

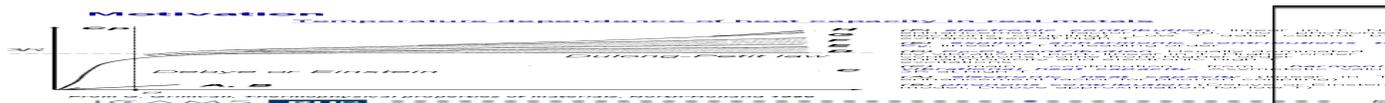


CALPHAD XL – Rio de Janeiro, Brasil
27th May 2011

CALPHAD connection to first-principles and microstructure simulations

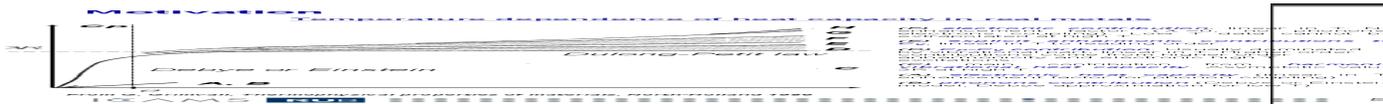
Suzana G. Fries

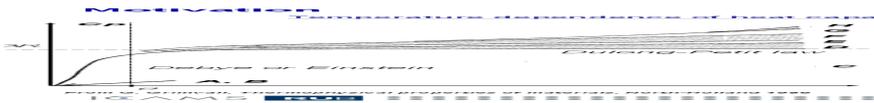
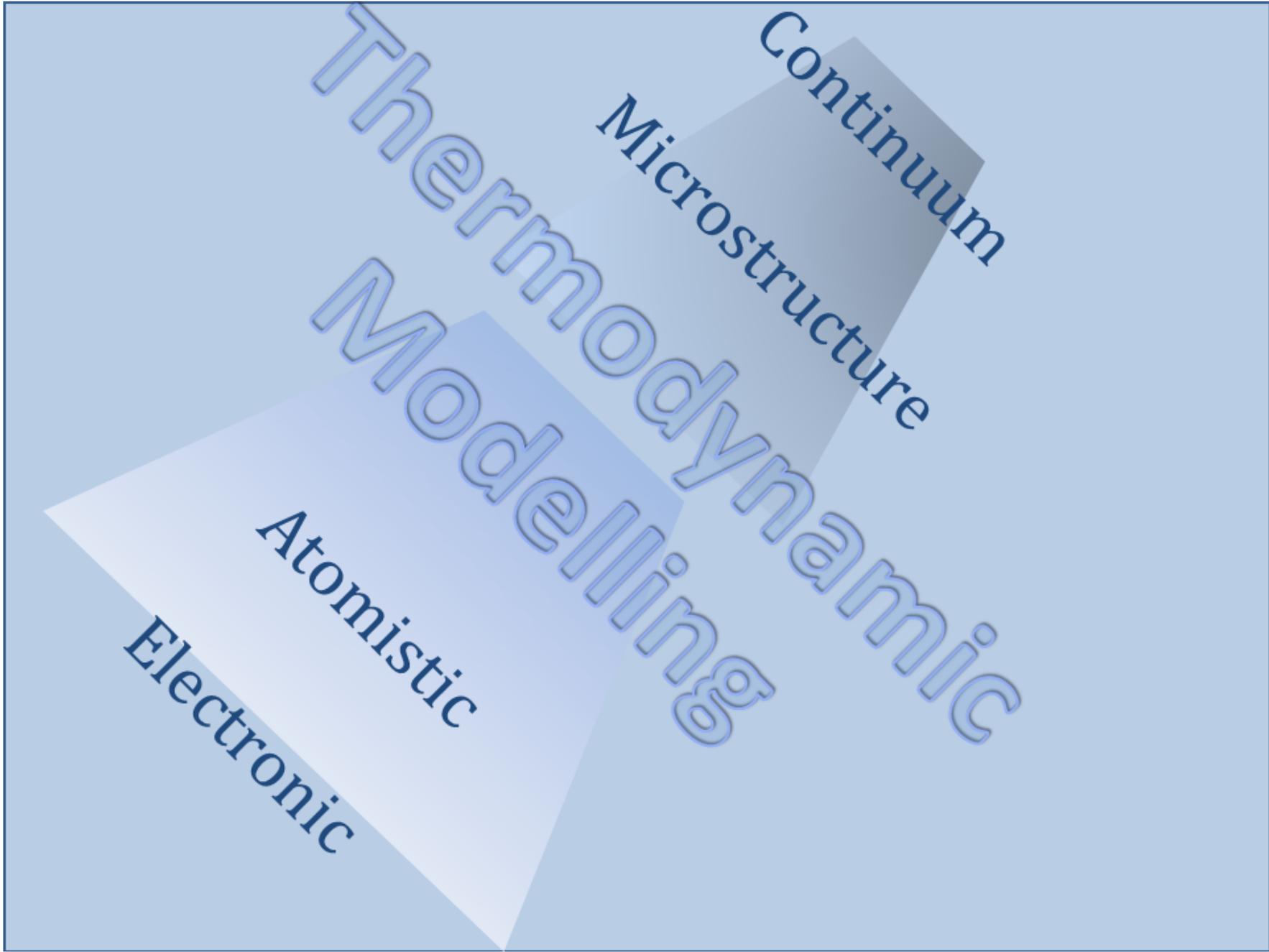
ICAMS, STKS, Ruhr University Bochum,
Bochum, Germany



The core of CALPHAD

Models based on **experimental evidence**
Description of some **reality** is an objective
Model **databases**

