Long time scale simulations to determine accurate ab initio free energies

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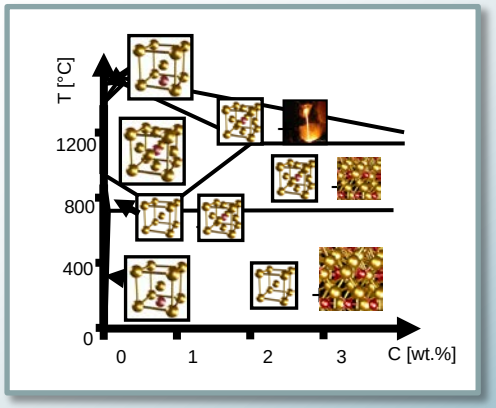
$$Z = \sum_{\{\vec{R}_I\}} e^{-E^{BOS}/k_B T}$$

Partition function

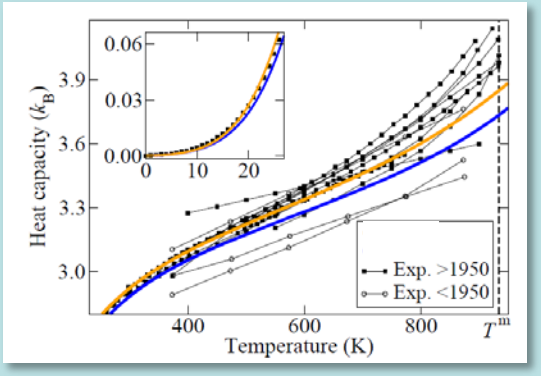
?



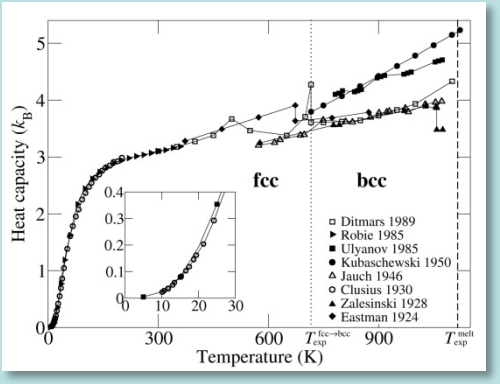
Phase diagram

Do we have to go beyond experiment?

Calorimetric measurements



fcc Al



fcc/bcc Mg

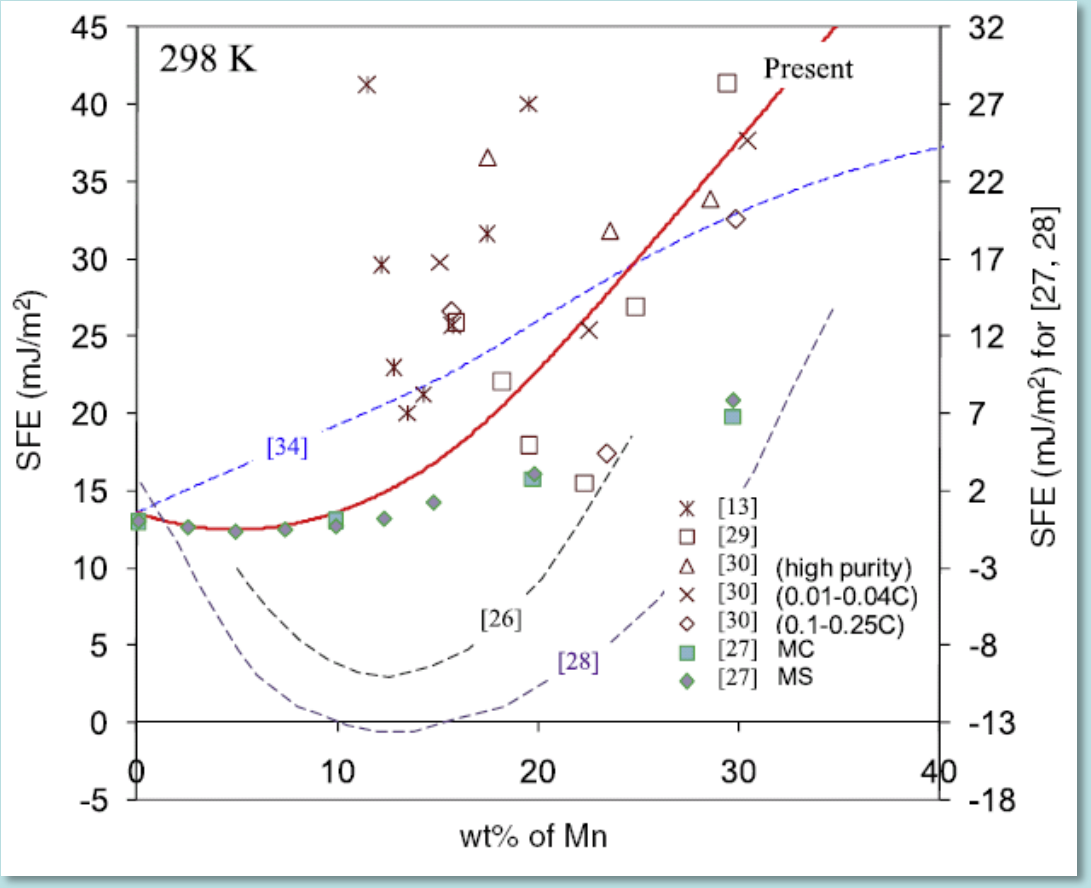
Fundamental input for all thermodynamic databases
→ But: Scatter of ~0.3 … 1 k_B

Point defects (vacancies): Formation energies and entropies

	Al	
	Exp.	DFT
E_f (eV)	0.7	0.6
S (k_B)	2.4	0.2

Do we have to go beyond experiment?

