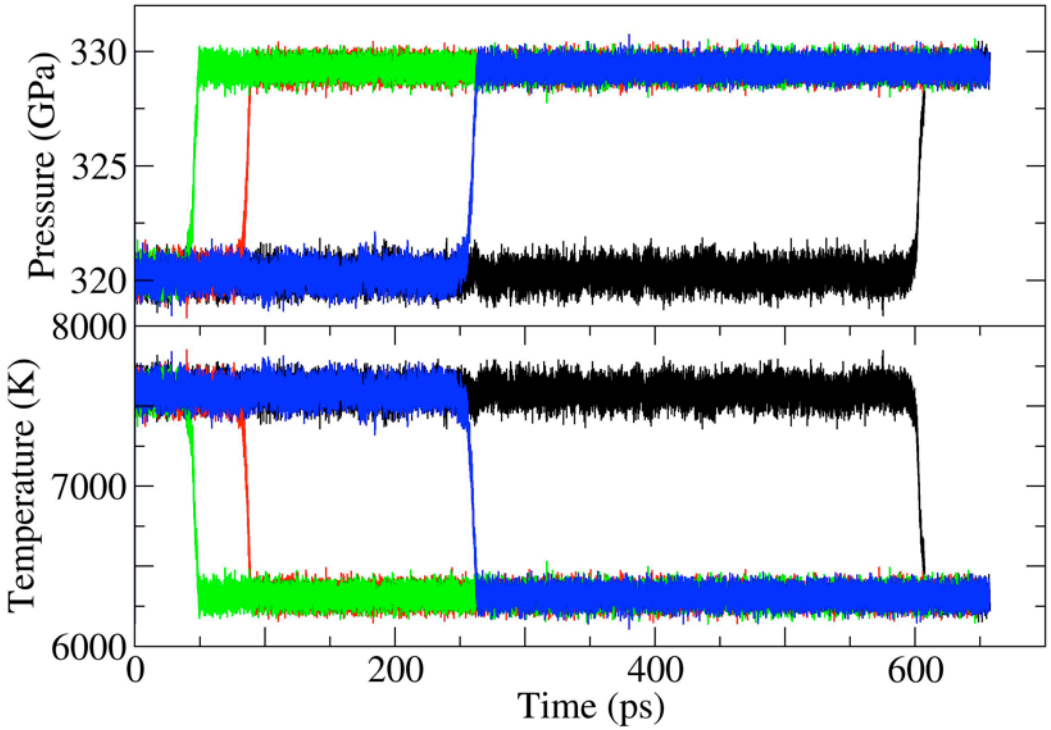
Homogeneous melting (Z method)

Belonoshko *et al.*, PRB **73**, 012201 (2006)

