Beyond the Margules-equation

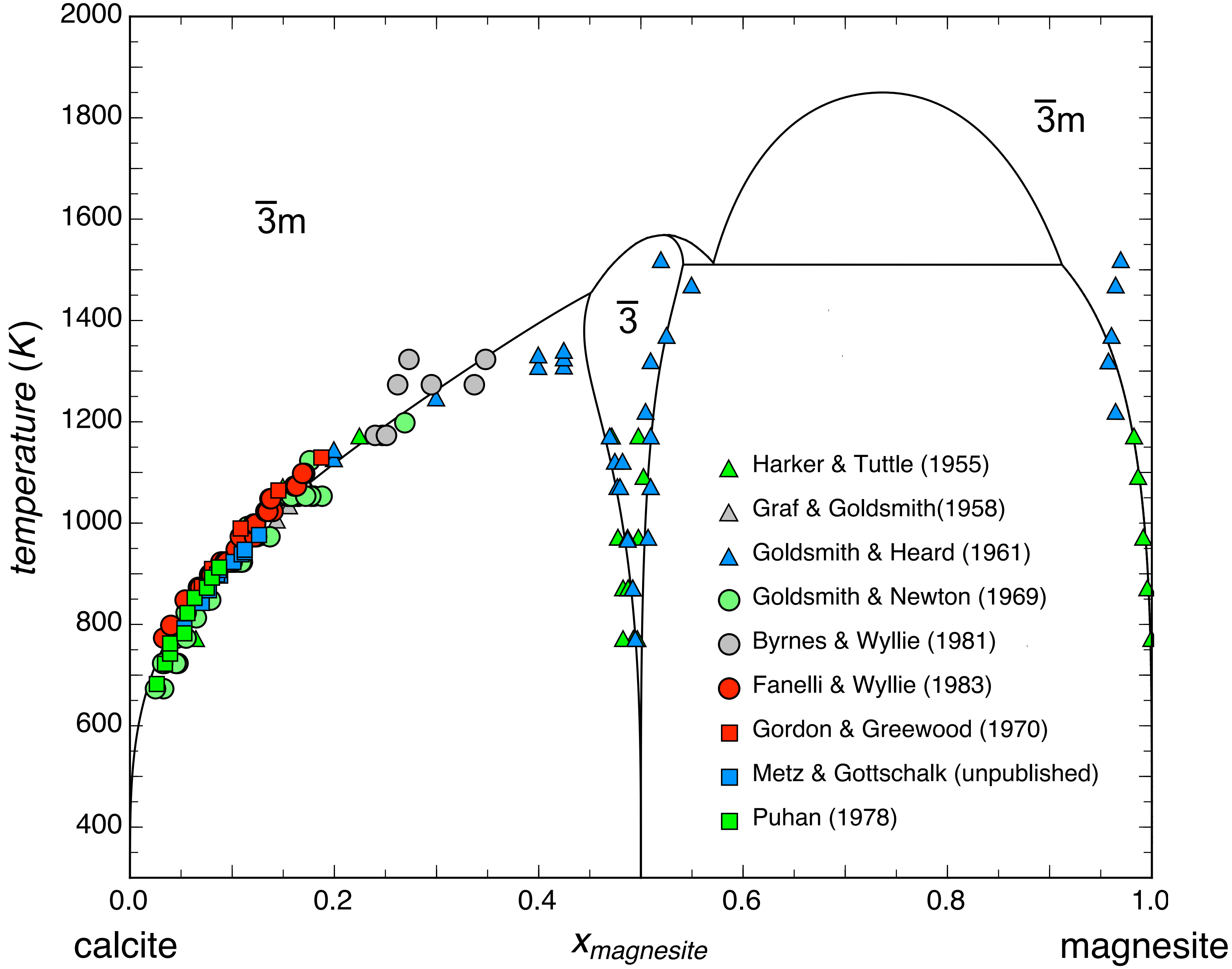
A treatment for multi-component solid solutions

Matthias Gottschalk

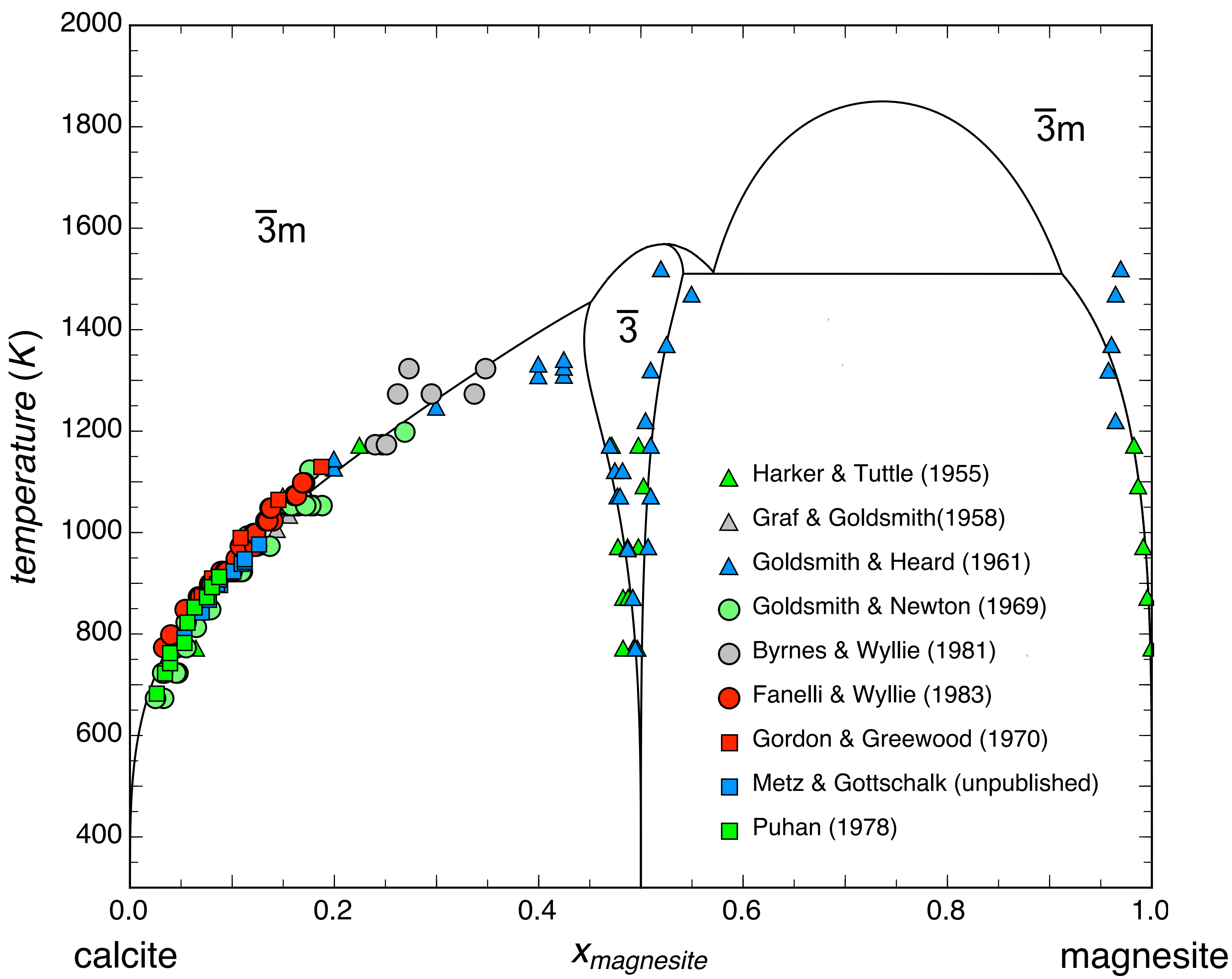
GFZ
Helmholtz-Zentrum
Potsdam

Helmholtz-Zentrum Potsdam
Deutsches GeoForschungsZentrum GFZ

thermodynamic treatment of solid solutions



thermodynamic treatment of solid solutions



- ideal mixing

$$s^{ideal} = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

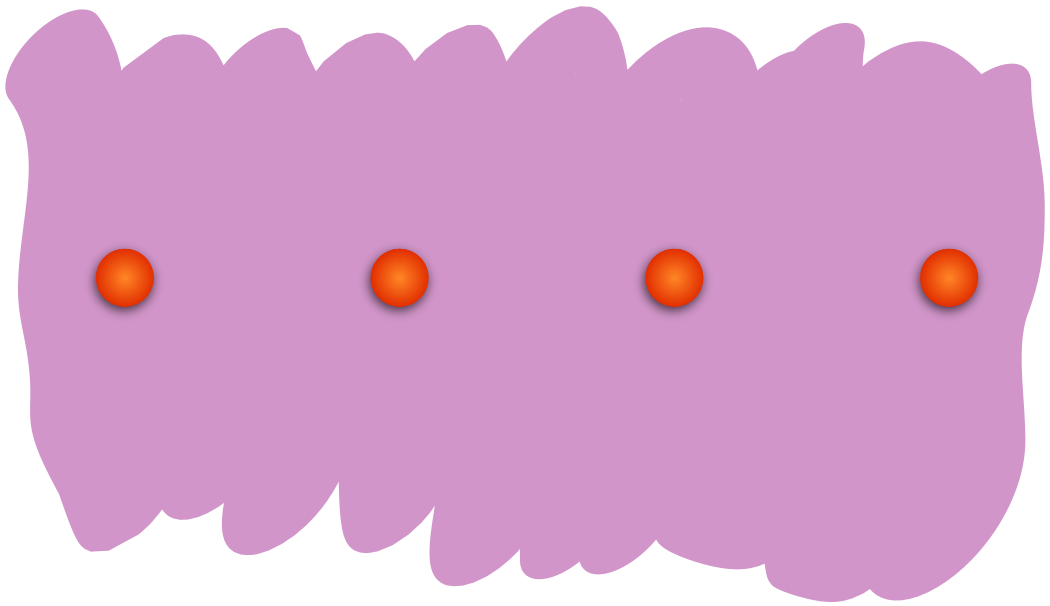
- regular or simple solution

$$h^{excess} = x_1 x_2 W_{12}$$

- Margules-equation

$$h^{excess} = x_1 x_2 \left(x_1 W_{112} + x_2 W_{122} \right)$$

cations with no interaction



$$h^{ss} = h_i^o$$

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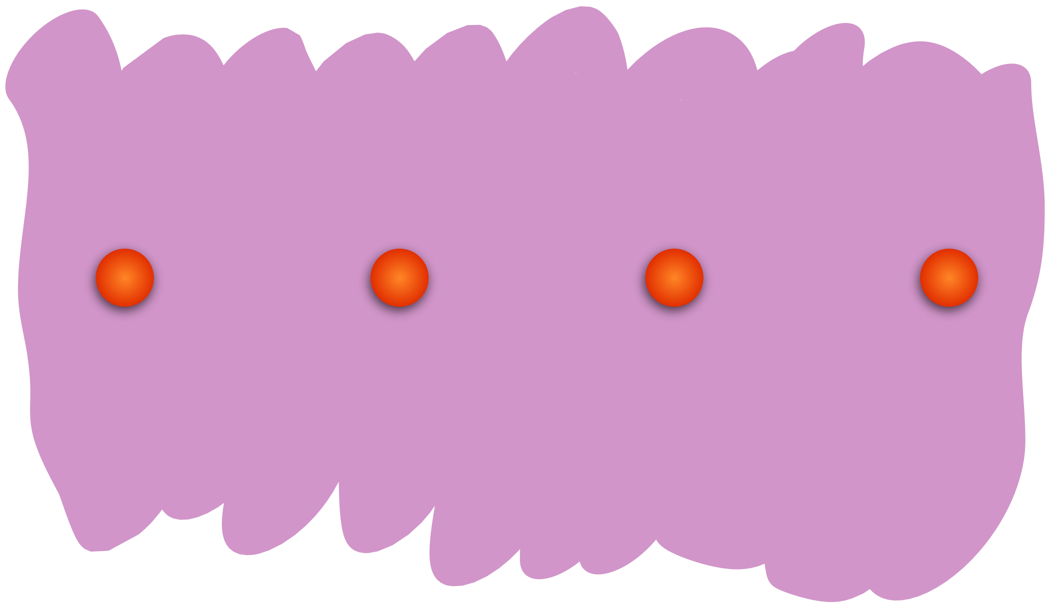
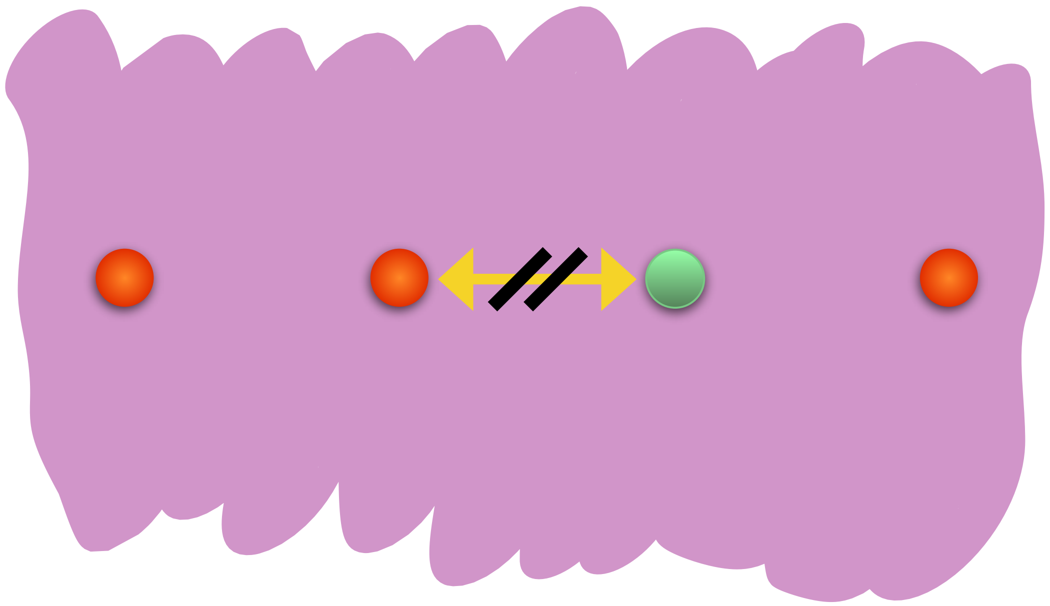


