Tools for atomic-scale model construction
Cluster expansions and force constants

Erik Fransson

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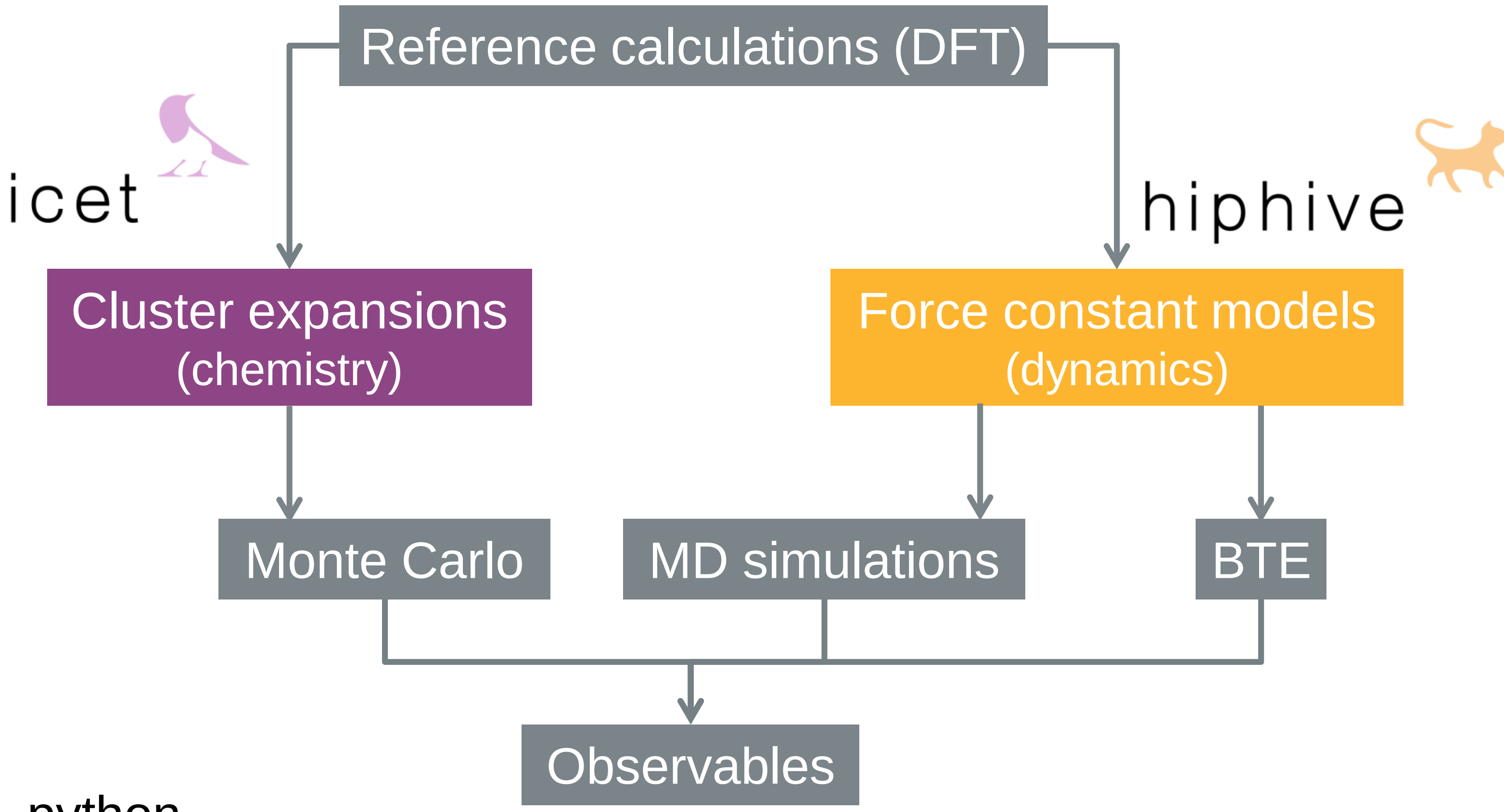
Chalmers University of Technology

Tools for atomic-scale model construction

$$\mathcal{Z} = \mathcal{Z}_{\mathrm{conf}}\mathcal{Z}_{\mathrm{vib}}\mathcal{Z}_{\mathrm{elec}}\cdots$$



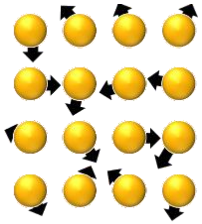
python

Force constant expansions

hiphive

Taylor expansion of the potential energy

$$E = E_0 + \sum_i \Phi_i u_i + \frac{1}{2!} \sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!} \sum_{ijk} \Phi_{ijk} u_i u_j u_k \ldots$$



u_i Displacement from static equilibrium position

Force constant expansions

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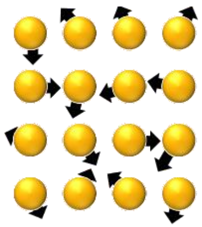
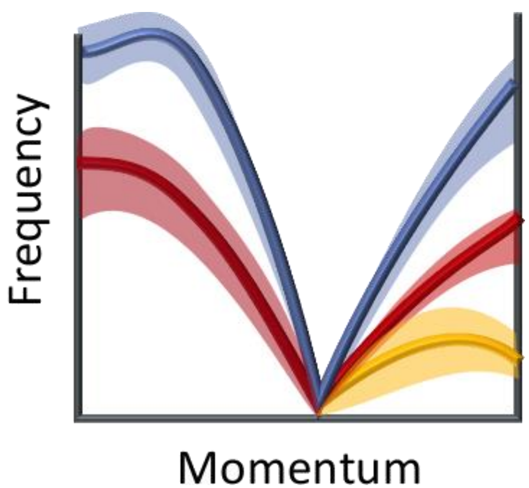


u_i Displacement from static equilibrium position

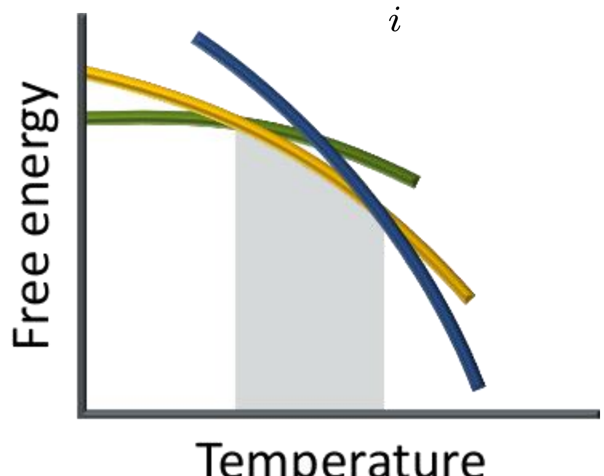
Phonon dispersions

$$\Phi_{ij} \rightarrow D_{\alpha\beta}(\boldsymbol{q}) \rightarrow \omega_k(\boldsymbol{q})$$



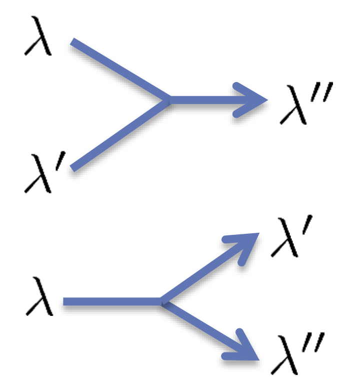
Free energies

$$F_{vib} = k_B T \sum_i \ln \omega_i$$



Transport

$$\kappa_l = \frac{1}{2V} \sum_{j\boldsymbol{q}} \lambda_{j\boldsymbol{q}}(T) v_{j\boldsymbol{q}} c_{j\boldsymbol{q}}(T)$$



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Force constant extraction

hiphive

$$E = E_0 + \sum_i \Phi_i u_i + \frac{1}{2!}\sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!}\sum_{ijk} \Phi_{ijk} u_i u_j u_k \ldots$$

"Direct" approach: systematic enumeration

$$\Phi_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j} \approx -\frac{F_i(u_j) - F_i(0)}{u_j}$$

Harmonic approximation → phonopy

Third-order FCs → phono3py, almaBTE

→ Poor scaling with system size and order

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Force constant extraction

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$$\Phi_{ij} = \frac{\partial^2 E}{\partial u_i \partial u_j}$$

$$\approx -\frac{F_i(u_j) - F_i(0)}{u_j}$$

"Regression" approach: fit to snapshots

→ TDEP & ALAMODE

Hellman *et al.* PRB 2011, Tadano *et al.* JPCM 2014

→ Compressive sensing

Zhou, Ozolins *et al.* PRL 2014

$$\Phi_{ij} = \Phi_{ij}(\boldsymbol{x})$$

$$\min(\|\boldsymbol{A}\boldsymbol{x} - \boldsymbol{f}\|_2^2)$$

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Generalizes regression approach
and makes it easily accessible