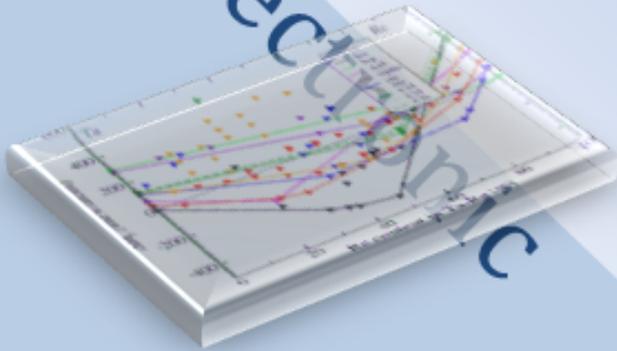
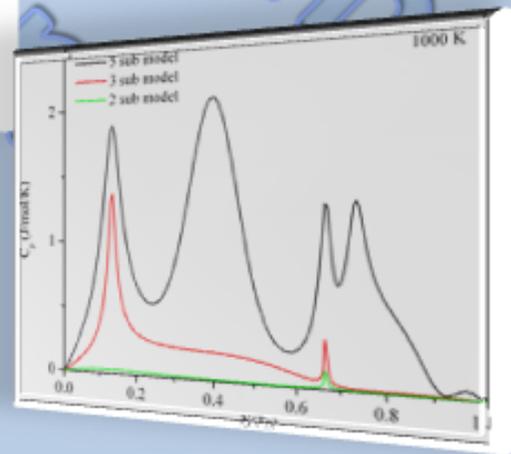
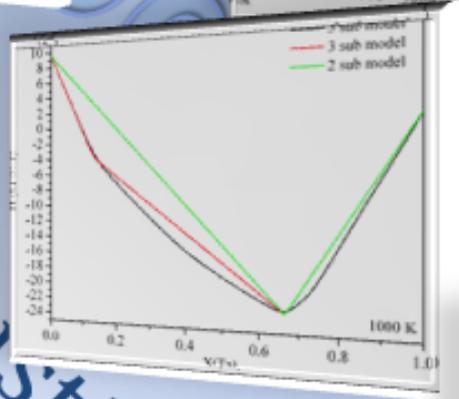
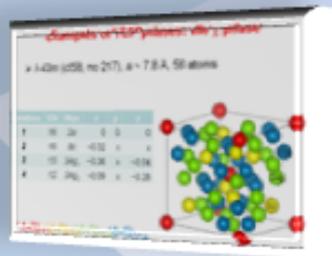
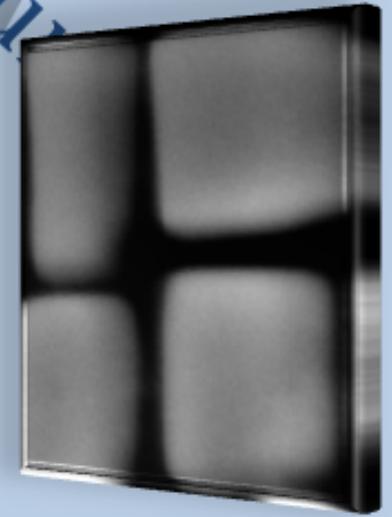
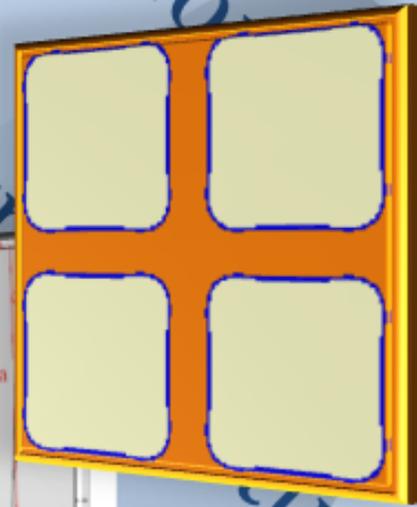
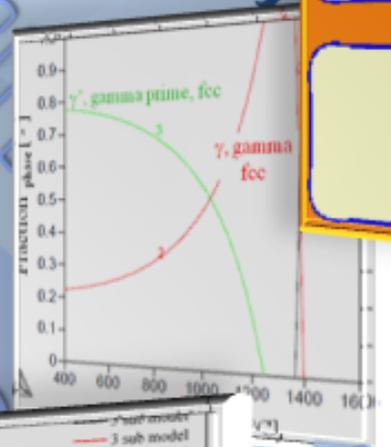
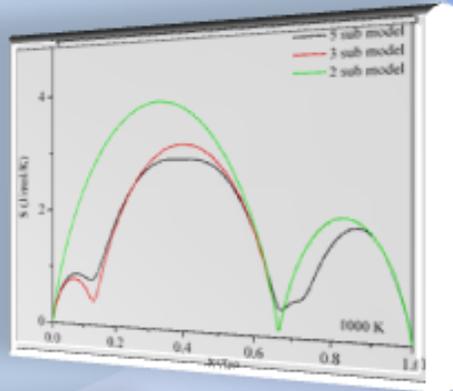




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Ni-superalloys
CALPHAD
SAPIENS
TCP



Atomistic
Electronic

Computational Thermodynamics

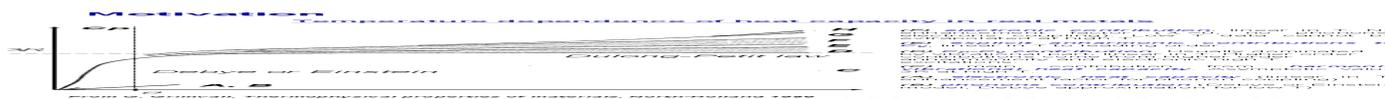
What is it?

- Name created by Bo Sundman in order to label KTH department where Kinetic and Thermodynamic databases for technical materials were being created using CALPHAD.

- -Nowadays the term is used in a generalized way, even when CALPHAD is not used.

The big advantage is that the label, now incorporates, for example, enthalpies of formation calculated by theoretical physicists using Density Functional Theory

Even if the objective is not to use the results in CALPHAD databases, the contribution for CALPHAD is done.



Computational Thermodynamics

What is it CALPHAD?

It is **not** a software!

It is a method!

Gibbs energies for all the stable phases of a systems are described by parametric models. These parameters are obtained in such a way that the Gibbs energy and its derivatives reproduce the experimental corresponding value at its best.

When this is done, by Gibbs energy minimization the phase diagram can be calculated!

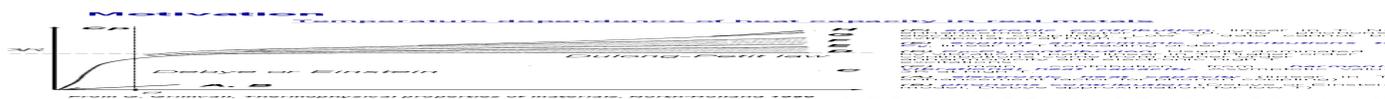
CALculated PHAse Diagrams

Big advantages: interpolations and extrapolations can be done . Less experiments are need.

Even some antecipation of higher order systems can be done!

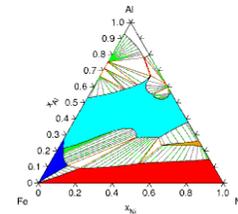
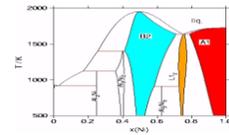
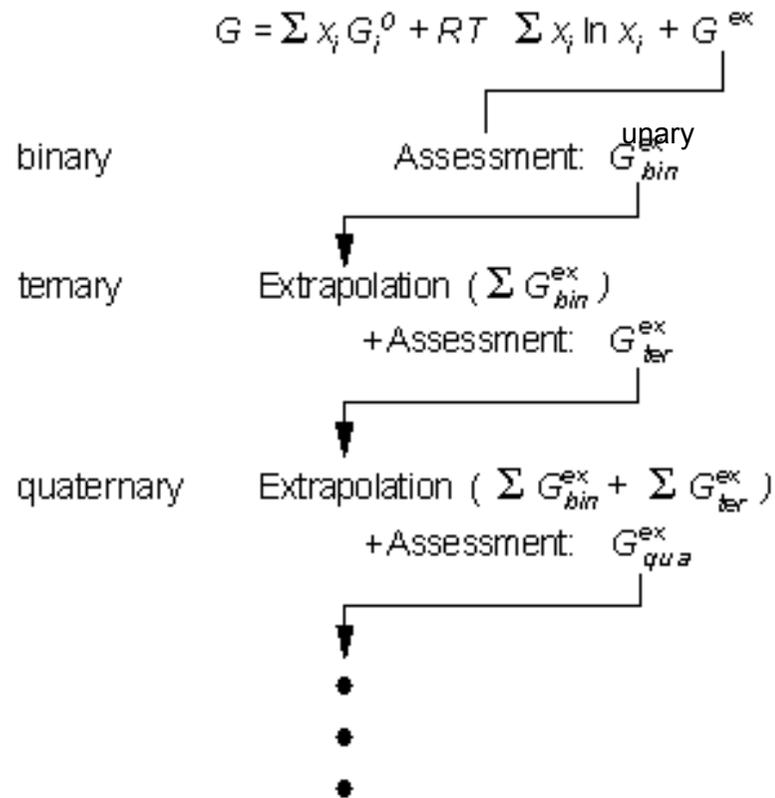
Interpolations are so good as the description...Extrapolations too and they are not trully predictable.

If there is a ternary compound that is not in the description it can not be guessed by the extrapolation from the binaries.

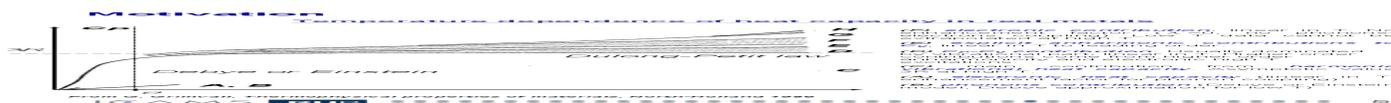


Computational Thermodynamics

The CALPHAD method.