$$h^{ss} = h_i^o$$

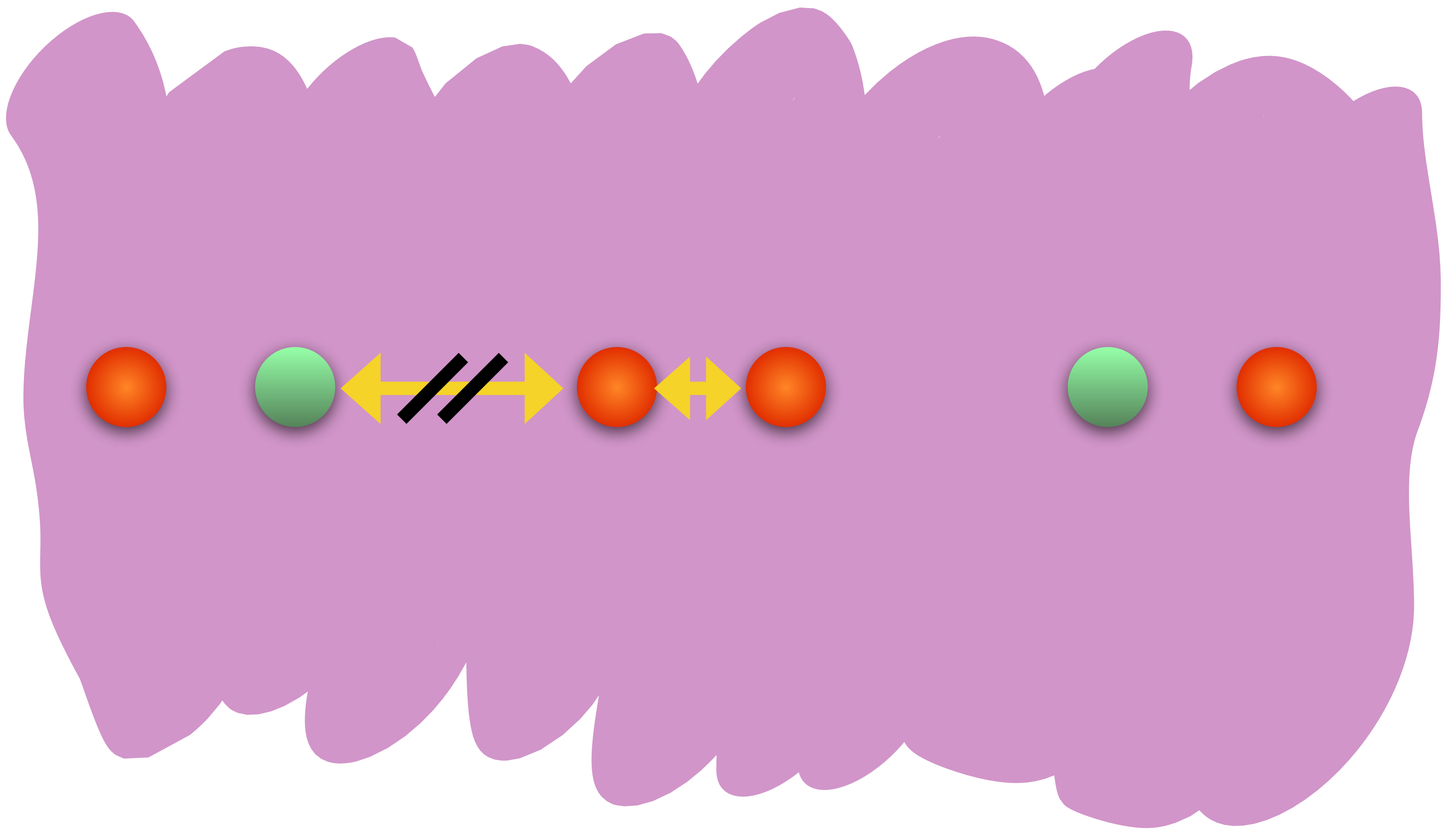


$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o = h^{mechanical}$$

c: number of components
x: mole fraction

$$h^{ss} = x_1 h_1^o + x_2 h_2^o$$

2-body cation interaction



$$h^{ss} = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j h_{(i:j)}$$

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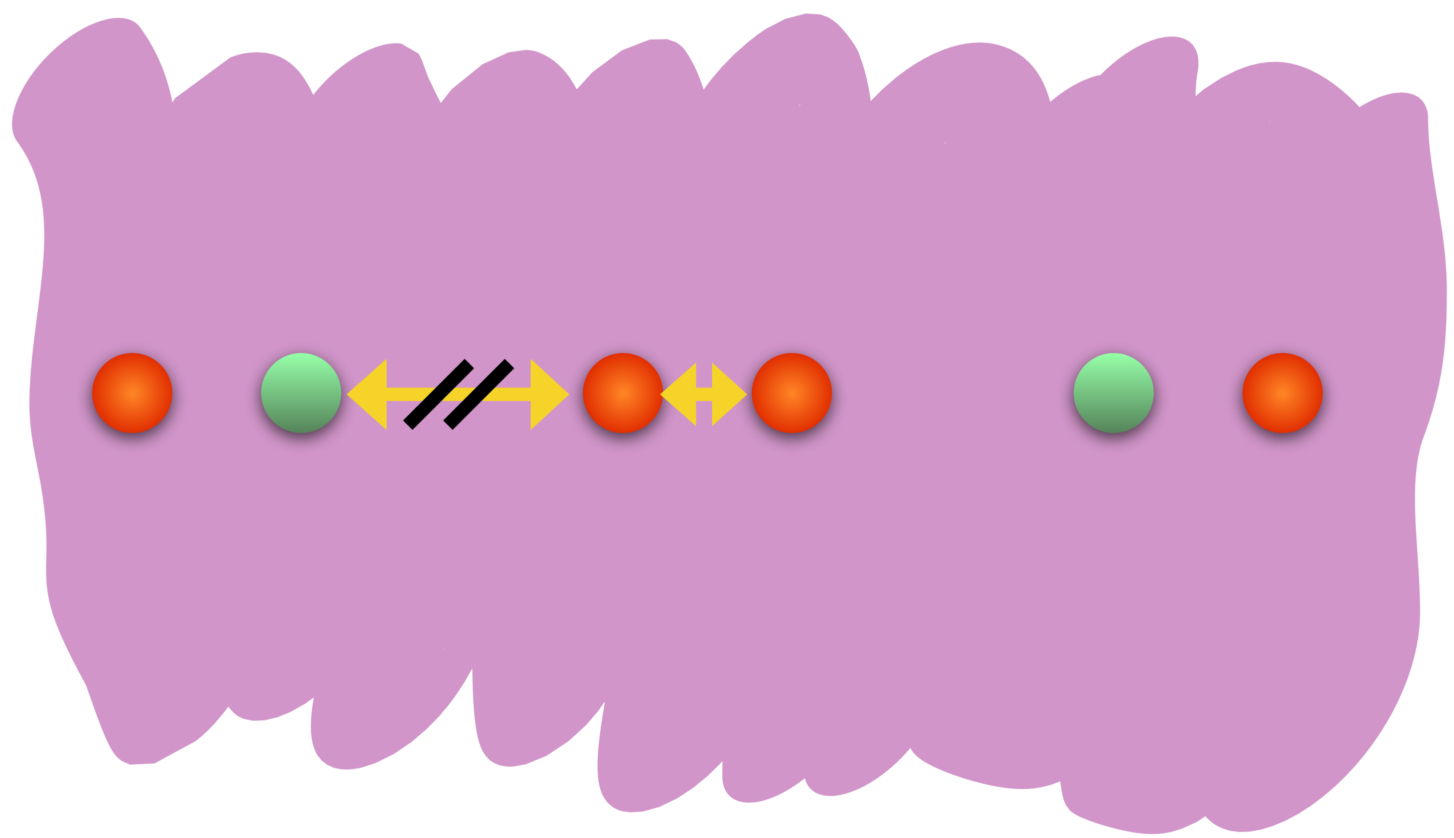
2-body cation interaction



$$h^{ss} = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j h_{(i:j)}$$

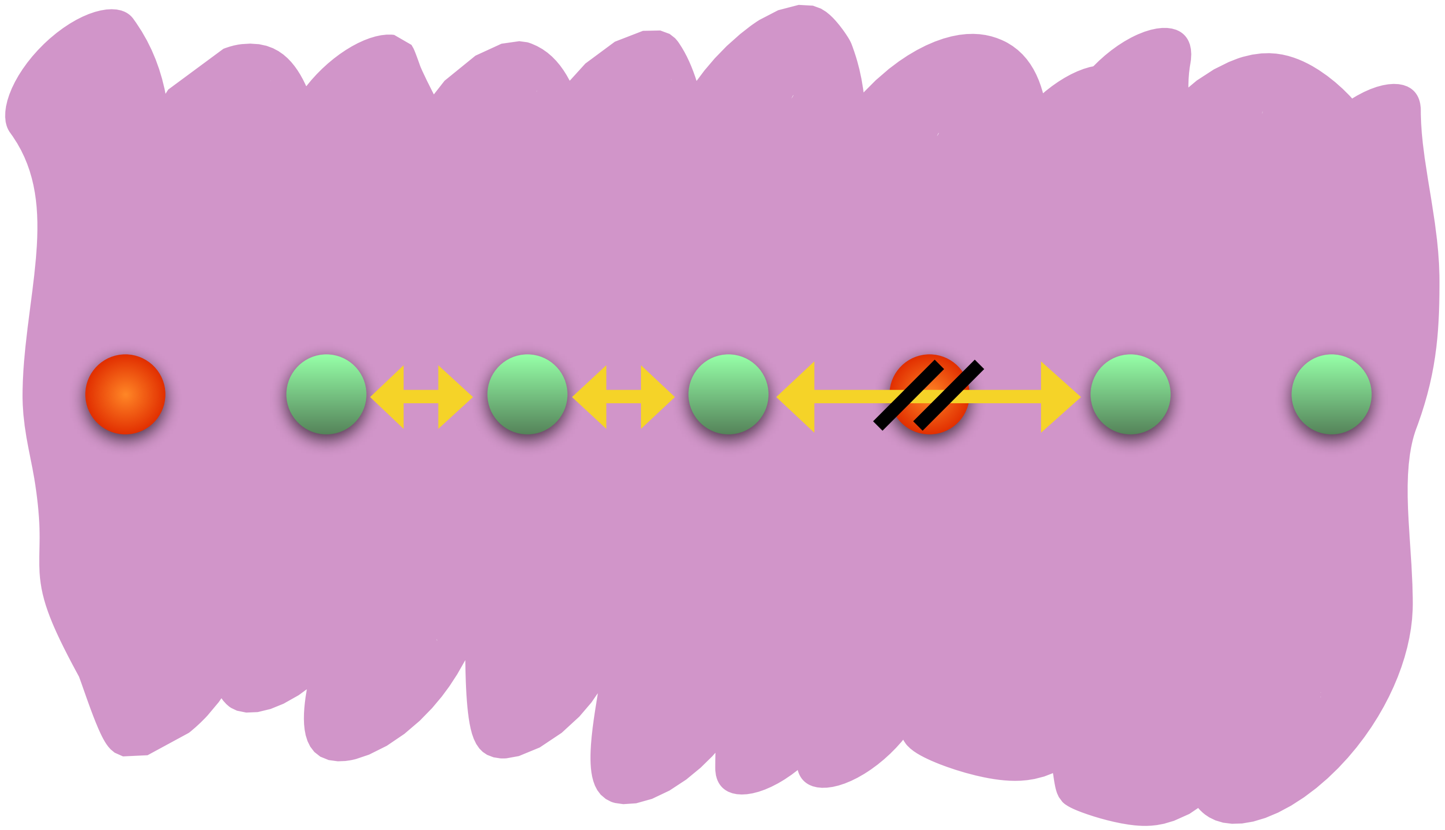
c: number of components
x: mole fraction

$$\boxed{\Delta H_{(i:j)} \triangleq 2h_{(i:j)} - h_{(i:i)} - h_{(j:j)} = 2h_{(i:j)} - h_i^o - h_j^o}$$