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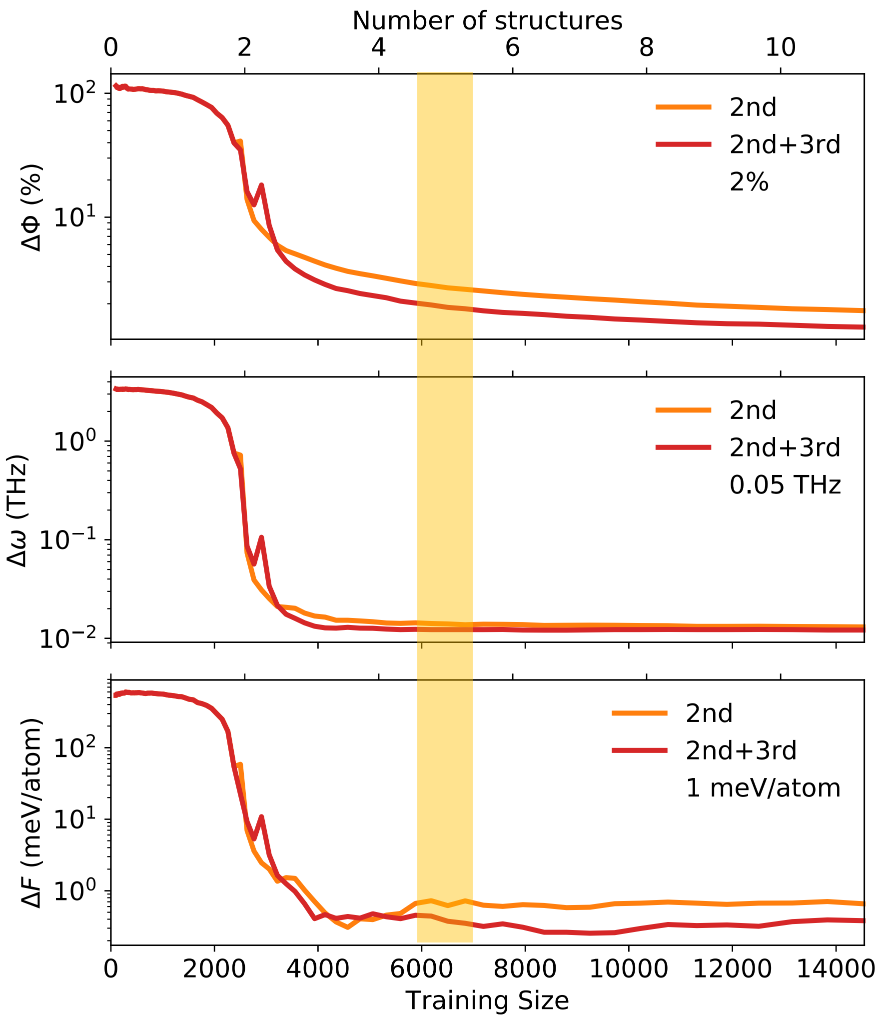
Efficiency 2nd-order: Vacancy in BCC-Ta

hiphive

Convergence with training size



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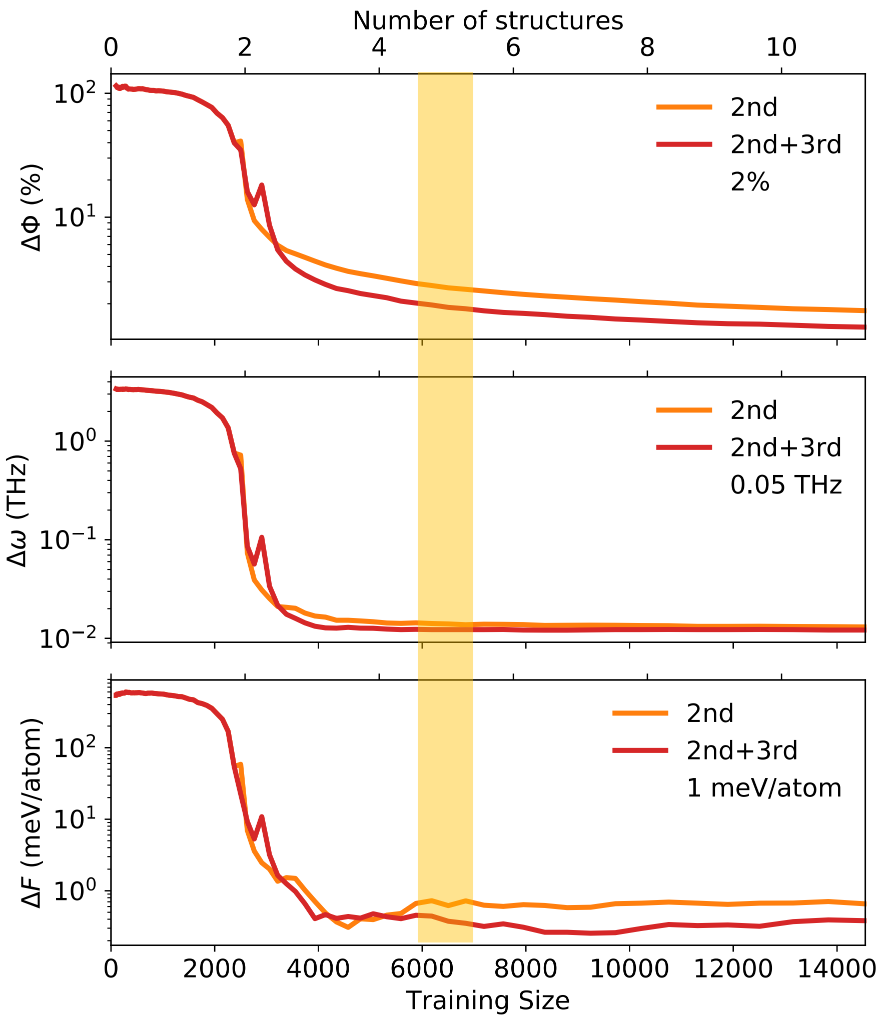
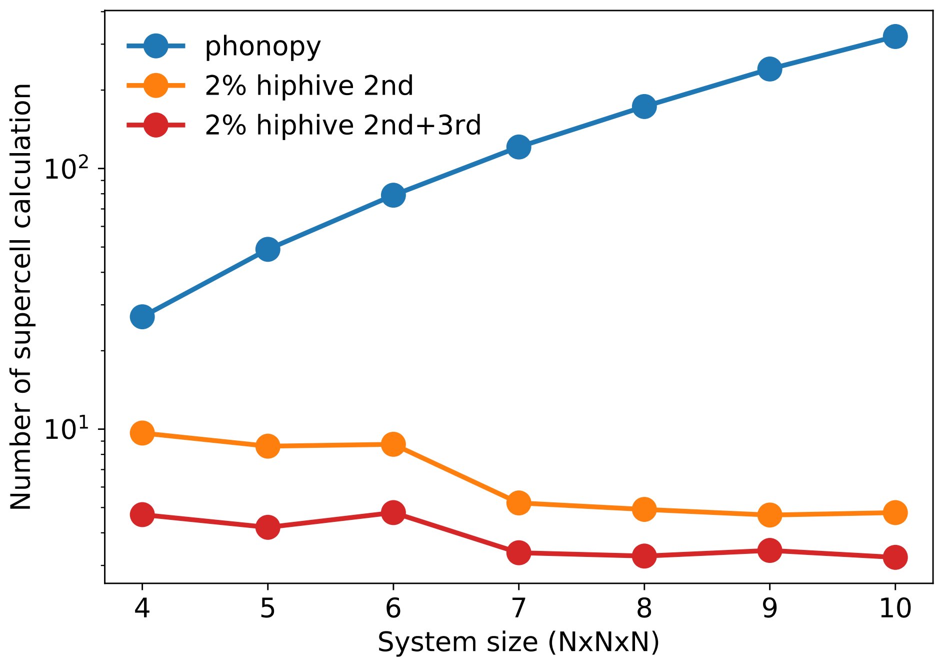


Scaling compared to direct-approach



Favorable size-scaling;
especially interesting for defects

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Efficiency 3rd-order: Silicon

Thermal conductivity of Silicon via Boltzmann transport

$$\kappa_l = \frac{1}{2V} \sum_{j\boldsymbol{q}} \lambda_{j\boldsymbol{q}}(T) v_{j\boldsymbol{q}} c_{j\boldsymbol{q}}(T)$$

$$\lambda_{j\boldsymbol{q}}(T) = \tau_{j\boldsymbol{q}}(T) v_{j\boldsymbol{q}}$$

Lifetime ($\tau_{j\boldsymbol{q}}$) — Group velocity ($v_{j\boldsymbol{q}}$)

Requires third-order force constants

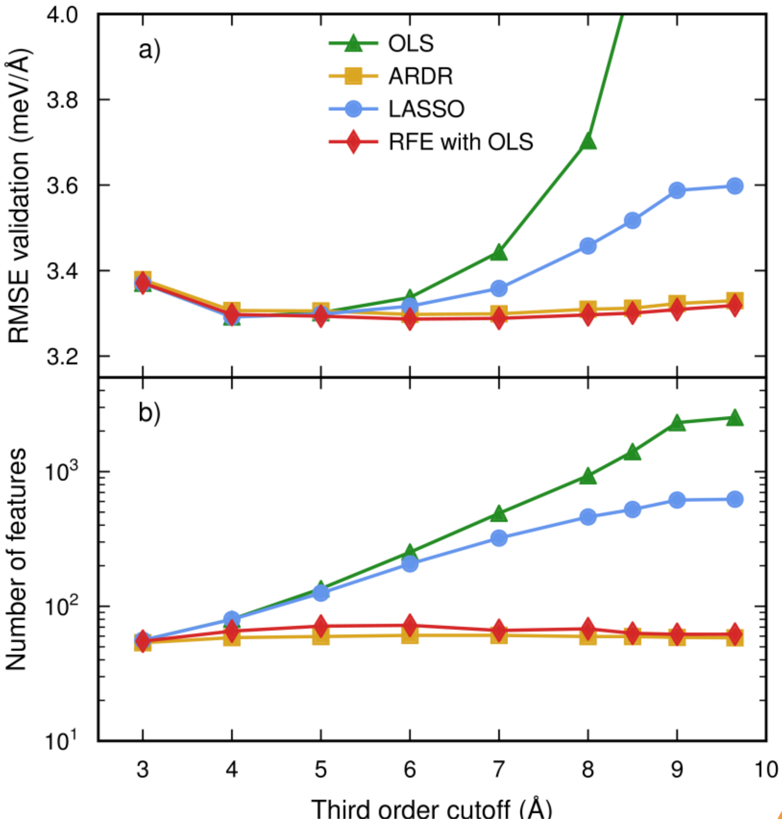
Efficiency 3rd-order: Silicon

hiphive

Thermal conductivity of Silicon via Boltzmann transport

Third-order cutoff selection

4Å



scikit learn

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Efficiency 3rd-order: Silicon