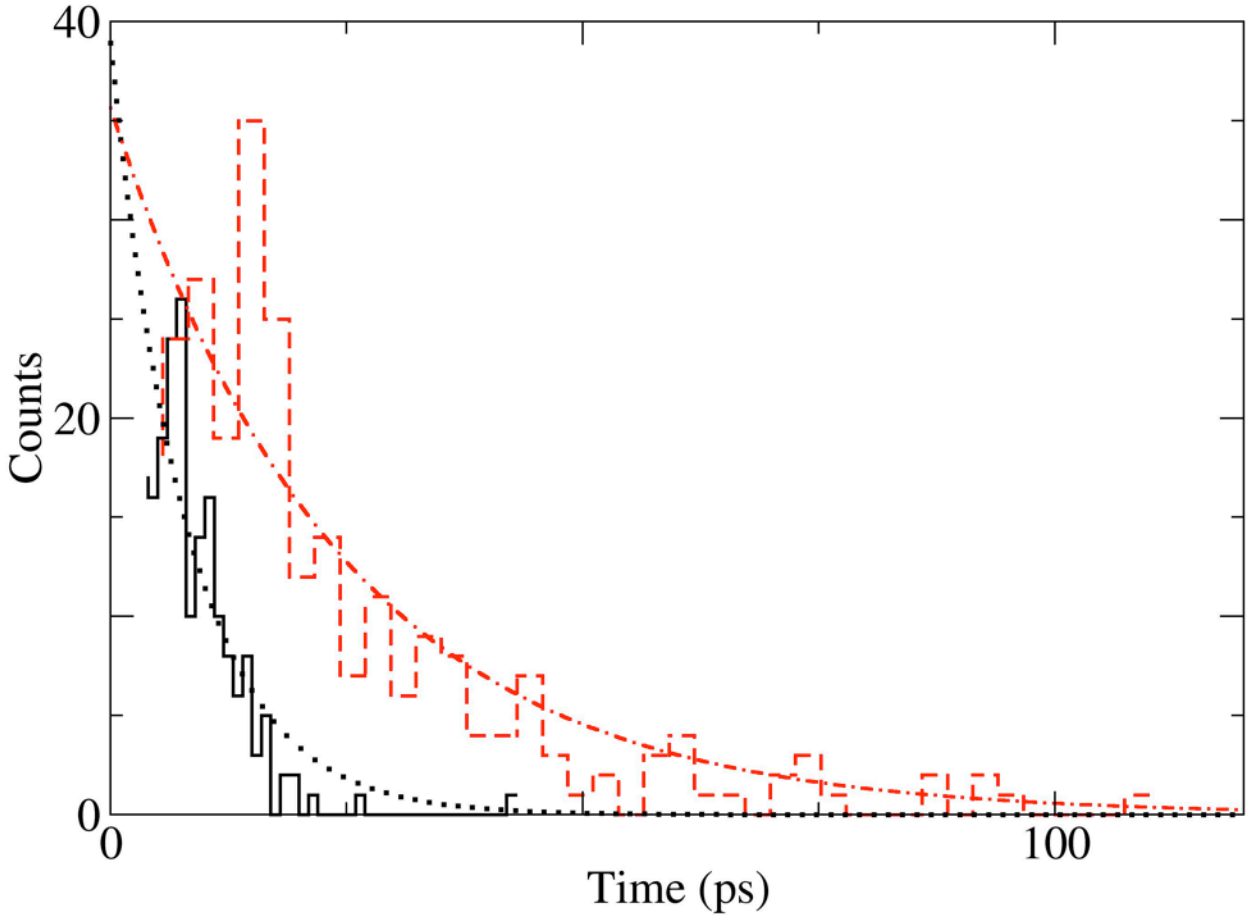


- What is the maximum energy E_{LS} a solid can have in a (N,V,E) simulation before melting ?
- It is the lowest energy on the given isochore within the field of thermodynamic stability of the liquid.
- This energy E_{LS} corresponds to a temperature T_{LS} above which the solid will always melt.
- Since E_{LS} is the lowest energy of the liquid on the given isochore, it should be the energy of the liquid in coexistence with the solid, so that it is associated to the melting temperature T_m, $E^s(V,T_{LS}) = E^l(V,T_m)$