Stacking fault energies (fcc Fe-Mn)



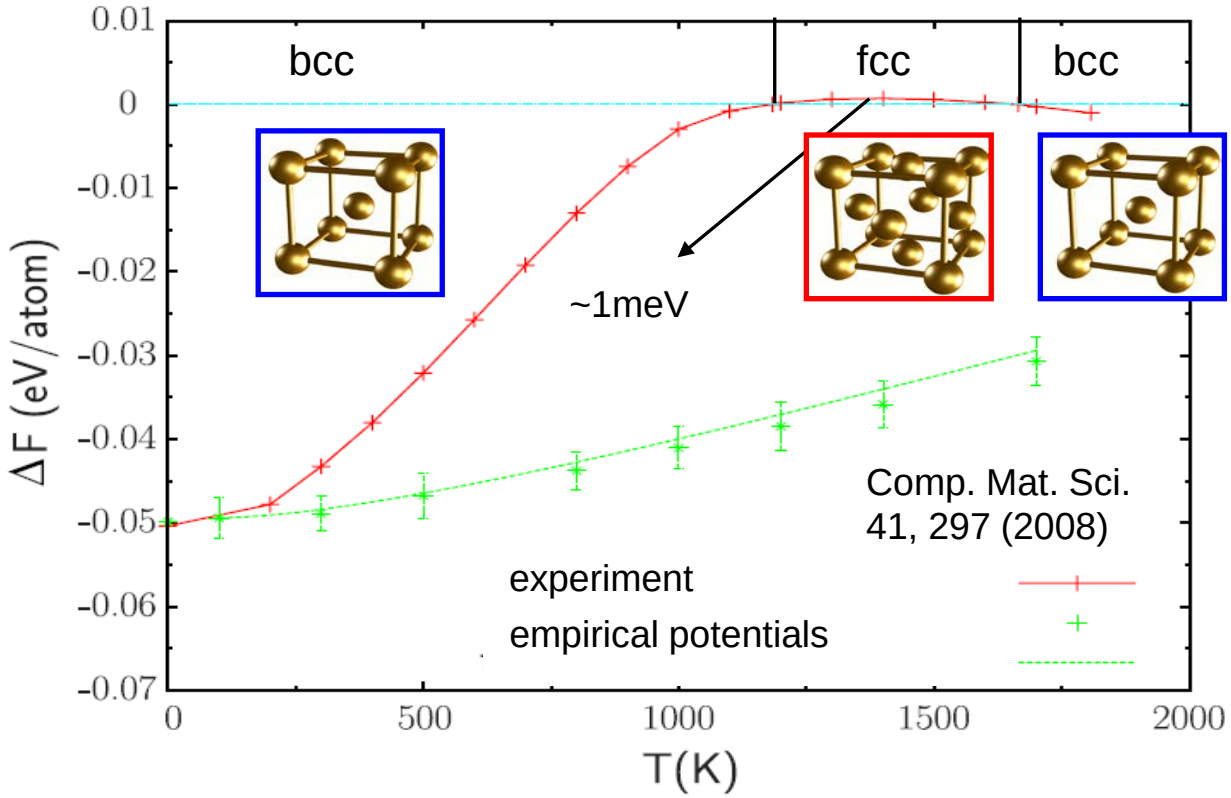
Key quantity to design novel high-strength steels

Additional complication
→ magnetism

Even chemical trends are hard to derive from existing data

Accuracy

Free energy difference between bcc and fcc iron



Energy resolution better 1 meV!

→ Can we achieve such accuracy with present day ab initio techniques?

Ab initio Thermodynamics

$$Z(V,T,x) = \left\langle e^{-E^{BOS}\left(\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}\right)/k_B T} \right\rangle_{V,T,x}$$

$$= \sum_{\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}} e^{-E^{BOS}\left(\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}\right)/k_B T} \Bigg|_{V,T,x}$$

Statistical averages over coordinates, magnetic moments, occupations, chemical compositions

Adiabatic approximation

$$= \sum_{\left\{\vec{R}_I\right\}} e^{-E^{BOS}\left(\left\{\vec{R}_I\right\}; \left\{Z_I, \sigma_I, f_i, \ldots\right\}_{fixed}\right)/k_B T} \Bigg|_{V,T,x}$$

Vibrational excitations

$$\times \sum_{\left\{f_i\right\}} e^{-E^{BOS}\left(\left\{f_i\right\}; \left\{\vec{R}_I, Z_I, \sigma_I, \ldots\right\}_{fixed}\right)/k_B T} \Bigg|_{V,T,x}$$

Electronic excitations

+ cross terms

e.g. electron-phonon interactions

Accuracy considerations

~0.1 meV/atom

~0.1 meV/atom

$$F(V,T) = E_{T=0\mathrm{K}} + F^{\mathrm{qh}} + F^{\mathrm{ah}} + F^{mag} + F^{\mathrm{el}} + F^{\mathrm{vac}} + F^{non-adiab}$$

challenging

< 1 meV/atom

10^7 configurations (~ 10 temperature steps)