hiphive

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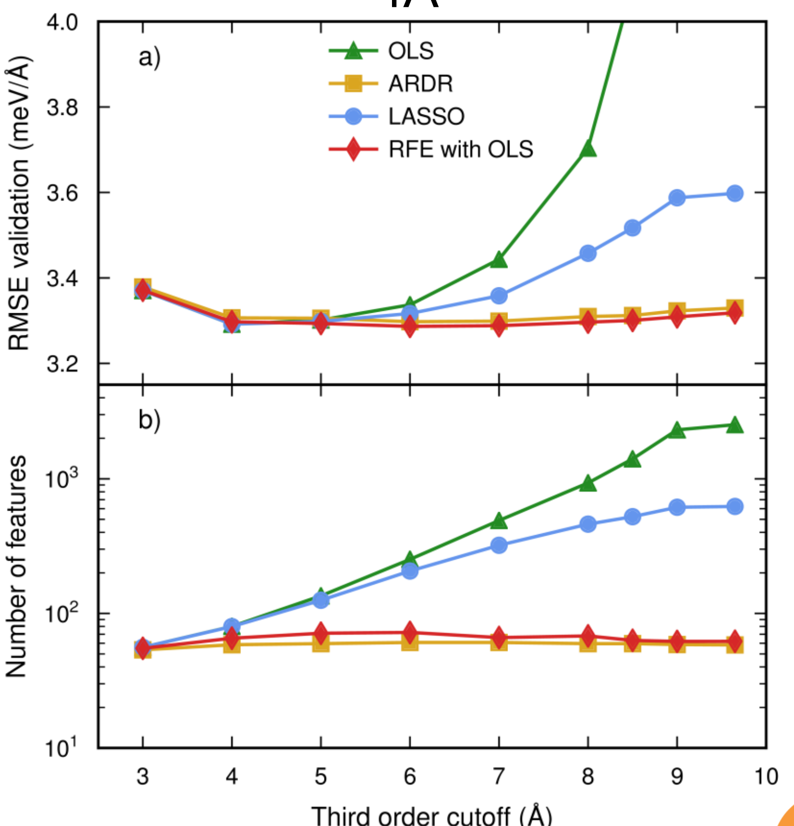
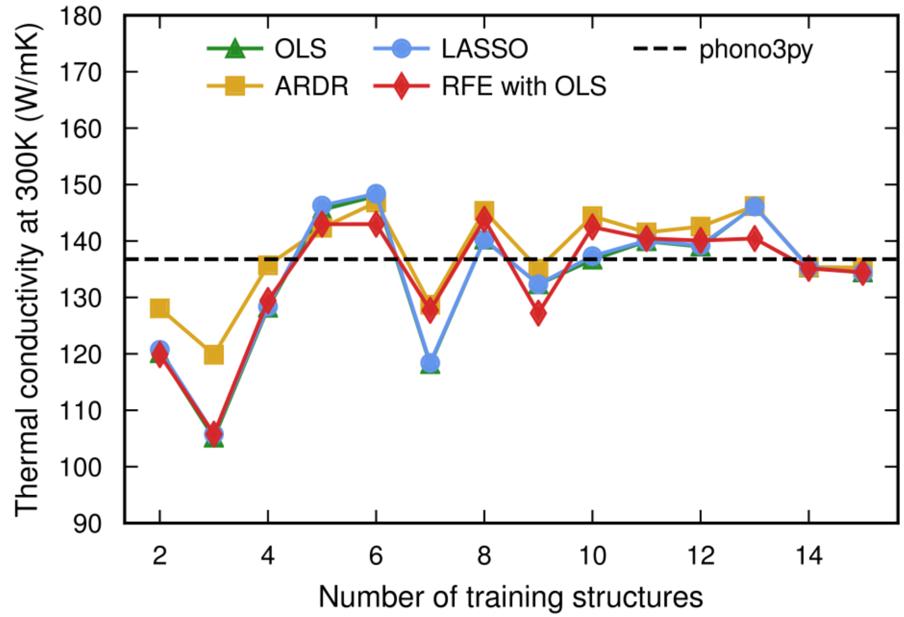


Thermal conductivity convergence



phono3py calculation 50-800 structures

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Anharmonicity in clathrates

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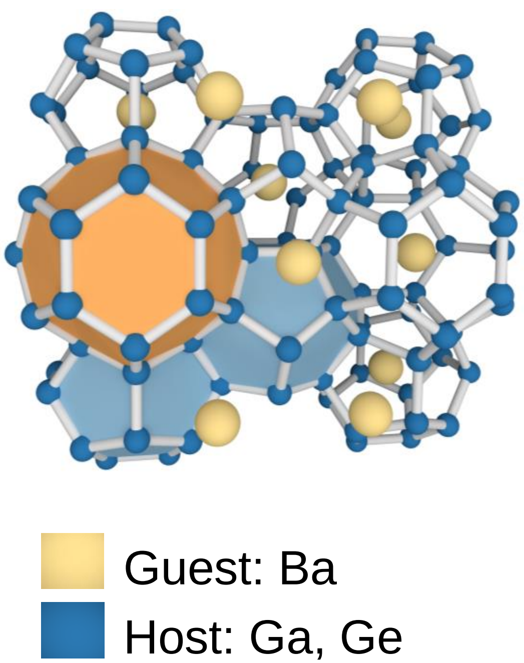
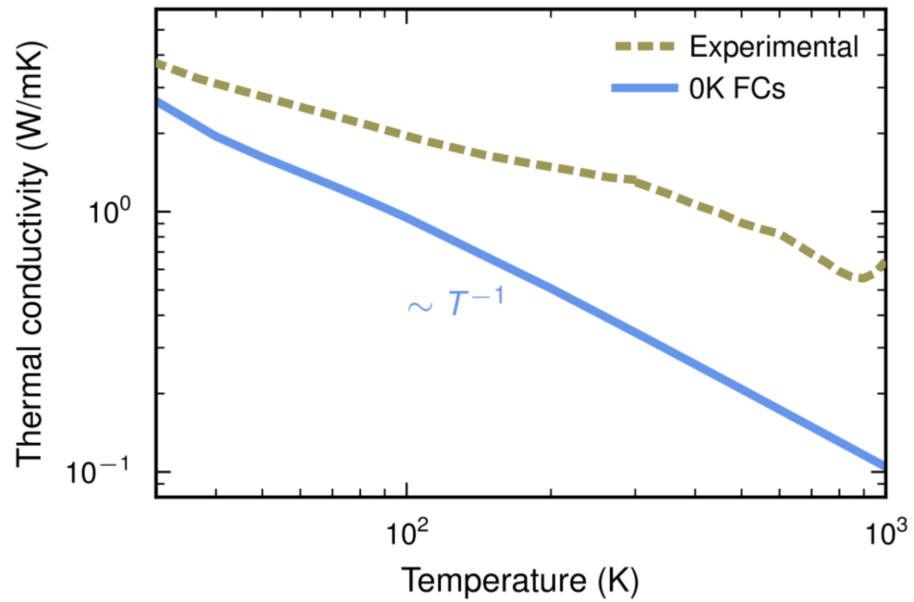
Inorganic clathrate $Ba_8Ga_{16}Ge_{30}$

- Anharmonic Ba (rattler) modes





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Anharmonicity in clathrates

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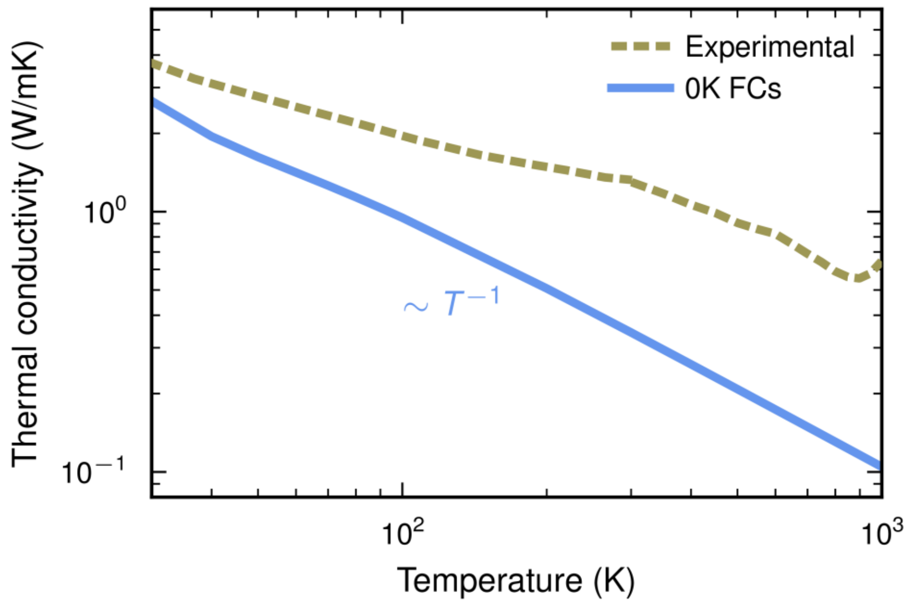
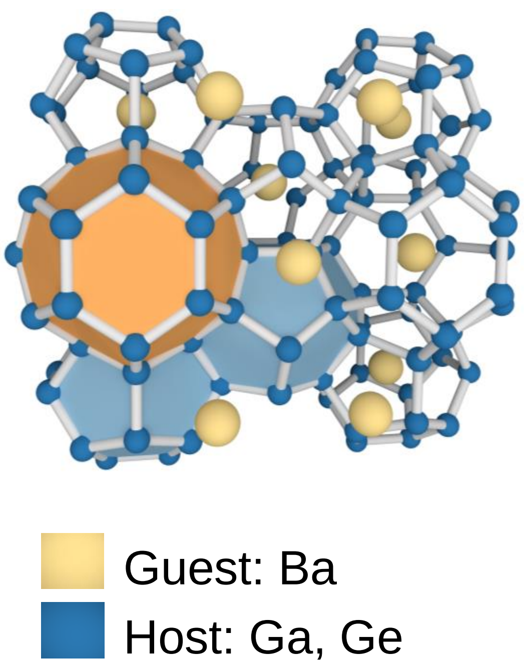
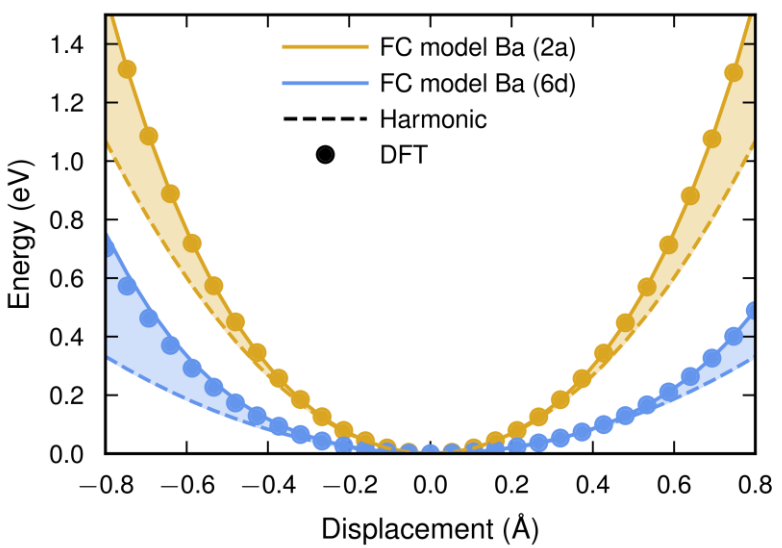
Inorganic clathrate $\mathrm{Ba_8Ga_{16}Ge_{30}}$

