Phase diagrams from ab-initio simulations

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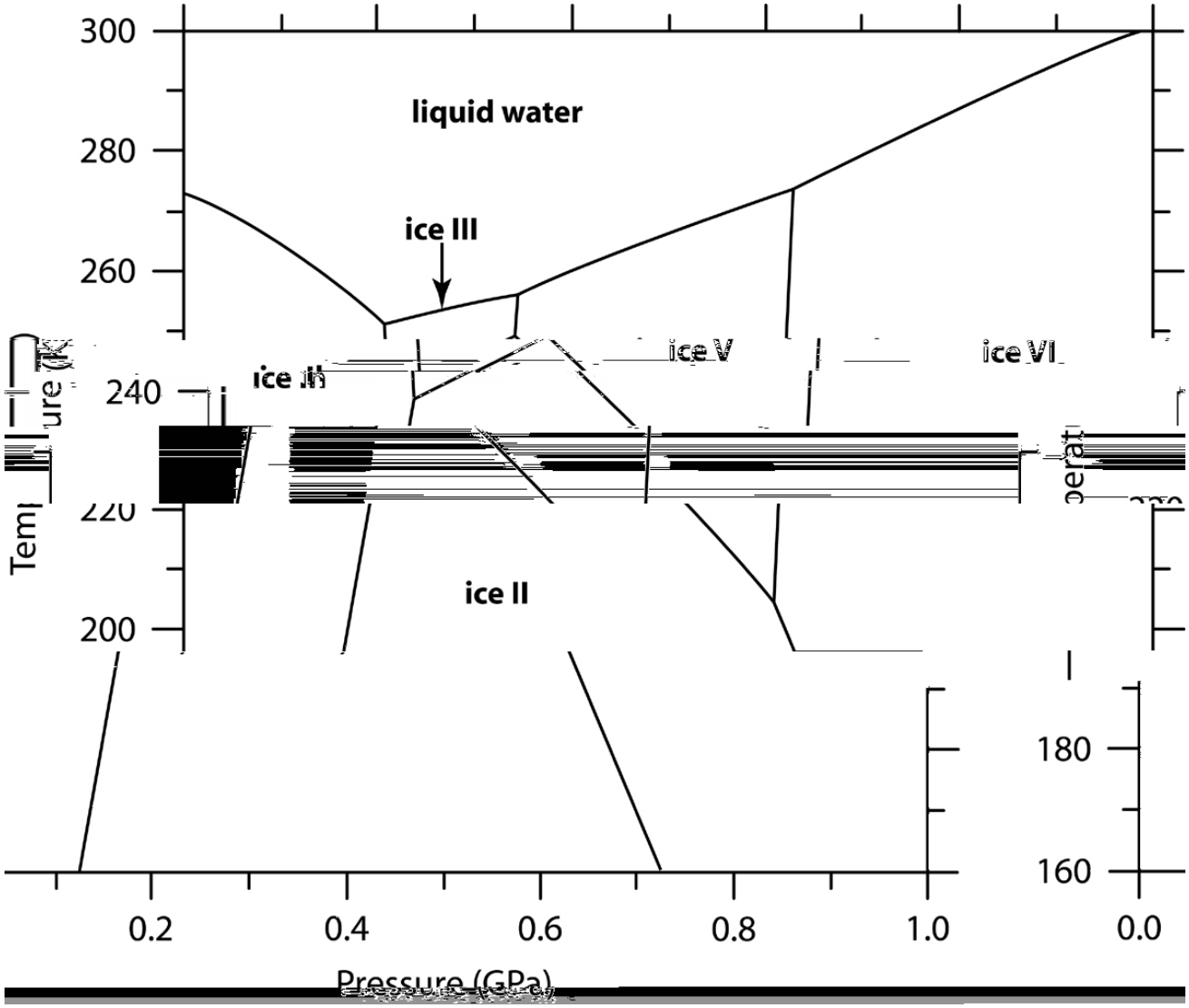
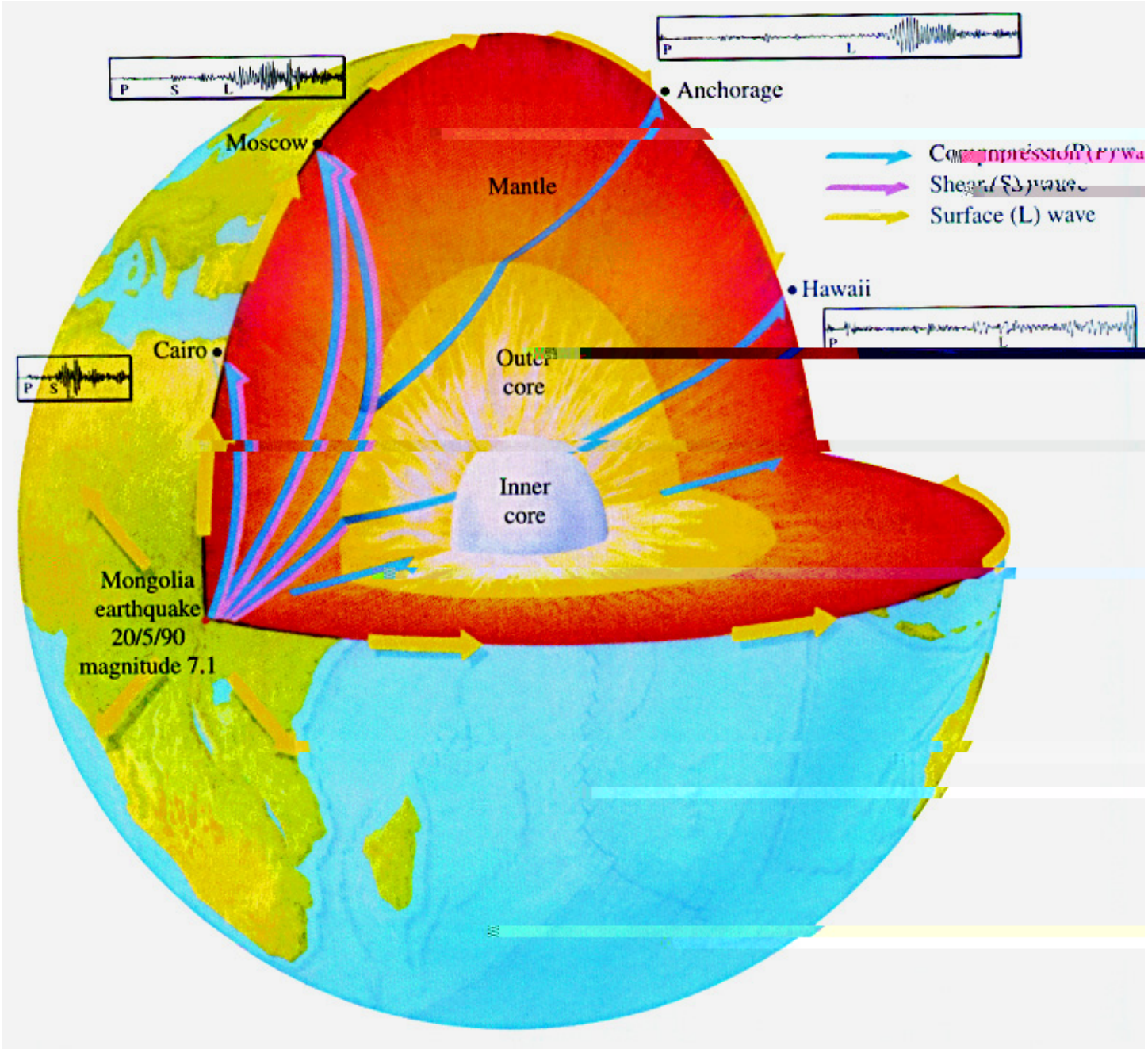
EPSRC Engineering and Physical Sciences Research Council

NATURAL ENVIRONMENT RESEARCH COUNCIL

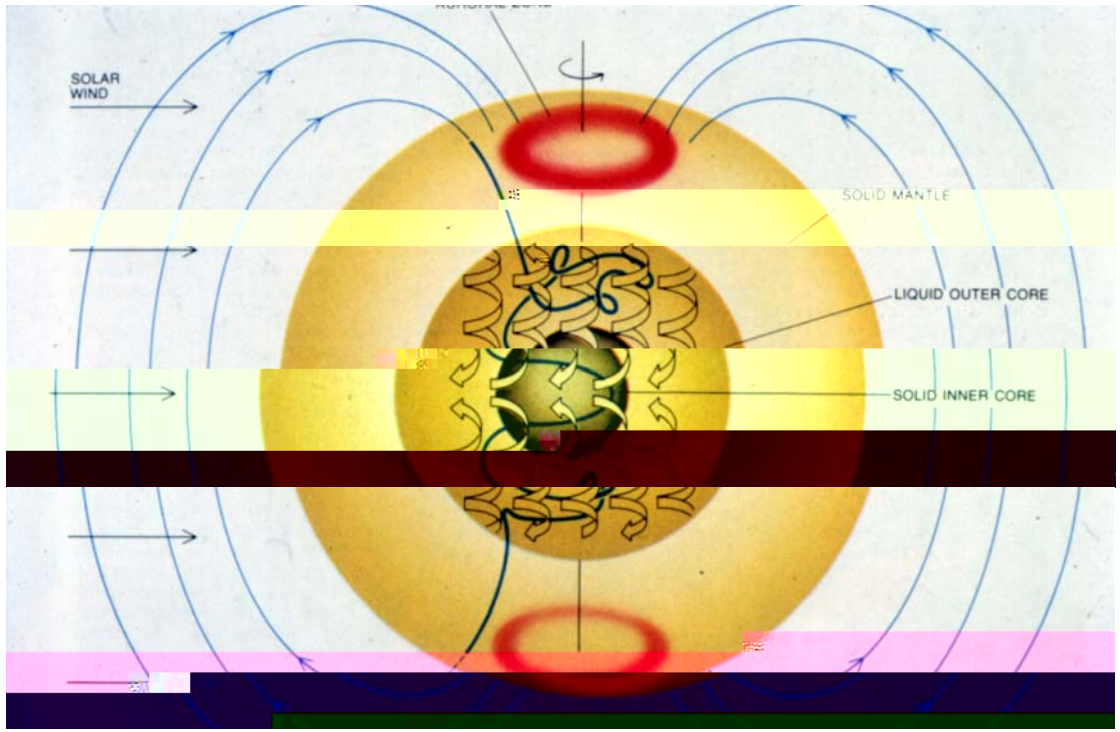
Phase diagram of ice



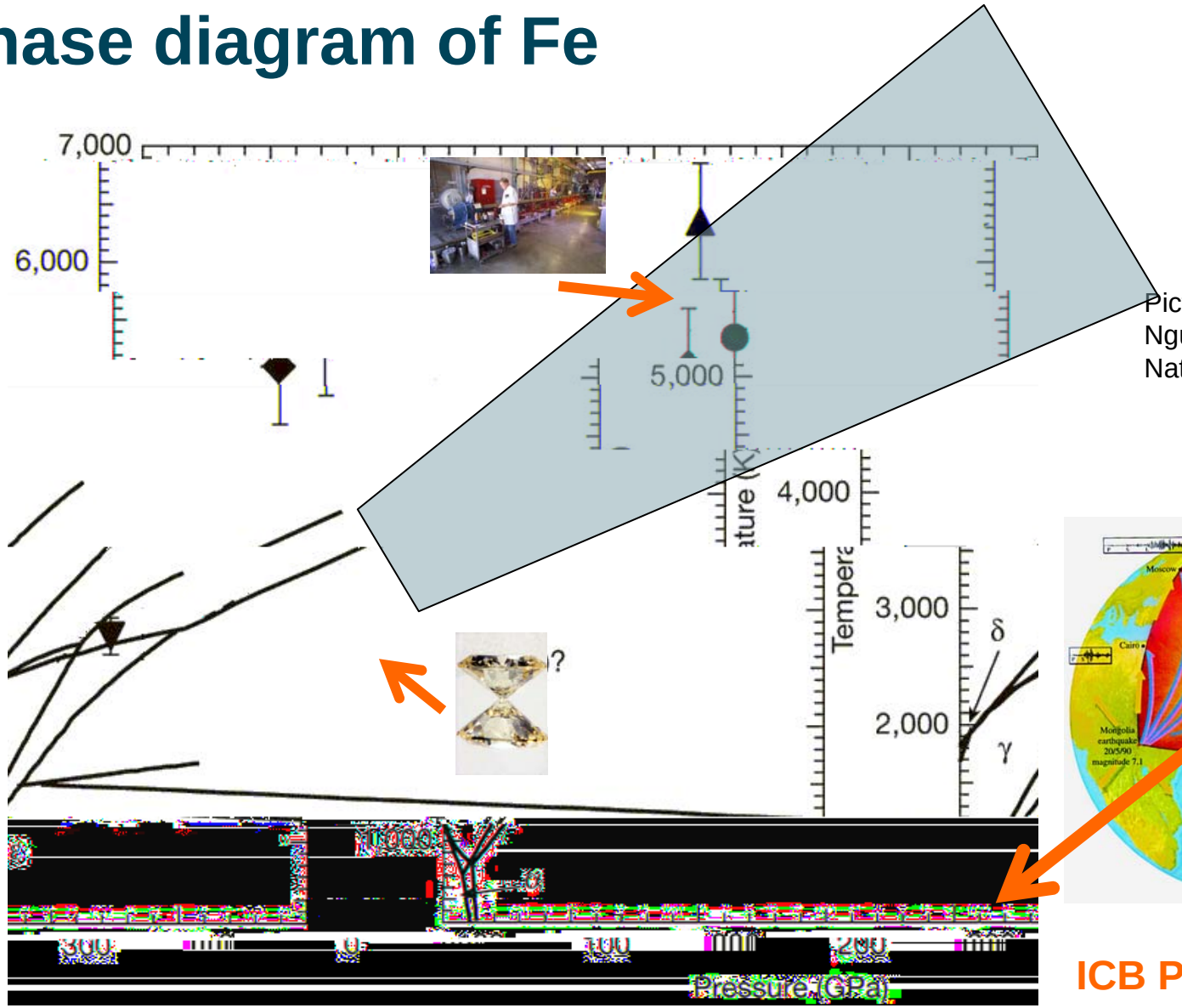

P S L
Moscow
P L
Anchorage
Mantle
Compression (P) wave
Shear (S) wave
Surface (L) wave
Hawaii
P L
Cairo
P S
Outer core
Inner core
Mongolia earthquake 20/5/90 magnitude 7.1