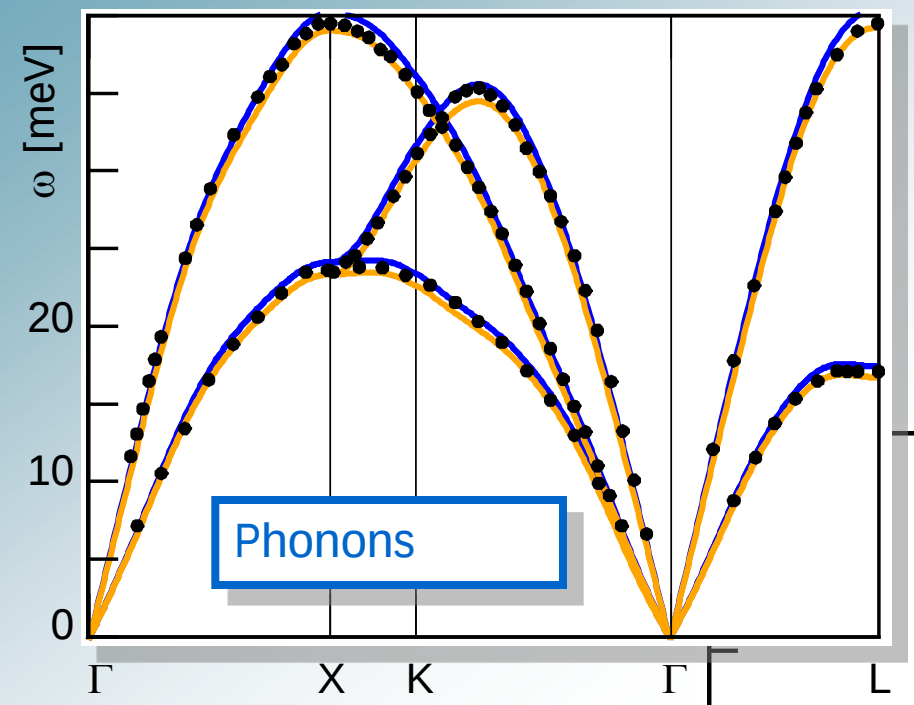
a few hours/days

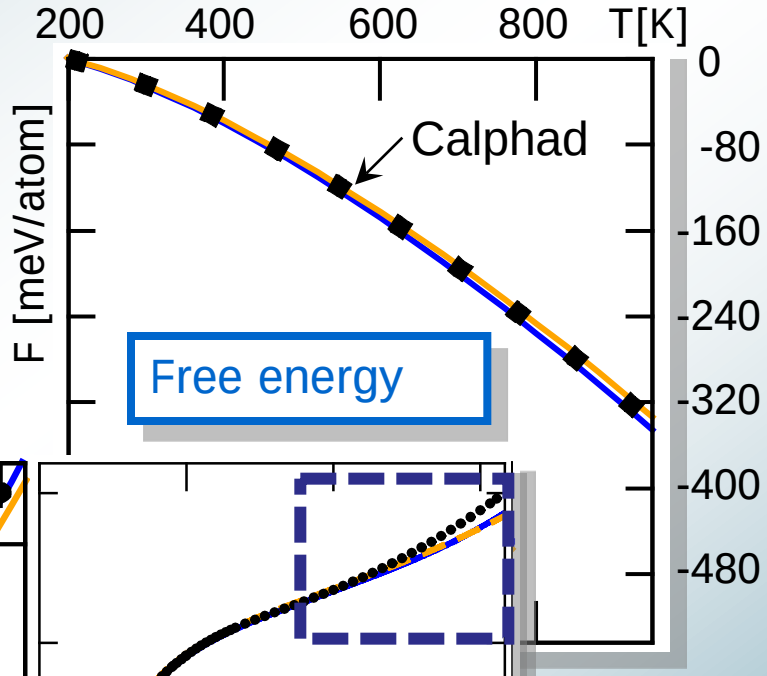
$$\langle E(T) \rangle = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_{t=t_0}^{t_0+\Delta t} E^{BOS}\left(\{\vec{R}_I(t)\}\right) dt$$

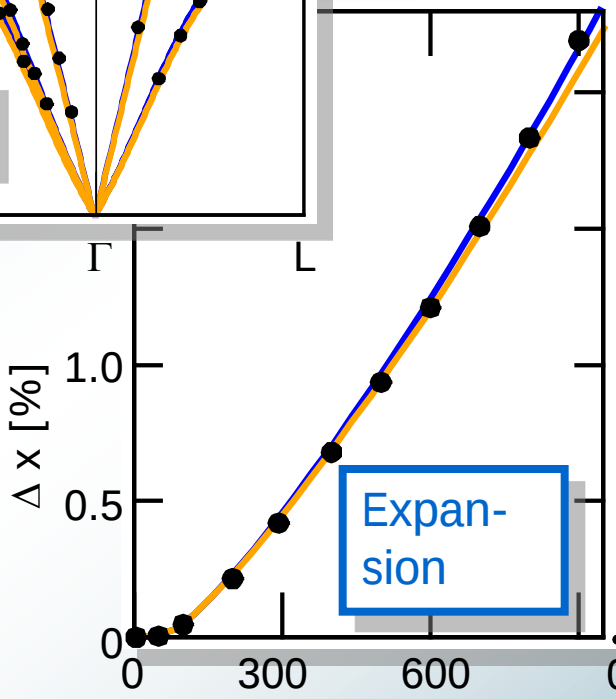
Statistical averages with 1meV accuracy

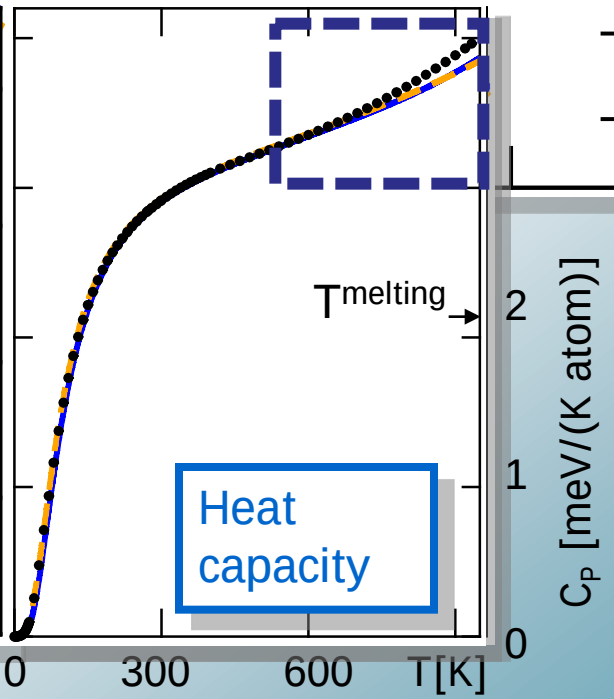
Are contributions beyond quasiharmonic approximation relevant?