$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o + \frac{1}{2} \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j \Delta H_{(i:j)}$$

mechanical excess

3-body cation interaction



$$h^{ss} = \sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c} x_i x_j x_k h_{(i:jk)}$$

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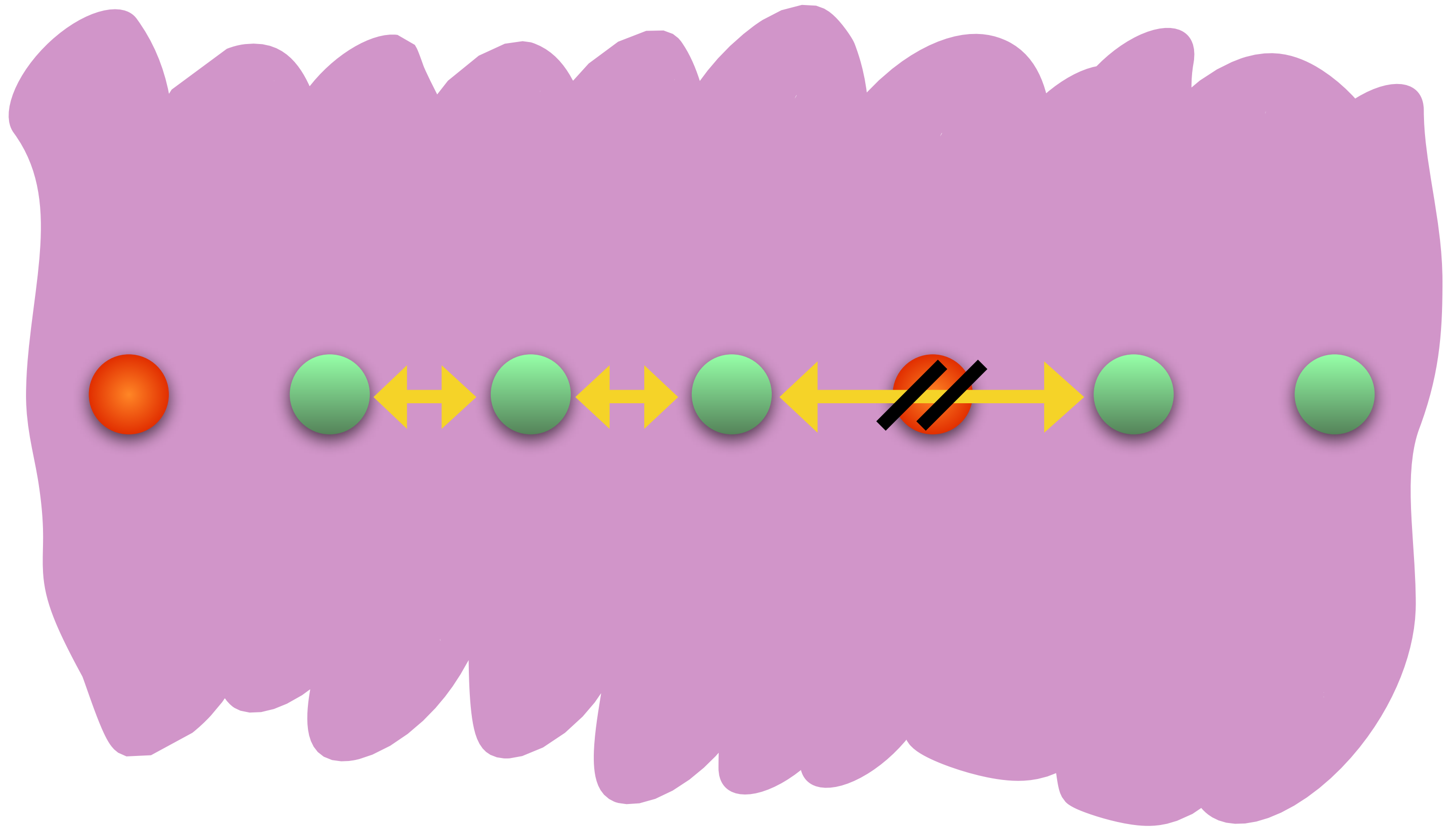
3-body cation interaction



$$h^{ss} = \sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c} x_i x_j x_k h_{(i:jk)}$$

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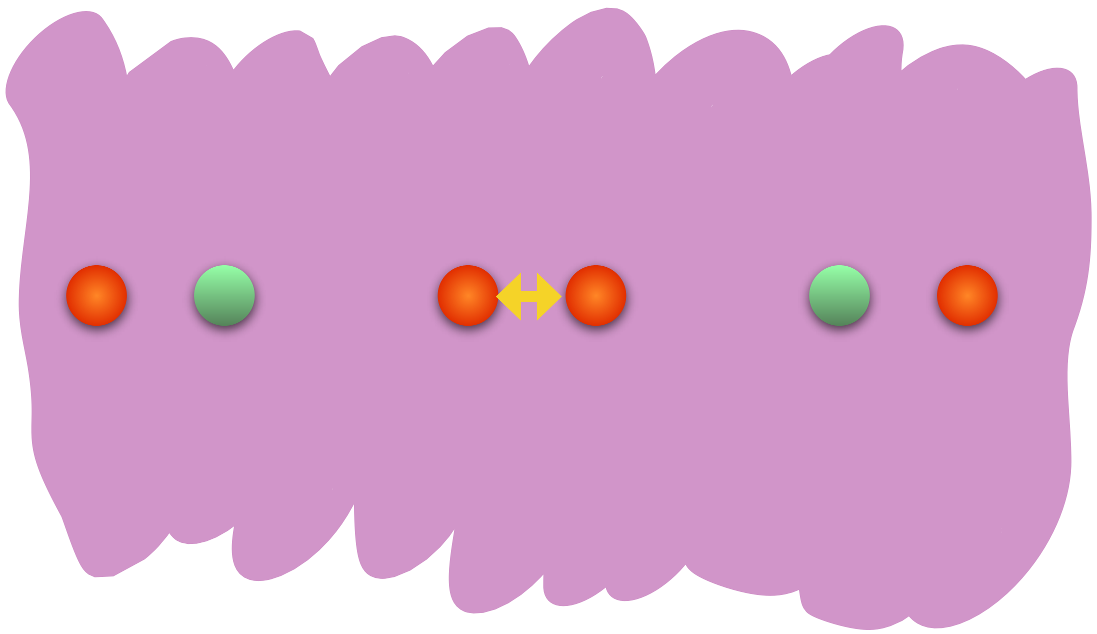
$$\boxed{\Delta H_{(i:jk)} \triangleq 3h_{(i:jk)} - h_{(i:ii)} - h_{(j:jj)} - h_{(k:kk)} = 3h_{(i:jk)} - h_i^o - h_j^o - h_k^o}$$

$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o + \frac{1}{3}\sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c} x_i x_j x_k \Delta H_{(i:jk)}$$

mechanical excess

relations to well known equations



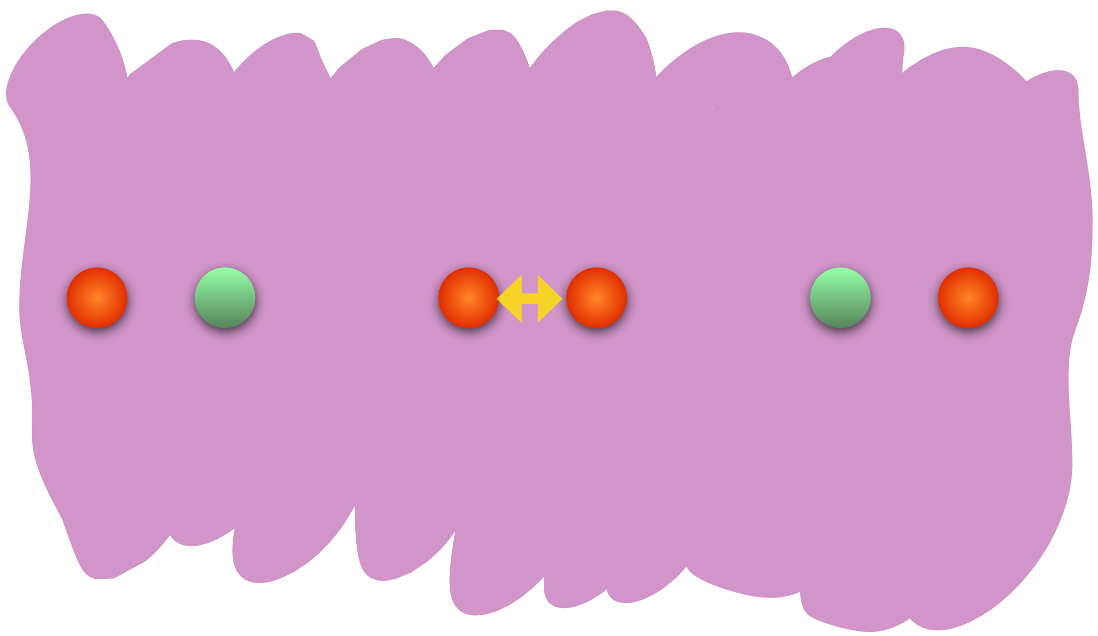
$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o + \frac{1}{2}\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j \Delta H_{(i:j)}$$

$$\boxed{\Delta H_{(i:j)} = \Delta H_{(j:i)} = \Delta H_{ij}}$$

$$h^{ss} = x_1 h_1^o + x_2 h_2^o + x_1 x_2 \Delta H_{12}$$

simple or regular solution

relations to well known equations



$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o + \frac{1}{2}\sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j \Delta H_{(i:j)}$$

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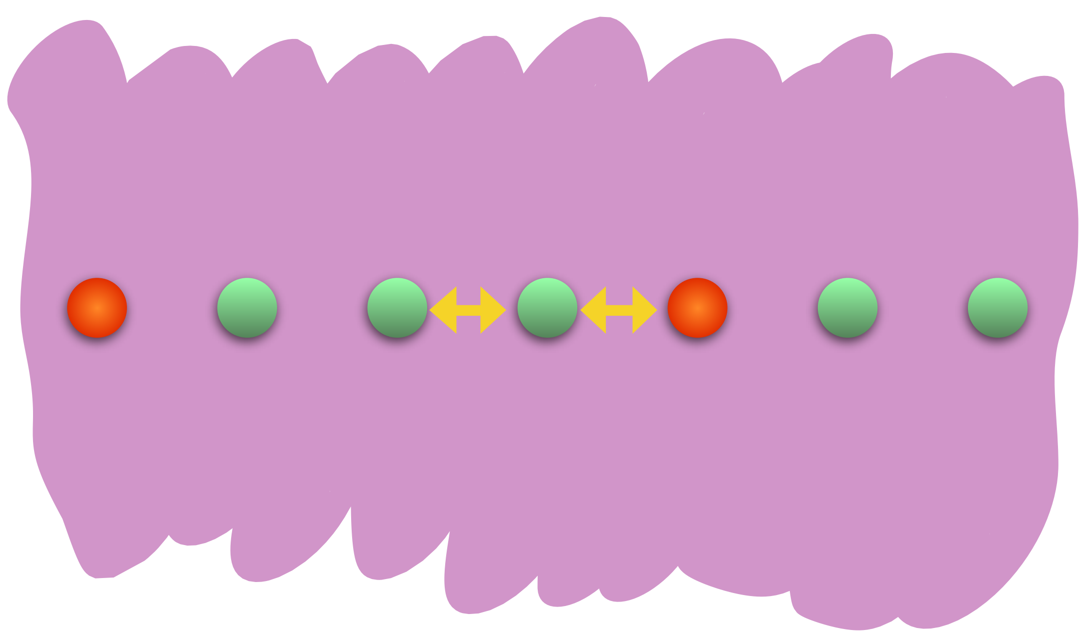