- Anharmonic Ba (rattler) modes
- Fourth-order model (6000 parameters)
- Reproduces anharmonicity of Ba







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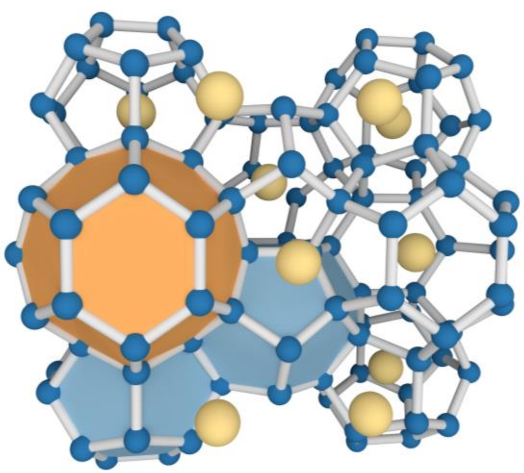
Anharmonicity in clathrates

hiphive

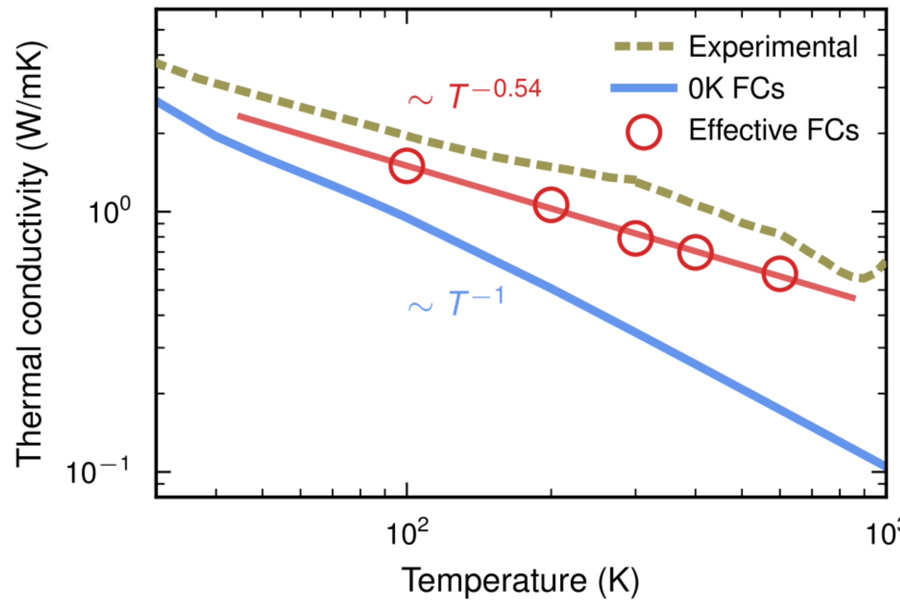
Inorganic clathrate $Ba_8Ga_{16}Ge_{30}$

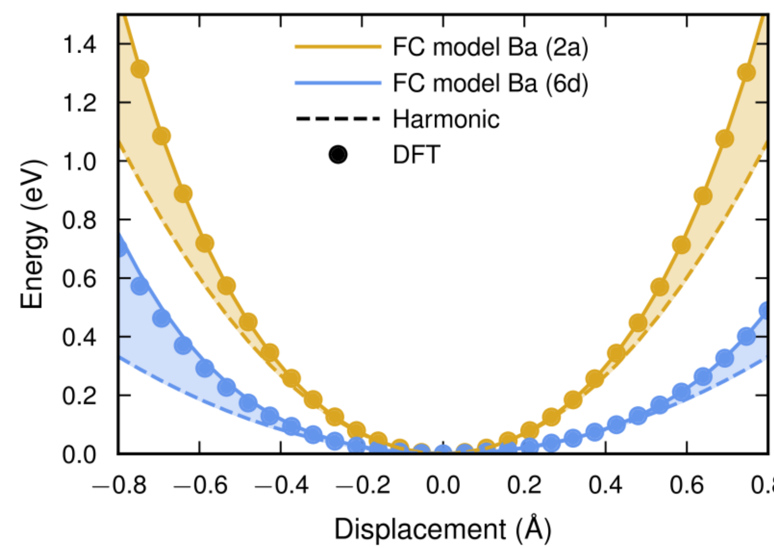
- Anharmonic Ba (rattler) modes
- Fourth-order model (6000 parameters)
- Reproduces anharmonicity of Ba
- Reproduces thermal conductivity



Guest: Ba

Host: Ga, Ge





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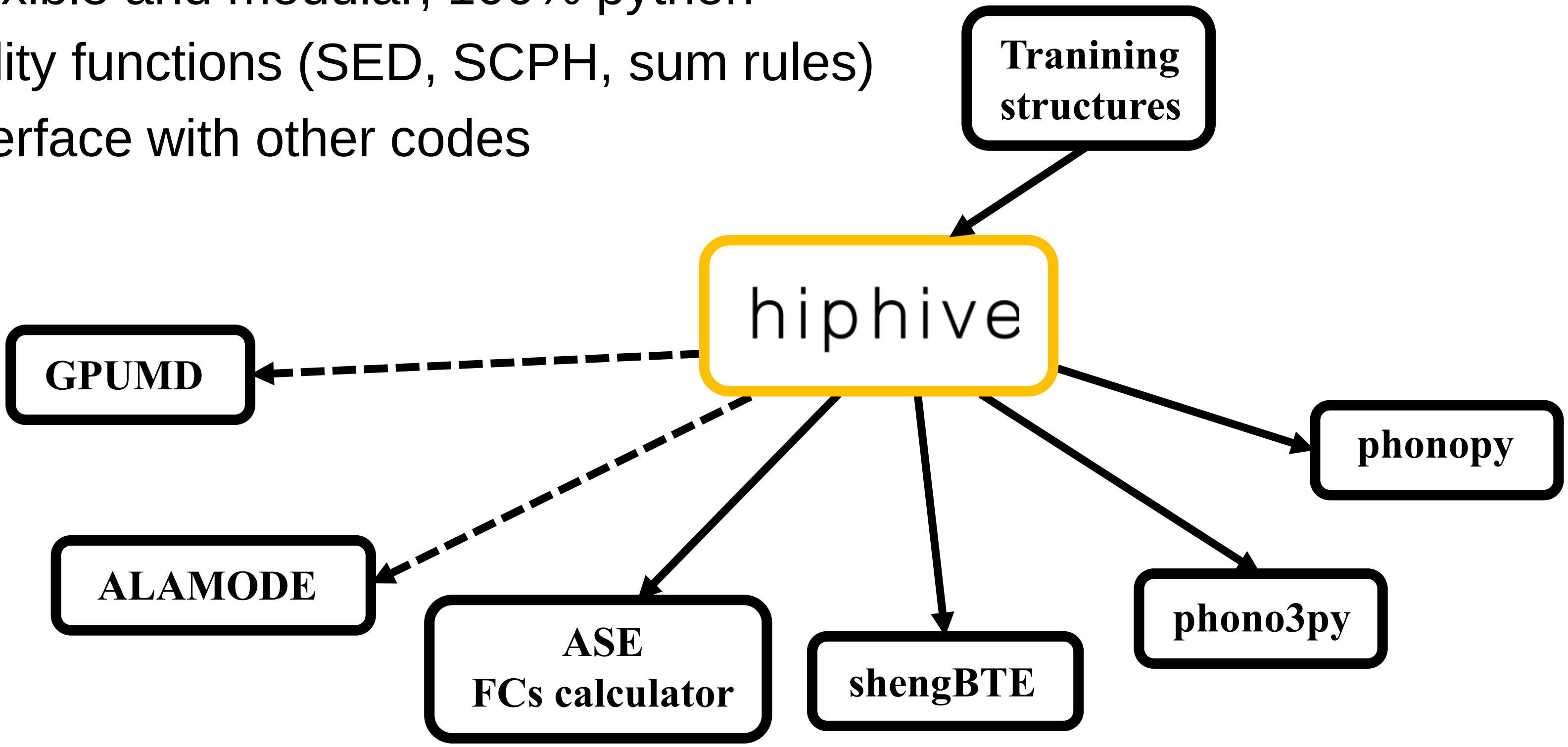
Force constants extraction tool