Example: Bulk (fcc) Aluminum

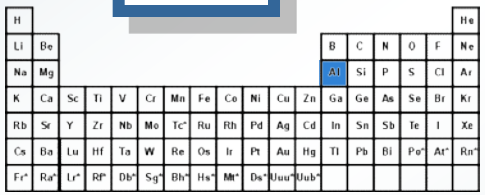








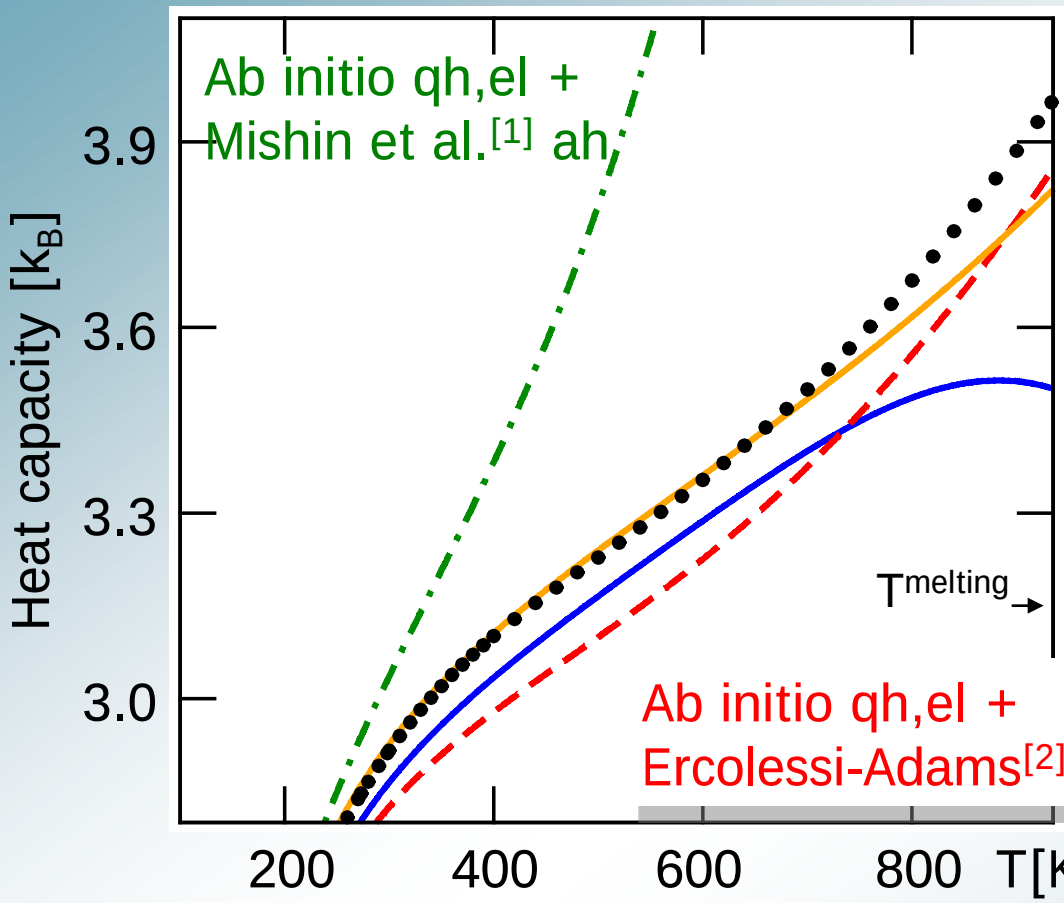
Al



How to sample over 10^7 configurations with ab initio accuracy?

Can we use empirical potentials to describe anharmonic contributions

Heat capacity of bulk Aluminum



Experiment[4]

Ab initio quasiharmonic + electronic

Ab initio qh,el + Mei-Davenport[3] ah

→ **None of the available empirical potentials is able to describe the anharmonic contribution**

[1] Y. Mishin, et al., Phys. Rev. B 59, 3393 (1999).
[2] F. Ercolessi and J. B. Adams, Europhys. Lett. 26, 583 (1994).
[3] J. Mei and J. Davenport, Phys. Rev. B 46, 21 (1992).
[4] D. A. Ditmars, et al., Int. J. of Thermophys. 6, 499 (1985).

Coarse graining configuration space

Main challenge:

Reduce number of (ab inition) configurations by several orders of magnitude

from MD or MC

$$\langle U(T) \rangle = \frac{1}{N} \sum_{i}^{N} E^{BOS}\left(\left\{\vec{R}_I(t_i)\right\}\right)$$

Two major concepts

Thermodynamic integration

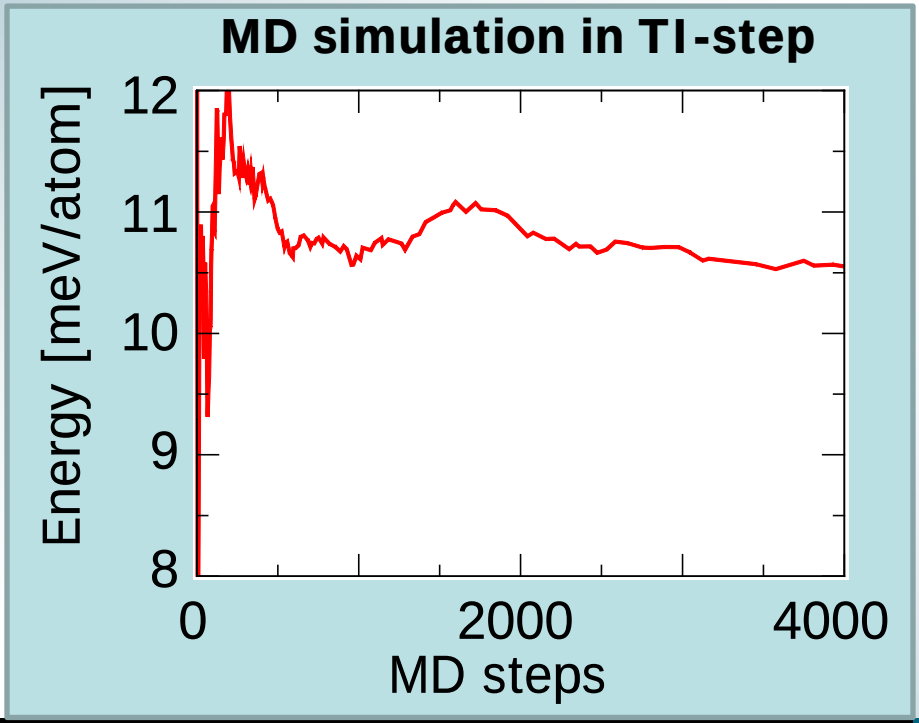
Free energy perturbation

Thermodynamic Integration

Key idea: Compute free energy change between reference system A and real system B

$$\Delta F(A \rightarrow B) = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

with $$U(\lambda) = U_A + \lambda (U_B - U_A)$$



Application straightforward if good reference is available

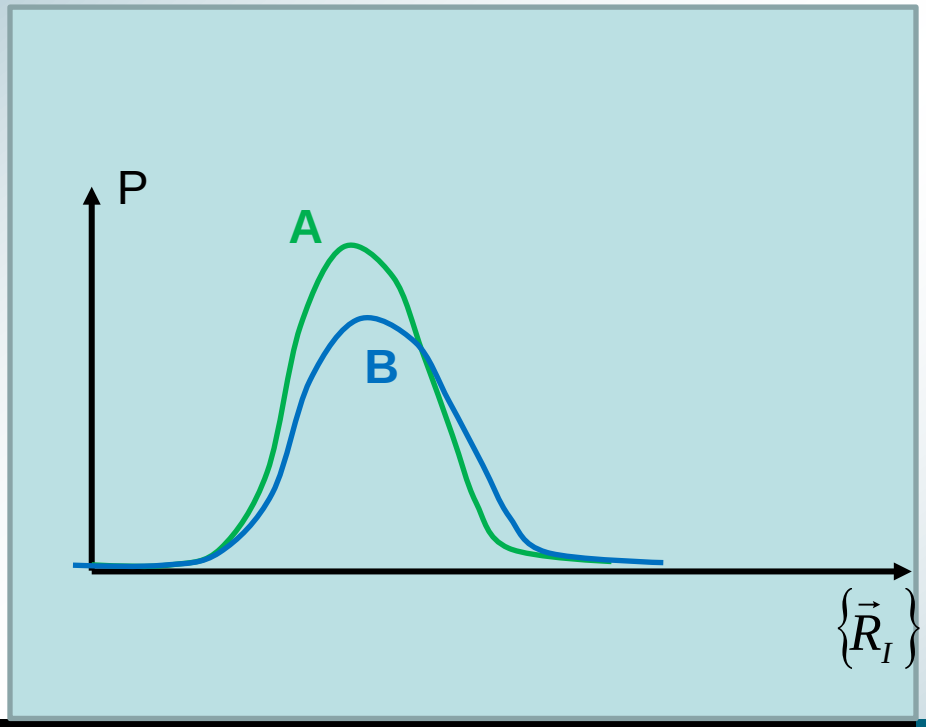
Typically the number of configurations can be reduced by 1-2 orders of magnitude
→ several 10^4 configurations

