Strategy

Ab initio Gibbs free energies calculations for solid and liquid iron:

$$G(P,T) = F + PV$$

Where F is the Helmholtz free energy, P is the pressure, V is the total volume of the system and T is the temperature.

At each fixed pressure P, $T_m(P)$ is determined by the condition:

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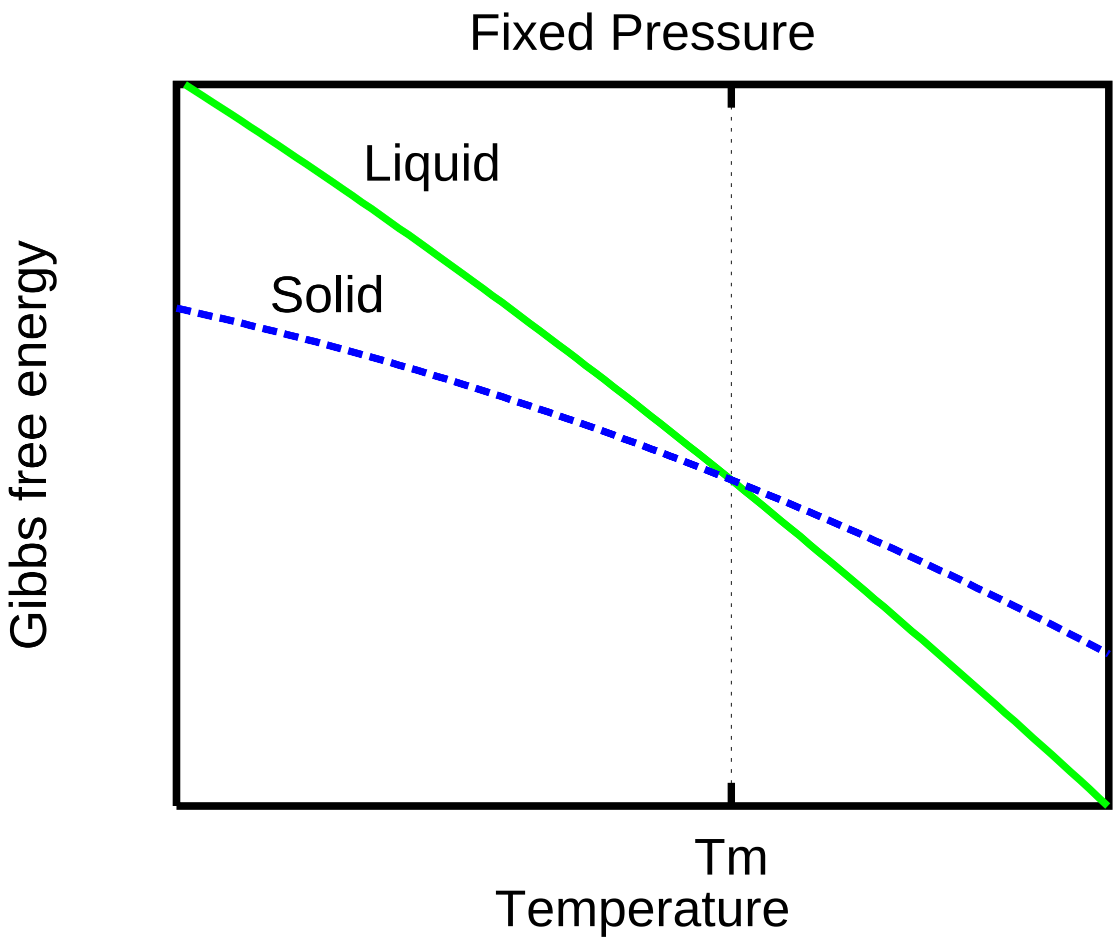
$$G_{liquid}(P,T) = G_{solid}(P,T)$$



Calculation of G(P,T):

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- *Ab initio* calculation of F(V,T) for a few volumes and temperatures, then fitting to an analitic form;

- P(V) $= -\frac{\partial F(V,T)}{\partial V}\Big|_T$;

- V(P) from inversion of P(V);

- G(P,T) = F(V(P),T) + PV(P)

Calculation of F(V,T):
Thermodynamic integration:

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$$\mathrm{F} = \mathrm{F}_0 + \int_0^1 d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda \qquad (1)$$

where F_0 is the free energy of a chosen reference system,

$$U_\lambda = \lambda U + (1-\lambda) U_0$$

where U_0 and U, are the potential energies of the reference and the *ab-initio* system respectively, and $\langle \cdot \rangle_\lambda$ means thermal average in the ensemble generated by U_λ.