The importance of the Earth's core

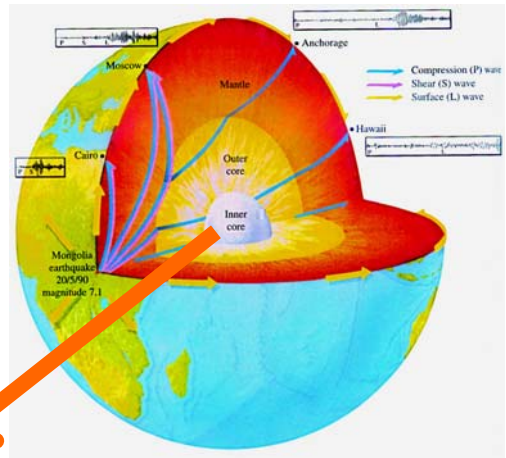
- Contains ~ 30% of the mass and ~ 15% of the volume of the Earth
- The Earth's core is the seat of major global processes.
- Convection in the outer core generates the Earth's magnetic field.
- Heat flow from the core helps drive Mantle convection.



Phase diagram of Fe



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



ICB P = 330 GPa

Theory

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

Quantum mechanics (Schrödinger equation, 1926)

$$H\psi = E\psi$$
$$H = T + V$$
$$\psi = \psi(r_1, \ldots r_N)$$

"The fundamental laws governing most of physics and all of chemistry are now completely known. The only problem is that the solution is much too difficult to be practicable."

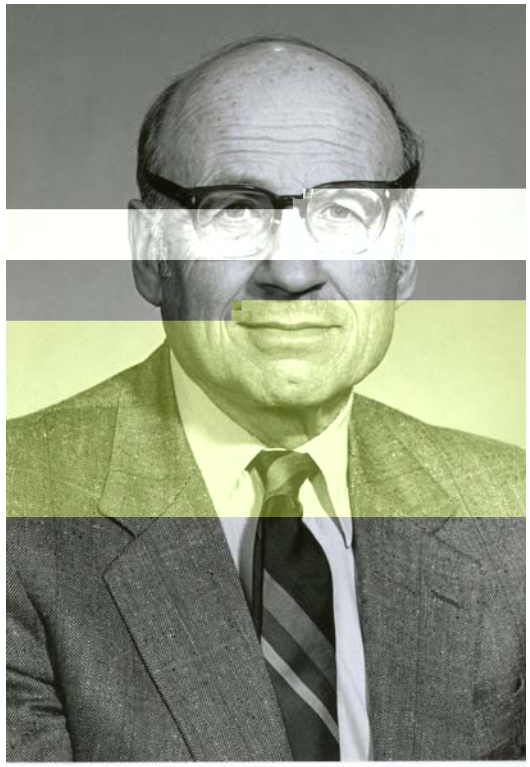
Paul Dirac

1929

Density Functional theory

Hohenberg & Kohn 1964

Kohn & Sham 1965



$$H\psi = E\psi$$

$$\psi(r_1, \ldots r_N)$$

$$\Downarrow$$

$$n(r)$$

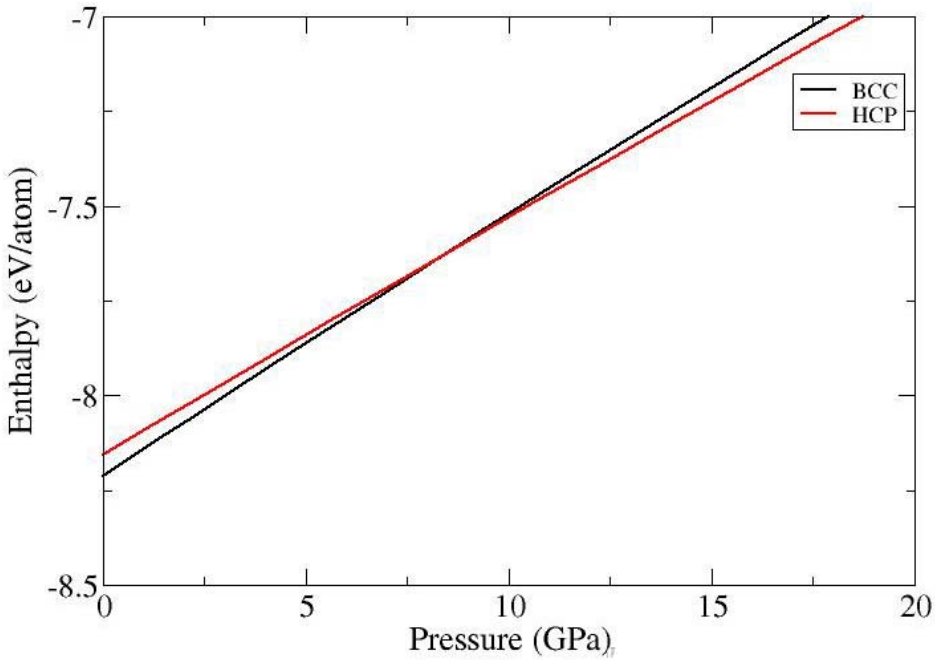
$$H_{KS}\psi_i = E_i\psi_i \quad i = 1, N$$

$$H_{KS} = T + V + V_H + V_{XC}$$

Phase stability:
Zero temperature

- Energy:
  - Internal energy: $E(V)$
  - Enthalpy: $H(p) = E(V) + pV$

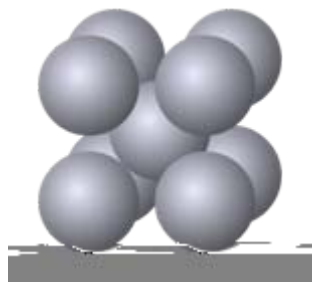
$$p = -dE/dV$$



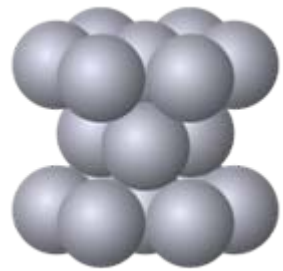
Equation of state (e.g. Birch-Murnaghan, Phys. Rev. **71**, 809 [1947]):

$$E(V) = E_0 + \frac{3}{2}V_0 K_0 \left[\frac{3}{4}(1+2\xi)\left(\frac{V_0}{V}\right)^{4/3} - \frac{\xi}{2}\left(\frac{V_0}{V}\right)^{2} - \frac{3}{2}(1+\xi)\left(\frac{V_0}{V}\right)^{2/3} + \frac{1}{2}\right]\xi + \frac{3}{2}$$

Body centred cubic (bcc)



Hexagonal closed packed (hcp)

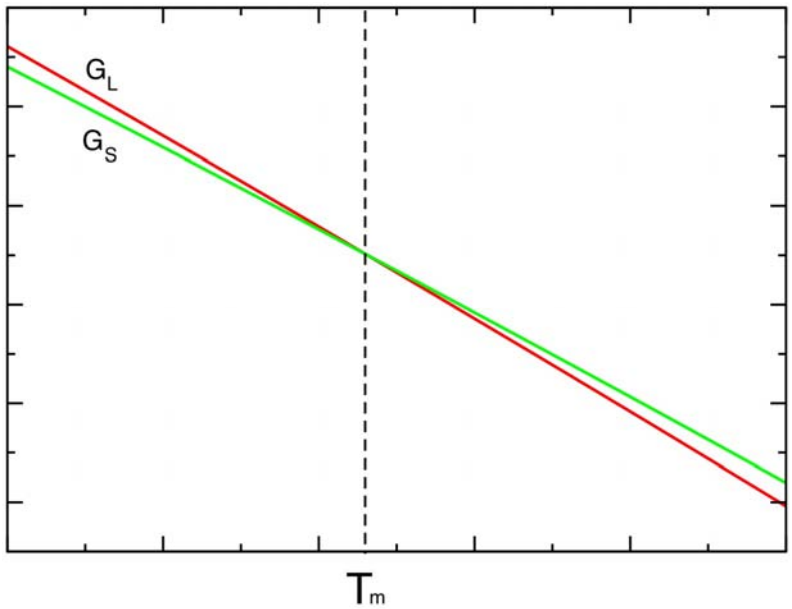


Finite temperature

- Free Energy:
  - Helmholtz free energy: $F(V,T) = E(V,T) - TS(V,T)$
  - Gibbs free energy: $G(p,T) = F(V,T) + pV$

$$p = -dF/dV$$

e.g. Melting:



The Helmholtz free energy

Solids: Low T

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

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

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

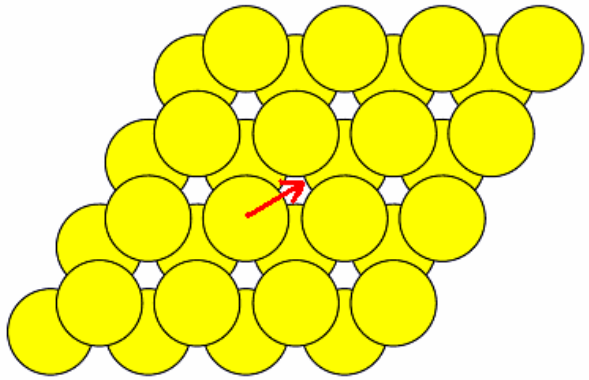
Force constant matrix: $F_\alpha(\quad) = \quad{}_\alpha(\quad\quad')\,u(\quad')$

$',$

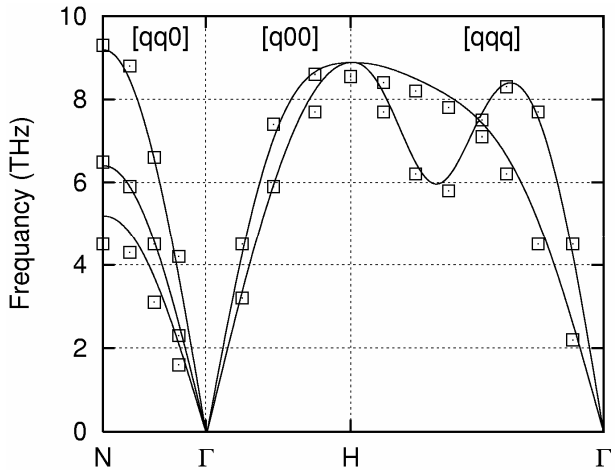
Small displacement method:

PHON code, freely available at:
http://chianti.geol.ucl.ac.uk/~dario

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



DFT phonons of Fe:



The Helmholtz free energy

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Liquids:

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

Thermodynamic integration

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

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

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

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

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

Thermodynamic integration

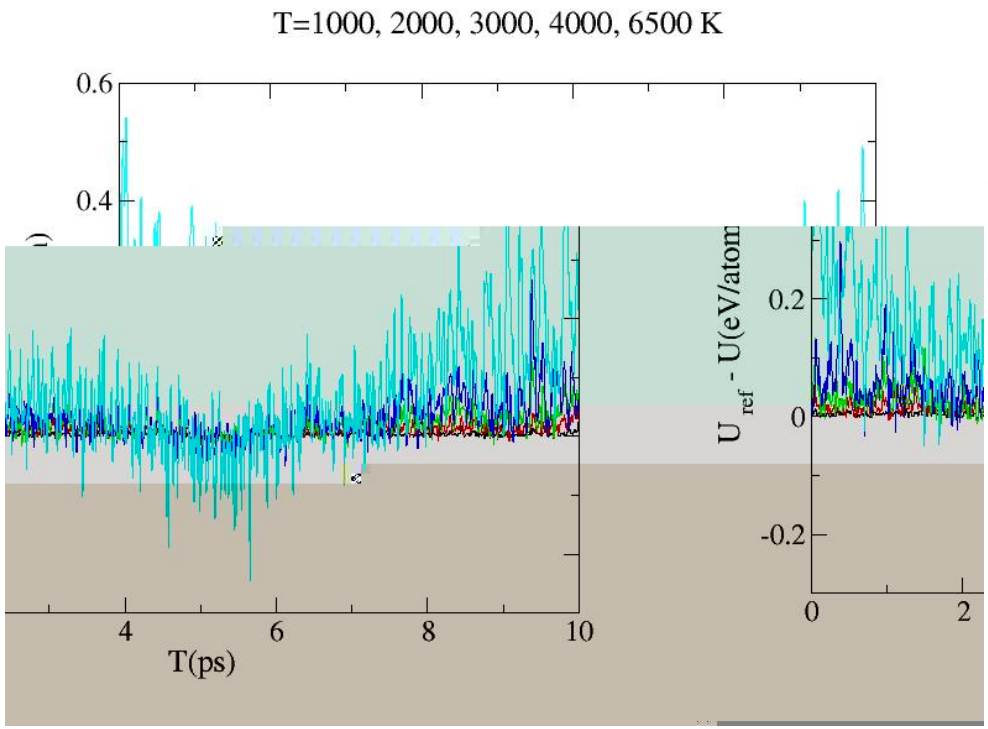
$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda$$