From Ursula Kattner

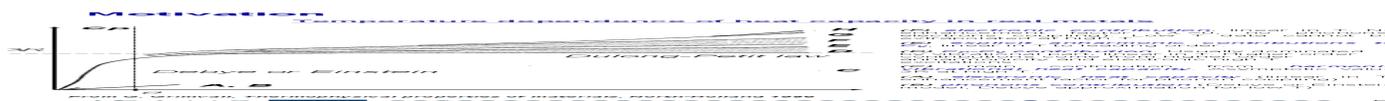


Computational Thermodynamics

The CALPHAD method.

- 1-Needs Gibbs energy databases.
- 2-Needs a Gibbs energy minimizer.

Only to say CALPHAD is not enough, one should say which database is used!
And they are several, even for the same material!!
Minimizers are also several, and if they use the same database,
the calculate results should be the same...



Computational Thermodynamics

For what?

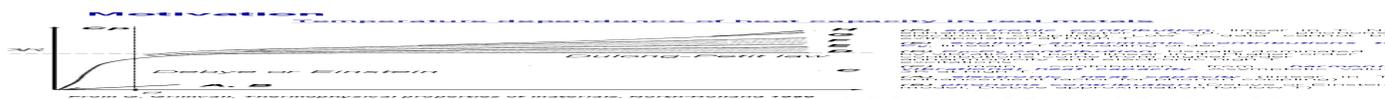
Even in the case one has a good Gibbs energy database, one still don't have the very relevant feature of materials properties: the microstructure

A microstructure pattern is not like a state variable. It depends on the processes!

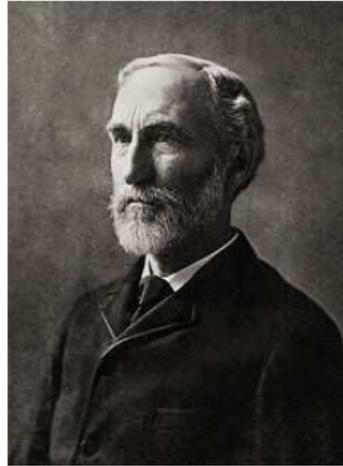
Then simulations are necessary. Phase Field is a powerful method

They are more realistic if they have some realistic information to where the whole system evolves.

To know the equilibrium thermodynamics is then a part of that simulations.



Gibbs energy



$$G = G(T, p, N_i)$$

entropy

$$S = - \left(\frac{\partial G_m}{\partial T} \right)_{p, N_i}$$

enthalpy

$$H = G + TS = G - T \left(\frac{\partial G}{\partial T} \right)_{p, N_i}$$

volume

$$V = \left(\frac{\partial G}{\partial p} \right)_{T, N_i}$$

Chemical potential of component i

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, N_{j \neq i}}$$

heat capacity

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{p, N_i}$$

thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial^2 G}{\partial p \partial T} \right)_{N_i}$$

isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_{T, N_i}$$

bulk modulus

$$B = \frac{1}{\kappa}$$



Computational Thermodynamics

Microstructure related quantities

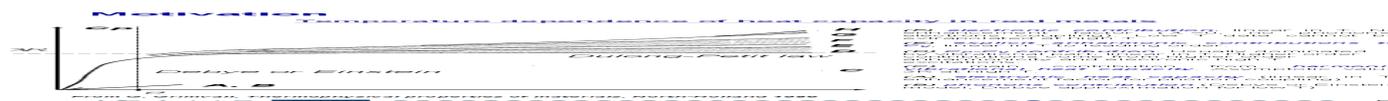
Even a material made by a single element can present different microstructures

- single crystal
- polycrystalline
 - -nanograins

All that results in different properties even if the chemistry is the same.

For the two last items there are interfaces!!

This is usually not in CALPHAD databases.



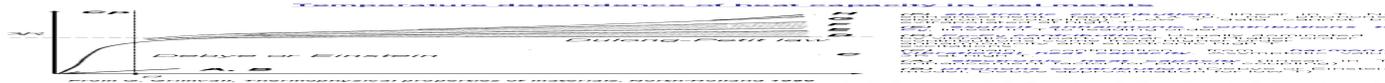
The general Gibbs energy expression is

$$G_m = G_m^{srf} - TS_m^{conf} + G_m^{xs} \quad (7)$$

The surface of reference for the model is the sum of Gibbs energies of all configurations with atom, i , on each sublattice, s , weighted by the site fractions, $y_i^{(s)}$. The σ phase has five sublattices with different numbers of sites and coordinations and can be described as

$(\text{Re,W})_4(\text{Re,W})_2(\text{Re,W})_8(\text{Re,W})_8(\text{Re,W})_8$, sites 1-5, respectively. This gives $2^5=32$ ordered configurations. Thus, the surface of reference becomes

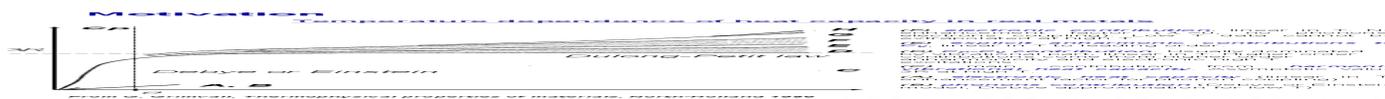
$$\begin{aligned} G^{srf} &= p_{ijklm} \circ G_{ijklm} \\ p_{ijklm} &= y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} y_m^{(5)} \end{aligned} \quad (8)$$



These compound energies, ${}^oG_{ijklm}$, are exactly the same FP energies calculated in the paper by Berne et al.

The only additional term necessary to calculate the Gibbs energy at any temperature is the entropy of mixing which is assumed to be ideal in CEF:

$$S^{conf} = -R \sum_s a^{(s)} \sum_{i=Re,W} y_i^{(s)} \ln(y_i^{(s)}) \quad (9)$$



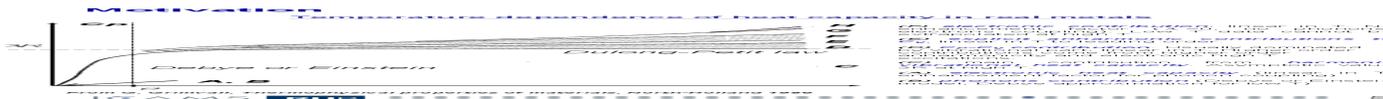
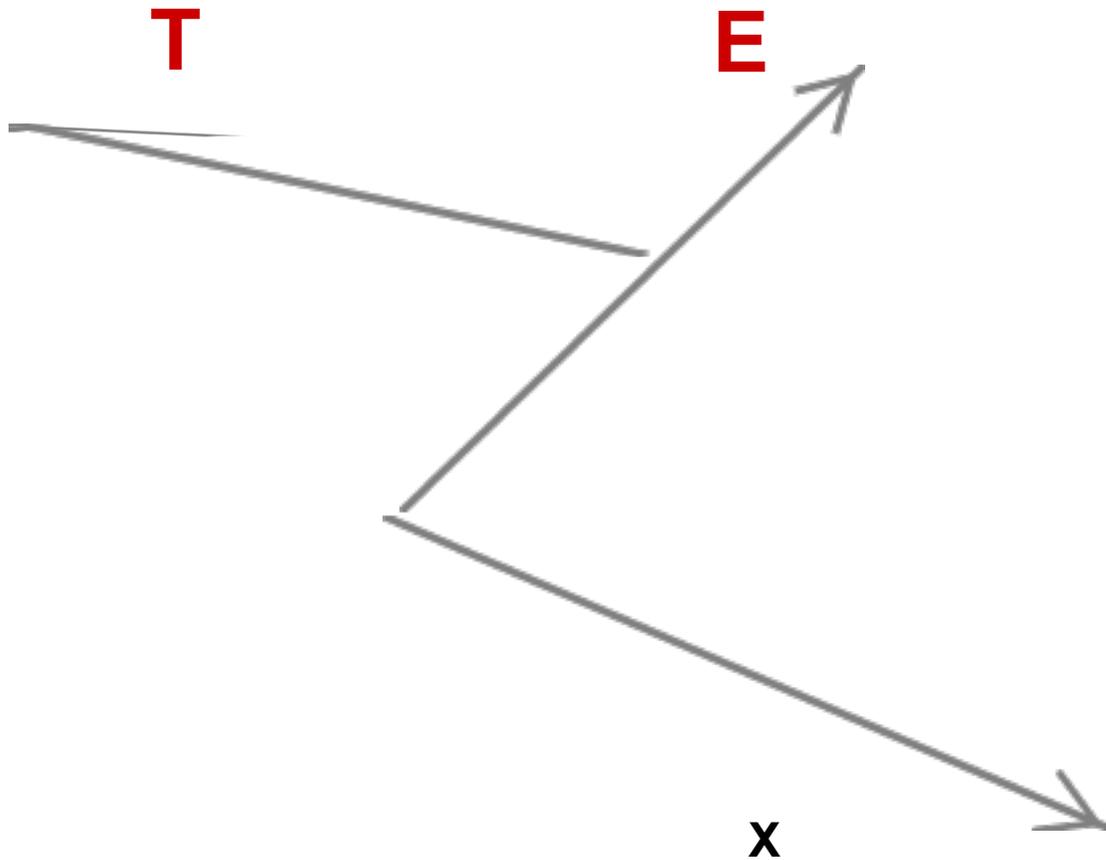
What is modeled?

