Liquid Iron

$$F^{ab}_{liquid}(V,T) = F^{ref}_{liquid}(V,T) + \Delta F(V,T)$$

Reference system:

Inverse Power Pair Potential

$$\phi(r) = \frac{A}{r^{\alpha}}$$

$$H_{ref} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\phi(|\mathbf{r}_i - \mathbf{r}_j|) + E(V,T)$$

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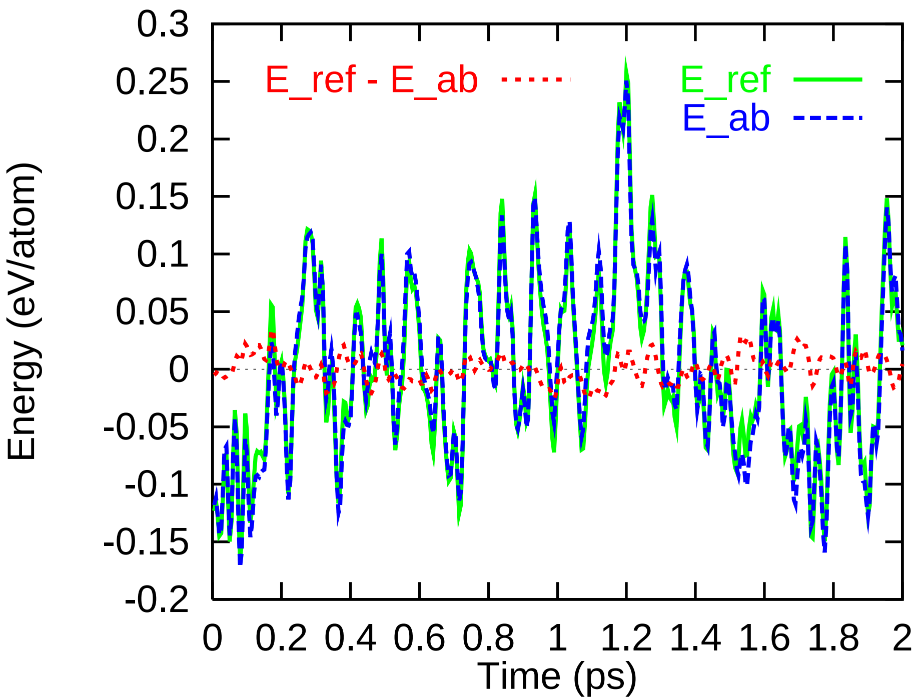
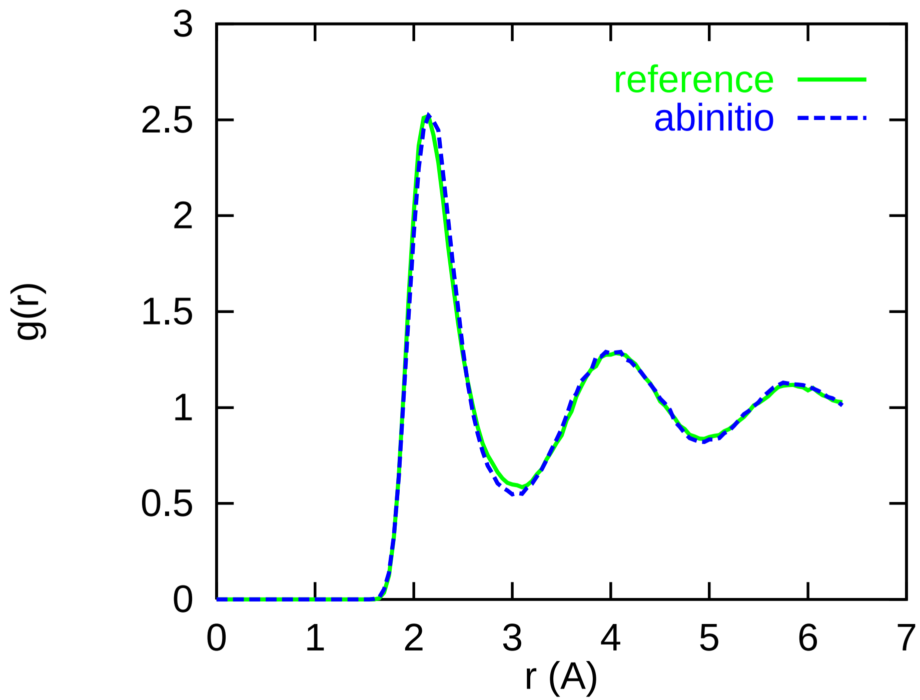
$$\delta(A,\alpha) = \langle (E_{ref}(A,\alpha) - E_{ab} - \langle E_{ref}(A,\alpha) - E_{ab} \rangle)^2 \rangle$$

where E_{ref} and E_{ab} are the potential energies of the reference system and the *ab-initio* system respectively, calculated on a set of positions generated with *ab initio* molecular dynamics.