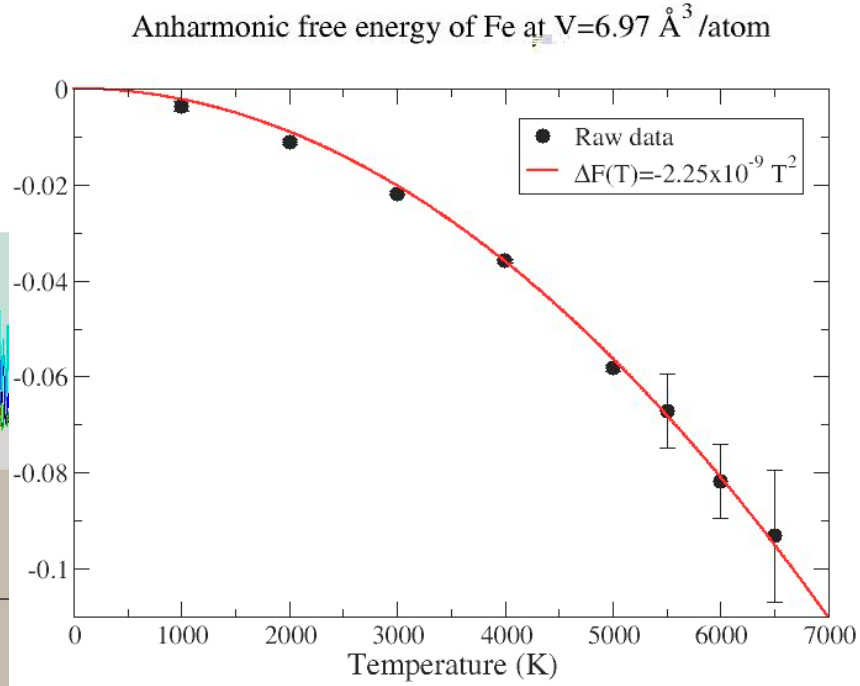
$$F = F_{ref} + \int_0^1 d\lambda \, \langle U - U_{ref} \rangle_\lambda = F_{ref} +$$

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

$$F = F_{harm} + \int_0^T dt \frac{d\lambda}{dt}\left(U - U_{harm}\right)_\lambda$$

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





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:

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

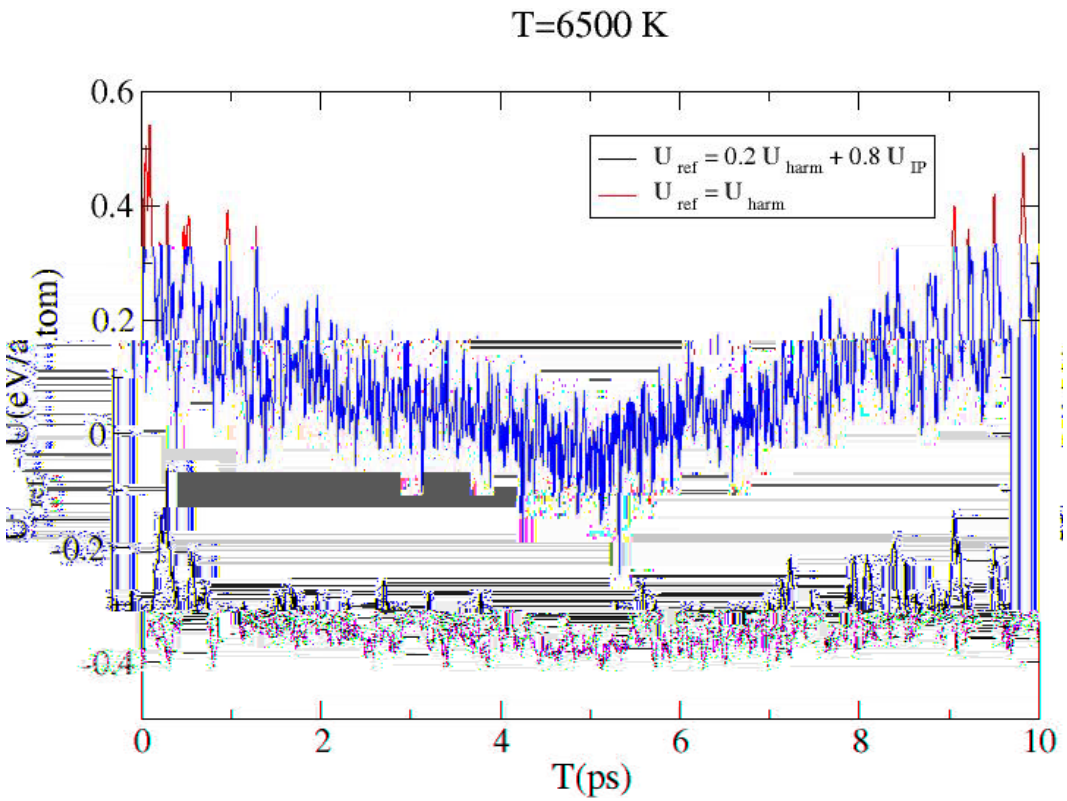
$$U_{harm} = \frac{1}{2} \sum_{i\alpha, j\beta} u_{i\alpha} \Phi_{i\alpha, j\beta} u_{j\beta}$$

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

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



Thermodynamic integration, a perturbative approach:

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

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

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

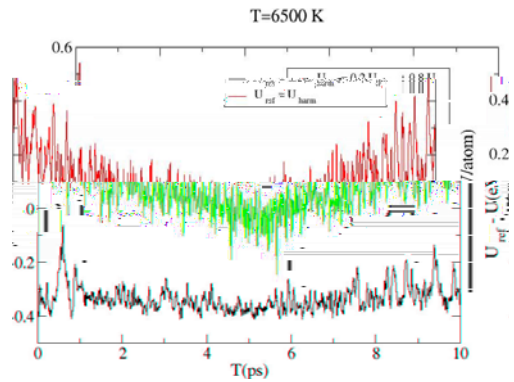
$$-\frac{1}{k_B T} \frac{\int_V dR \, \left(\frac{\partial U_\lambda}{\partial \lambda} \right)^2 e^{-U_\lambda(R)/k_B T}}{\int_V dR \, e^{-U_\lambda(R)/k_B T}} - \left(\frac{\int_V dR \, \frac{\partial U_\lambda}{\partial \lambda} e^{-U_\lambda(R)/k_B T}}{\int_V dR \, e^{-U_\lambda(R)/k_B T}} \right)^2 = -\frac{1}{k_B T} \left\langle \delta \Delta U_\lambda^2 \right\rangle_\lambda$$

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

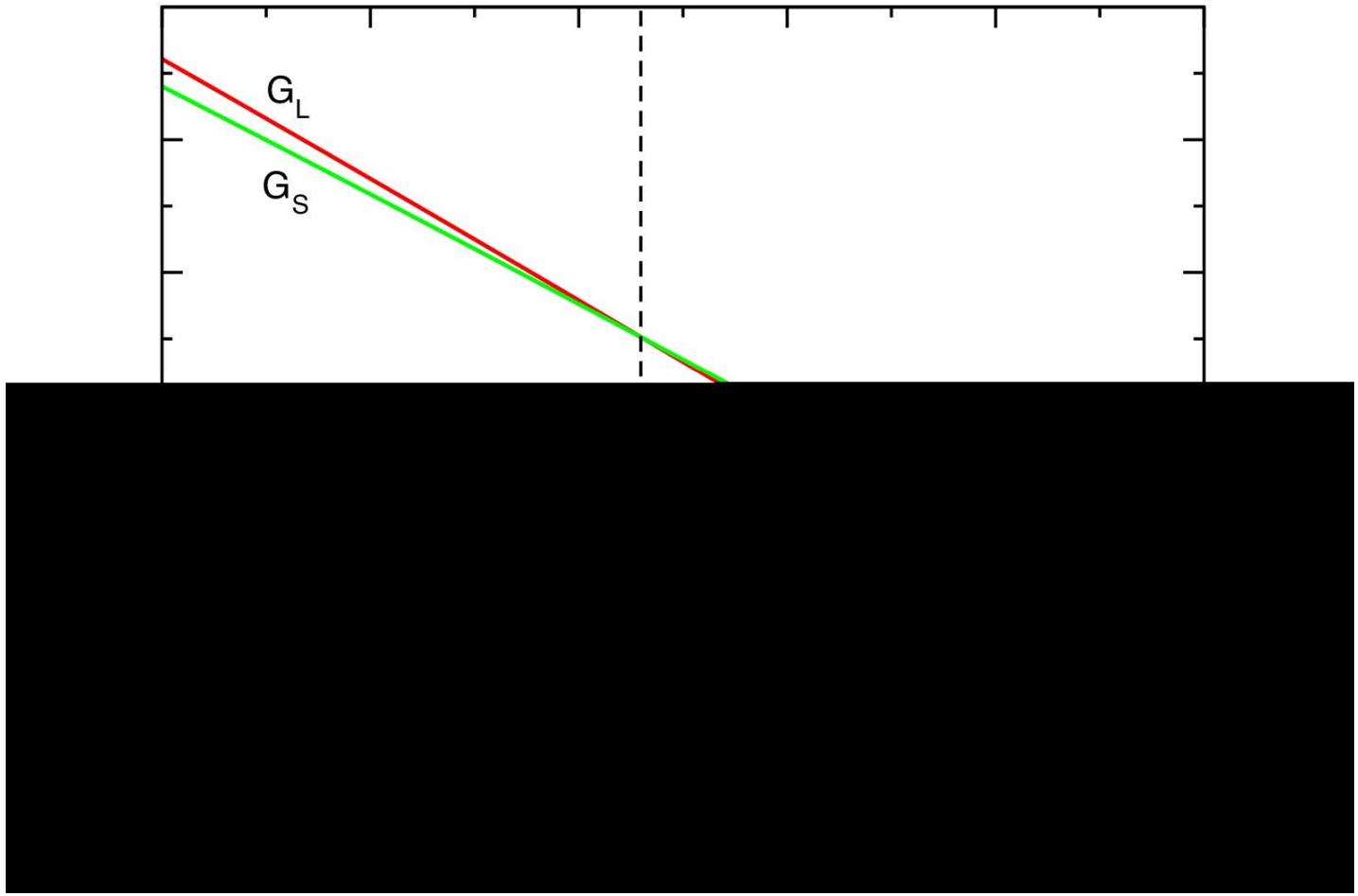
$$\left\langle U - U_{ref} \right\rangle_\lambda = \left\langle U - U_{ref} \right\rangle_{\lambda=0} - \frac{\lambda}{k_B T}\left\langle \delta\Delta U_0^2 \right\rangle_0 + o(\lambda^2)$$

$$\int_0^1 d\lambda \left\langle U - U_{ref} \right\rangle_\lambda \quad \left\langle U - U_{ref} \right\rangle_{\lambda=0} - \frac{1}{2k_B T}\left\langle \delta\Delta U_0^2 \right\rangle_0$$

Only need to run simulations with one potential (the reference potential for example).