E: Thermodynamic potential
and its derivatives

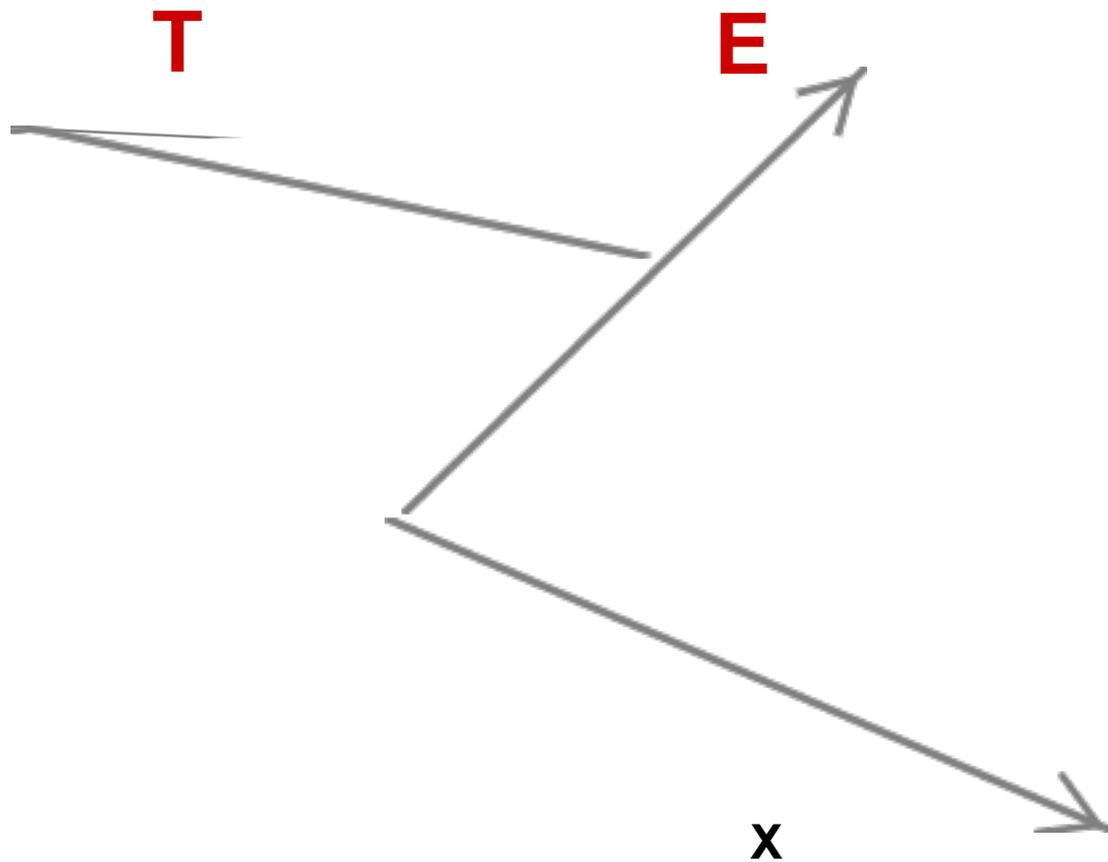
$G(P,T,N)$

$F(V,T,N)$

...



What is modeled?

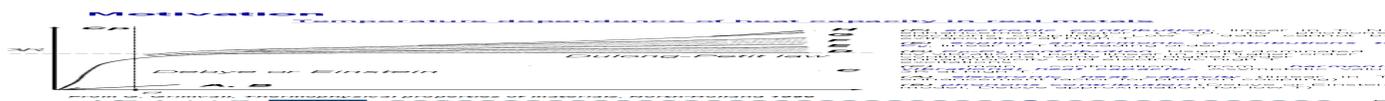
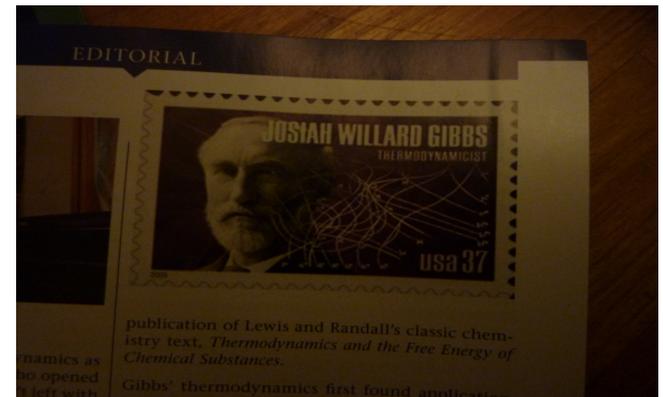


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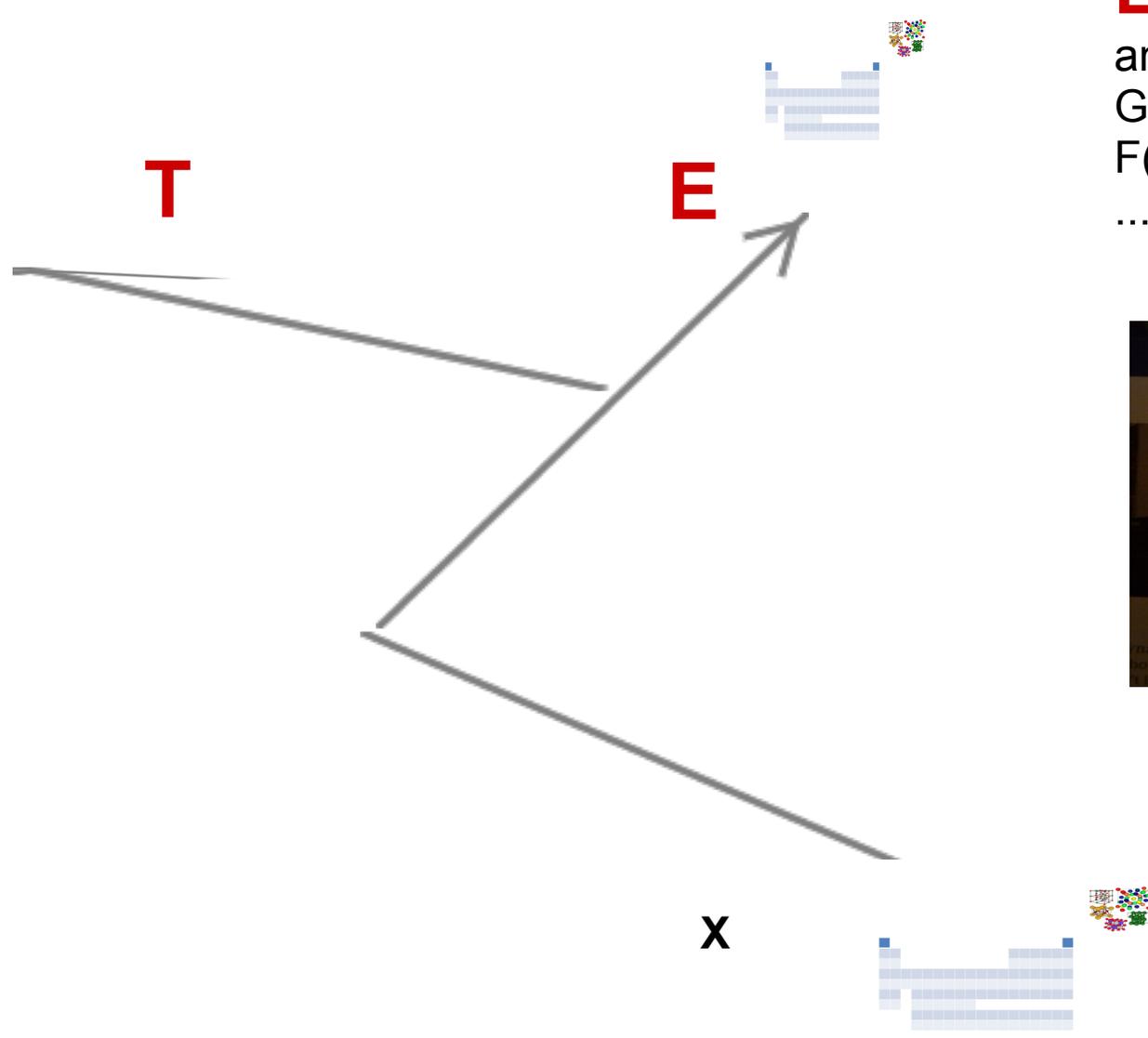
$$\kappa = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_{T, N_i}$$