- Flexible and modular, 100% python
- Utility functions (SED, SCPH, sum rules)
- Interface with other codes



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Eriksson *et al.*, Adv. Theory Simul. **2019**, 1800184 icet

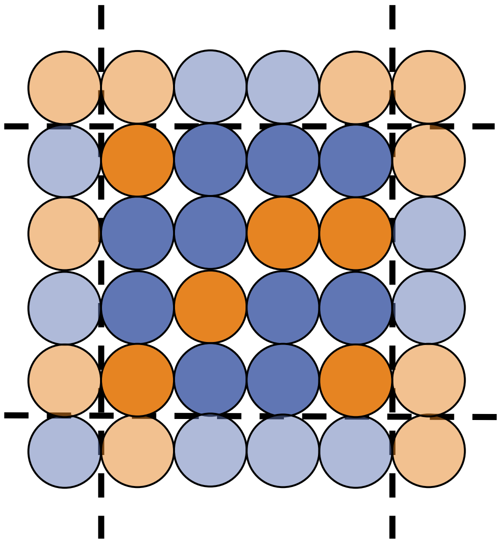
Ångqvist *et al.*, Adv. Theory Simul. **2019**, 1900015

Cluster Expansions

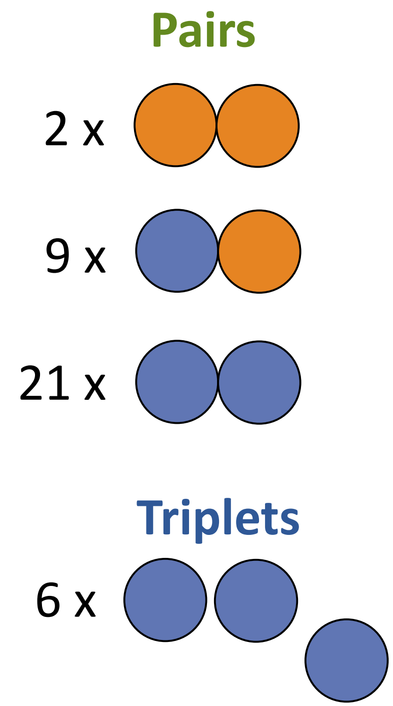
icet

Expansion of the total energy in site occupations

$$E(\boldsymbol{\sigma}) = E_0 + \sum_i J_i \sigma_i + \sum_{ij} J_{ij} \sigma_i \sigma_j + \sum_{ijk} J_{ijk} \sigma_i \sigma_j \sigma_k + \ldots$$



Decompose into “clusters”



$\boldsymbol{\sigma}$ Occupation vector

Need efficient means to extract effective cluster interactions (ECIs) J_α

→ Again a linear problem

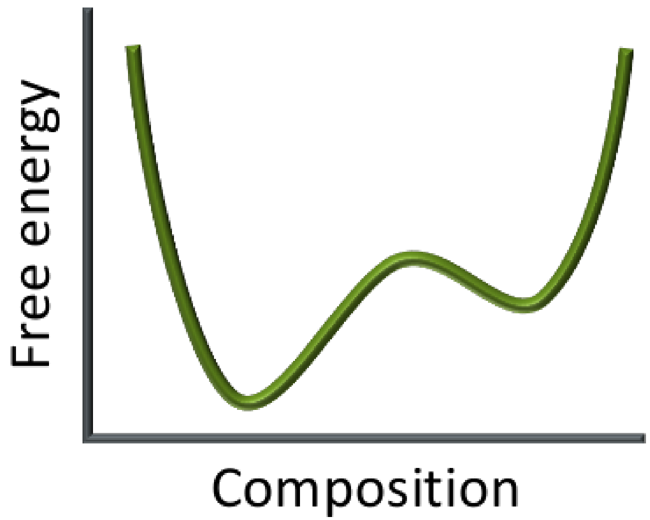
Cluster Expansions

icet

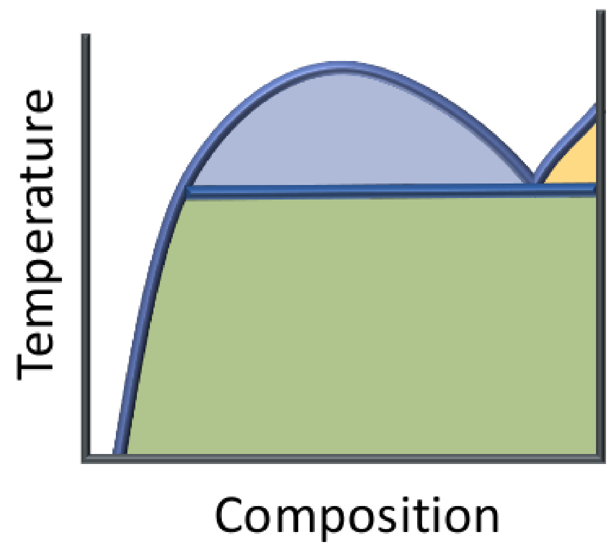
Expansion of the total energy in site occupations

$$E(\boldsymbol{\sigma}) = E_0 + \sum_i J_i \sigma_i + \sum_{ij} J_{ij} \sigma_i \sigma_j + \sum_{ijk} J_{ijk} \sigma_i \sigma_j \sigma_k + \ldots$$

Free energies



Phase diagrams



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CE construction for a Ag-Pd alloy

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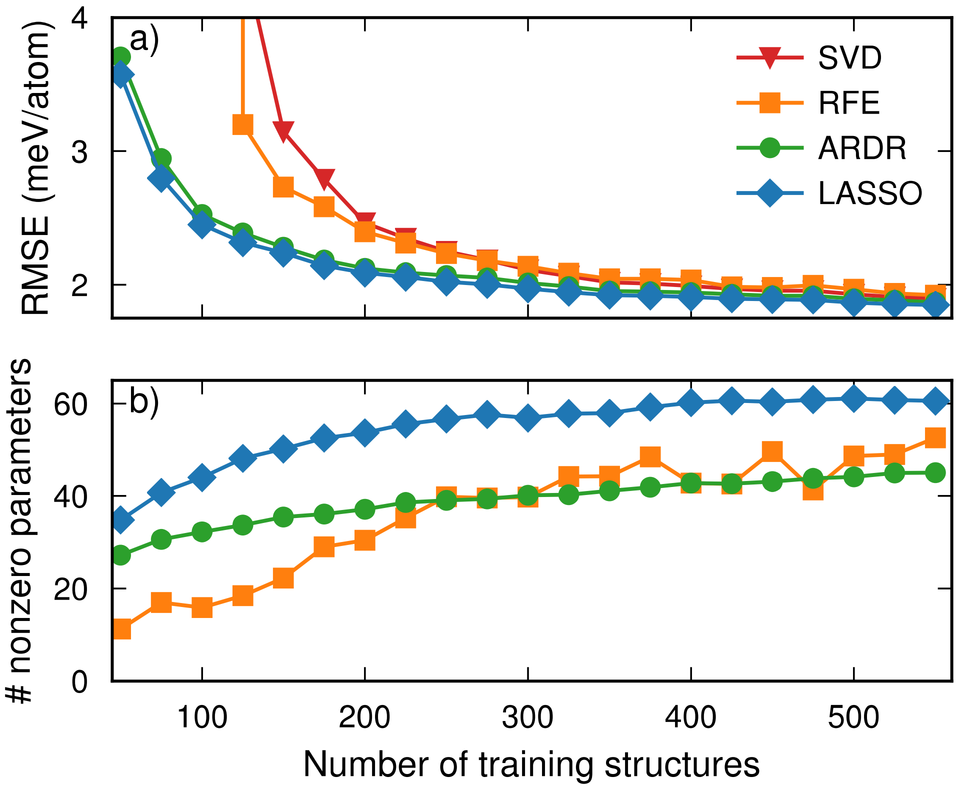

zerolet + singlet
+ 24 pairs
+ 20 triplets
+ 35 quadruplets
= 81 parameters

ARDR: fast convergence and sparse solution
LASSO: more false-positives
RFE: requires more structures