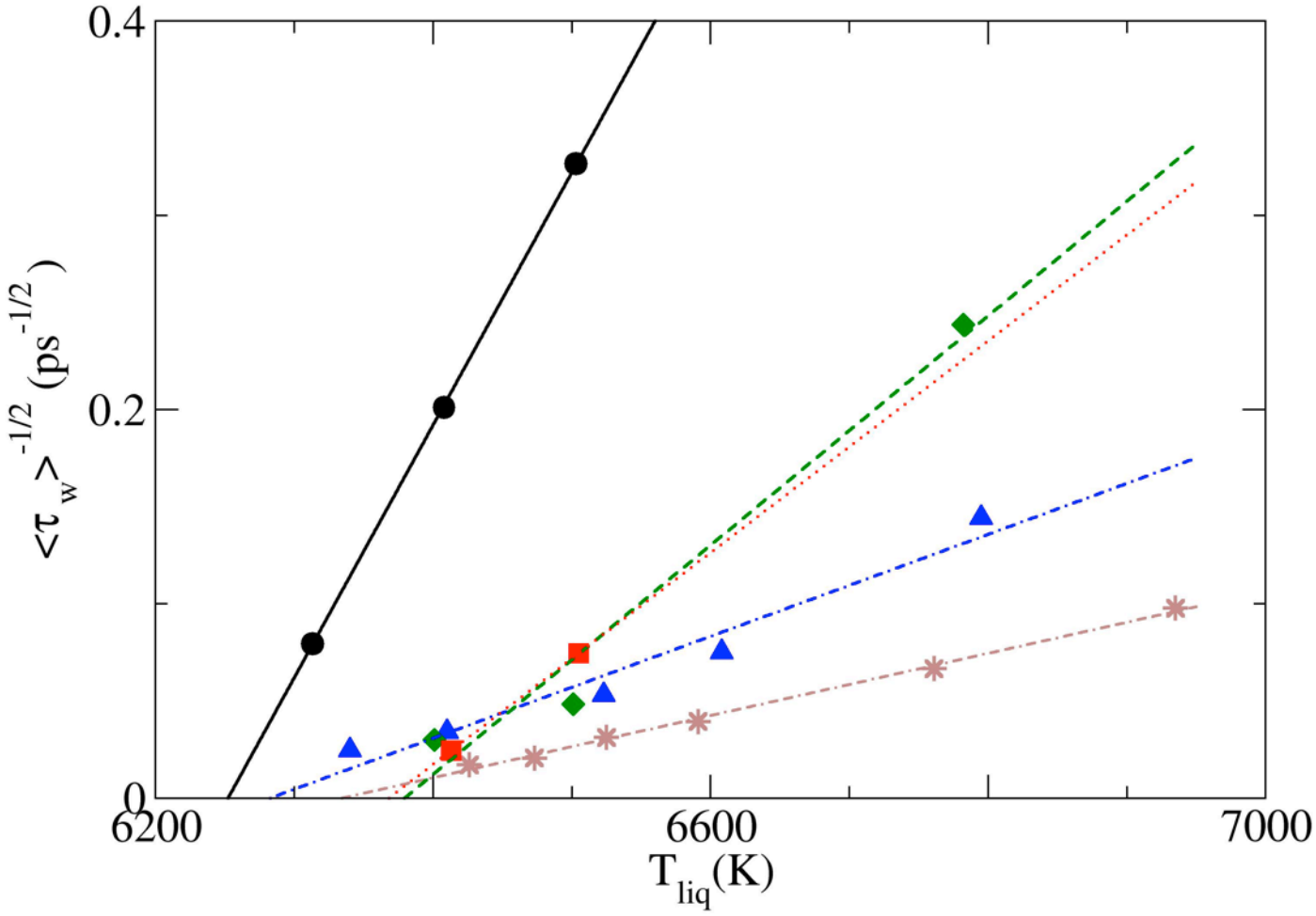
Fe, EAM, 7776 atoms



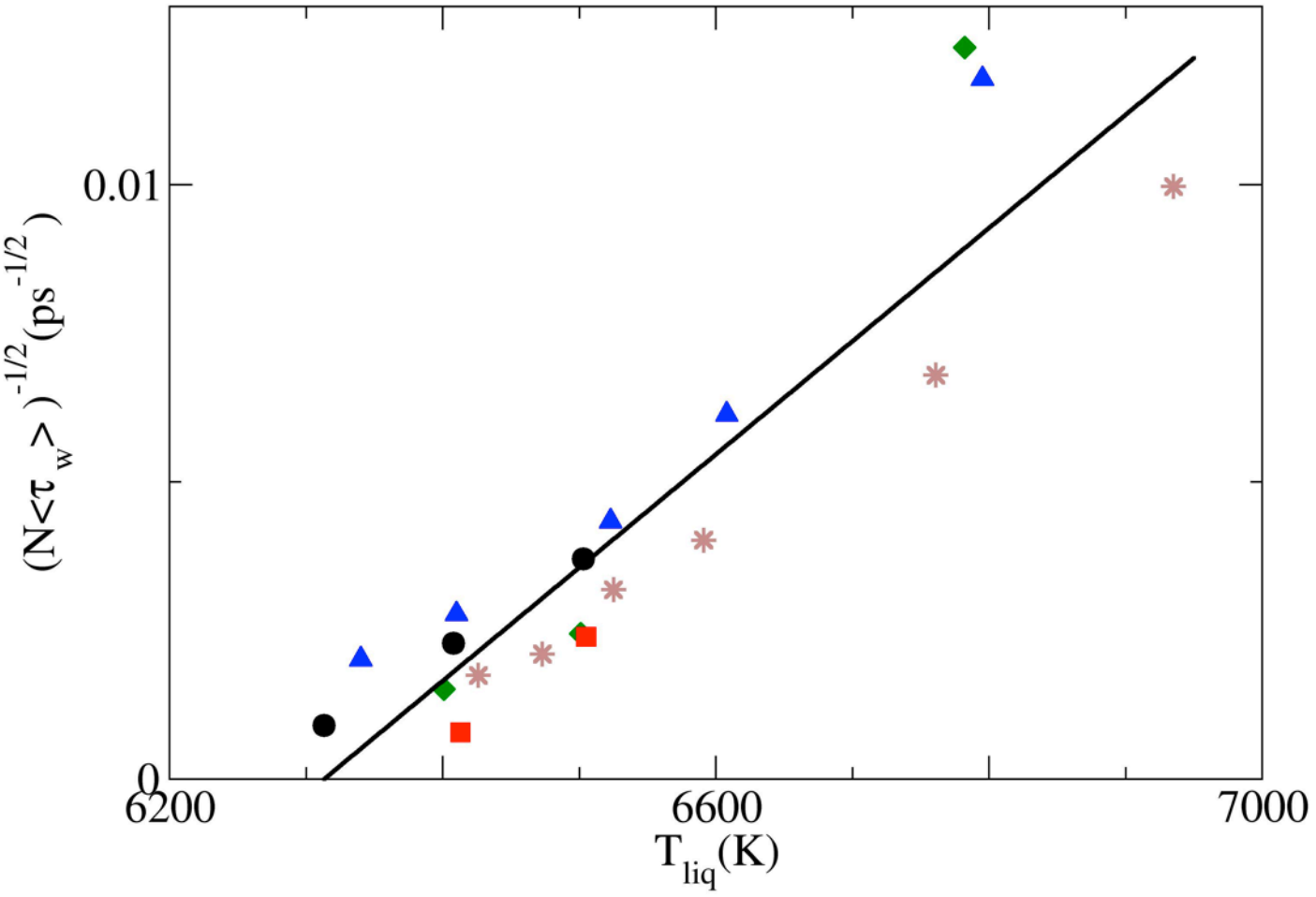
D. Alfe`, C. Cazorla and M. J. Gillan, J. Chem. Phys. ***135****, 024102 (2011)*