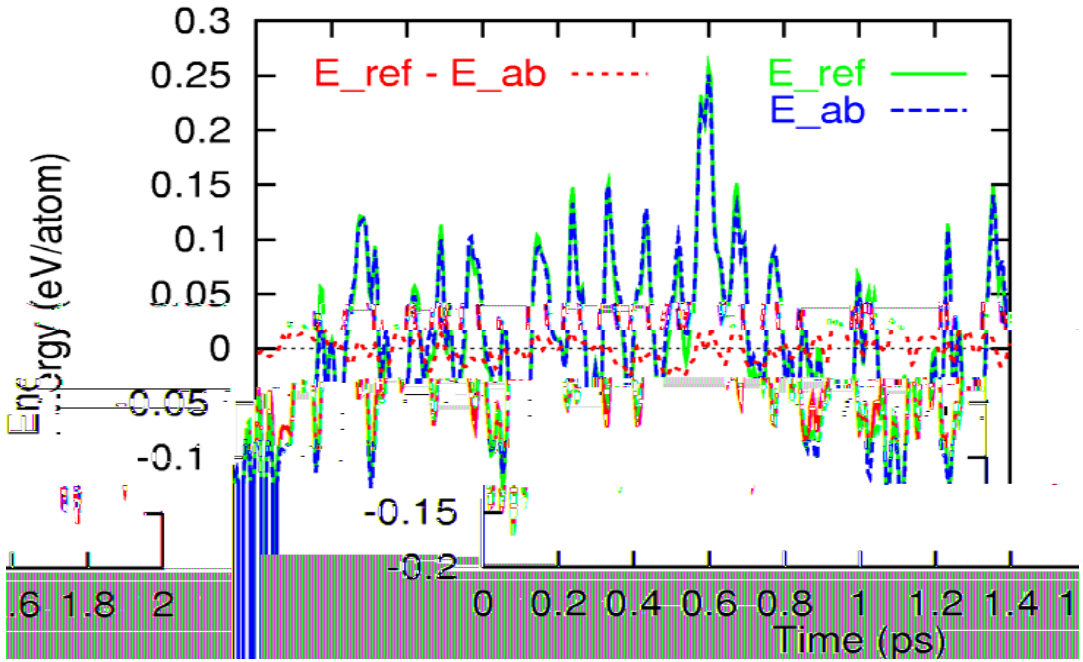
Melting of Fe

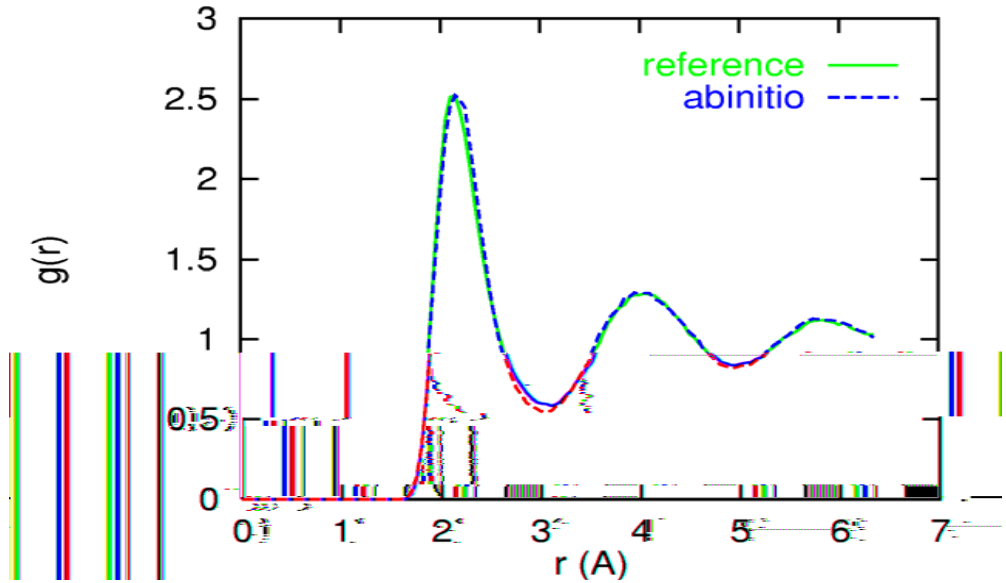


Liquid Fe

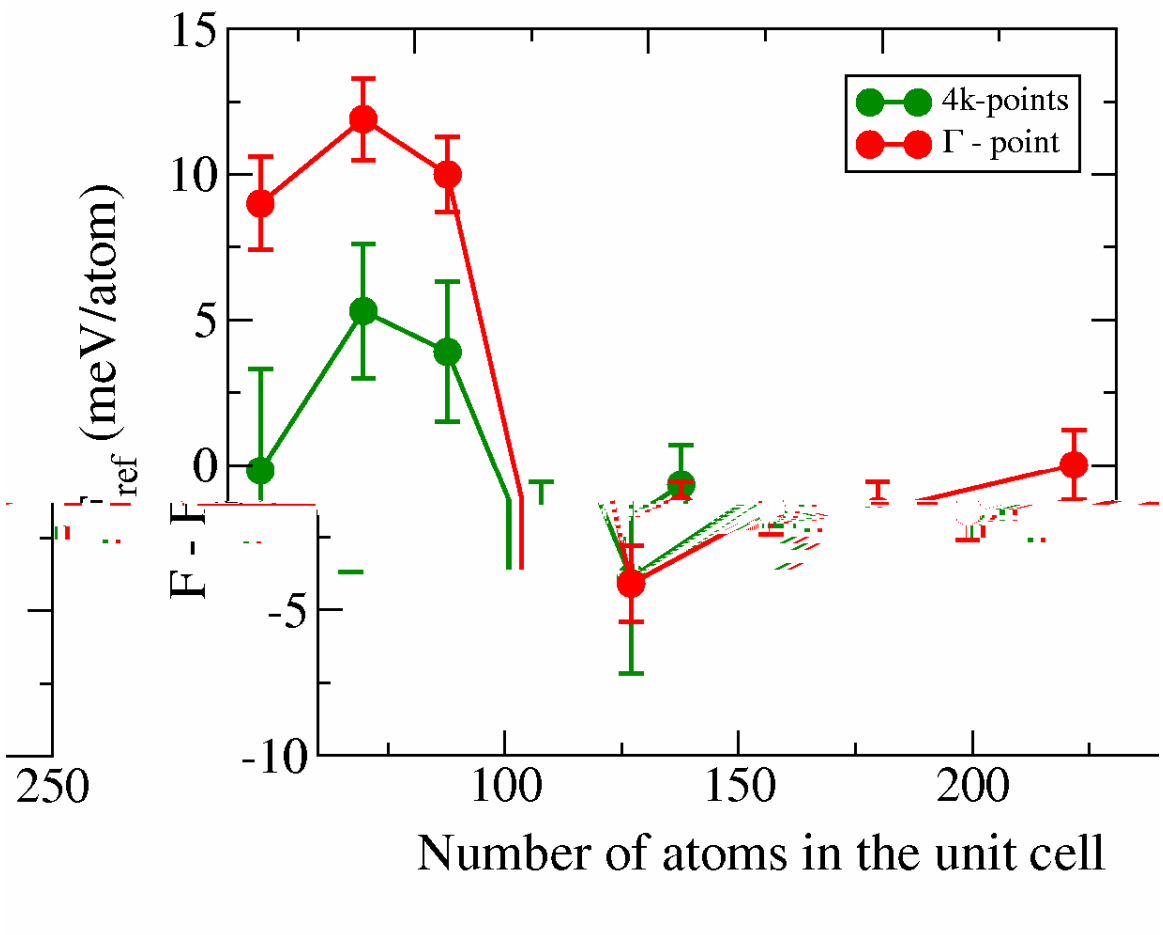
$$U_{ref} = \frac{1}{2}\sum_{i \neq j} \frac{A}{\left|r_i - r_j\right|^B}$$

$$B = 5.86$$



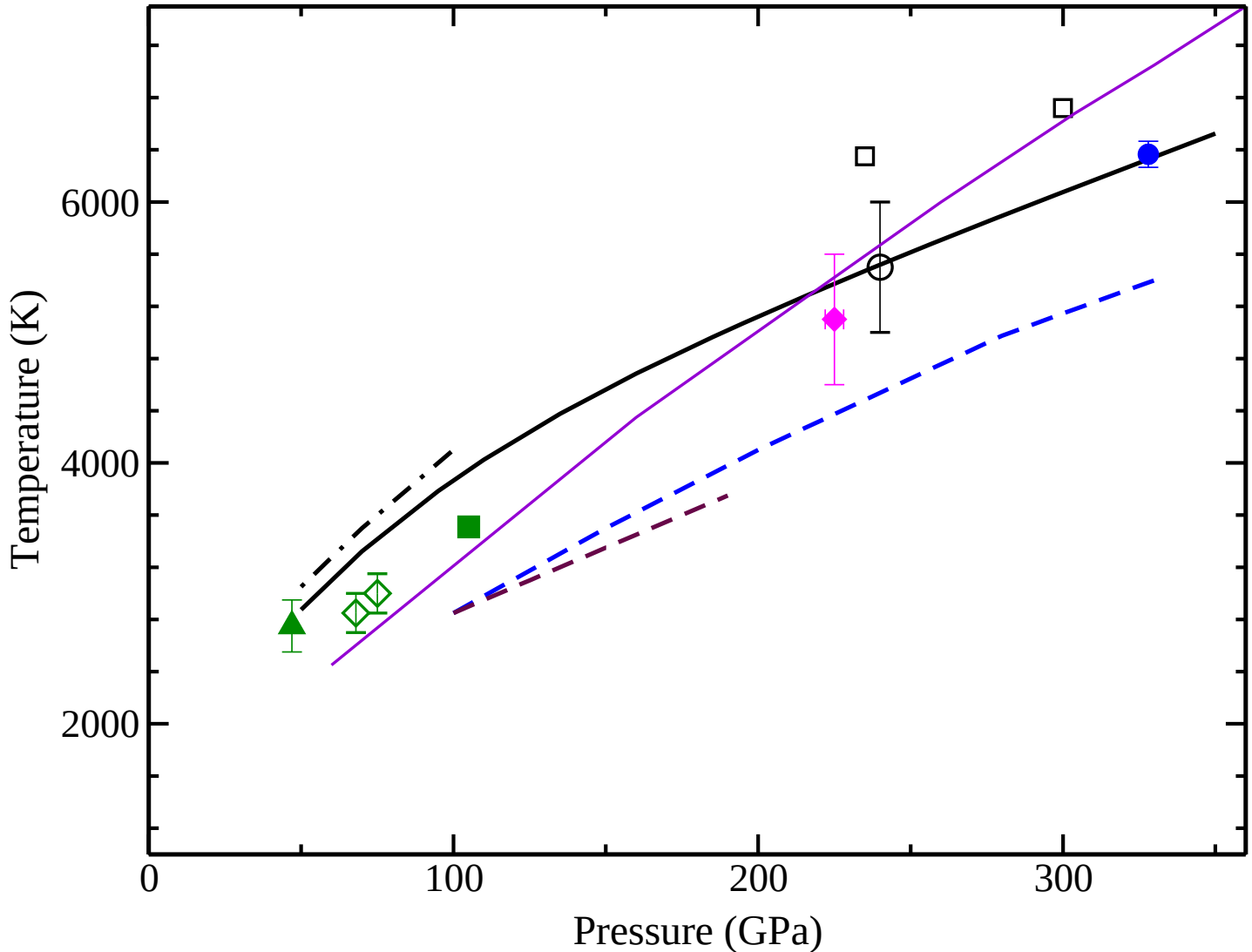


Size tests

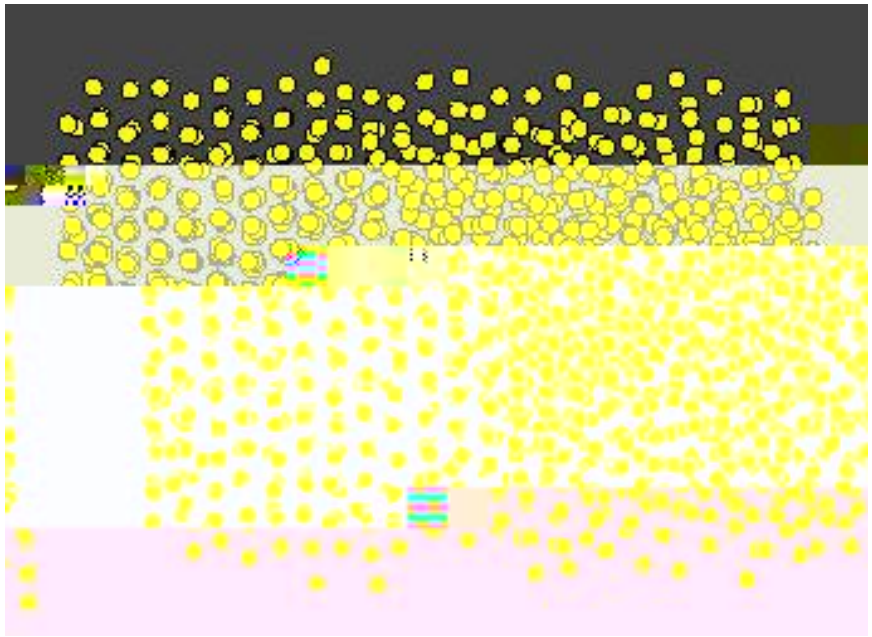


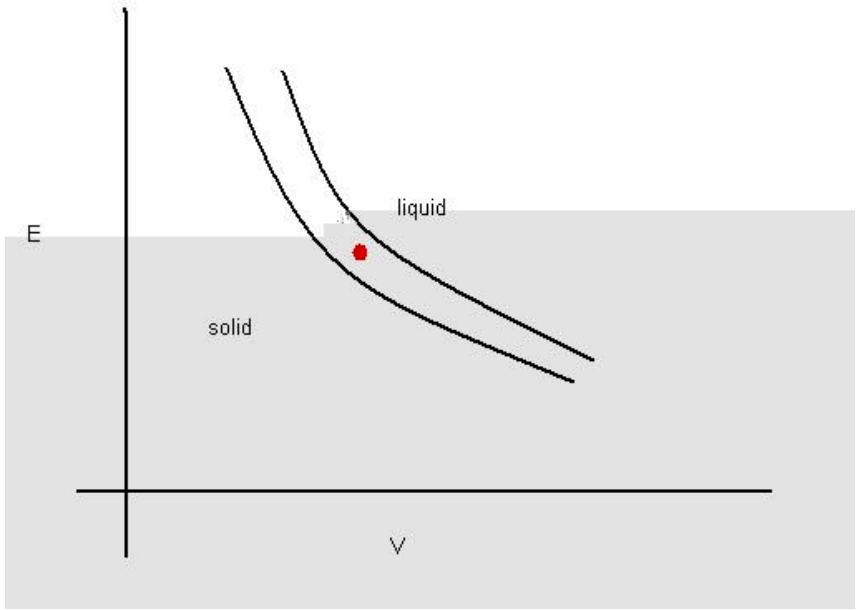
$$\Delta T \approx 100\ K \ \rightarrow\ \Delta G \approx 10\ meV\ /\ atom$$