Ångqvist *et al.*, Adv. Theory Simul. **2019**, 1900015

CE construction for a Ag-Pd alloy

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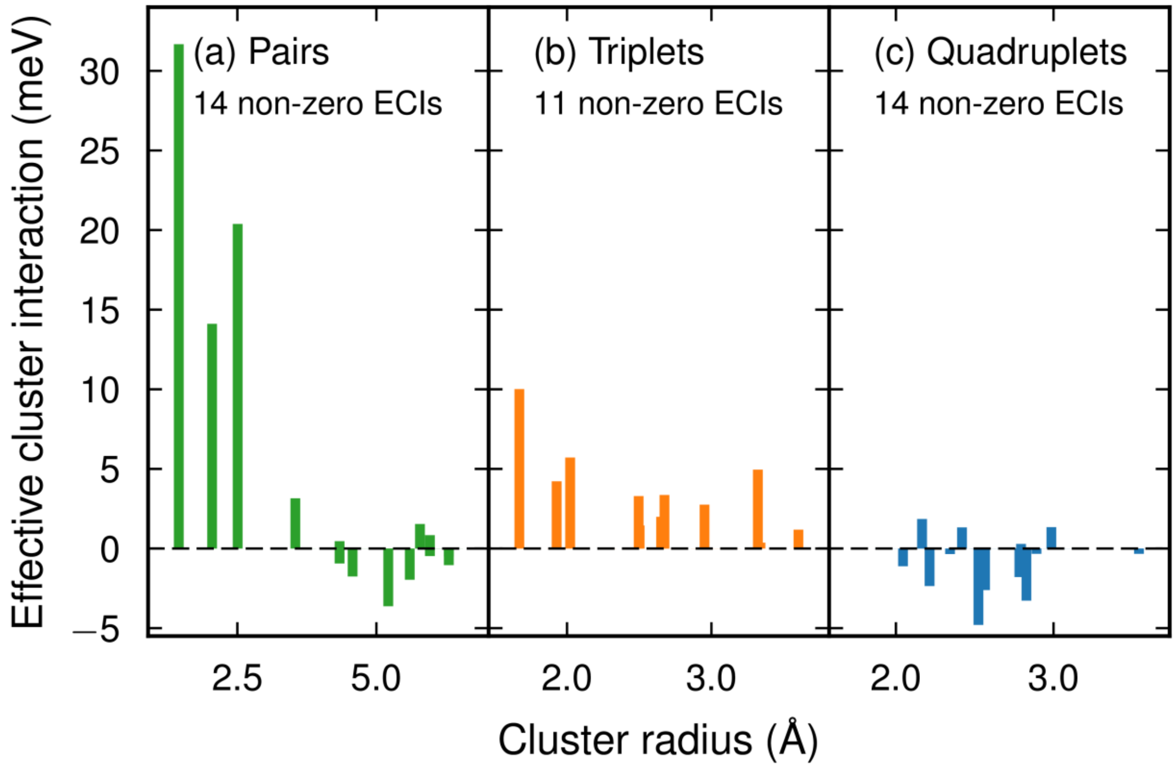

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Ångqvist *et al.*, Adv. Theory Simul. **2019**, 1900015

Ag-Pd alloy: CE sampling

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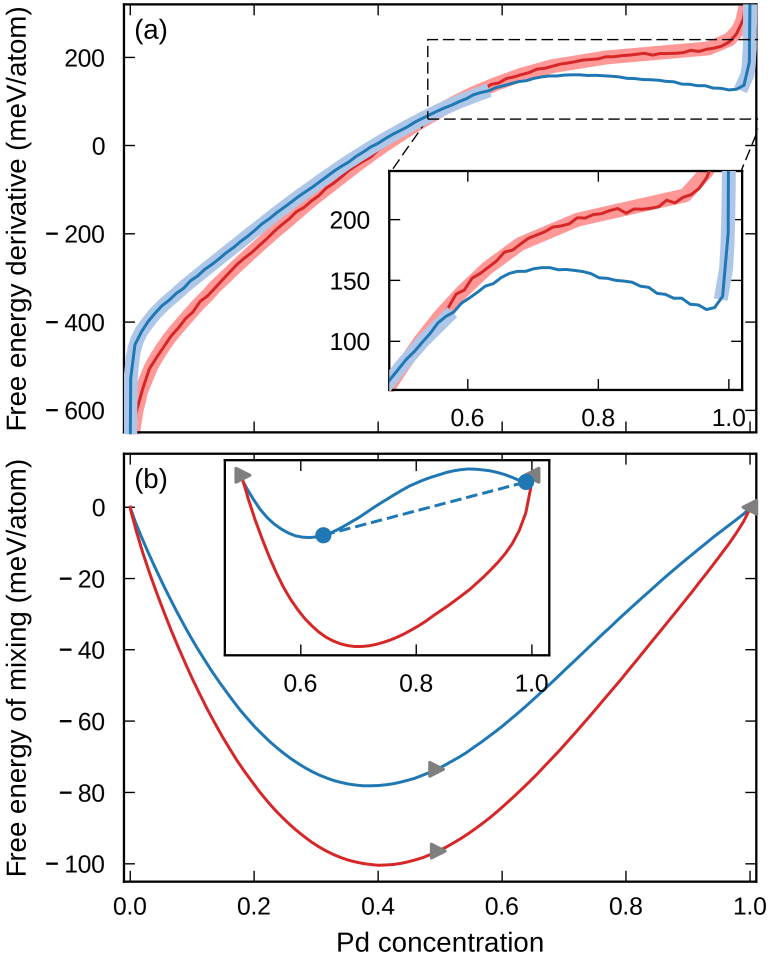
Monte Carlo simulations
at 800 K and 400 K



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Ångqvist *et al.*, Adv. Theory Simul. **2019**, 1900015

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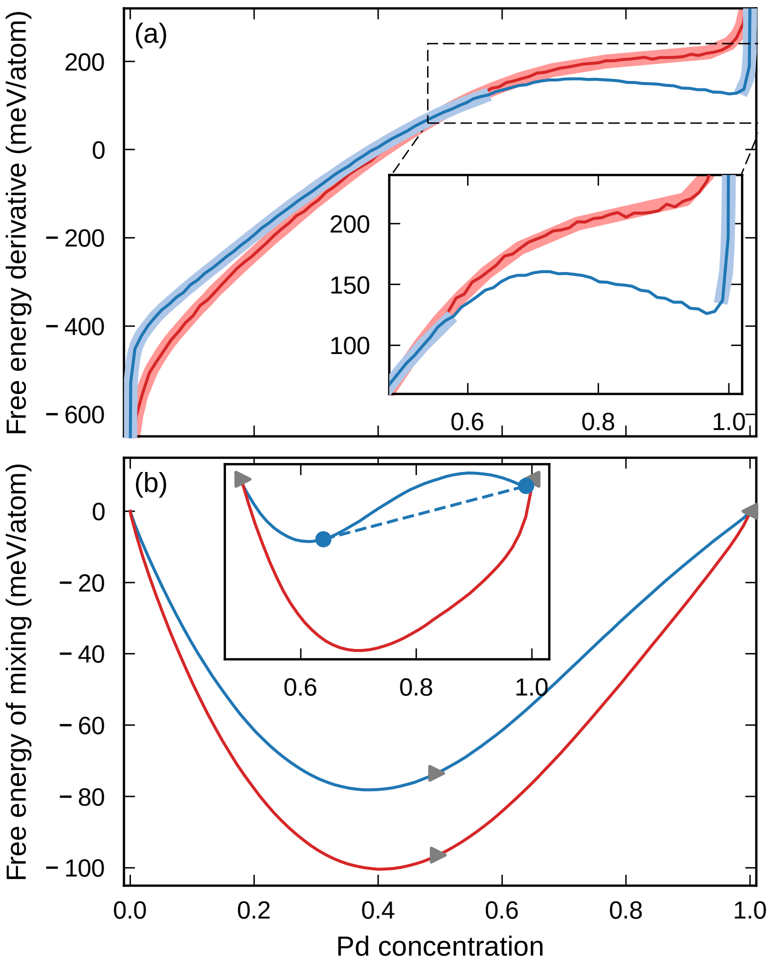
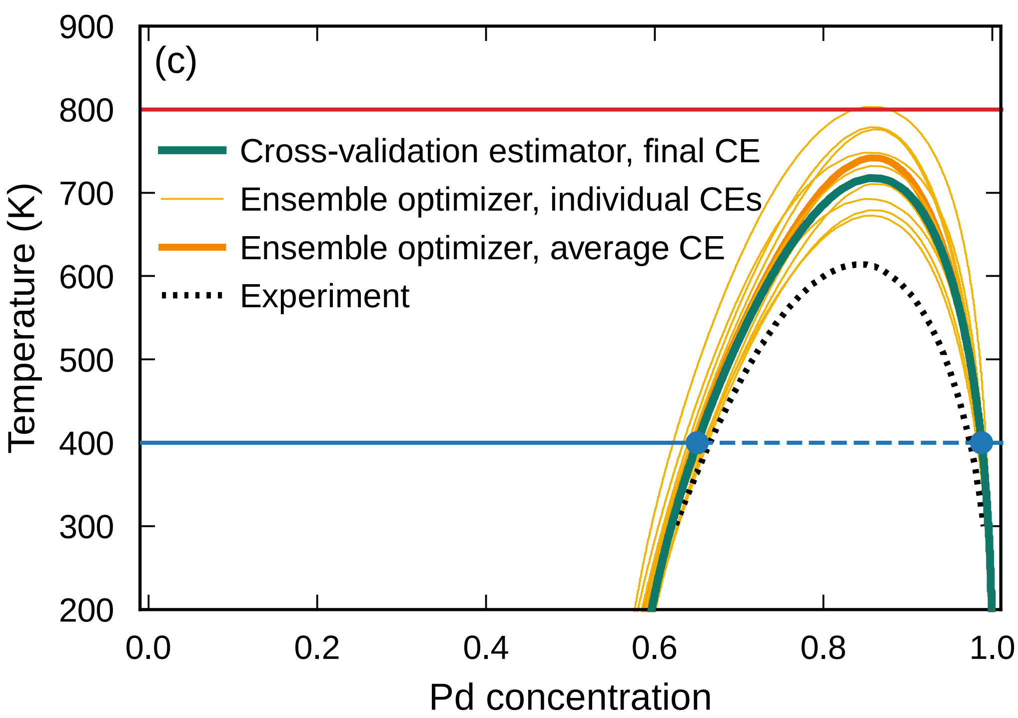