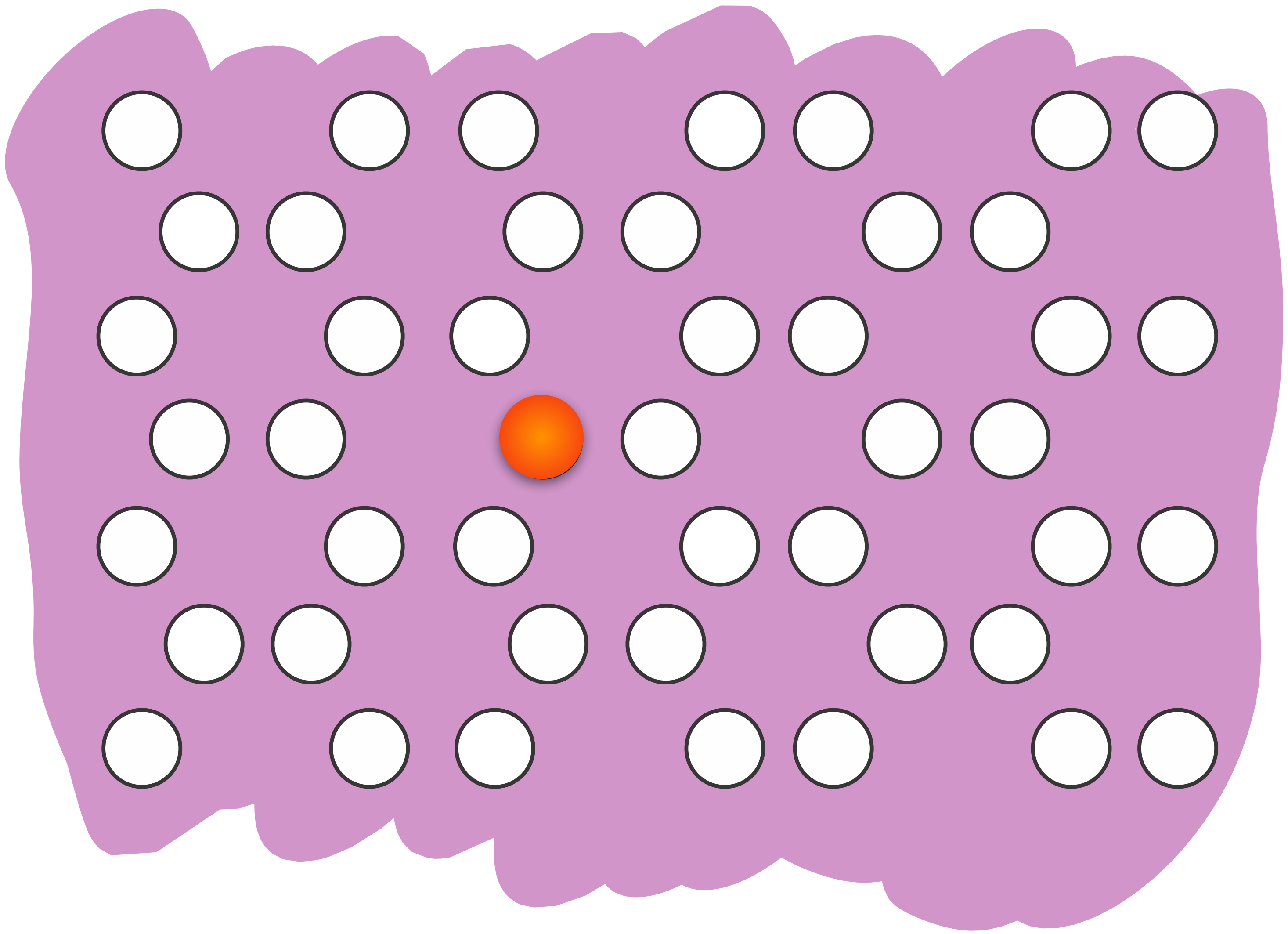
$$h^{ss} = \sum_{i=1}^{c} x_i h_i^o + \frac{1}{3}\sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c} x_i x_j x_k \Delta H_{(i:jk)}$$

$$\boxed{\Delta H_{(i:jk)} = \Delta H_{(j:ik)} = \Delta H_{(k:ij)} = \cdots = \Delta H_{ijk}}$$

$$h^{ss} = x_1 h_1^o + x_2 h_2^o + x_1 x_2 \left(x_1 \Delta H_{112} + x_2 \Delta H_{122} \right)$$

Margules (1895)

general formulation



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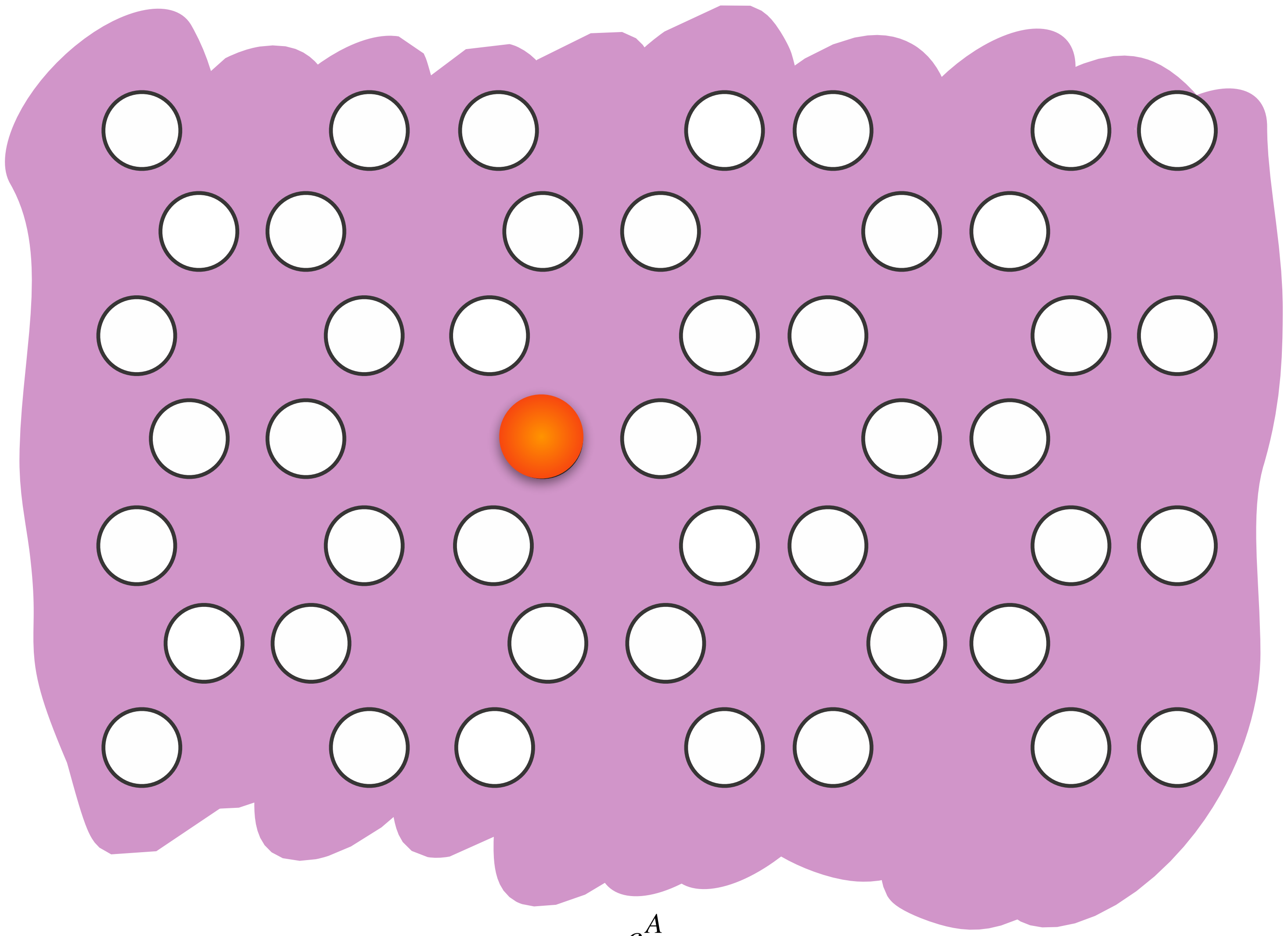
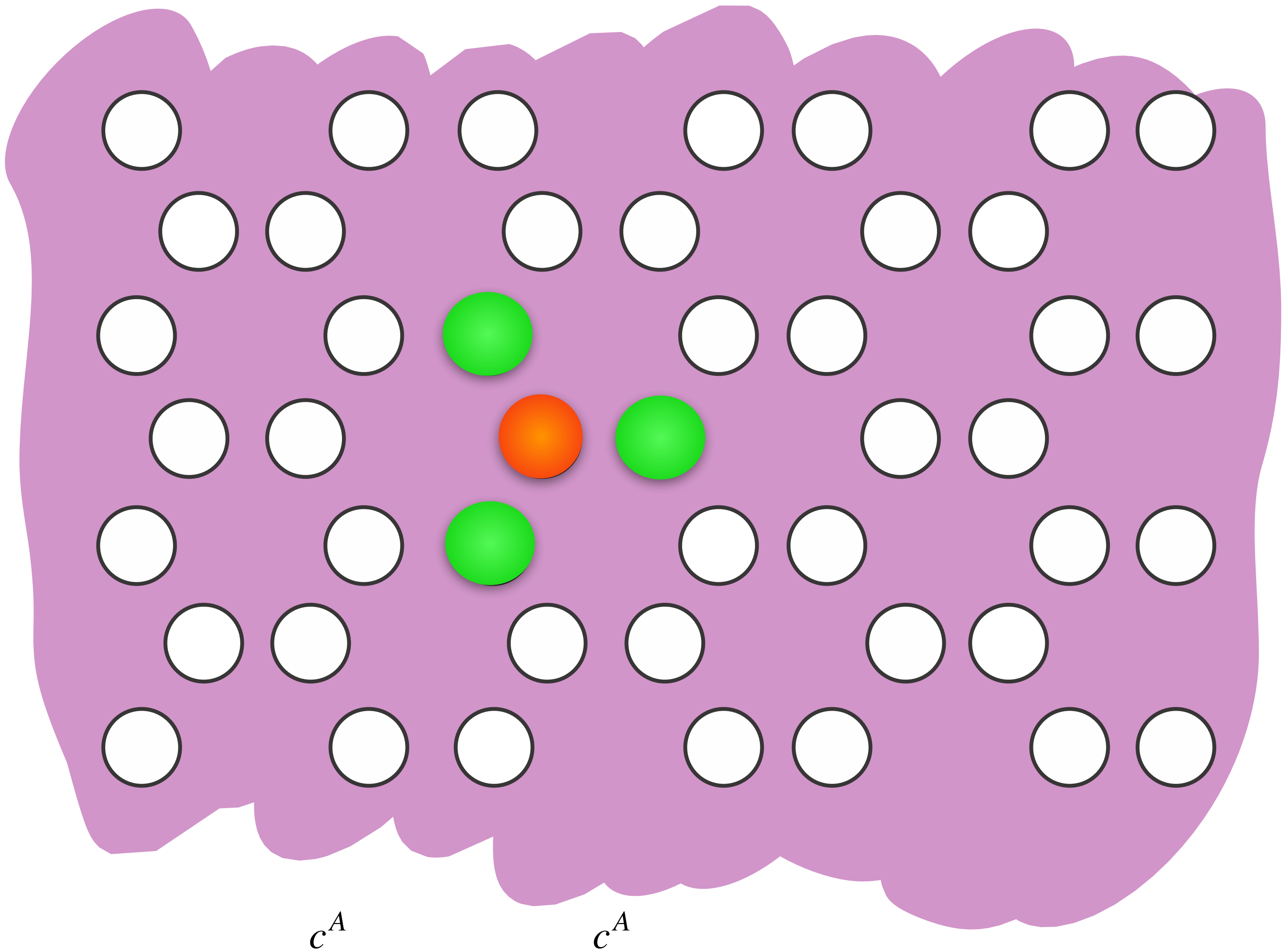