Finite size and k-point sampling tests

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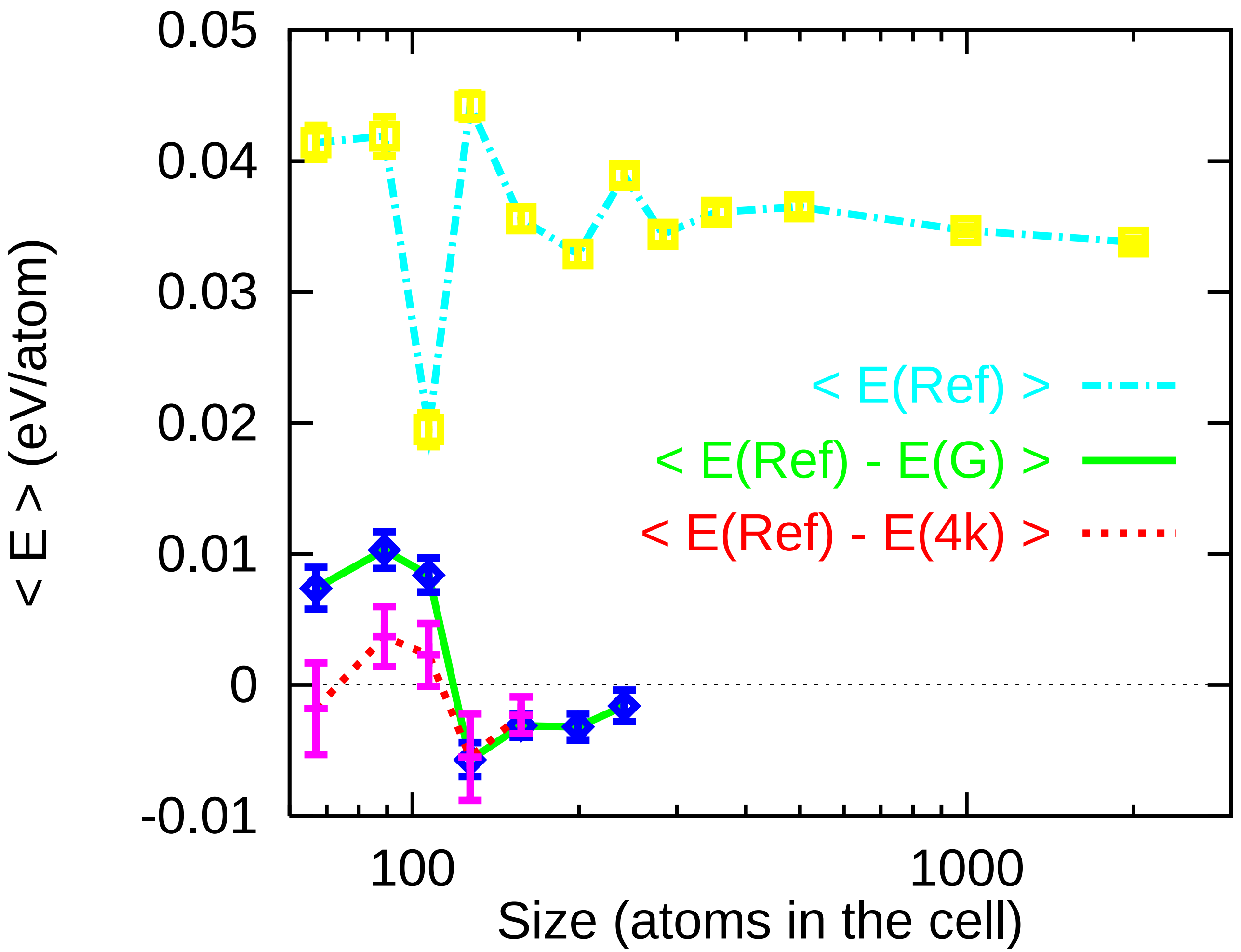

Calculation of $F^{ab}_{liquid}(V,T)$:

We used a 67 atoms unit cell and the Γ point only.

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Key points:

- A and α are basically independent on V and T
- The minimum of $\delta(A, \alpha)$ is small

$$\Downarrow$$

The reference system describes very well the liquid.

$$\Downarrow$$

Thermodynamic integration from H_{ref} to $H_{abinitio}$ is cheap:

- The statistical error on $\langle \Delta U \rangle_\lambda = \langle \partial U_\lambda / \partial \lambda \rangle_\lambda$ is $\approx 2\ meV/atom$ for a simulation of 2 ps.
- Few λ's are needed to calculate the integral in

- Few λ's are needed to calculate the integral in (1).

The integral in (1) is small, $\Delta F \approx -10\ meV/atom$ for all a set of thermodynamic states (V,T) spanning from CMB to ICB conditions.

$$F^{ab}_{liquid}(V,T) = F^{ref}_{liquid}(V,T) + \Delta F + C$$

where $C \approx 10\ meV/atom$ is a correction due to the finite-size/k-points sampling effects.

Calculation of $F^{ref}_{liquid}(V,T)$:

$$F^{ref}_{liquid}(V,T) = F^{ref}_{inverse}(V,T) + E(V,T)$$

Thermodynamic integration is performed to calculate

Thermodynamic integration is performed to calculate $F^{ref}_{inverse}(V,T)$; in this case the reference system is the Lennard-Jones system. We used a 499 atoms cell. Because of the simple form of the inverse power potential, all the a-dimensional quantities depend only on the variable

$$\zeta = \frac{An^{\alpha/3}}{k_B T}$$

where $n = N/V$ is the number density. Hence:

$$\frac{F^{ref}_{inverse}(V,T)}{k_B T} = f(\zeta)$$

and a single isotherm is sufficient to determine the value of $F^{ref}_{inverse}(V,T)$ for every V and T.

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