Not affordable on highest ab initio level

Free energy perturbation

Key idea: Compute free energy change between reference system A and real system B

$$\Delta F(A \rightarrow B) = -k_B T \ln \left\langle \exp\left(-\frac{E_B - E_A}{k_B T} \right) \right\rangle_A$$



Performance increases with quality of reference

For large differences to reference the method becomes inefficient/ fails

For the targeted accuracy less efficient than thermodynamic integration

How to boost coarse graining?

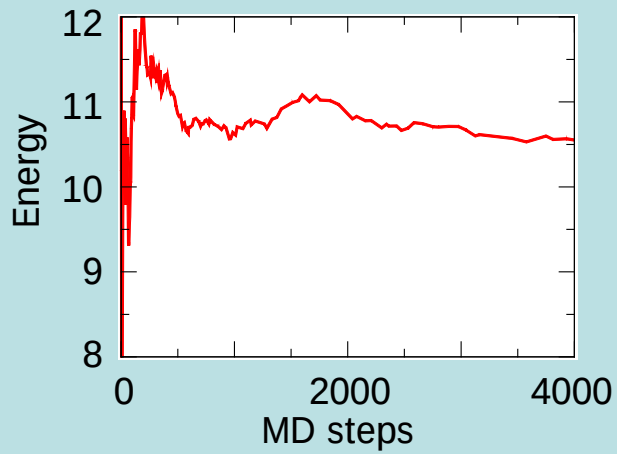
Cycles in thermodynamic integration

$$\Delta F(A \rightarrow B) = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

λ integration (2-10 steps)

→ Improved ref. reduces step number

Thermodynamic average (10^3…10^4 MD steps)



→ Performance bottleneck

Solution

λ integration (2-10 steps)

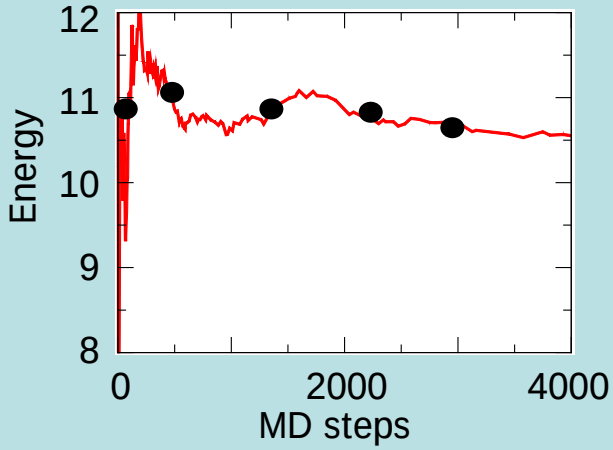
→ Improved reference reduces step number

→ Here: Quasiharmonic reference

Thermodynamic average (10^3…10^4 MD steps)

→ Use free energy perturbation approach

→ Use low/medium converged DFT as reference

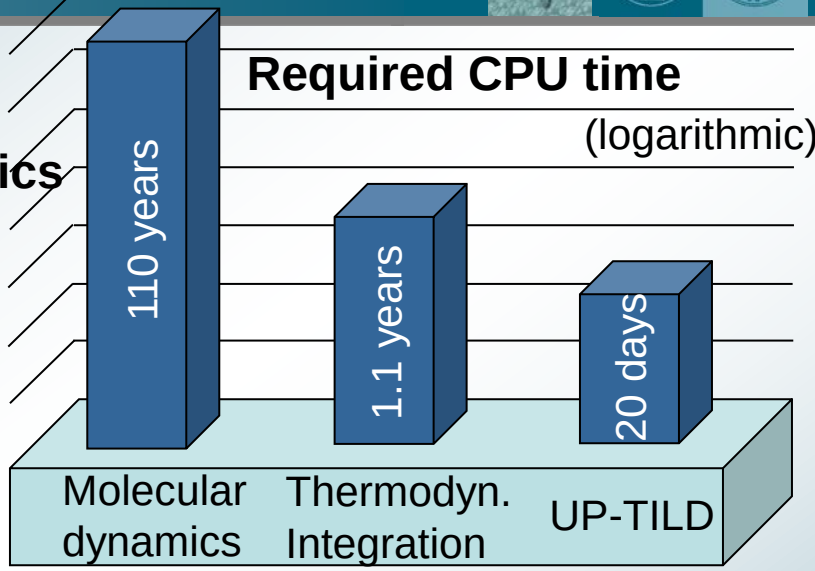


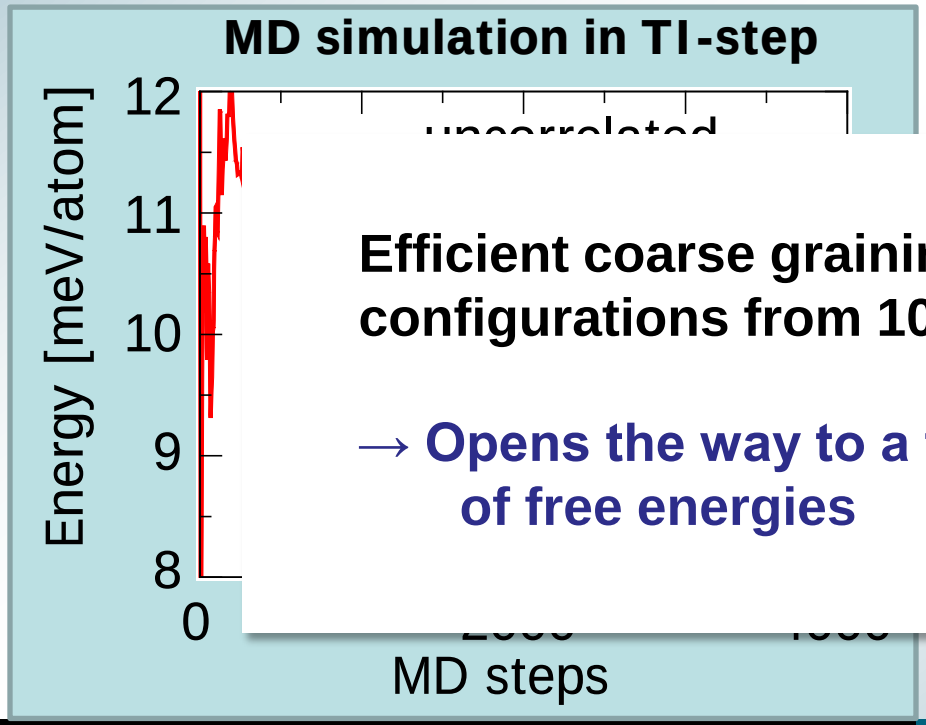
→ **Typically reduces number of configurations by 10^2**