bulk modulus

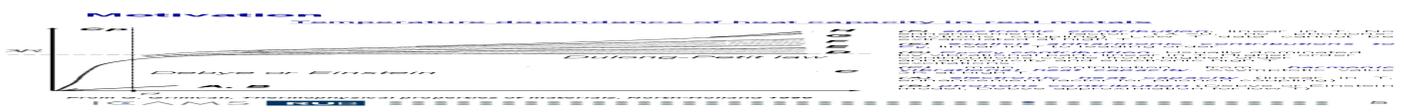
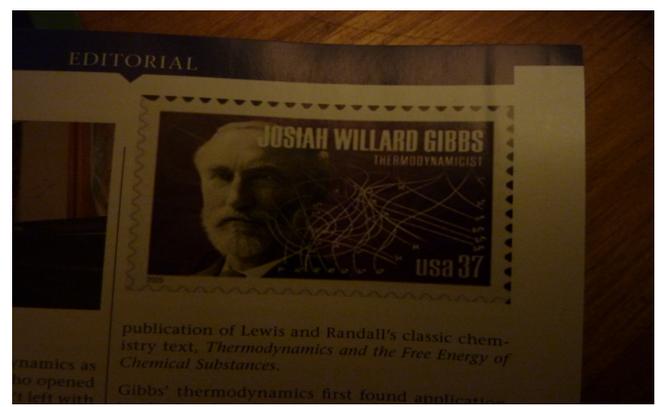
$$B = \frac{1}{\kappa}$$



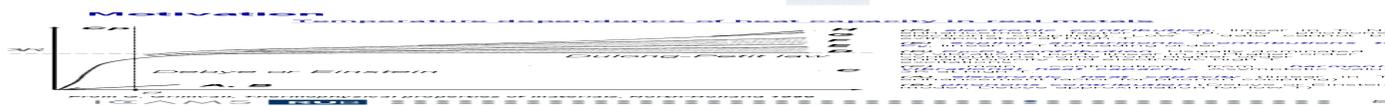
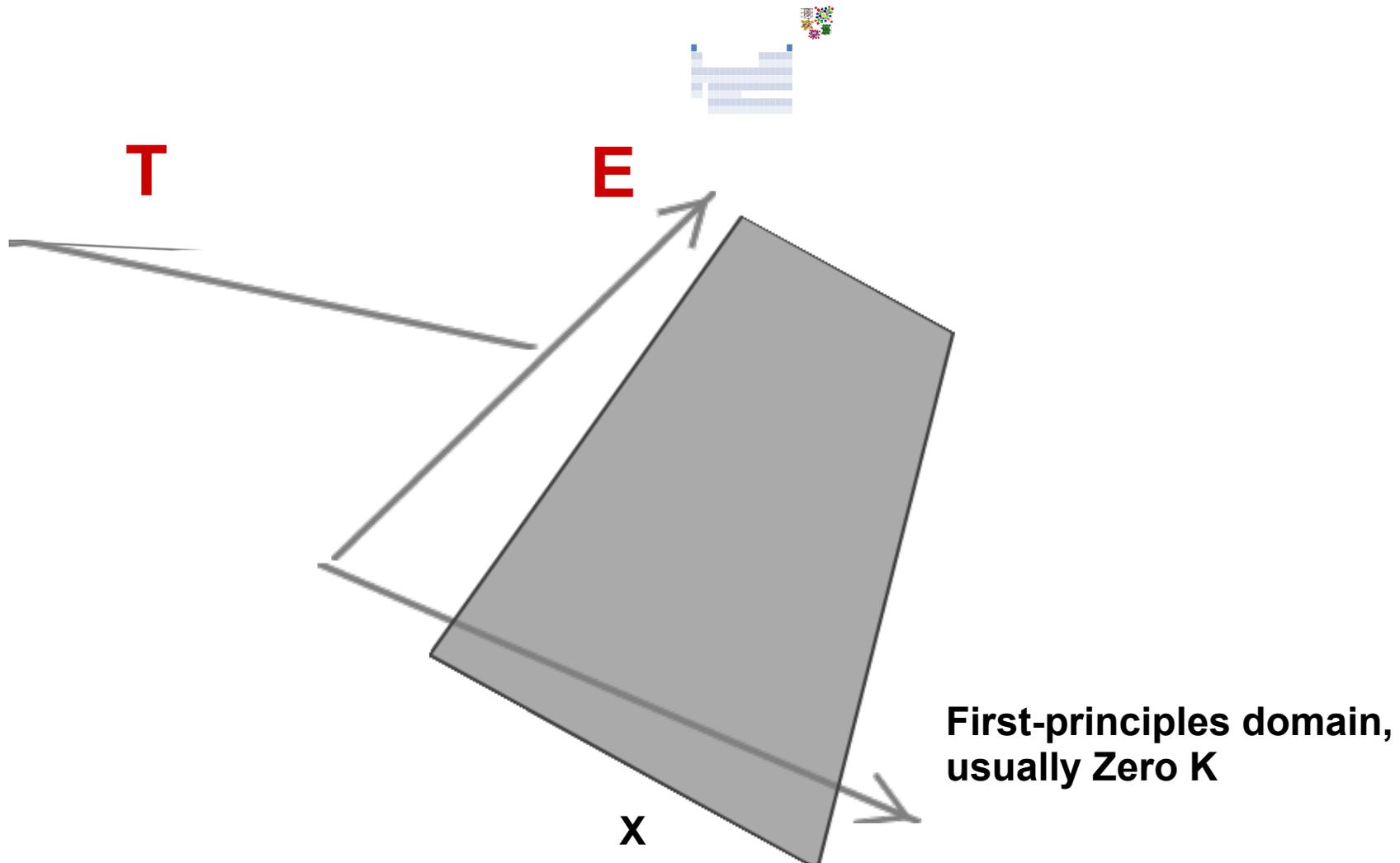
What do we would like to have?