The melting curve of Fe

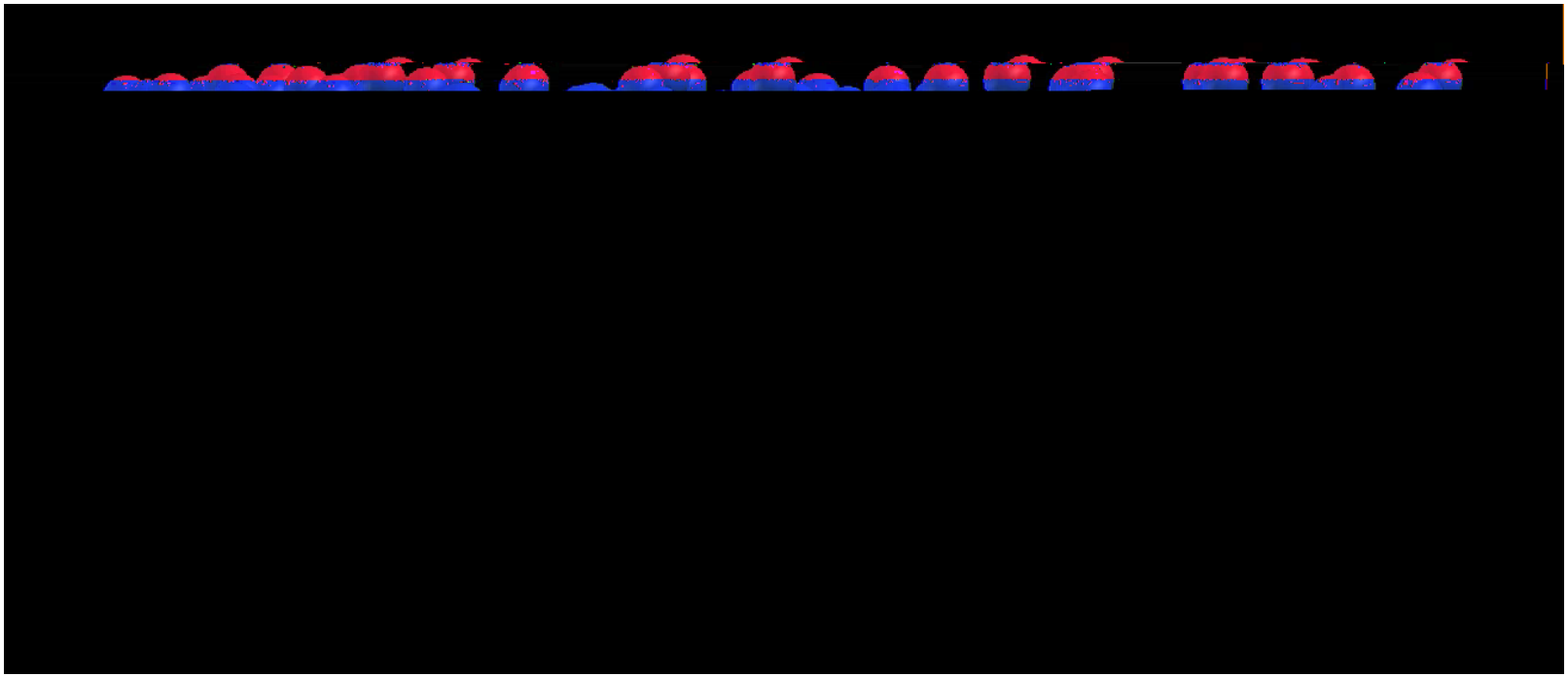


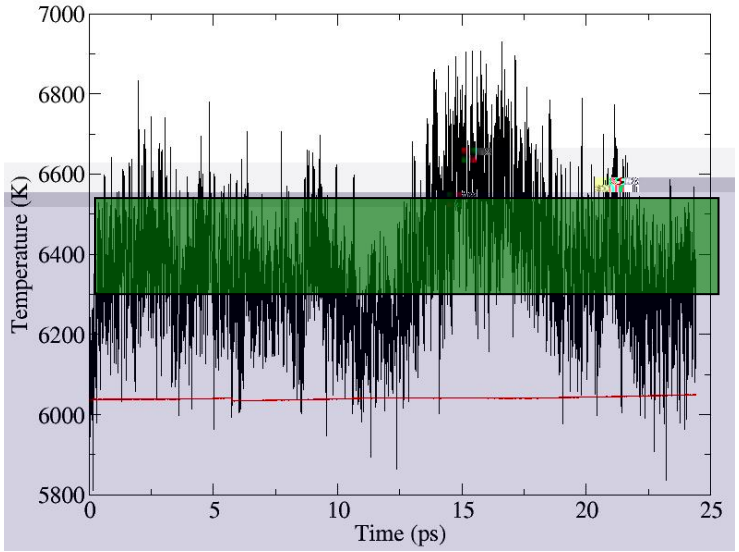
Melting: coexistence of phases

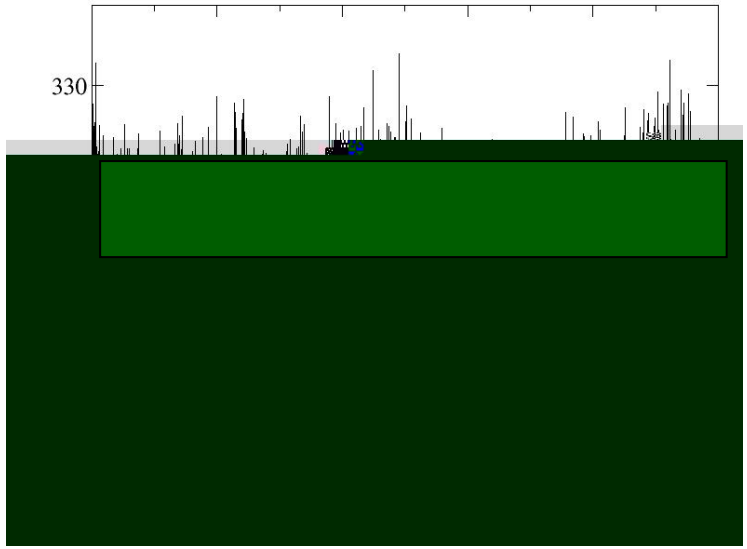




NVE ensemble: for fixed V, if E is between solid and liquid values, simulation will give coexisting solid and liquid



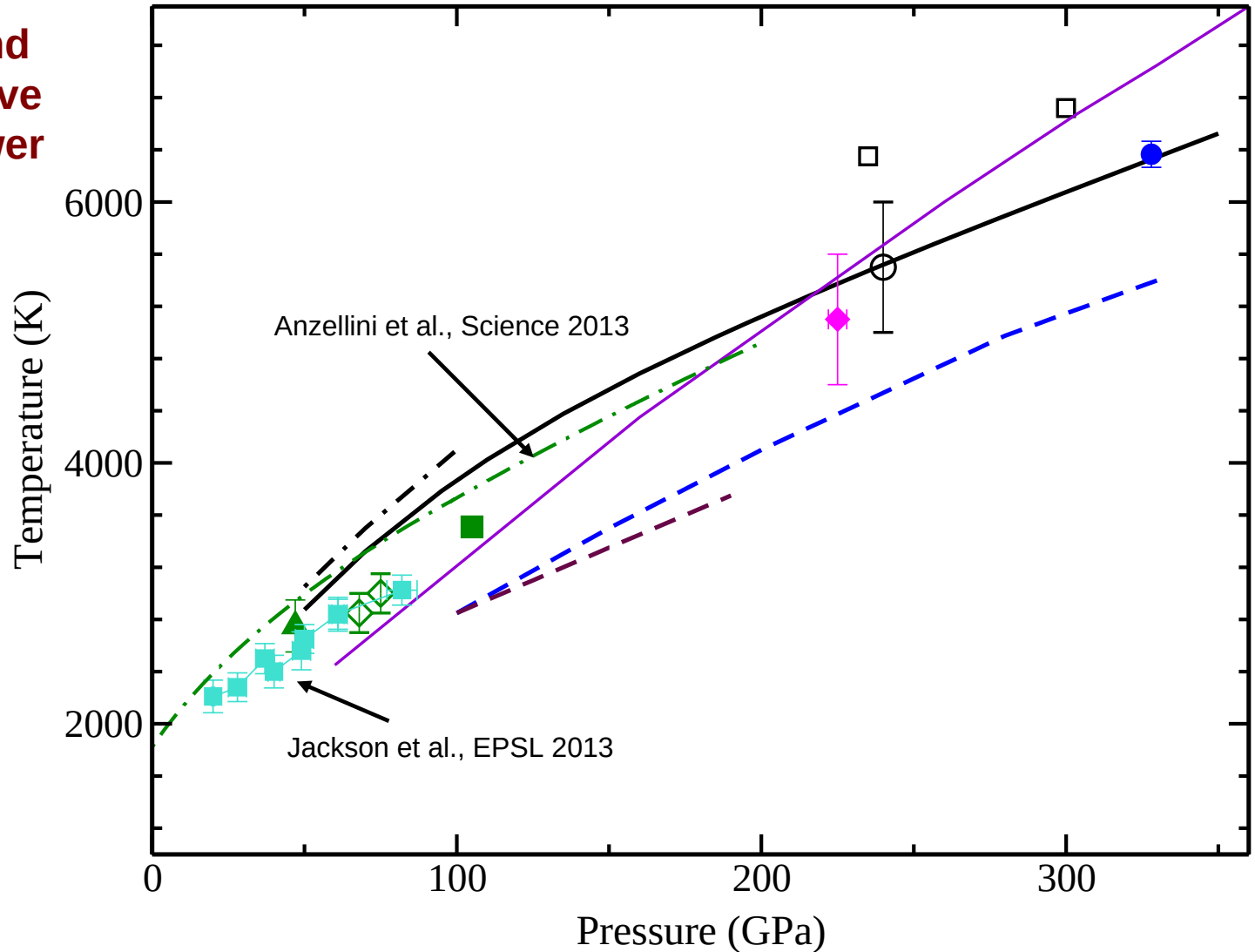




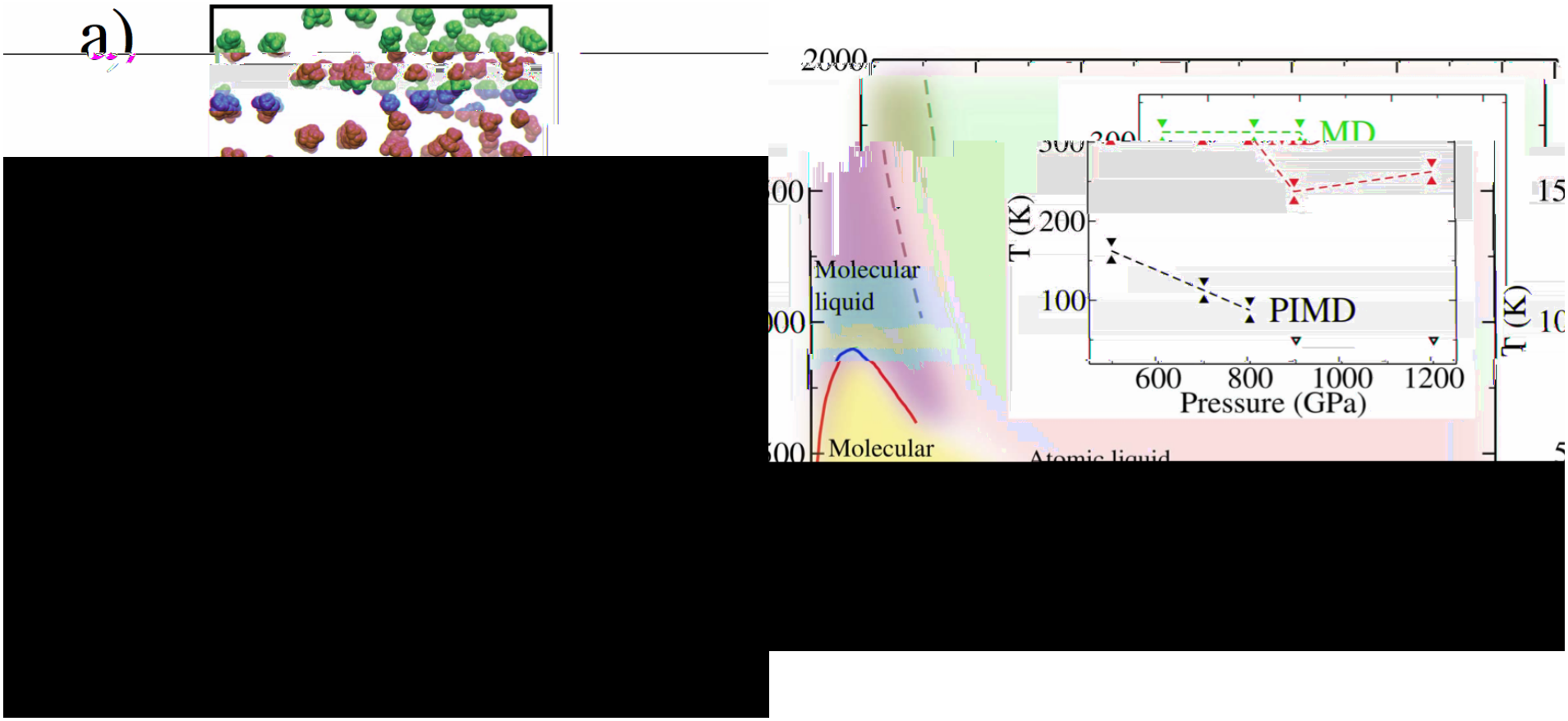
*D. Alfè, Phys. Rev. B, **79**, 060601(R) (2009)*