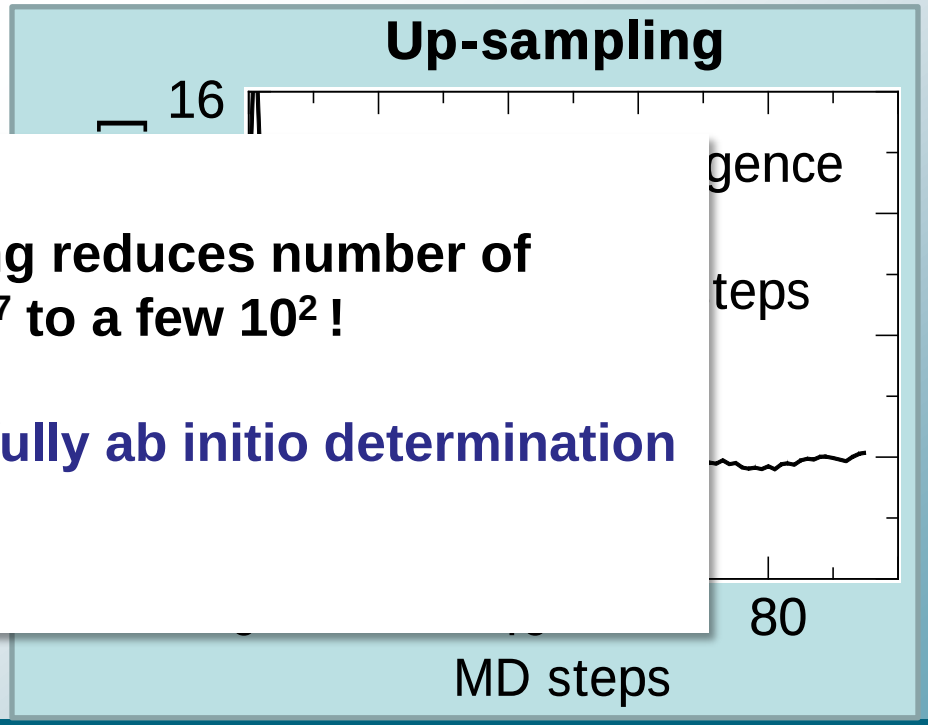
Performance of the new approach

- **Wavefunction extrapolation**
- **Thermodyn. integr. (TI) with Langevin dynamics**
- **Ensemble average instead of time average (parallelization)**
- **Up-sampling in λ–TI step**
- **etc.**

Grabowski et al., Phys. Rev. B79, 134106 (2009).





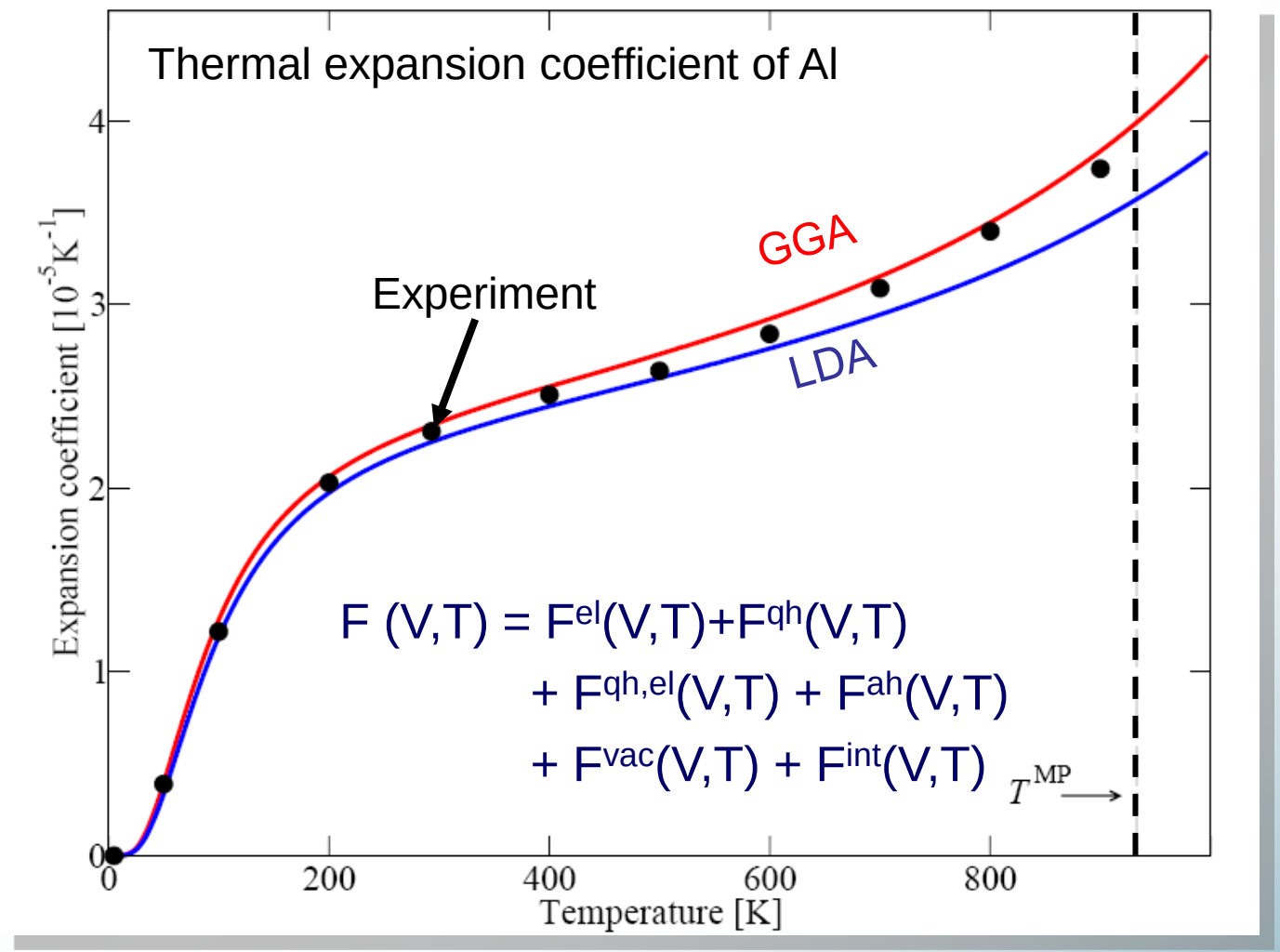


Efficient coarse graining reduces number of configurations from 10^7 to a few 10^2 !