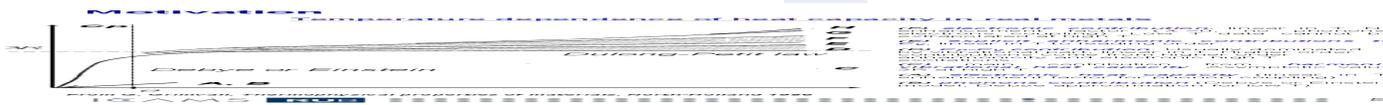
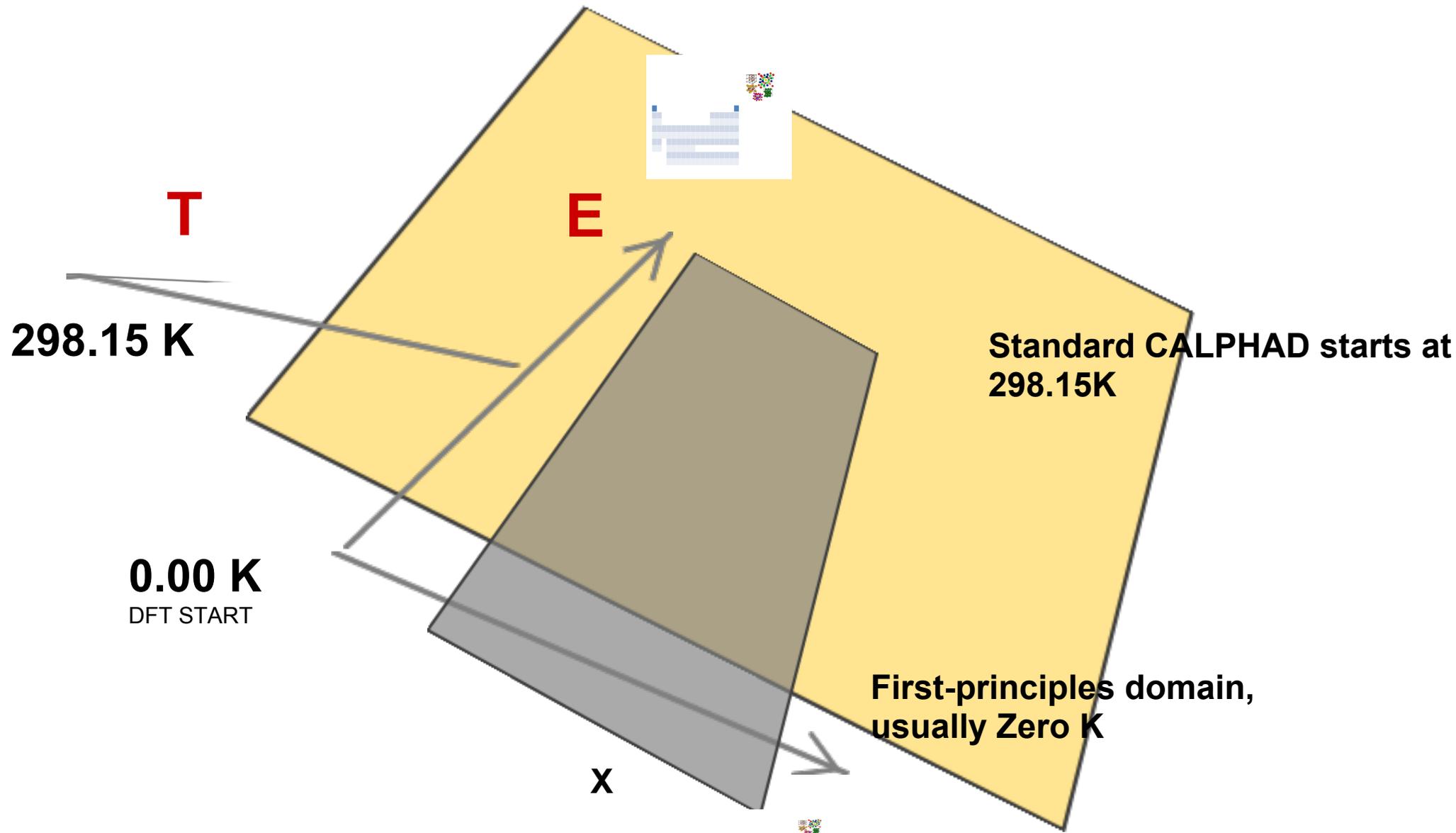
E: Thermodynamic potential
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 $G(P,T,N)$
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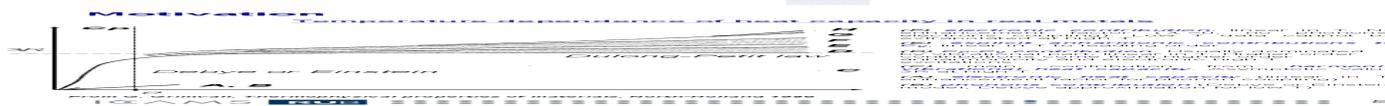
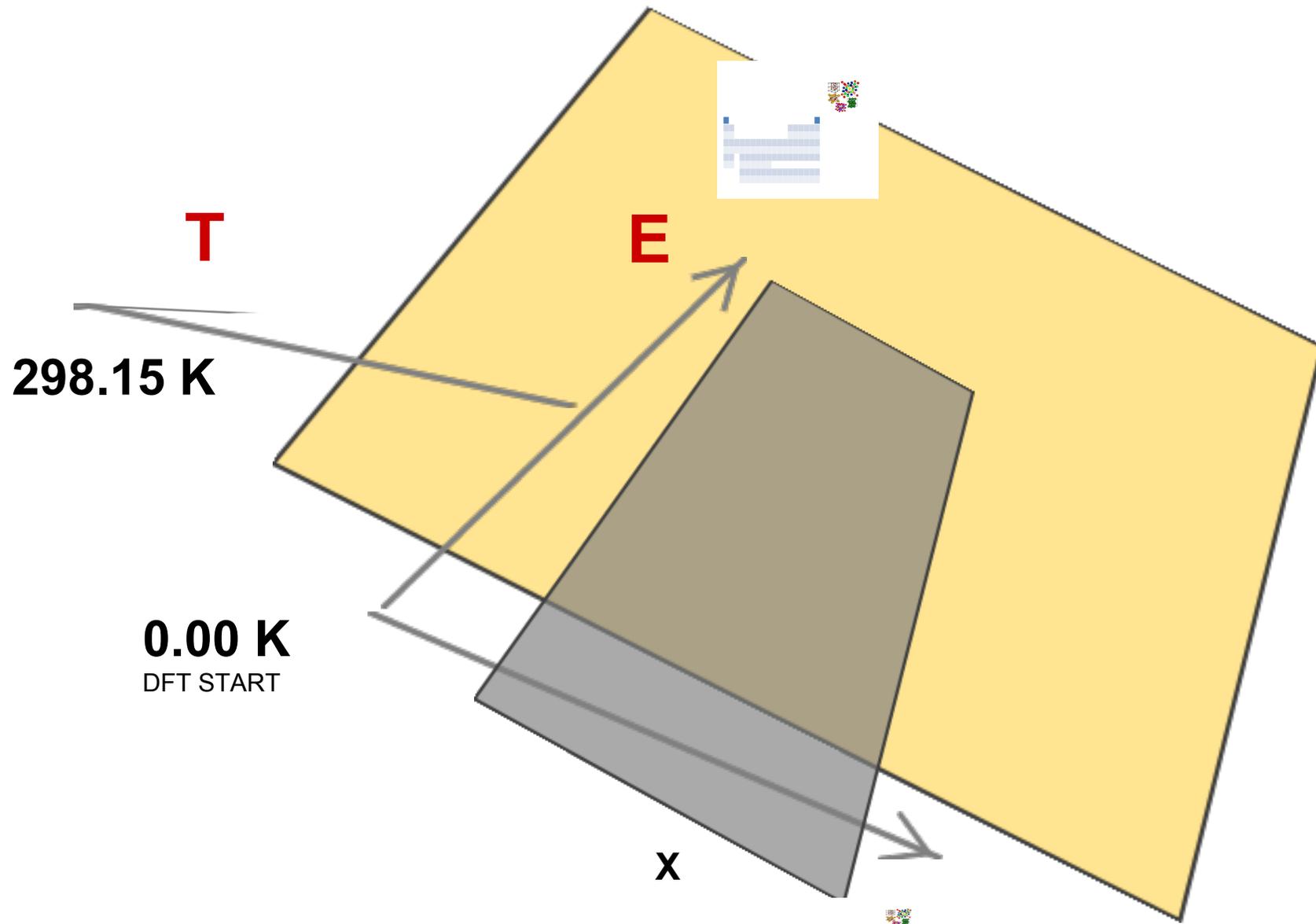
Being trully predictive...the big challenge.