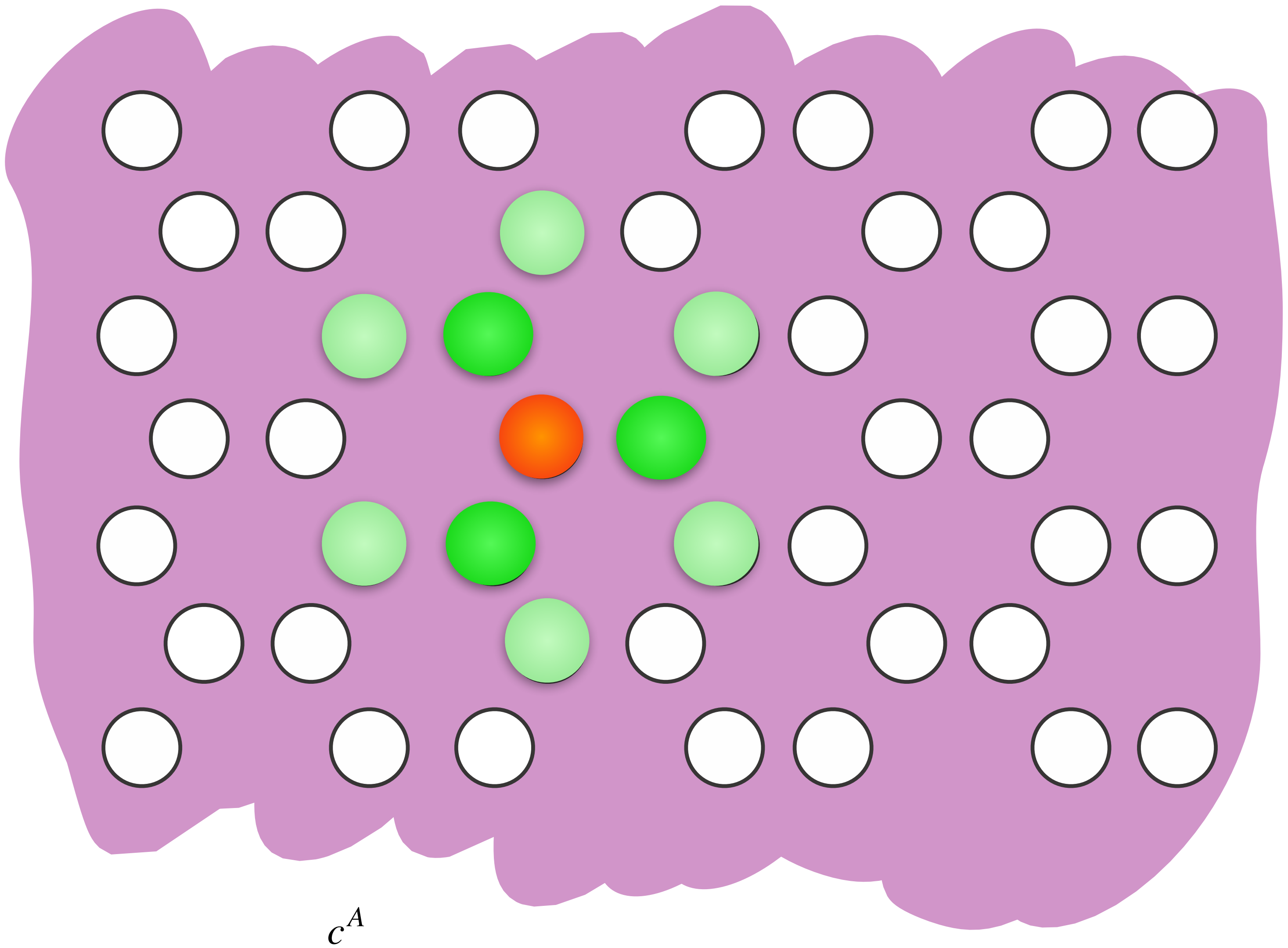
$$h^{ss} = \sum_{i=1}^{c^A} x_i^A h_i^o$$

general formulation



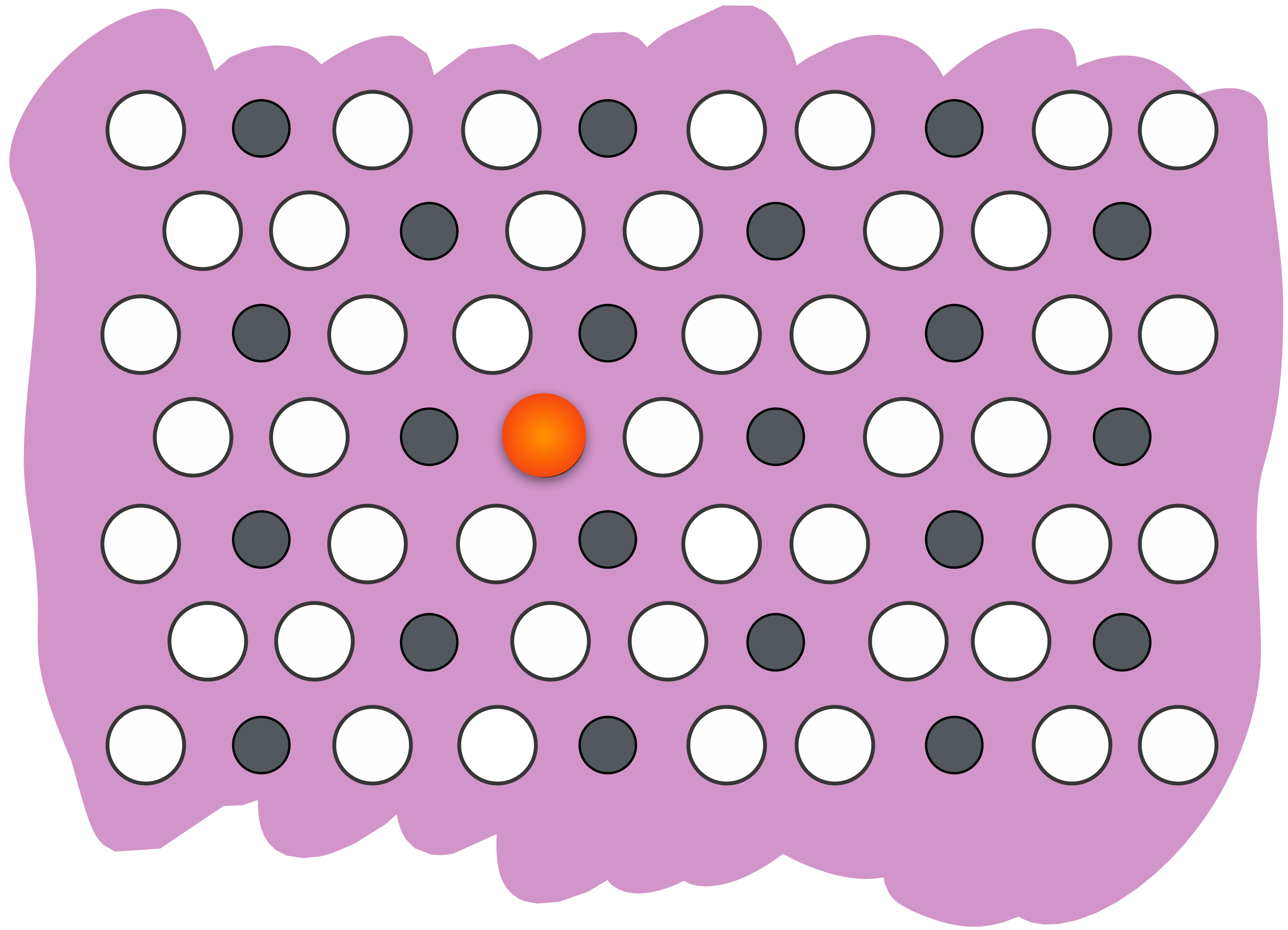
$$h^{ss} = \sum_{i=1}^{c^A} x_i^A h_i^o + \sum_{i,j,k,l}^{c^A} x_i^A x_j^A x_k^A x_l^A \Delta H_{(i:jkl)}$$

general formulation

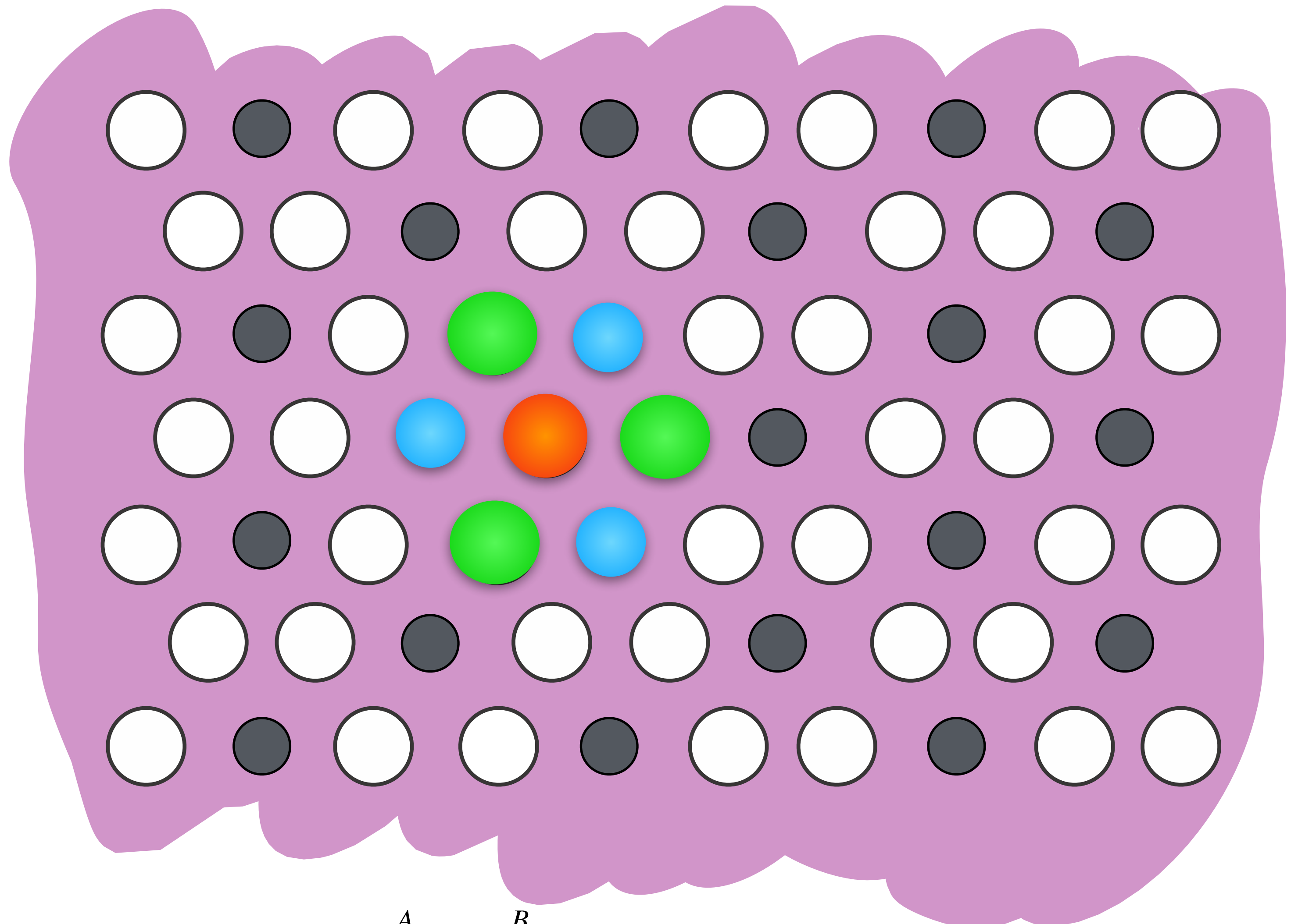


$$h^{ss} = \sum_{i=1}^{c^A} x_i^A h_i^o + \sum_{i,j,k,l,m,n,o,p,q,r}^{c^A} x_i^A x_j^A x_k^A x_l^A x_m^A x_n^A x_o^A x_p^A x_q^A x_r^A \Delta H_{(i:jkl/mnopqr)}$$