The melting curve of Fe

Free energy and coexistence give the same answer



Melting curve of H



J. Chen, X-Z Li et al. Nature Comm. 2013

Theory

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

Quantum Monte Carlo

Variational Monte Carlo:

Energy E_V depends on $_T$

$$E_V = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \geq E_0$$

Diffusion Monte Carlo:

$$-\frac{\partial \phi(\mathbf{x},t)}{i\partial t} = \left(\hat{H} - E_T\right)\phi(\mathbf{x},t)$$

Extracting the ground state: substitute $= it$

$$-\frac{\partial \phi(\mathbf{x},\tau)}{\partial \tau} = \frac{1}{2}\sum_{i=1}^{N} \Delta_i \phi(\mathbf{x},\tau) + (V - E_T)\phi(\mathbf{x},\tau)$$

$$\tau \to \infty, \quad \phi(\mathbf{x},\tau) \to \Phi_0(\mathbf{x})$$

Imaginary time Schroedinger equation with $V = 0$: Diffusion equation

$$-\frac{\partial\phi(\mathbf{x},\tau)}{\partial\tau} = \frac{1}{2}\sum_{i=1}^{N}\Delta_i\phi(\mathbf{x},\tau)$$

$_i = 0$: Rate equation

$$-\frac{\partial\phi(\mathbf{x},\tau)}{\partial\tau} = (V - E_T)\phi(\mathbf{x},\tau)$$

Diffusing particles (walkers) with birth/death process

$\leftrightarrow$

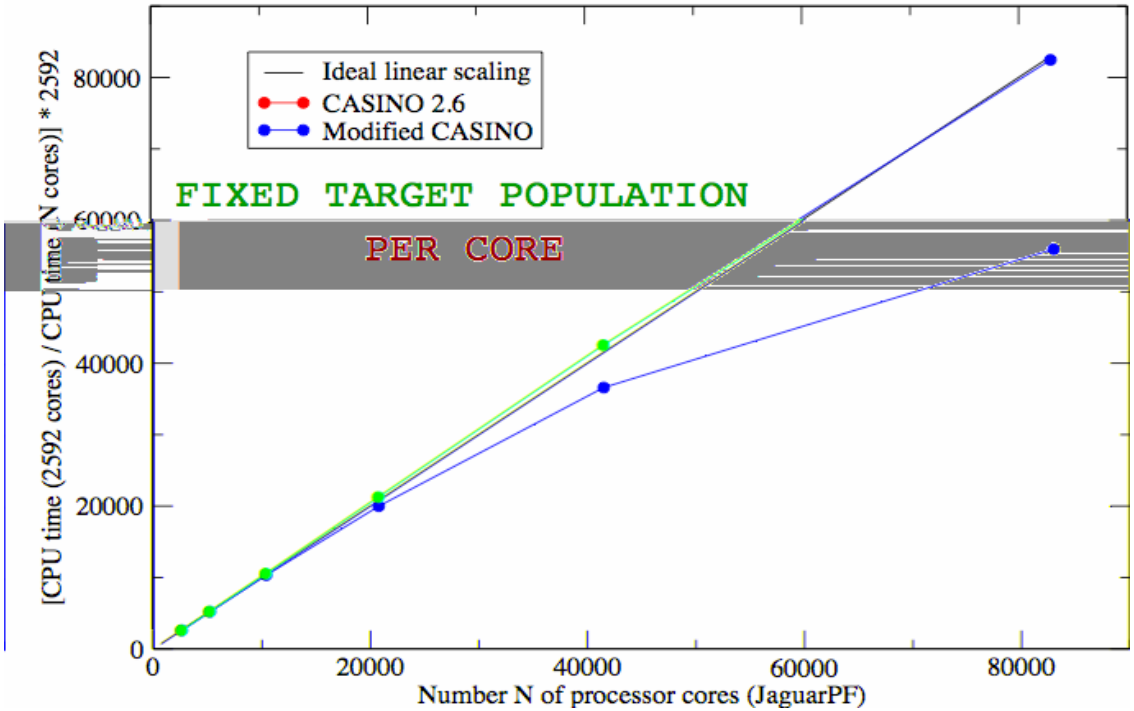
distribution function

Approximations:

- Fixed nodes approximation:
- Pseudopotentials (locality approximation)

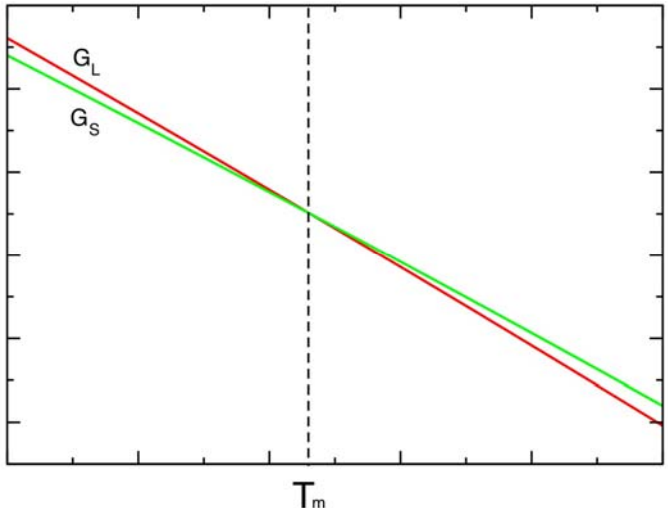
DMC is ~ 10^4 times more expensive than DFT

QMC scaling on JaguarPF (Cray XT6, 300,000 cores at ONRL)



M.J. Gillan, M.D. Towler and D. Alfè, "*Petascale computing opens new vistas for quantum Monte Carlo*", Psi-k Highlight of the Month, February 2011.

Melting of Fe from QMC:



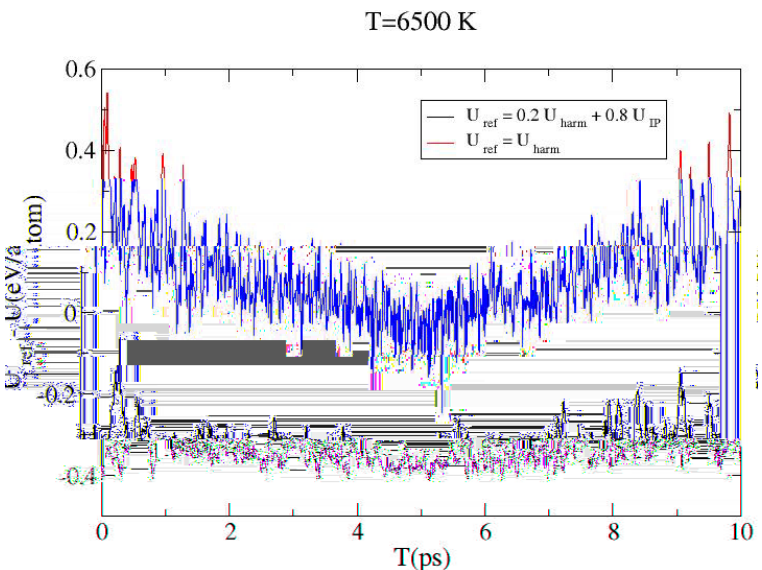
Free energy corrections from DFT to QMC:

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

Thermodynamic integration, a perturbative approach:

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

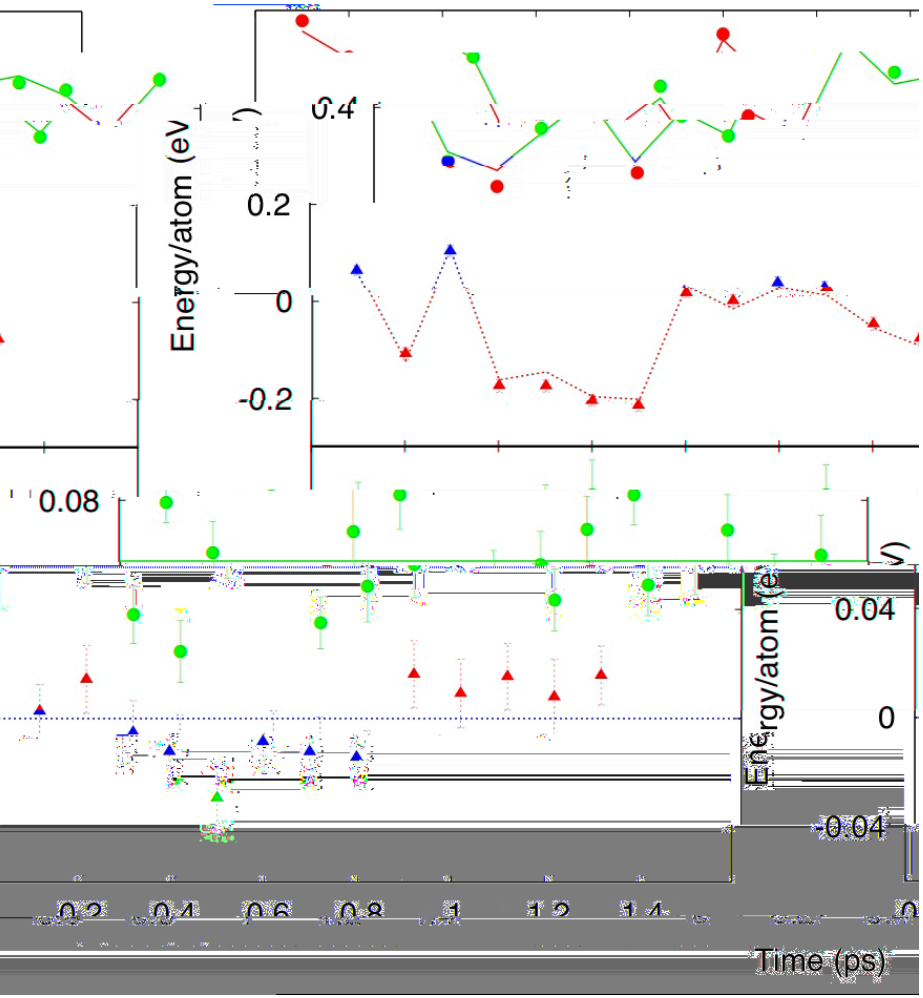
$$\left\langle U - U_{ref} \right\rangle_\lambda = \left\langle U - U_{ref} \right\rangle_{\lambda=0} + \lambda \left. \frac{\partial \left\langle U - U_{ref} \right\rangle_\lambda}{\partial \lambda} \right|_{\lambda=0} + o(\lambda^2)$$