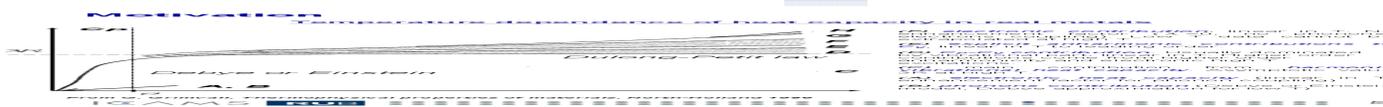
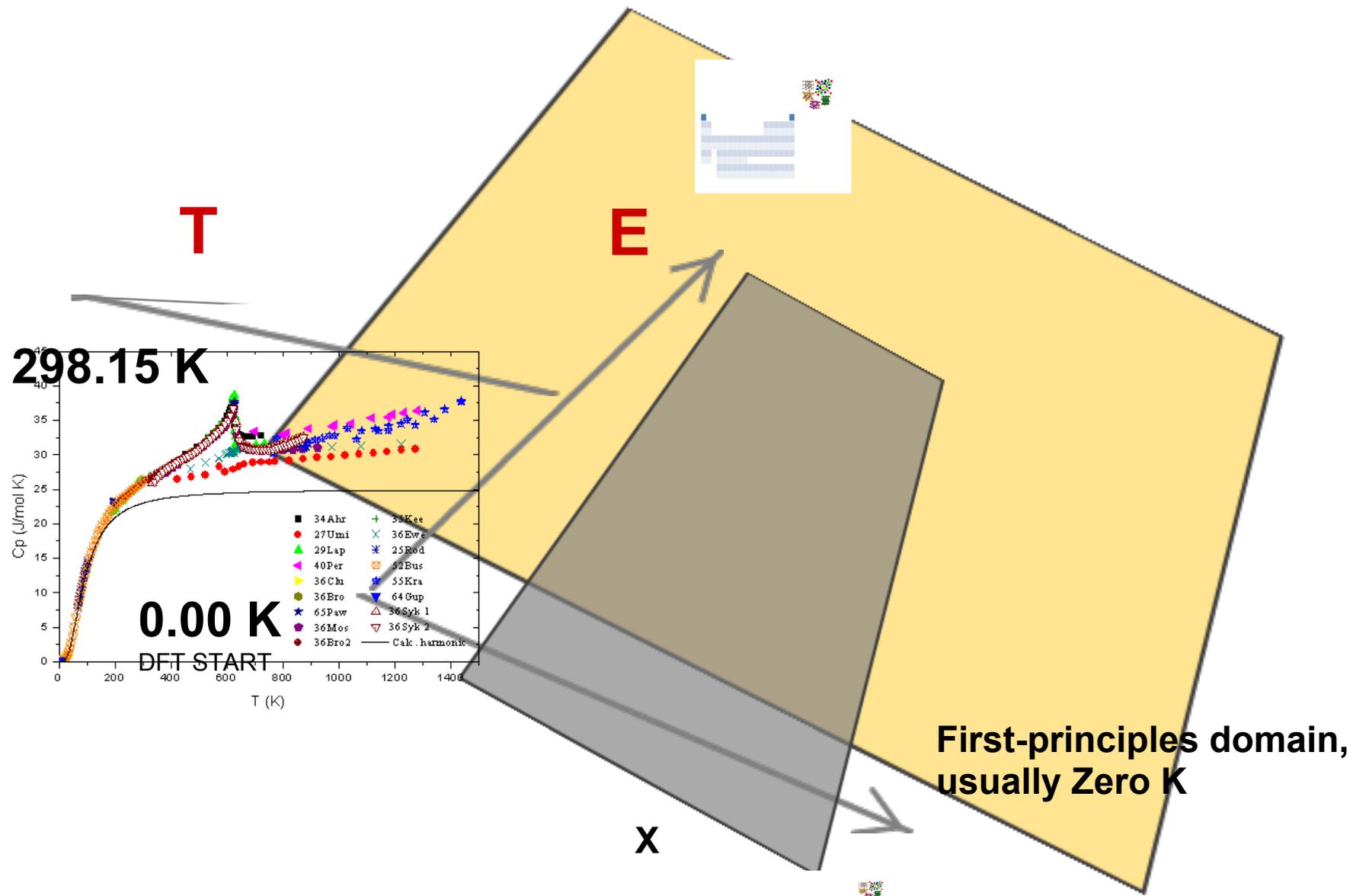
Connecting the approaches



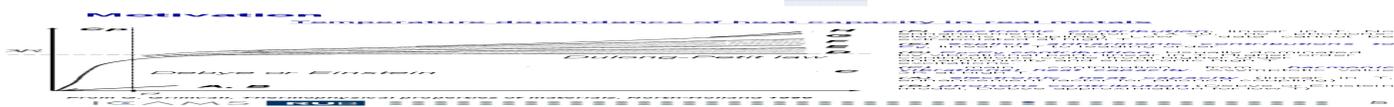
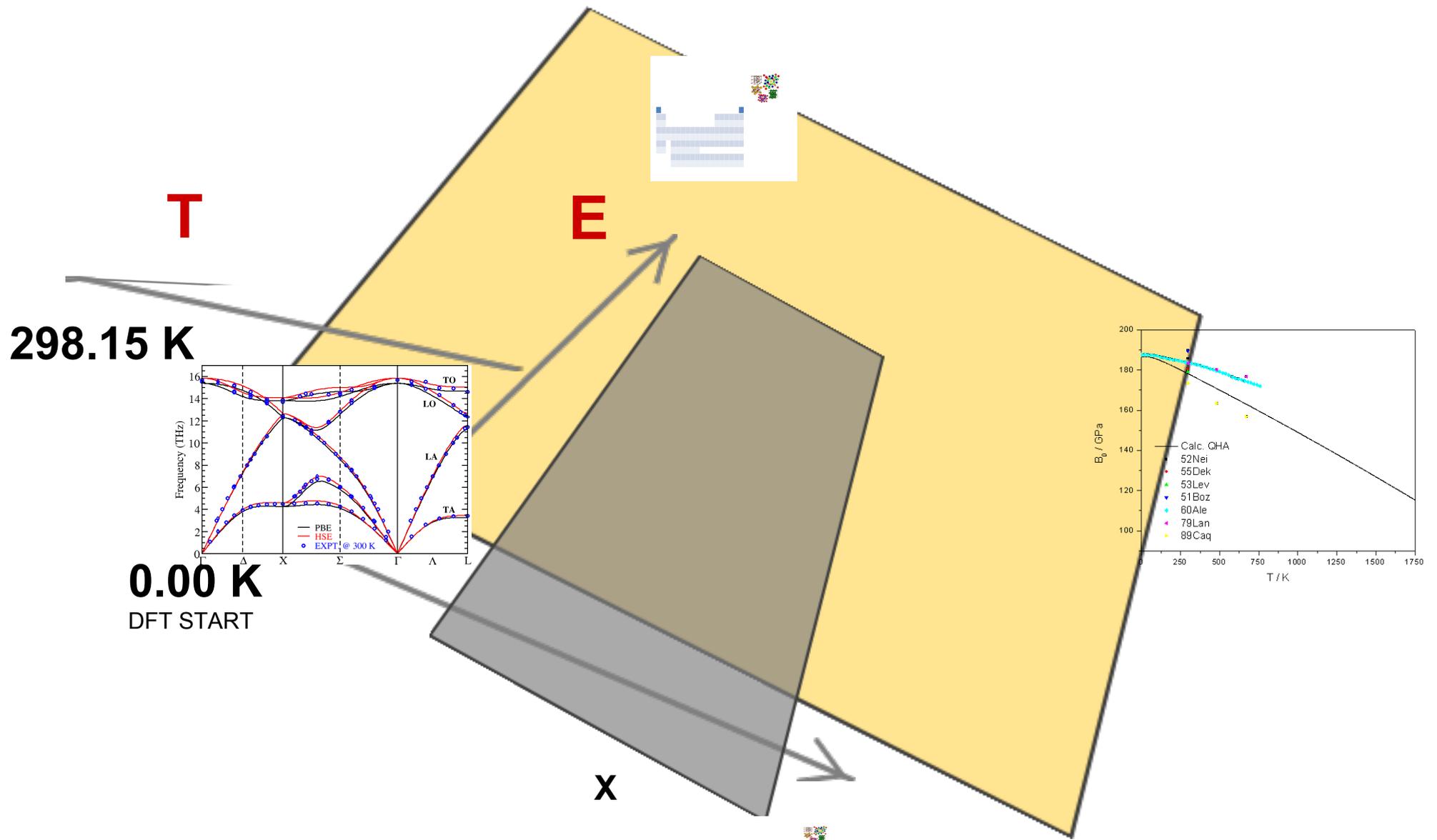
New kind of experimental values