D. Alfe`, C. Cazorla and M. J. Gillan, J. Chem. Phys. ***135****, 024102 (2011)*

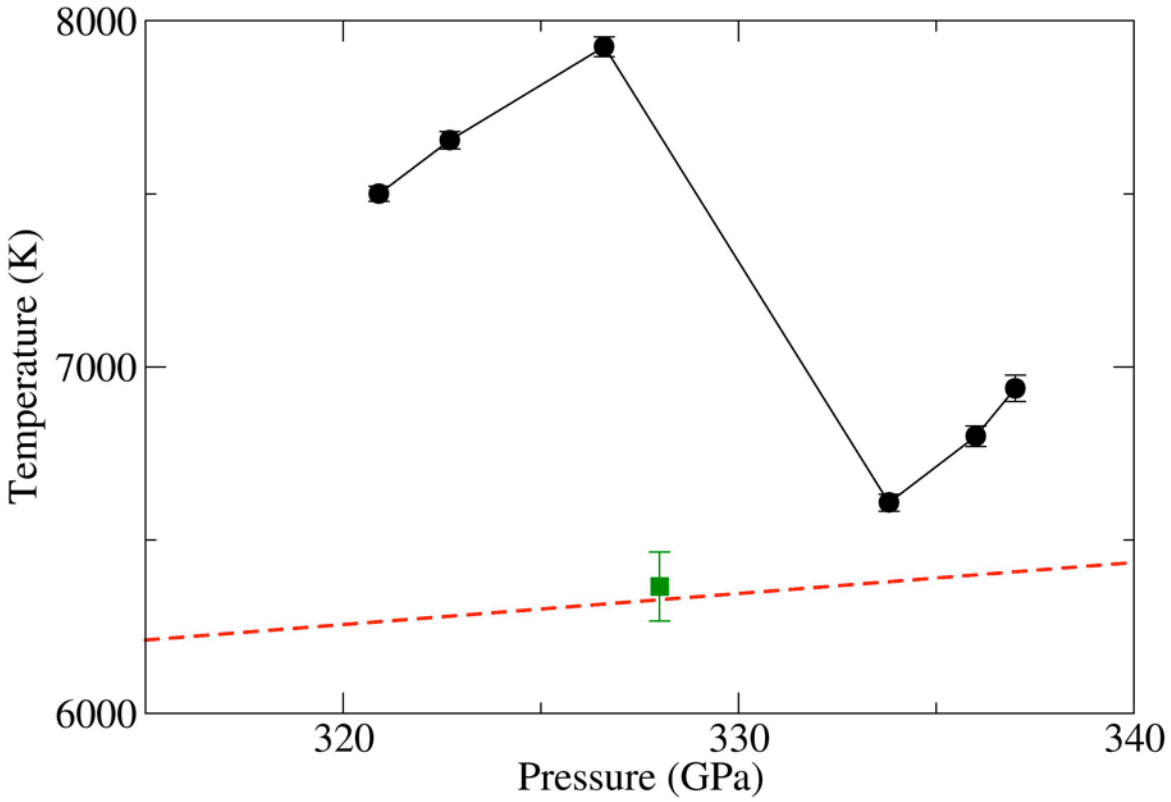


D. Alfe`, C. Cazorla and M. J. Gillan, J. Chem. Phys. ***135****, 024102 (2011)*



D. Alfe`, C. Cazorla and M. J. Gillan, J. Chem. Phys. ***135****, 024102 (2011)*

Fe, DFT, 150 atoms, 50 ps



D. Alfe`, C. Cazorla and M. J. Gillan, J. Chem. Phys. ***135****, 024102 (2011)*

Conclusions

- Methods for phase stability: if applied consistently give the same answer.
- Free energy
  - Small systems if reference potential is good
  - Access to thermodynamics
  - (Human) labour intensive
- Coexistence
  - Computer does most of the work
  - Large systems
  - Only melting
- Z
  - Simple (but really ?)
  - Hundreds (thousands) simulations required
  - Only melting

Acknowledgments

- Simone Taioli (BKF, Trento)
- Claudio Cazorla (ICMAB-CSIC, Barcelona)
- Mike Gillan (UCL)

- EPSRC (HECToR time allocation, UK)
- ORNL (JaguarPF time allocation, USA)