Solid Iron

h.c.p.

$$F_{solid}(V,T) = F_{solid}^{harm}(V,T) + \Delta F(V,T)$$

Harmonic system:

$$U_{harm} = U_0(V,T) + \frac{1}{2}\sum_{i\alpha,j\beta} u_{i\alpha}\Phi_{i\alpha,j\beta}(V,T)u_{j\beta}$$

where U_0 is the perfect lattice energy and $\Phi_{i\alpha,j\beta}$ is the force-constant matrix.
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$$F_{solid}^{harm}(V,T) = U_0(V,T) + \frac{k_B T}{\Omega_{BZ}} \sum_s \int_{BZ} \ln\left[\frac{\hbar\omega_{\mathbf{q},s}}{k_B T}\right] d\mathbf{q}$$

$$= U_0(V,T) + k_B T \ln\left[\frac{\hbar\bar{\omega}}{k_B T}\right]$$

where $\omega_{\mathbf{q},s}$ is the s-th branch of the phonon frequencies at wave-vector $\mathbf{q}$. The $\omega_{\mathbf{q},s}$'s are calculated by diagonalization of the dynamical matrix $D_{\alpha\beta}(\mathbf{q})$:

$$D_{\alpha\beta}(\mathbf{q})(V,T) = \frac{1}{M} \sum_j \Phi_{i\alpha,j\beta}(V,T) \exp[i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)]$$

where $\mathbf{R}_j$ is the position of lattice site j and M is the mass of the atoms.

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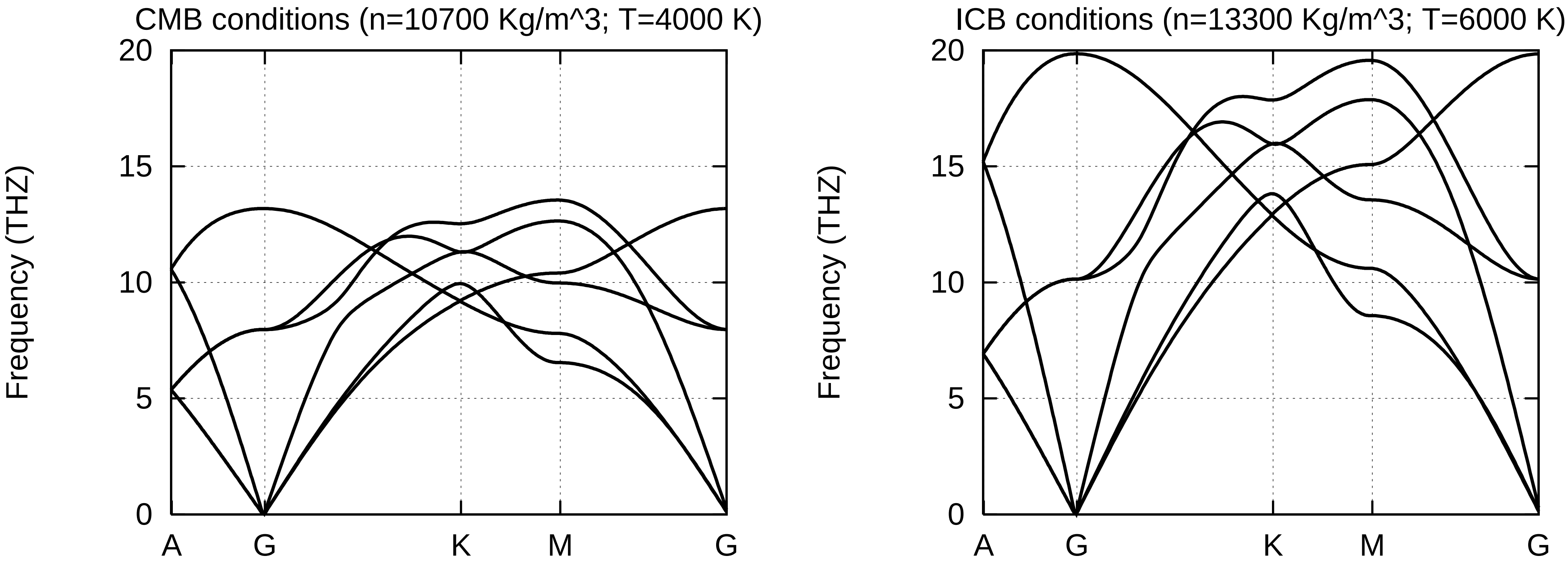
The calculation of $\Phi_{i\alpha,j\beta}$ is done using:

$$F_{i\alpha} = -\sum_{j\beta} \Phi_{i\alpha,j\beta} u_{j\beta}$$

where $F_{i\alpha}$ is the α component of the force on the atom in $\mathbf{R}_i$ induced by a displacement $u_{j\beta}$ of the atom in $\mathbf{R}_j$. This relation is applied directly by calculating the forces on the atoms in a large periodically repeated cell for chosen displacements.
We have used a $3 \times 3 \times 2$ supercell for the h.c.p. crystal, which gives free energies converged within $\approx 2\ meV/atom$.

Phonon dispersions:



We have calculated phonons at different volumes and temperatures. Then, we have fitted the 'average frequency', $\ln \bar{\omega}(V, T)$ to a polinomial in V and T.

Anharmonicity, $\Delta F(V, T)$:

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To calculate $\Delta F(V,T)$ we use again thermodynamic integration. This is done in two steps. In the first we generate a second reference system as a linear combination of the Harmonic and the Inverse Power potential:

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

where c_1 and c_2 are chosen so as to minimize the fluctuations of $U - U_{ref}$. Then, we do two thermodynamic integrations. The first from the harmonic system U_{harm} to the reference system U_{ref}, which is the largest contribution to $\Delta F(V,T)$, but this does not involve ab-initio calculations. The second from the reference system U_{ref} to the ab-initio U, this is a not involve ab-initio calculations. The second from the reference system U_{ref} to the ab-initio U, this is a small correction which can be calculated with a relatively small number of ab-initio calculations.

In classical statistical mechanics, $\Delta F(V,T)$ is expected to go as T^2 at low temperatures, and in fact we find that $\Delta F(V,T) = a(V)T^2$ gives a good representation of our results for all the temperatures studied. The volume dependence of $a(V)$ is adequately represented by $a(V) = \alpha_1 + \alpha_2 V$, with $\alpha = 2.2 \times 10^{-9}$ eV K^{-2} and $\alpha_2 = -6.0 \times 10^{-10}$ eV Å^{-3} per atom.