Cp at low temperature



Phonons spectra, bulk modulus, etc



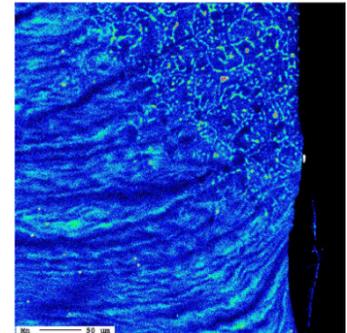
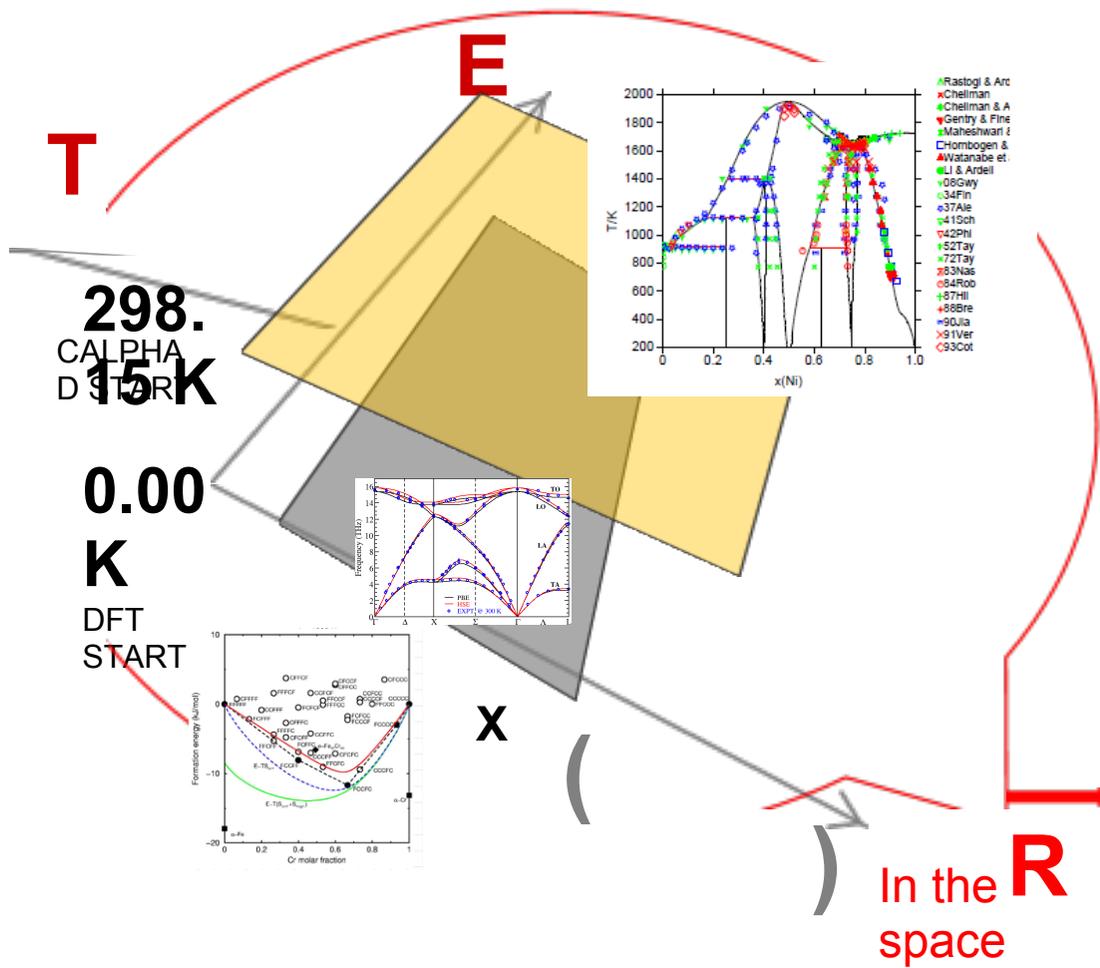


Bulk modulus

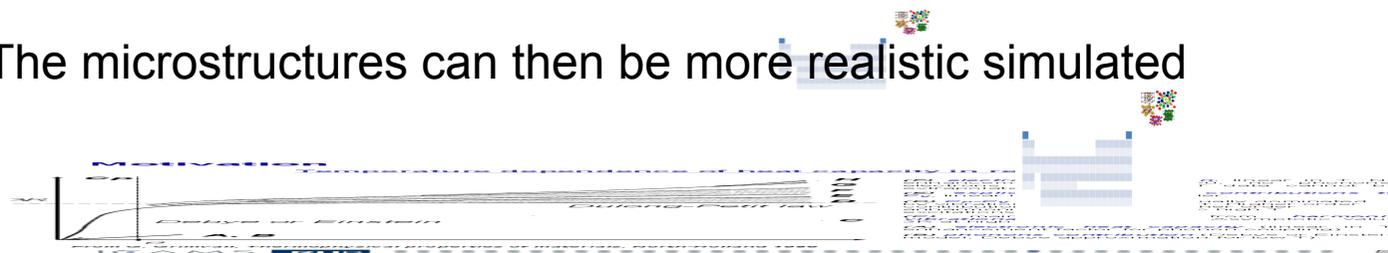
Thermal expansion

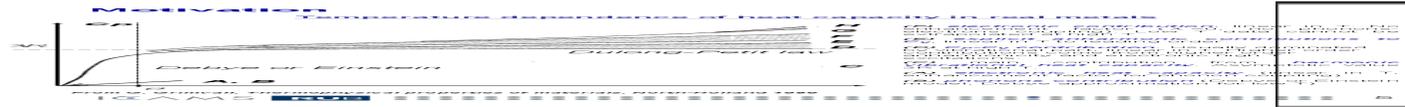
Heat capacity

Microstructure Simulation



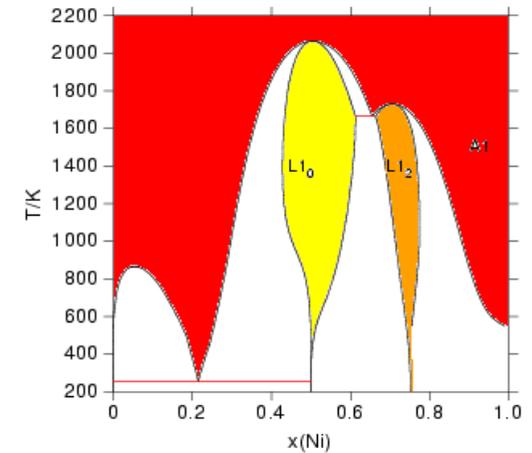
The microstructures can then be more realistic simulated





Fundamentals

$T=0$ $S=0$



CPA vs
Cluster Expansion

Short and long
range order
necessary