Phase diagram



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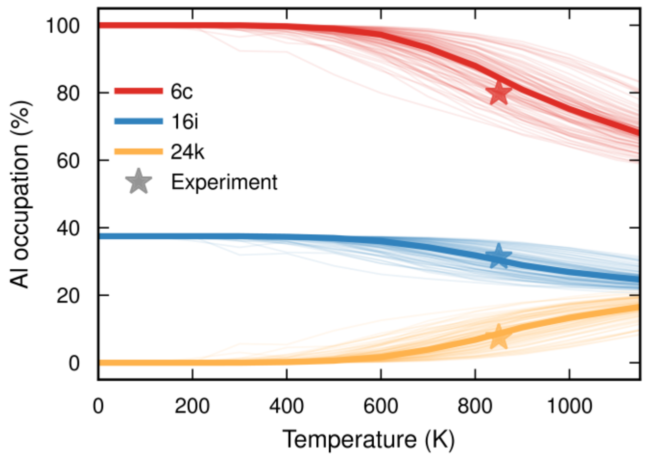
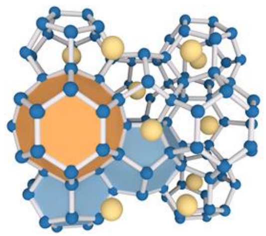
Ångqvist *et al.*, Adv. Theory Simul. **2019**, 1900015

Clathrates

- Chemical order → thermoelectric performance

Ångqvist *et al.* **2017**





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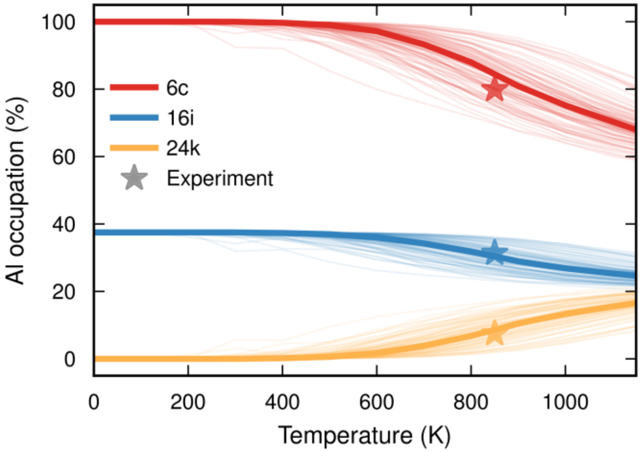
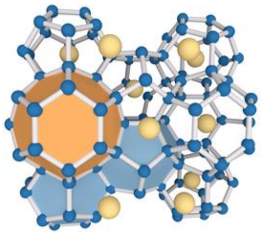
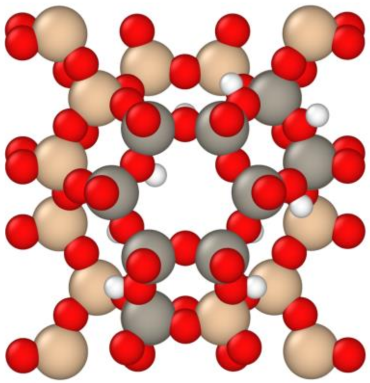




Zeolites

- Aluminium distribution on framework
- Löwenstein's rule violated

Magnus Fant 2019



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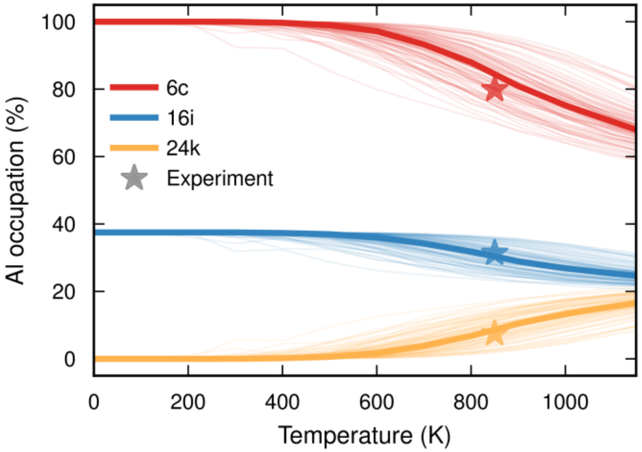

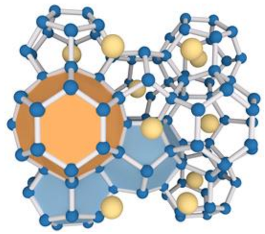

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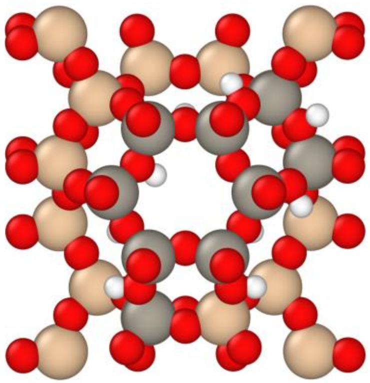
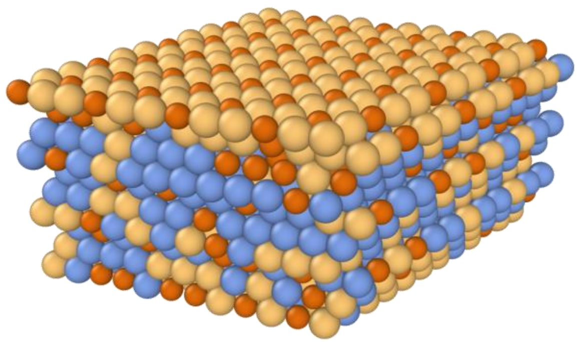
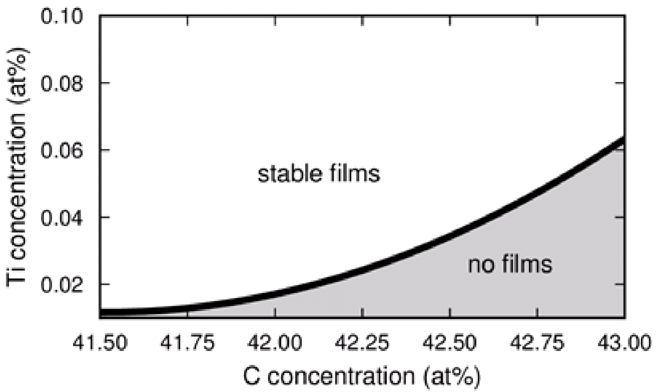


Interface systems

- Surface segregation in PdAuCu (Pernilla Tanner 2019)
- Stability of WC-Co interfacial phases (Martin Gren 2019)





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icet features

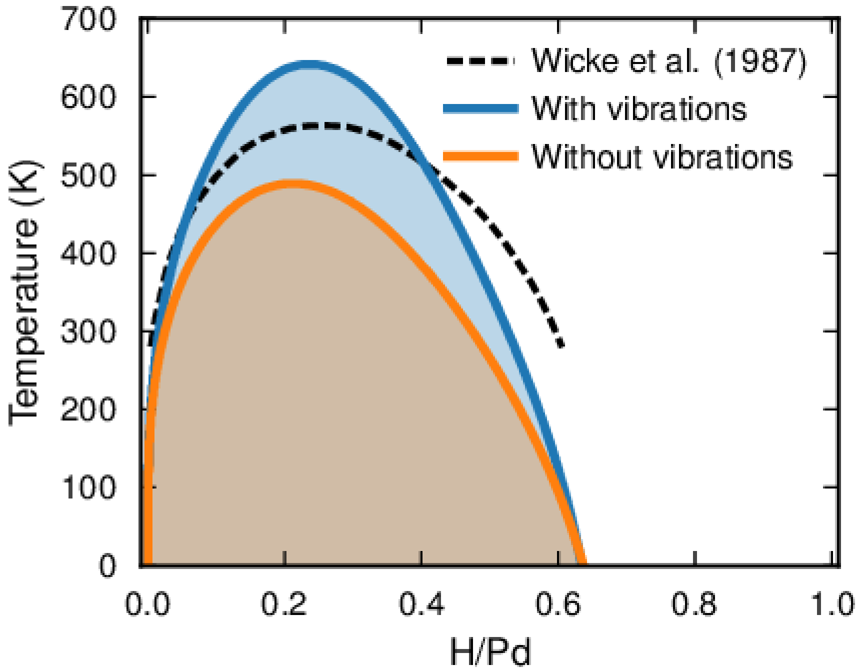
- **Structure generation**
  - Enumeration
  - SQS (Special Quasi-random Structures)
  - Ground-states via MIP (Mixed Integer programming)
- **Training via scikit-learn**
  - LASSO, ARDR, RFE, …
- **Monte Carlo sampling**
  - Canonical ensemble
  - Semi-Grand canonical ensemble
  - Variance-constrained semi-grand canonical ensemble
  - Simulated annealing
  - Wang-Landau sampling

Future work: Configurational + Vibrational

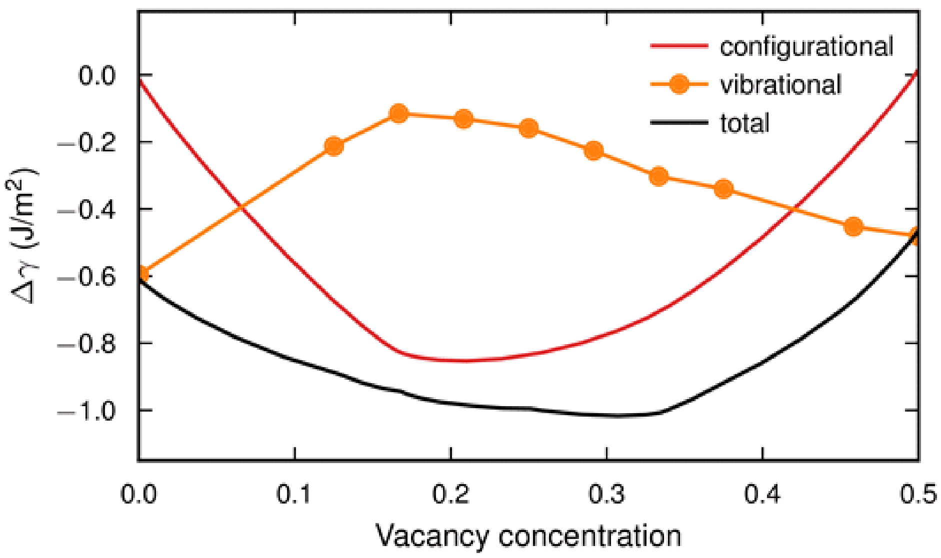
$$\mathcal{Z} = \mathcal{Z}_{\mathrm{conf}}\mathcal{Z}_{\mathrm{vib}}$$