general formulation

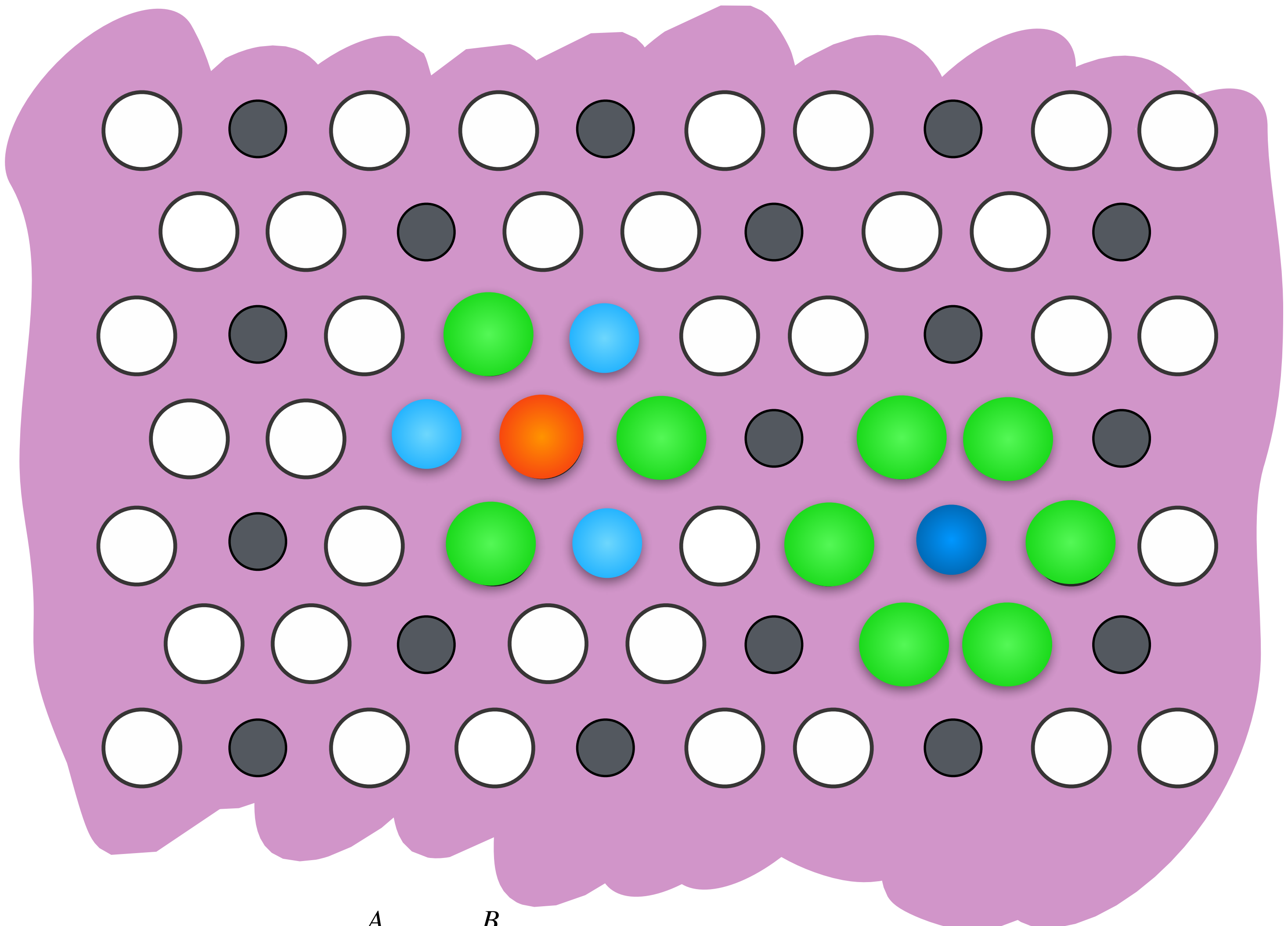


general formulation



$$h^{\text{excesss on } A} = 2\sum_{i,j,k,l}^{c^A}\sum_{m,n,o}^{c^B} x_i^A x_j^A x_k^A x_l^A x_m^B x_n^B x_o^B \Delta H_{(i:jkl)(mno)}$$

general formulation

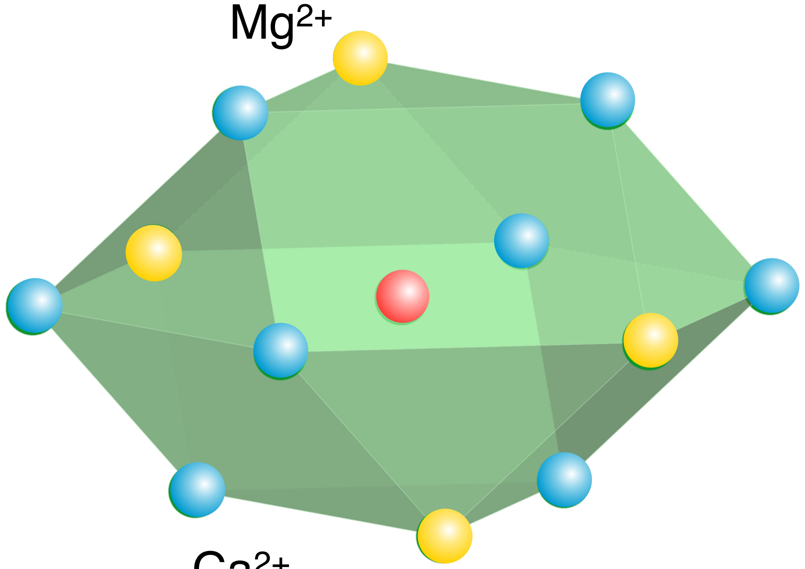


$$h^{\text{excesss on }A} = 2\sum_{i,j,k,l}^{c^A}\sum_{m,n,o}^{c^B} x_i^A x_j^A x_k^A x_l^A x_m^B x_n^B x_o^B \Delta H_{(i:jkl)(mno)}$$

$$h^{\text{excesss on }B} = \sum_{i}^{c^B}\sum_{j,k,l,m,n,o}^{c^A} x_i^B x_j^A x_k^A x_l^A x_m^A x_n^A x_o^A \Delta H_{(i)(jklmno)}$$

$$h^{ss} = \sum_i^{c^A}\sum_j^{c^B} x_i^A x_j^B h_{ij}^o + h^{\text{excesss on }A} + h^{\text{excesss on }B}$$

$CaCO_3$-$MgCO_3$



$$h^{ss} = \sum_{i}^{c^A} \sum_{j}^{c^B} x_i^A x_j^B h_{ij}^o$$

$$+ \sum_{i,j,k,l,m,n,o}^{c^A} \sum_{p,q,r,s,t,u}^{c^B} x_i^A x_j^A x_k^A x_l^A x_m^A x_n^A x_o^A x_p^B x_q^B x_r^B x_s^B x_t^B x_u^B \Delta H_{(i:jklmno)(pqrstu)}$$

$$+ \sum_{i,j,k,l,m,n,o}^{c^B} \sum_{p,q,r,s,t,u}^{c^A} x_i^B x_j^B x_k^B x_l^B x_m^B x_n^B x_o^B x_p^A x_q^A x_r^A x_s^A x_t^A x_u^A \Delta H_{(i:jklmno)(pqrstu)}$$

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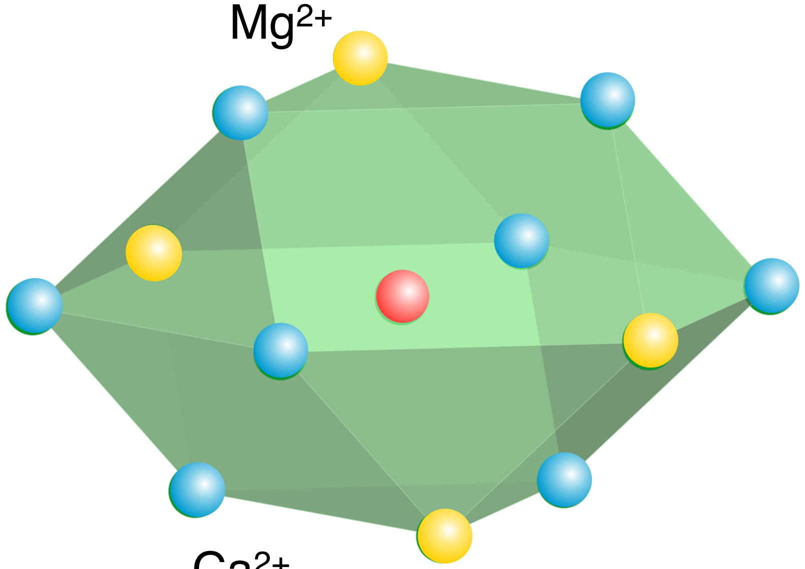

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$\Delta H_{(i:jklmno)(pqrstu)}$ → 8192 parameters

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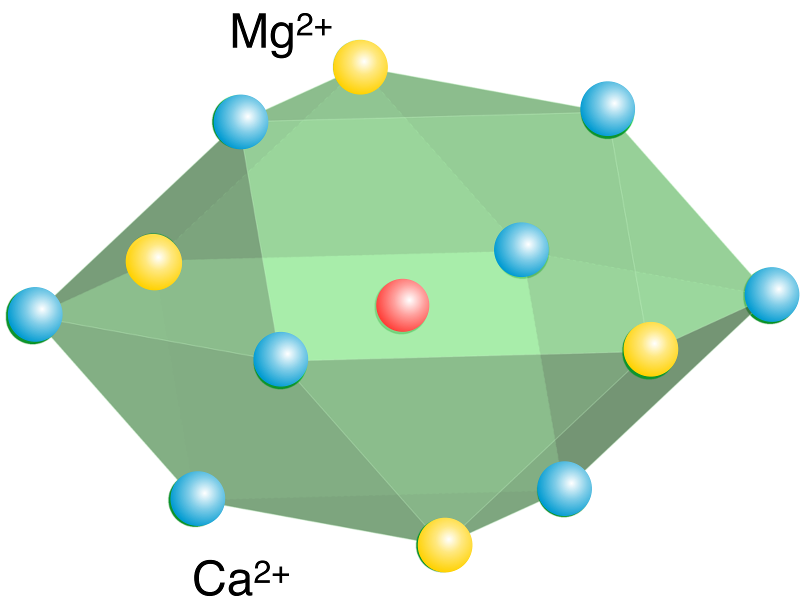

$$h^{ss} = \sum_{i}^{c^A} \sum_{j}^{c^B} x_i^A x_j^B h_{ij}^o$$
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$$+ \sum_{i,j,k,l,m,n,o}^{c^B} \sum_{p,q,r,s,t,u}^{c^A} x_i^B x_j^B x_k^B x_l^B x_m^B x_n^B x_o^B x_p^A x_q^A x_r^A x_s^A x_t^A x_u^A \Delta H_{(i:jklmno)(pqrstu)}$$

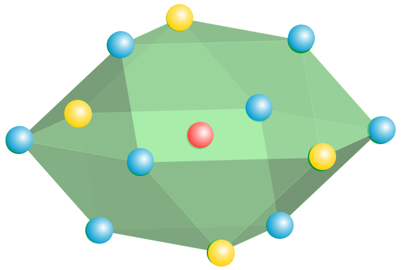
$\Delta H_{(i:jklmno)(pqrstu)}$ → 8192 parameters

$\Delta H_{(1:111122)(112222)}$ → sites sorted

1: Ca
2: Mg

(1:6)(6)
94 non zero parameters

force-field calculations: 8x8x1 supercell



384 configurations
in each supercell

10000 supercells

force-field potentials by
Austen et al. (2005)

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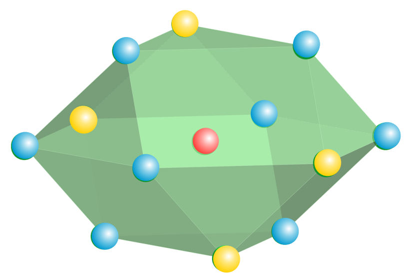

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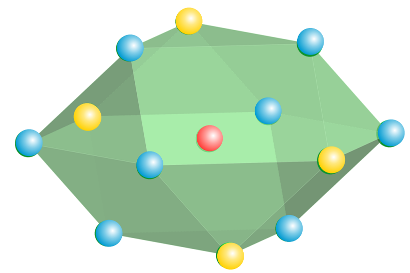