→ Opens the way to a fully ab initio determination of free energies

Benchmark against experiment

Thermal expansion coefficient



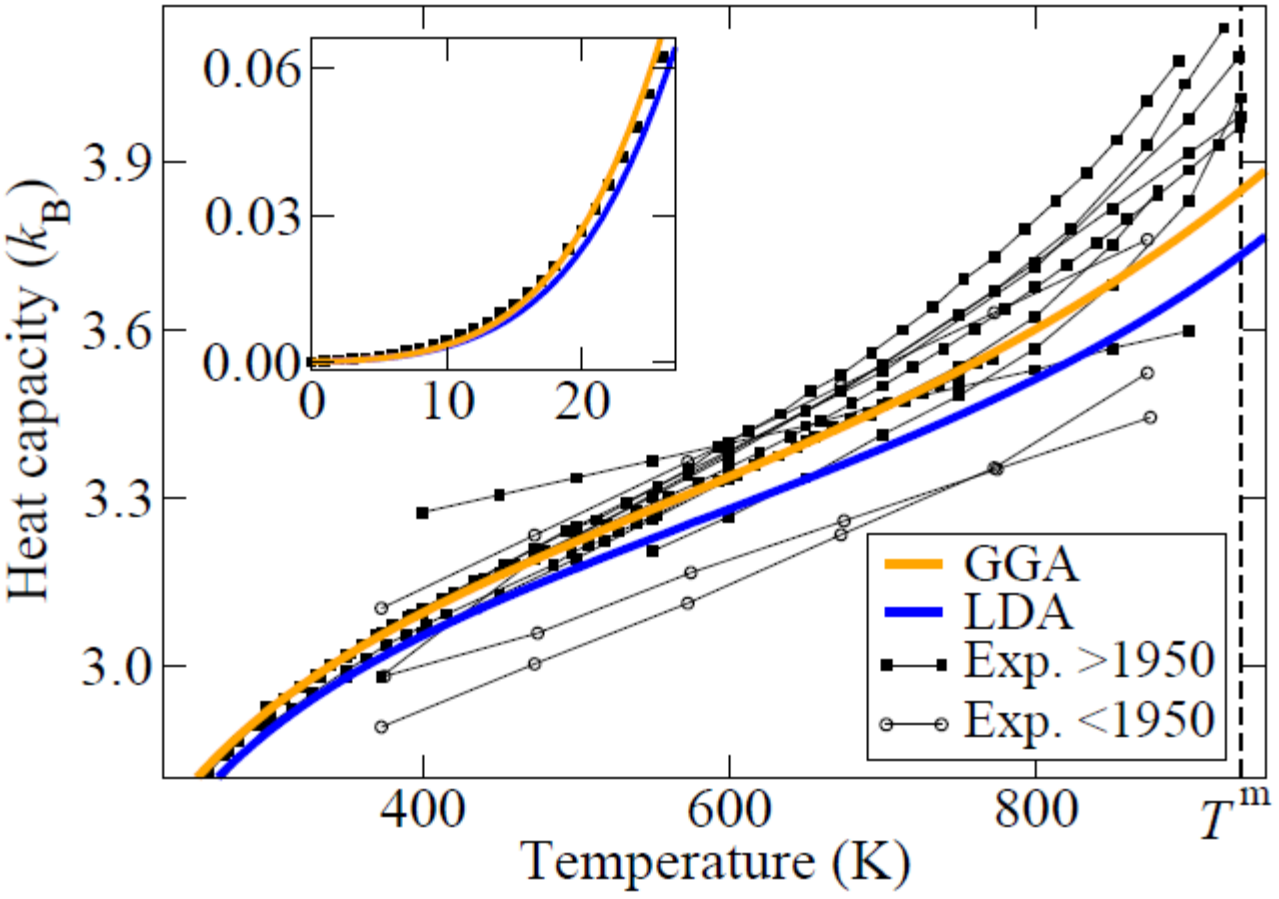
→ Excellent agreement with experiment

→ Systematic trend: LDA and GGA provide approximate measure of error bars

Grabowski,Ismer, Hickel, Neugebauer, Phys. Rev. B 79, 134106 (2009)