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

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

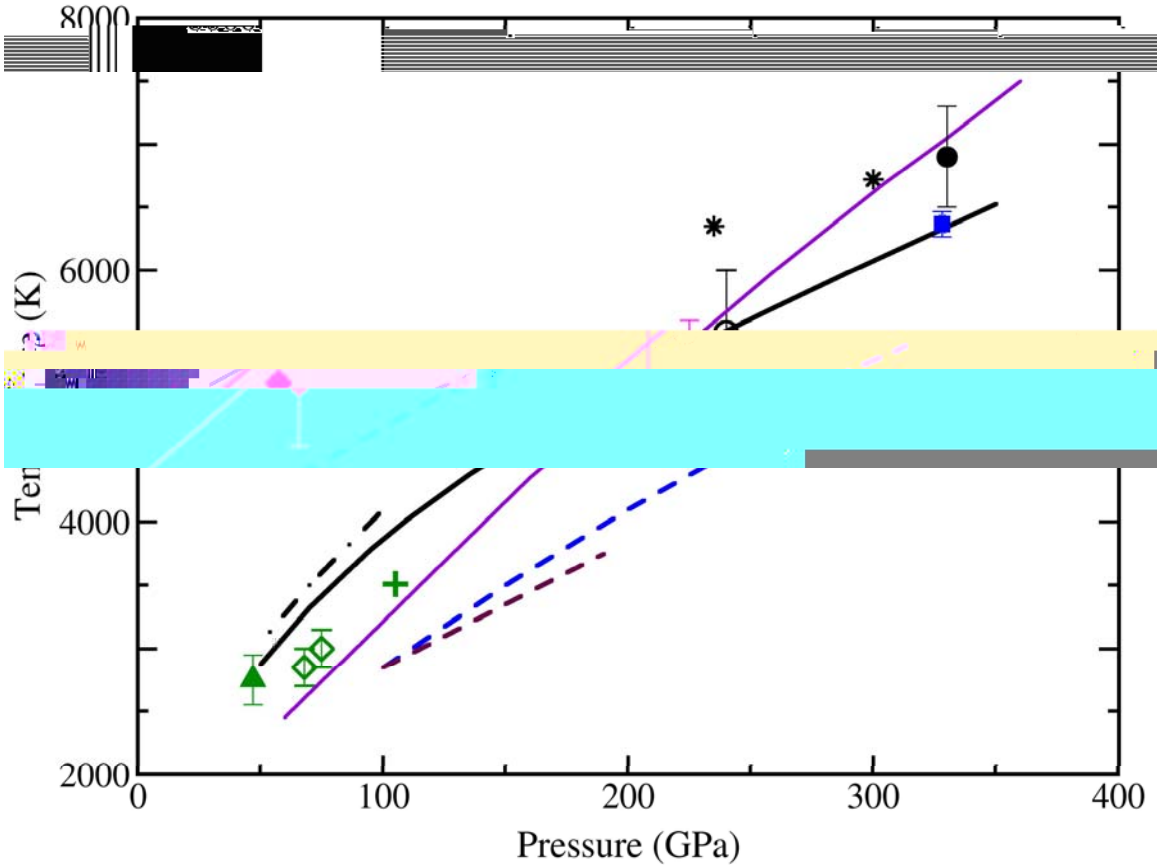
QMC correction to the DFT Fe melting curve



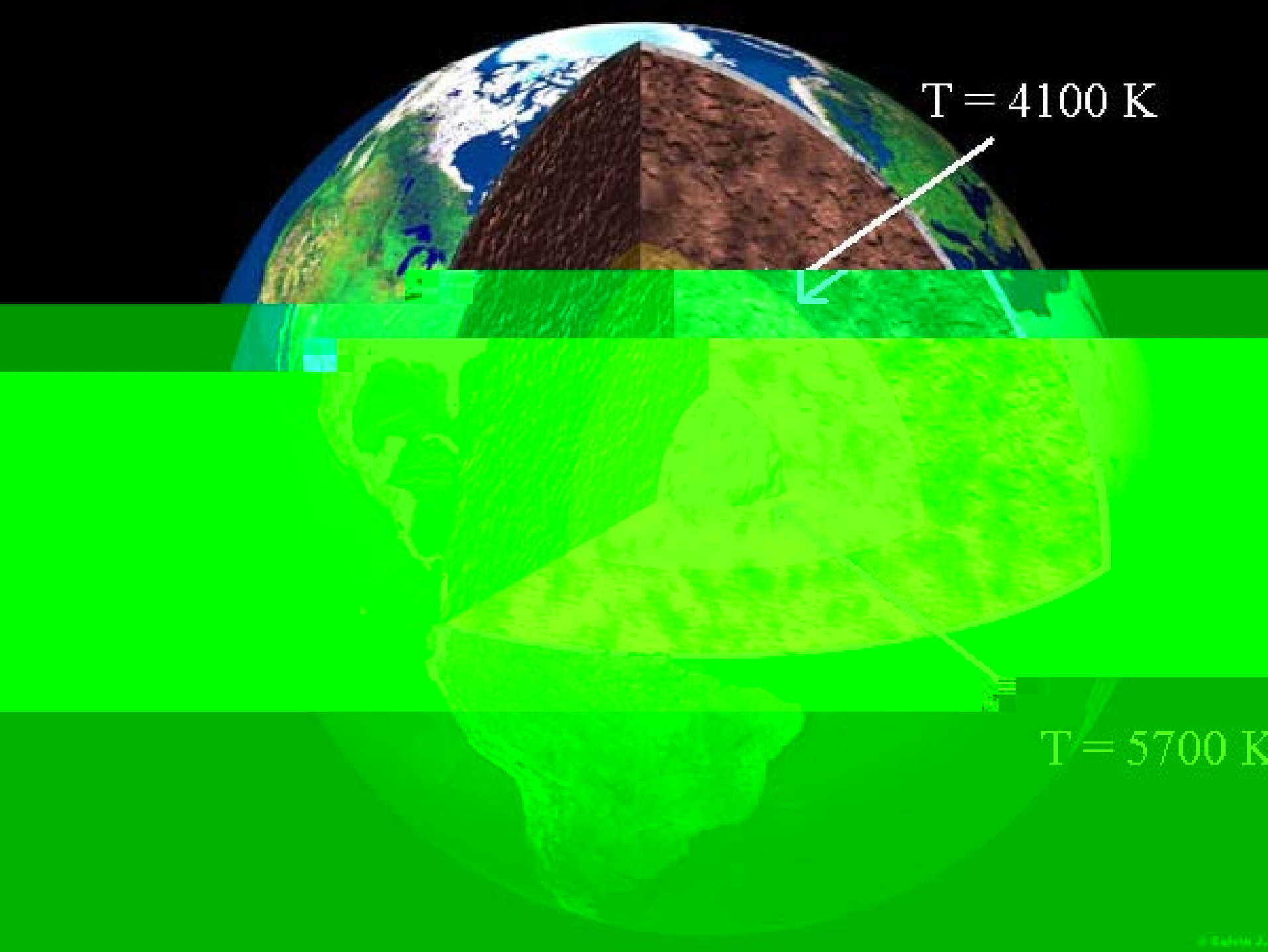
$$\Delta G^{ls}(T_m^{ref}) = 0.05 \pm 0.02 \text{ eV/atom}$$

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

Melting curve of Fe



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

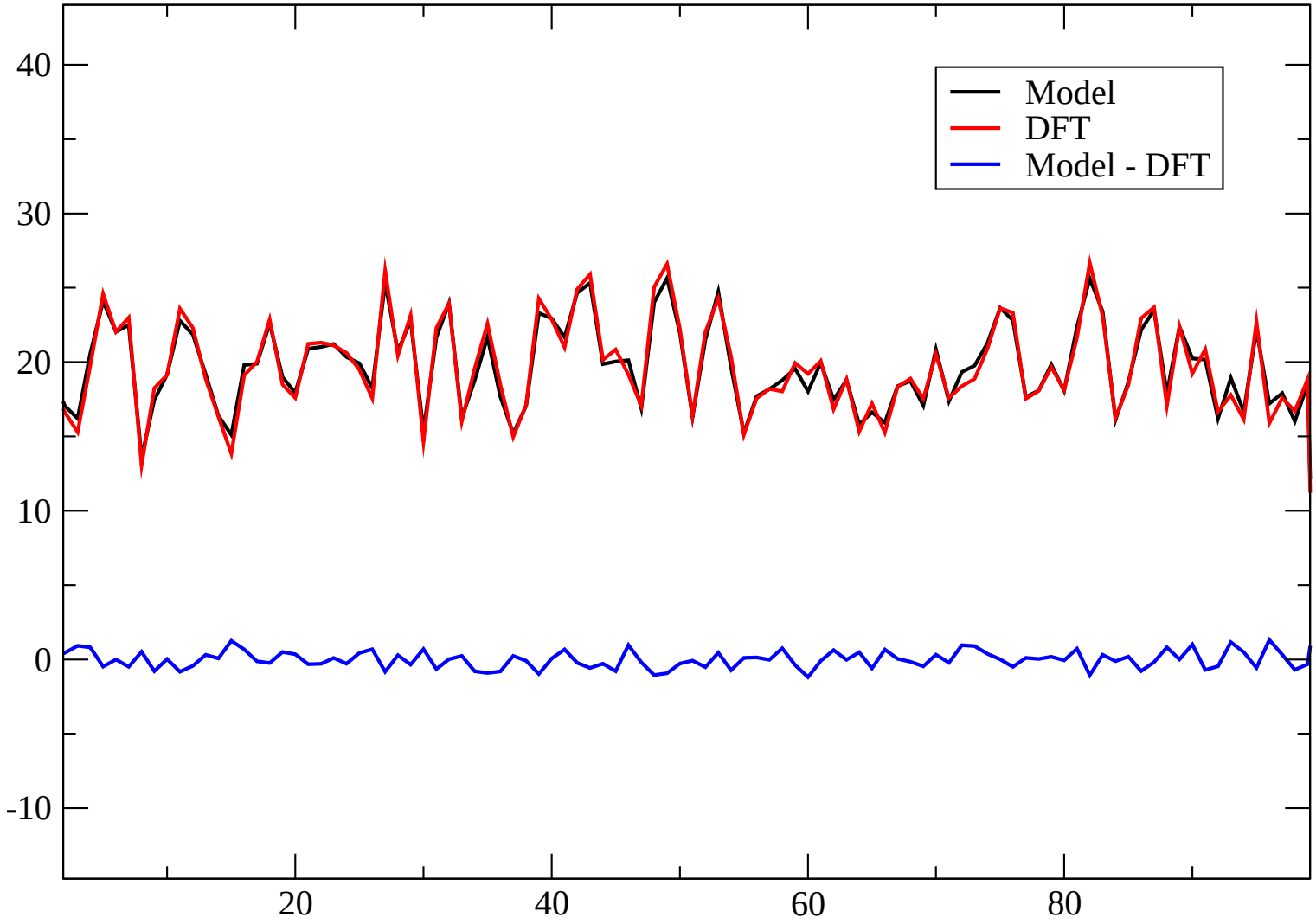

T = 4100 K
T = 5700 K

Theory

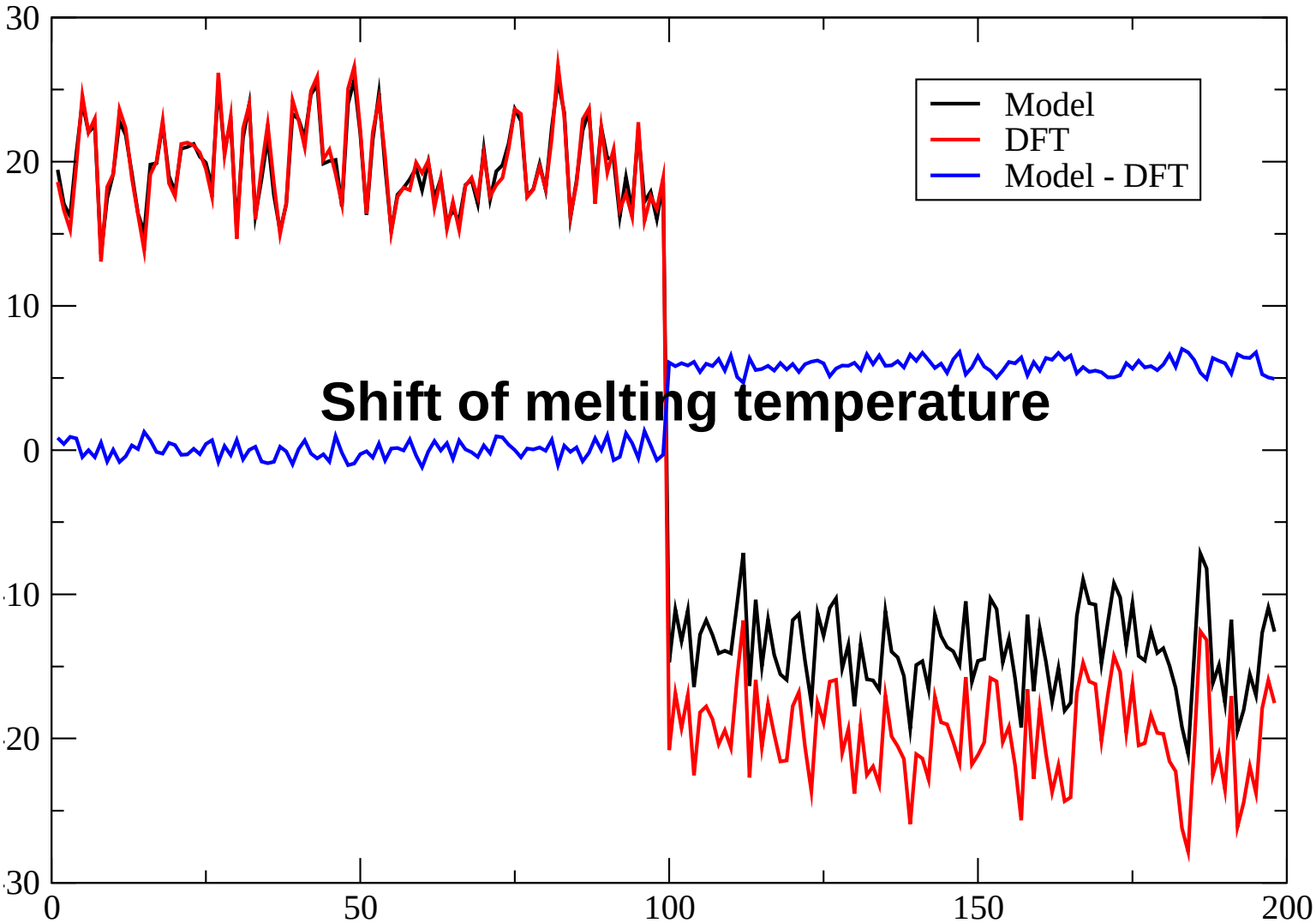
- Statistical mechanics
  - Free energies
  - Coexistence of phases
  - Coexistence of phases + free energies
- Interatomic interactions
  - Empirical potentials
  - Density functional theory
  - Quantum Monte Carlo