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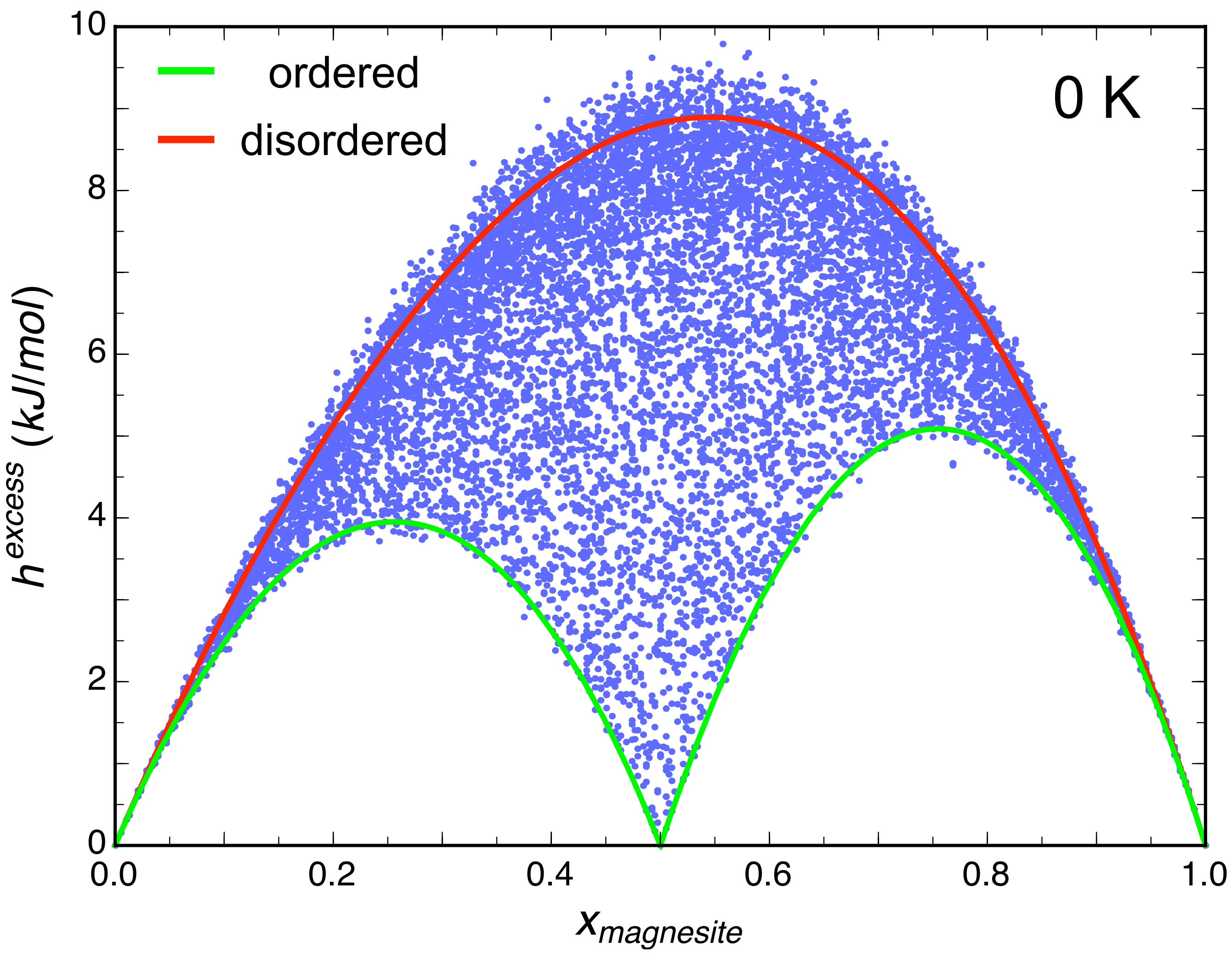
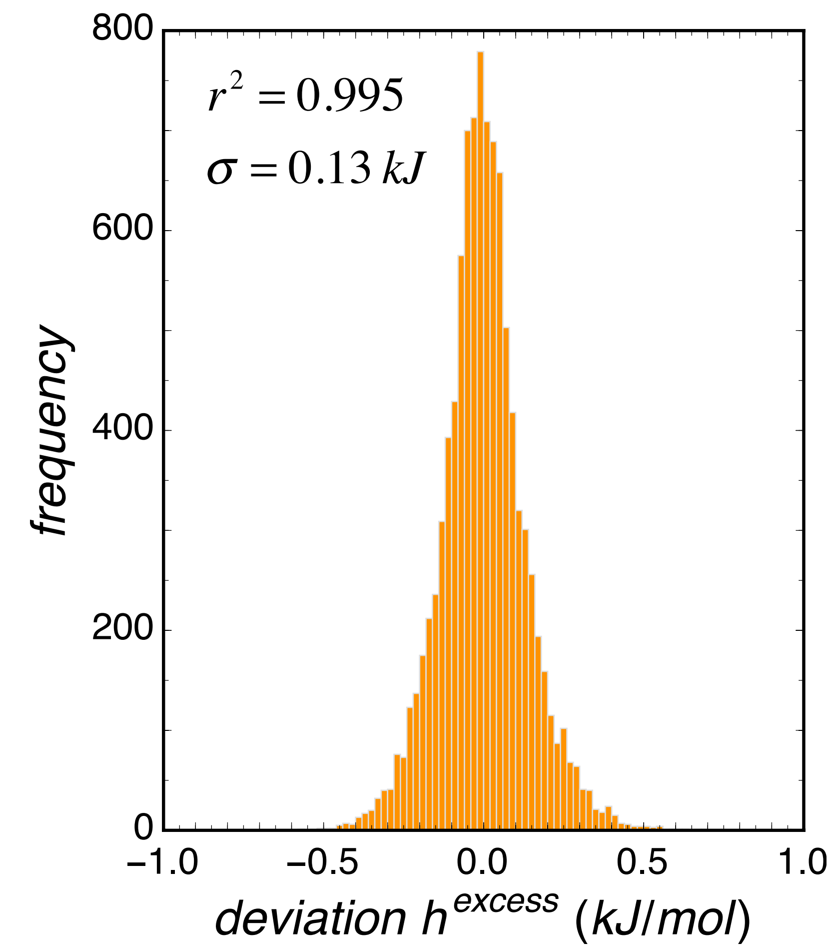
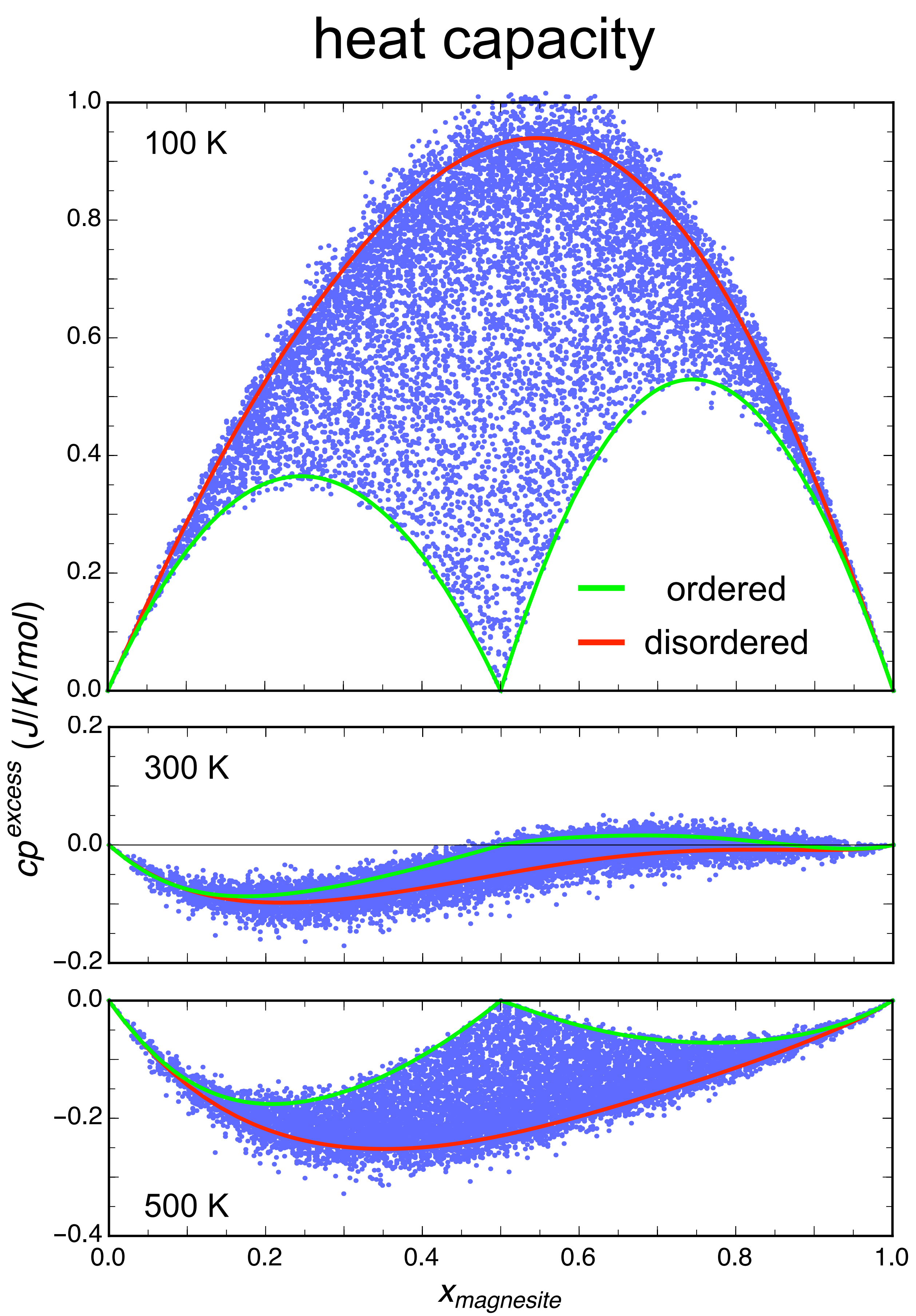
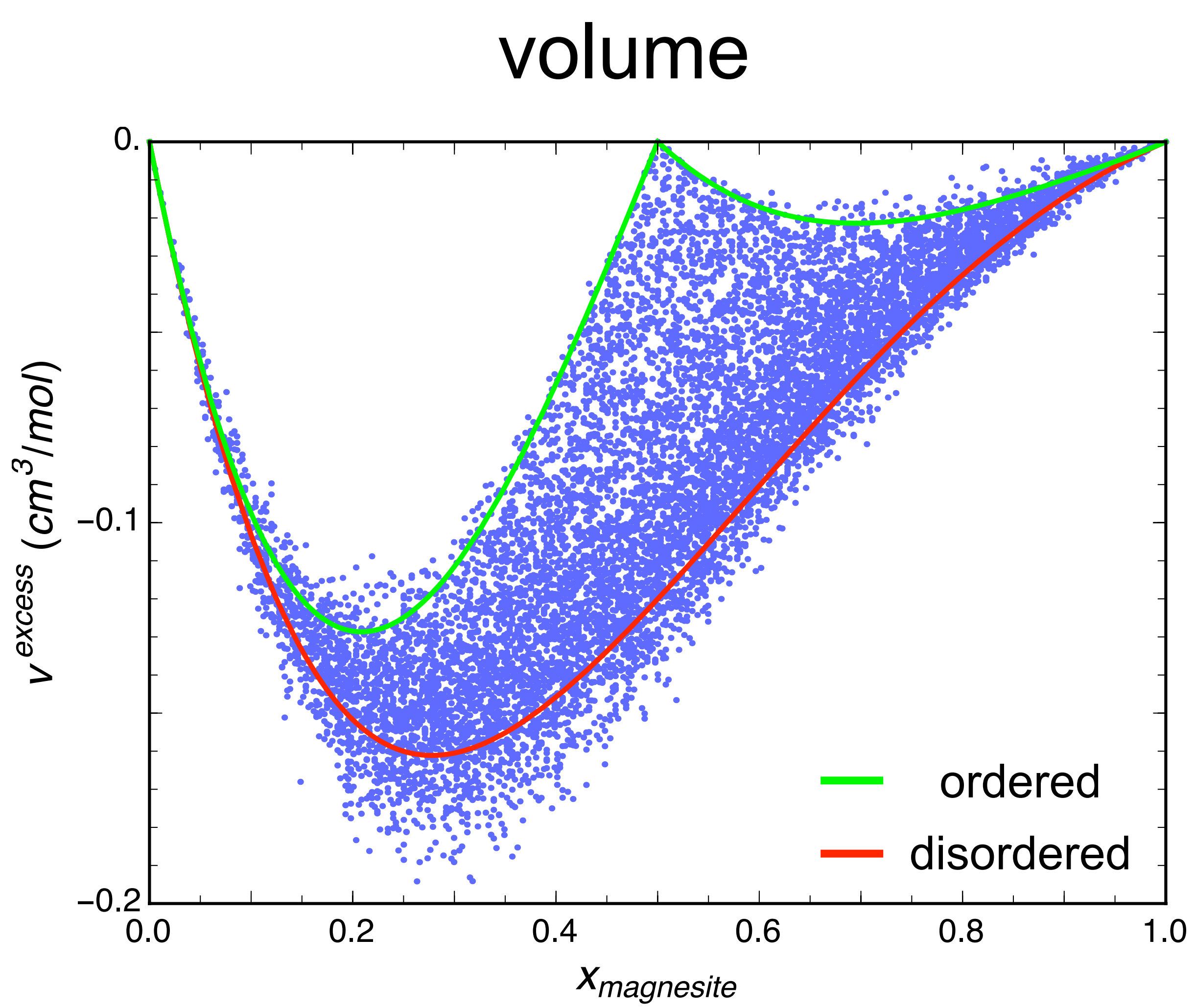