Heat Capacity

Heat capacity of Al

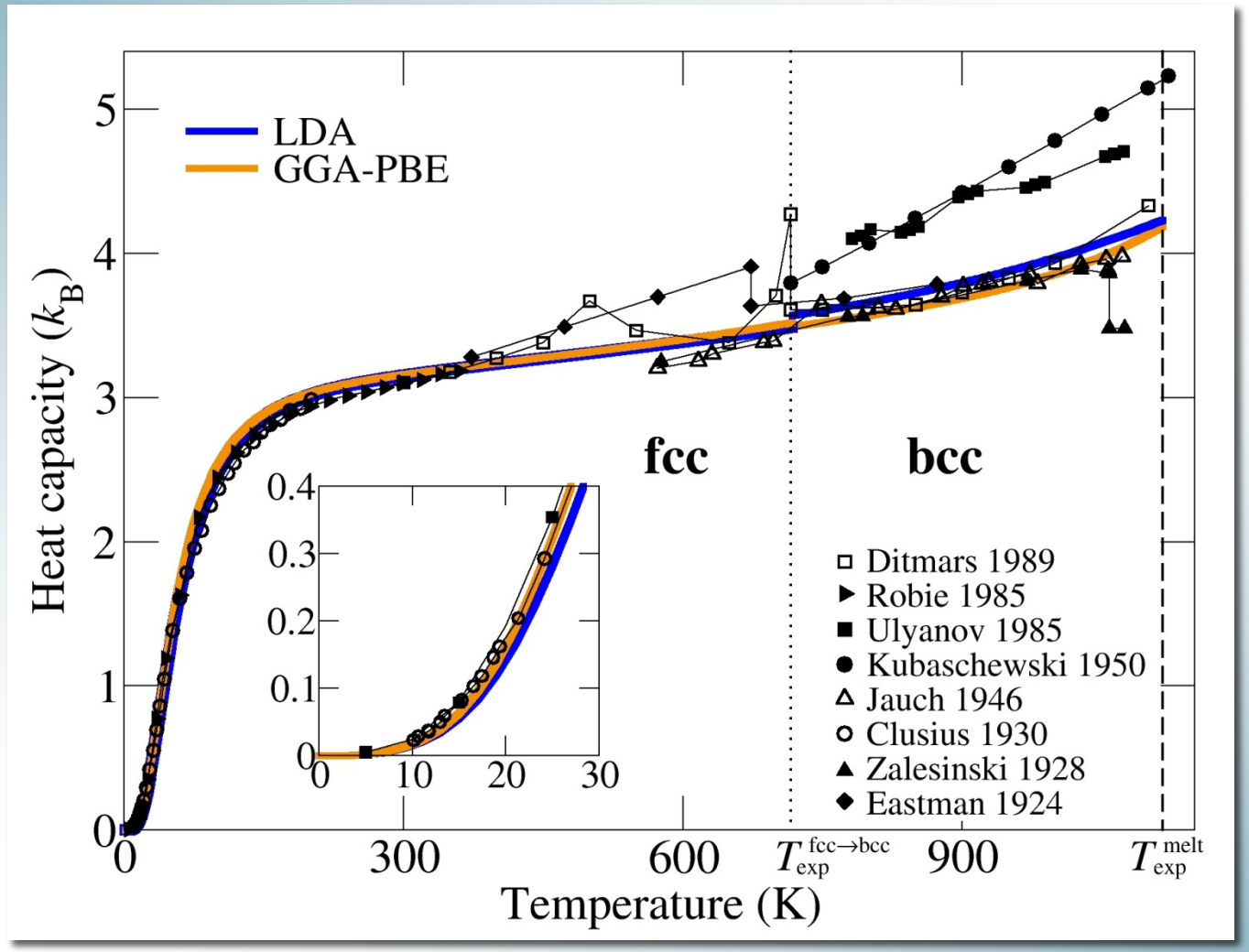


→ DFT gives lower bound to all recent experiments

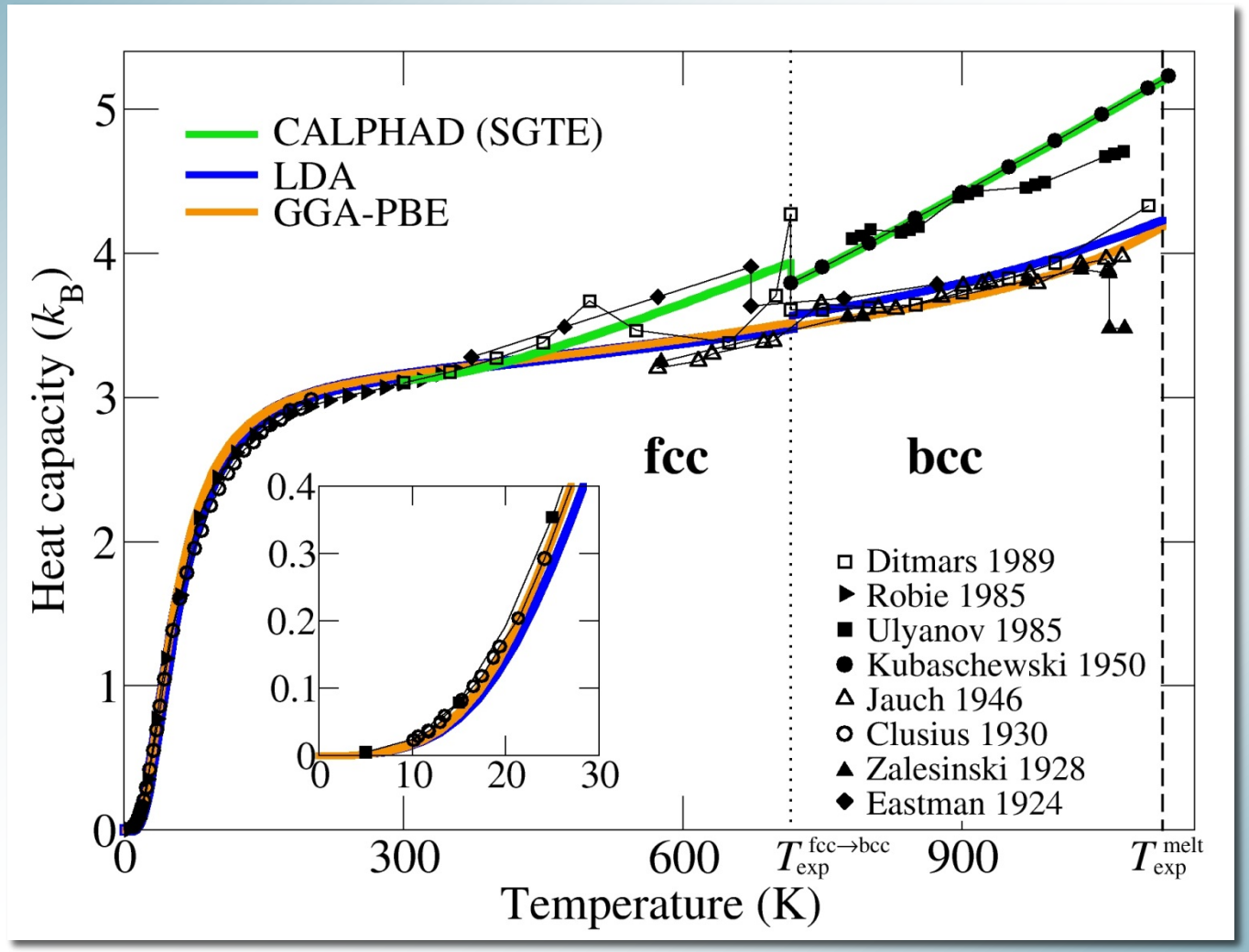
Applications

Assessment of experimental data

Calcium: Heat capacity



Calcium: Heat capacity



Ab initio thermodynamics (Conclusions)

Newly developed approaches allow to systematically improve performance of DFT to describe finite temperature properties

Accuracy often exceeds experimental data even of stable phases

→ Provide excellent basis to compute thermodynamic data

Thanks to the department

Thanks for your attention