Coupling between configurational and vibrational dofs
→ Very computational expensive

Alloys



WC phases



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Tutorials

icet tutorial Thursday 1pm

```
# setup
cs = ClusterSpace(atoms, [6.0, 5.0], ['Ag', 'Pd'])
sc = StructureContainer(cs)
for structure in training_structures:
    sc.add_structure(structure)

# training
opt = Optimizer(sc.get_fit_data(), fit_method='ardr')
opt.train()
ce = ClusterExpansion(cs, opt.parameters)

# sample
calc = ClusterExpansionCalculator(ce, atoms)
mc = CanonicalEnsemble(atoms, calc, temperature=600)
mc.run(1000)
```

hiphive tutorial Thursday 3pm

```
# setup
cs = ClusterSpace(atoms, [8.0, 6.0])
sc = StructureContainer(cs)
for structure in training_structures:
    sc.add_structure(structure)

# training
opt = Optimizer(sc.get_fit_data(), fit_method='rfe')
opt.train()
fcp = ForceConstantPotential(cs, opt.parameters)

# write to phono3py format
fcs = fcp.get_force_constants(supercell)
fcs.write_to_phonopy('fc2.hdf5')
fcs.write_to_phono3py('fc3.hdf5')
```

The end

icet

- Mattias Ångqvist
- William Muñoz
- Magnus Rahm
- Erik Fransson
- Joakim Brorsson
- Céline Durniak
- Piotr Rozyczko
- Thomas Rod
- Paul Erhart

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- Fredrik Eriksson
- Erik Fransson
- Paul Erhart

EUROPEAN SPALLATION SOURCE

https://materialsmodeling.org/software

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Knut och Alice Wallenbergs Stiftelse

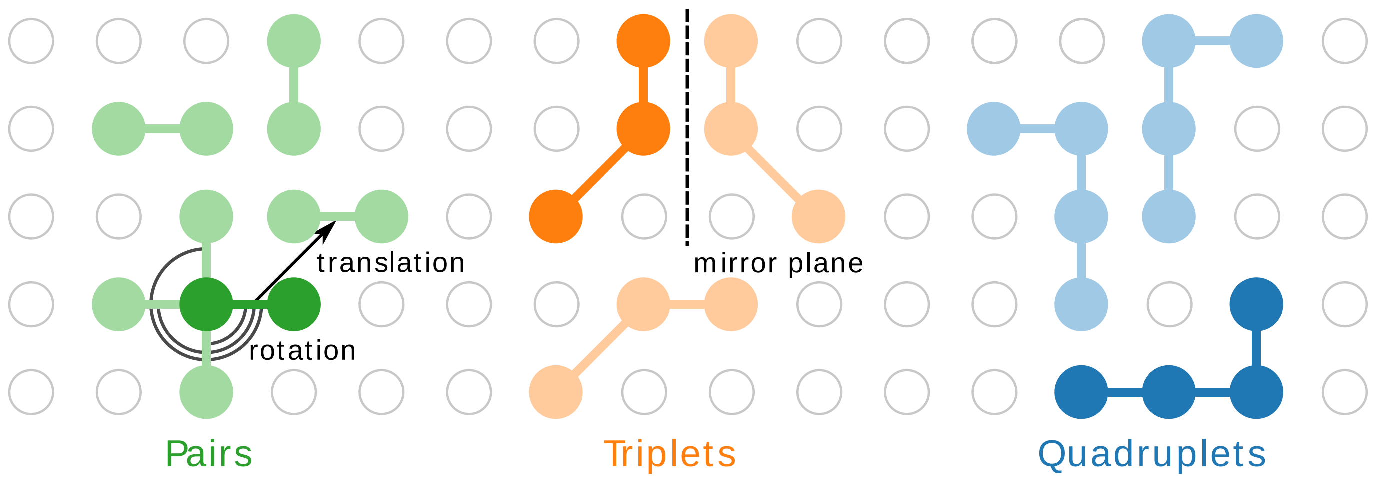
Vetenskapsrådet

Extra

Cluster decomposition

General procedure

1. Generate list of clusters
2. Obtain symmetry operations
3. Categorize clusters into orbits
4. Identify independent parameters
5. Apply sum rules

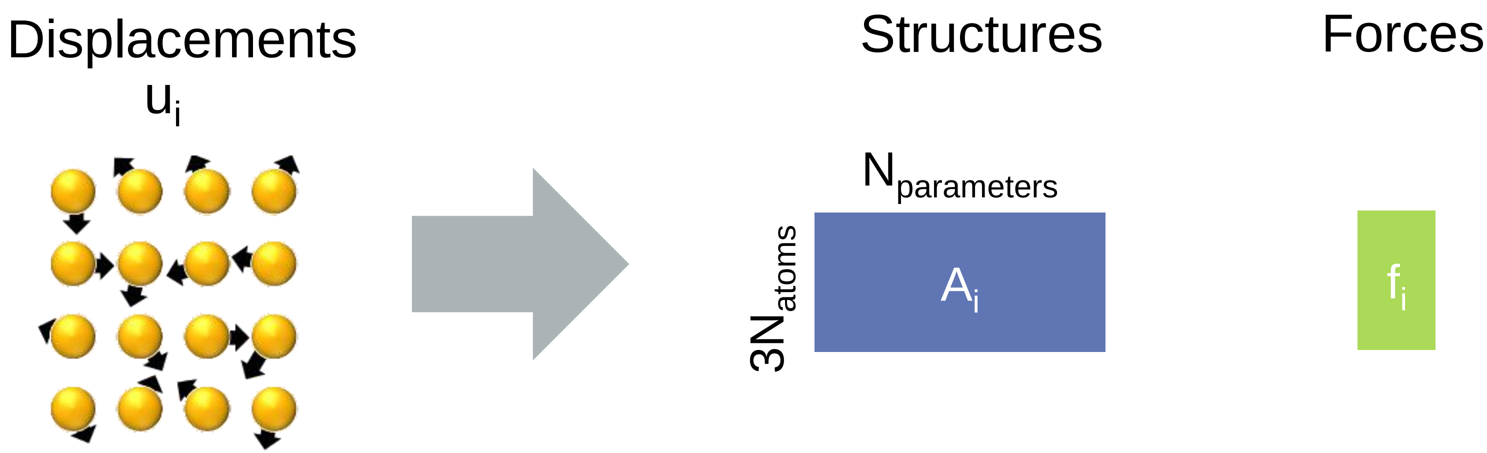


Structure decomposition

1. Generate structure e.g., by applying random displacements or superposing normal modes

2. Convert displacements u_i into “cluster vectors”
   → each structure yields a matrix A_i with $N_{parameters}$ columns and $3N_{atoms}$ rows

3. Each structure comes with a target force vector



Parameter optimization

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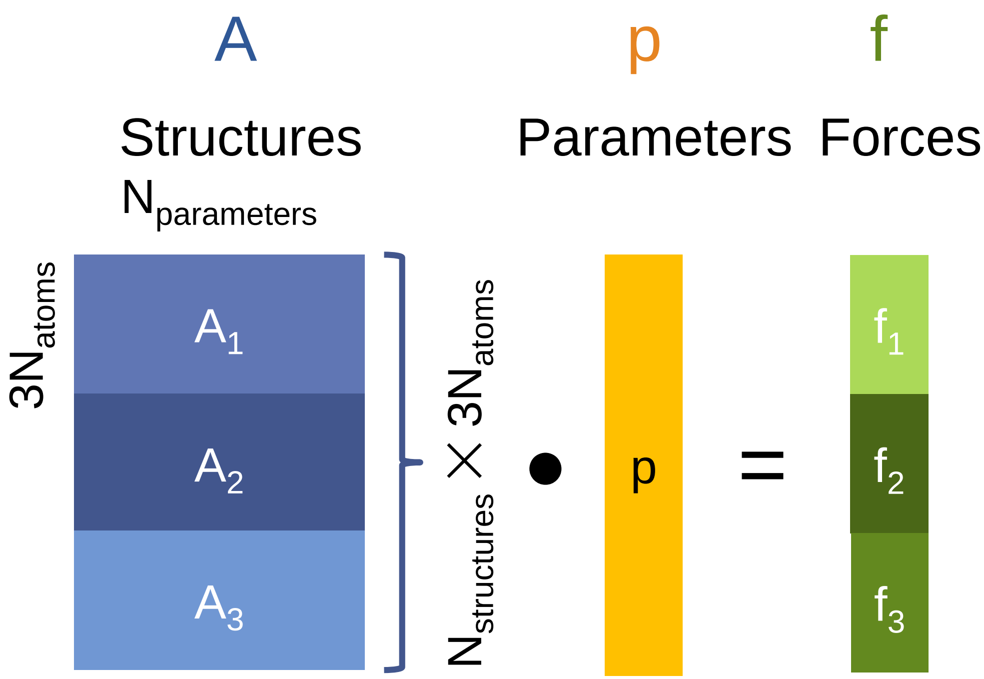
1. Compile multiple structures into one (large) fit matrix A
2. Solve the linear problem Ap=f



How?

Least-squares

$$||\boldsymbol{Ap} - \boldsymbol{f}||_2 < \epsilon$$

Ridge-regression/LASSO/

$$||\boldsymbol{Ap} - \boldsymbol{f}||_2^2 + \alpha||\boldsymbol{p}||_1 + \beta||\boldsymbol{p}||_2^2$$

Automatic relevance determination regression (ARDR)

Recursive feature elimination (RFE)

+ Cross-validation