Combining coexistence and free energies

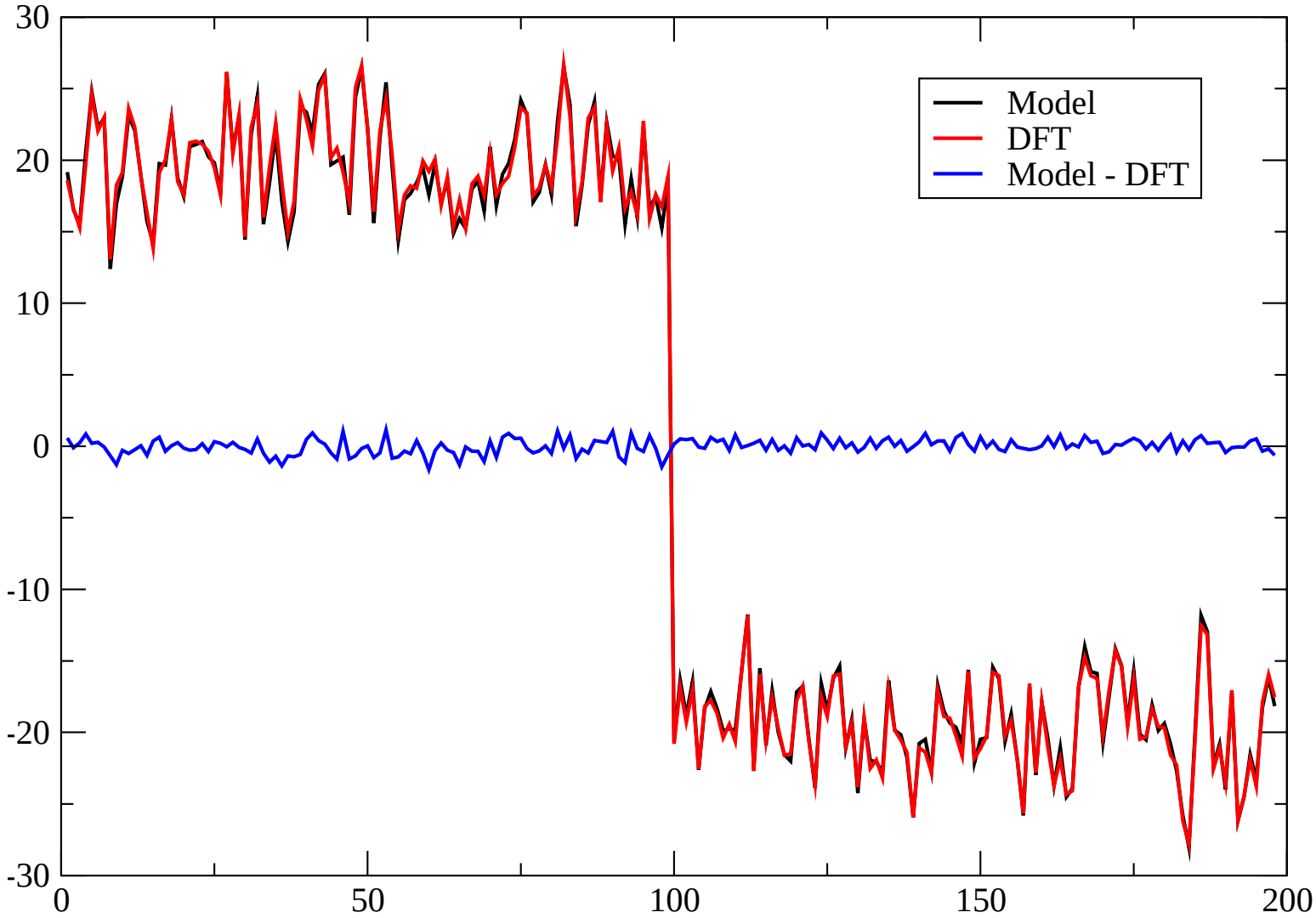
Fitting a model (e.g. using only the liquid):



Performance of the model also on the solid:



Fitting a model (using both liquid and solid):



Potential fitting summary:

- For best results use data from both phases (liquid and solid, or solid and solid, or even several different solids if interested in complex phase diagrams).
- If potential is only fitted to one phase then transferability is not guaranteed, and it will usually result in a (possibly large) shift of the phase boundary that needs to be corrected for.

Strategy for melting of Ta, Mo and Ni:

Coexistence of phases with classical potential:

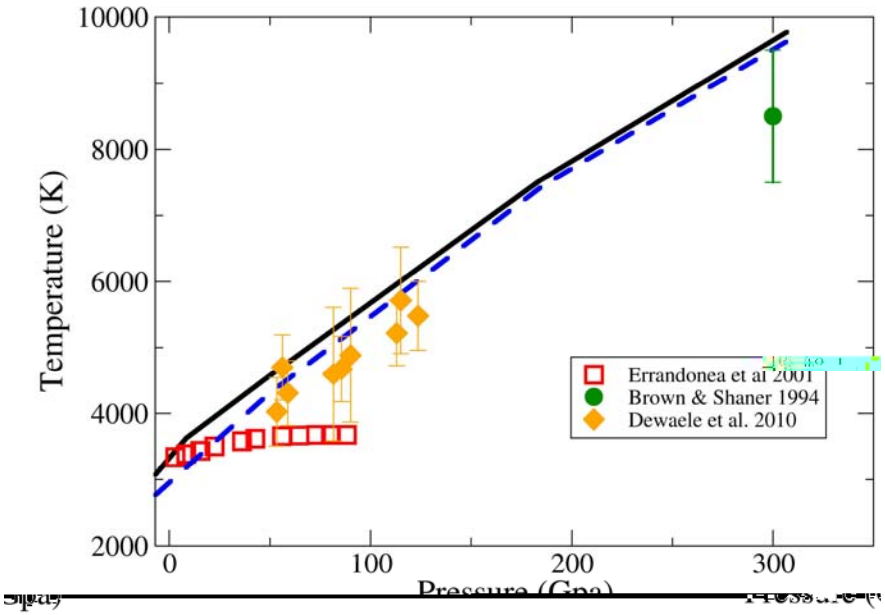
$$U_{\mathrm{ref}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{\mathrm{N}}) = \frac{1}{2}\varepsilon\sum_{i\neq j}\left(\frac{a}{r_{ij}}\right)^{n} - C\varepsilon\sum_{i}\sum_{j(\neq i)}\left(\frac{a}{r_{ij}}\right)^{m}{}^{1/2}$$

Free energy corrections:

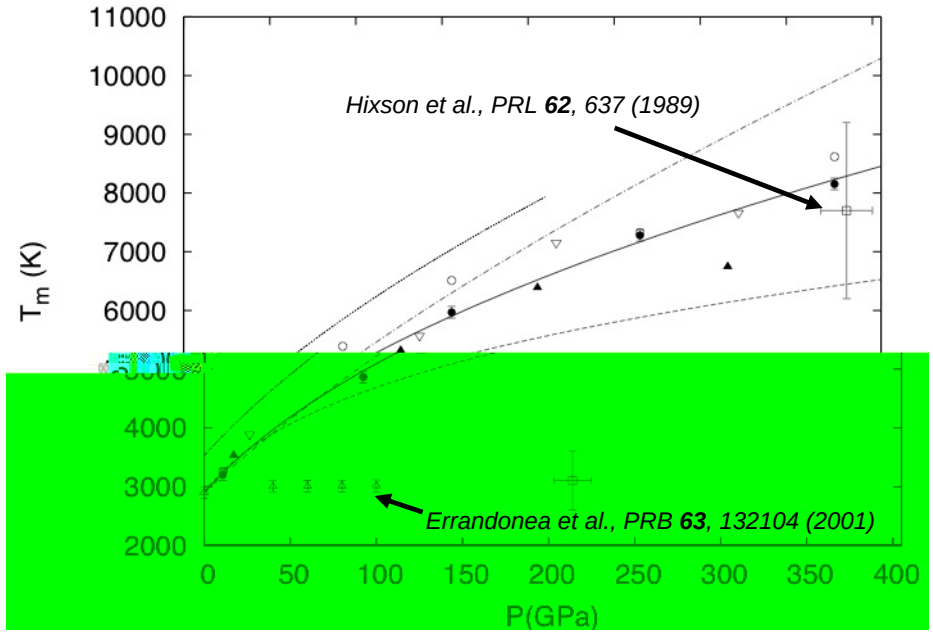
$$\delta T_m = \frac{\Delta G^{ls}(T_m^{ref})}{S_{ref}^{ls}}$$

Melting curves of Ta and Mo

Tantalum

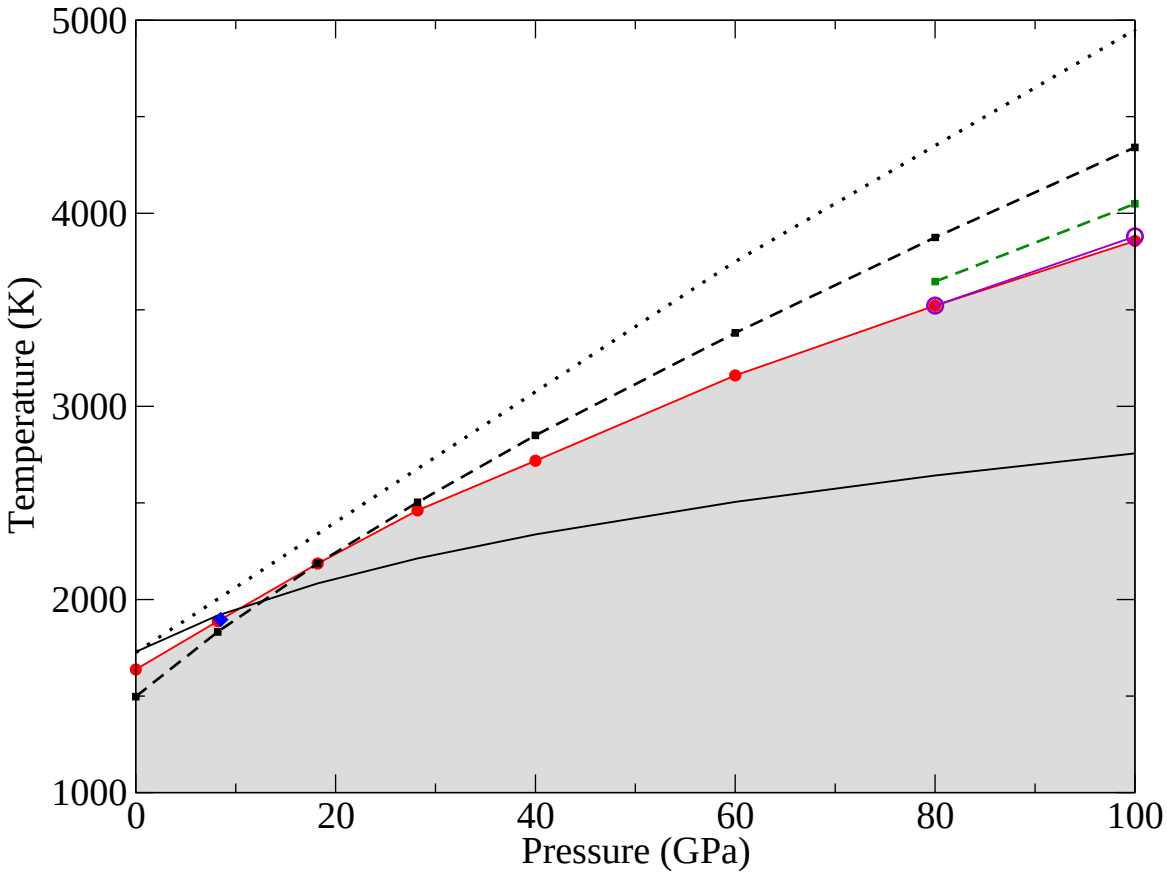


Molybdenum



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

Melting curve of Ni



M. Pozzo and D. Alfè, *submitted*

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
- Coexistence + free energy
  - Large systems only with reference potential
  - Needs good reference potentials
  - Only melting

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