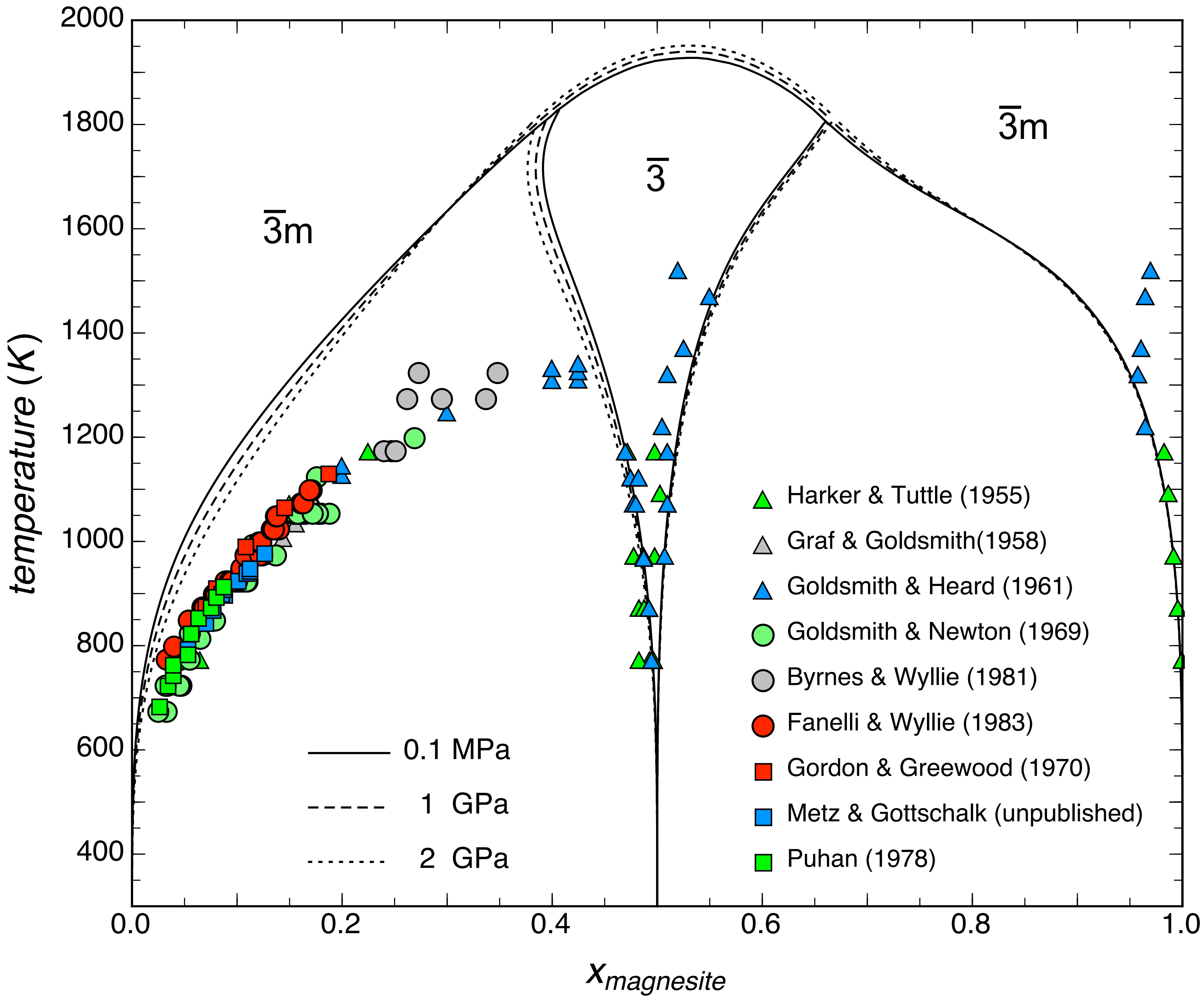


heat capacity and volume





force-field phase diagram



- artificial phase diagram
- potentials by Austen et al. (2005)
- potential fitted against volumes and elastic properties
- no cation-cation potential available
- good for dolomite-magnesite
- not so good for calcite-dolomite
- 15% reduction of the enthalpy will result in a better phase diagram

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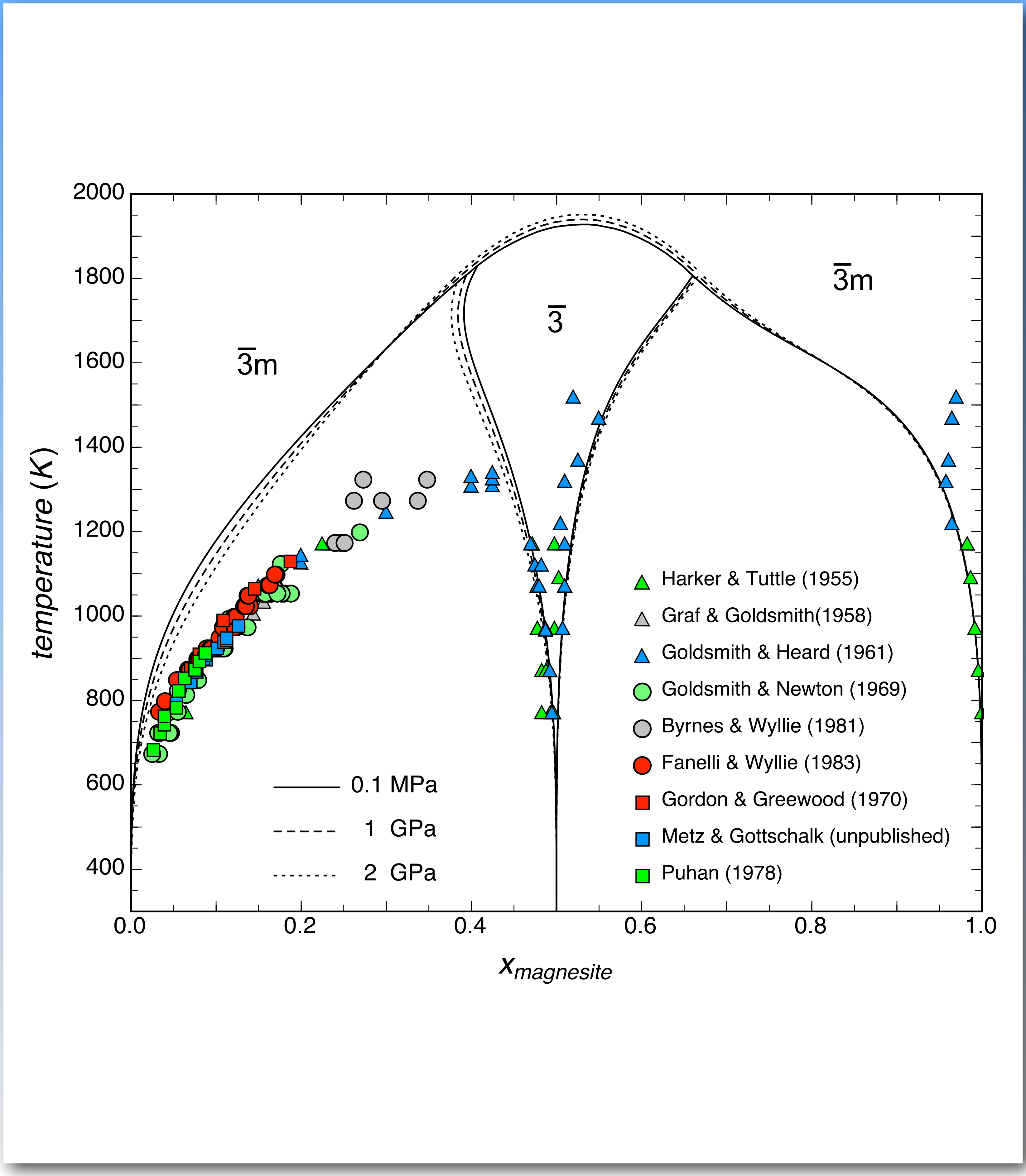

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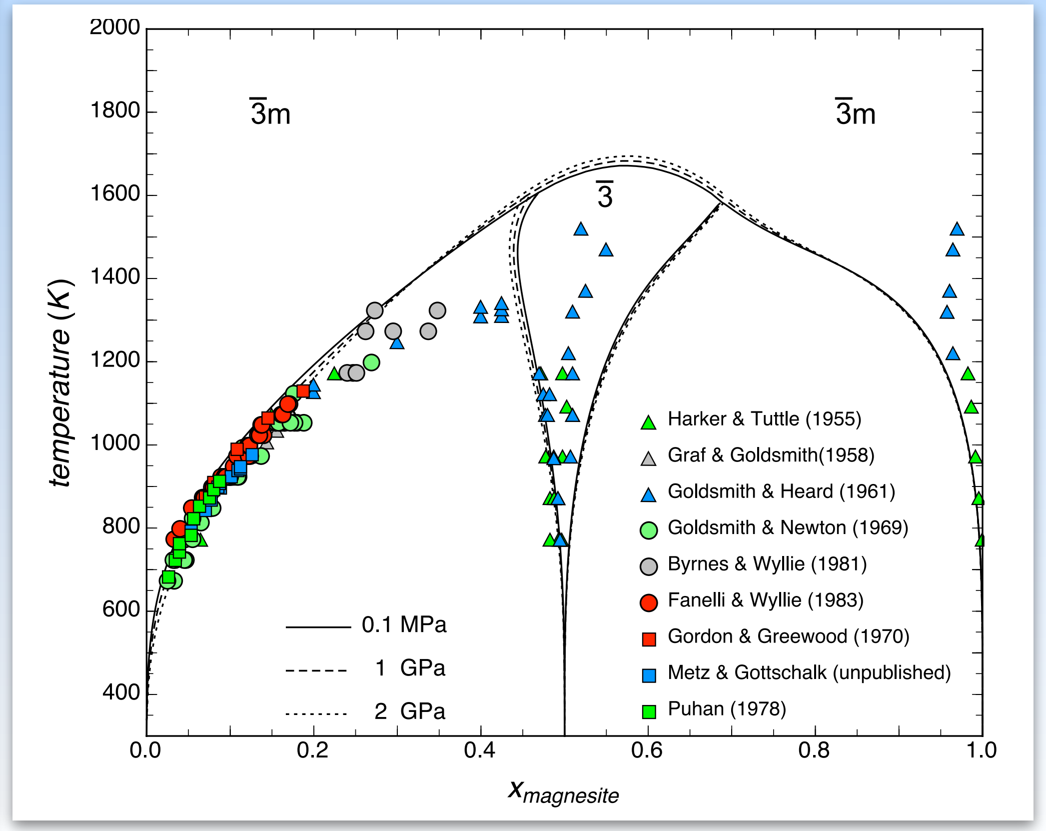
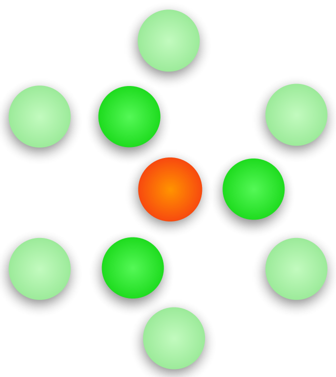


advantages of the configurational model

$$\Delta H_{(i:jkl/mnoqpr)} =$$ 

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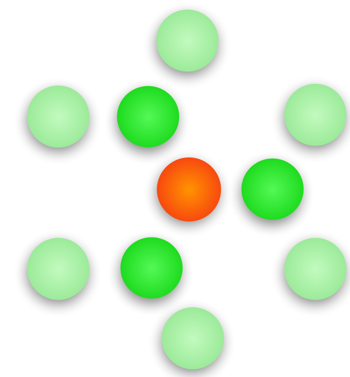

- energy ΔH of the local configuration
- not based on bonds
- not pairwise additive
- differentiable analytical expression
- coupled substitutions
- trace elements
- multi-component solid solutions
- the one-time computational effort is moderate

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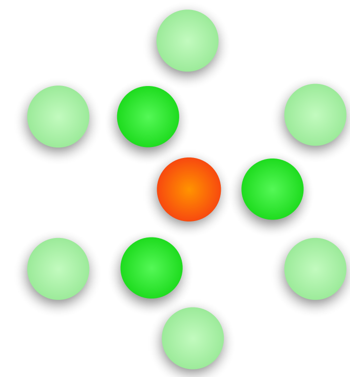

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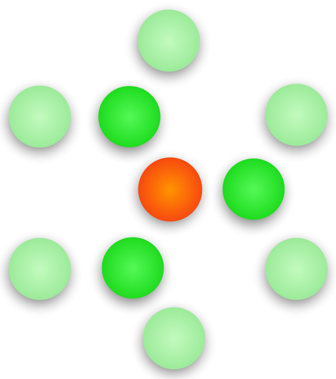
$$\Delta H_{(i:jkl/mnoqpr)} =$$ 

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- we need better force-field potentials to do energies

Max Margules

23.4.1856 - 4.10.1920

Meteorologist and Physical Chemist

He refused to give weather forecasts saying, that this unethical and character damaging.