DE LA RECHERCHE À L'INDUSTRIE

KineCluE : hands-on tutorial

CECAM 2024: Long time multi-scale simulations of activated events: from theory to pratice

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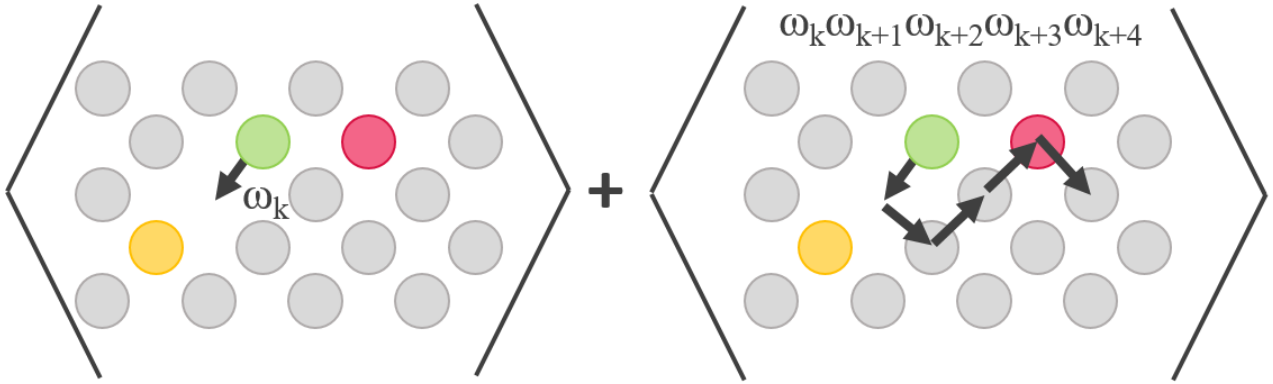
Thermodynamics of Irreversible Processes

The ***Onsager equation*** is a thermodynamic formulation of fluxes in out-of-equilibrium systems

$$\vec{J}_i = -\sum_j L_{ij} \vec{\nabla} \mu_j$$

To compute the flux you need to know the ***transport coefficients*** (L_{ij}'s) which are ***equilibrium properties*** (fluctuation-dissipation theorem) independent of driving forces

L_{ij}'s represent the average mobility of a given atomic species. It is related to atomic jump frequencies + the kinetic correlations which arise from the integration of all possible trajectories

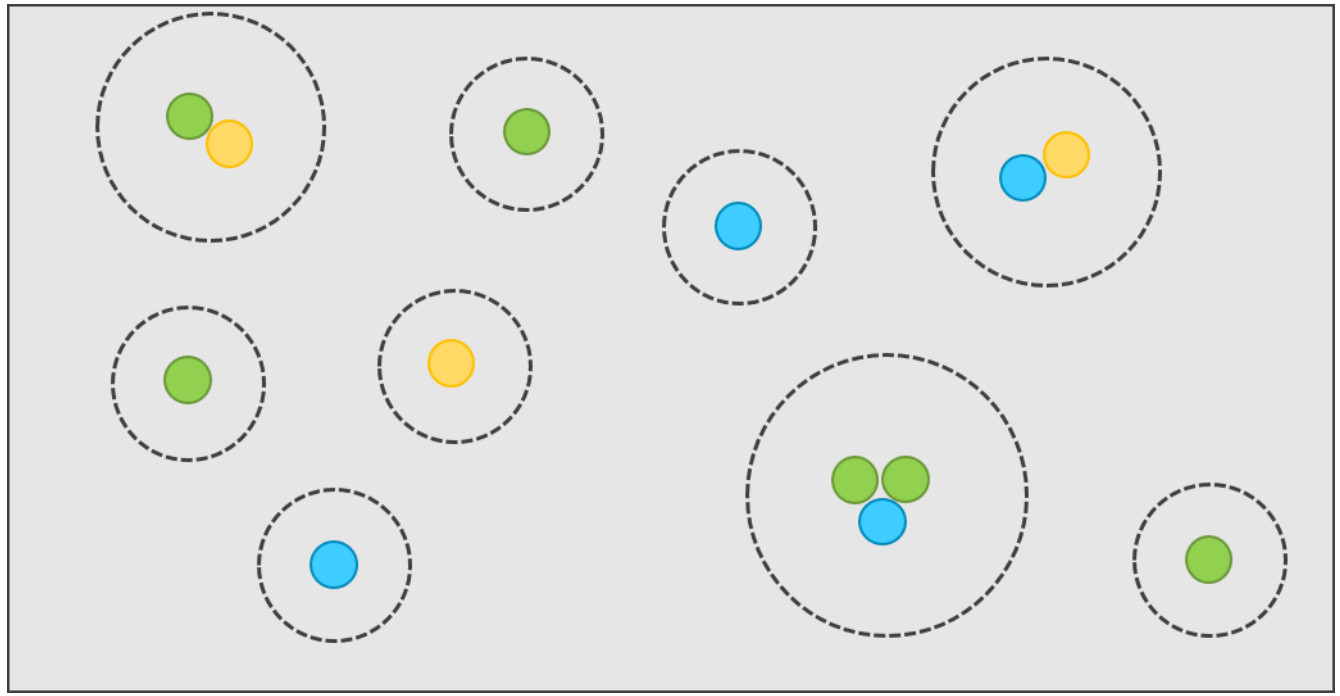


Our aim today, and the aim of KineCluE is to provide a framework to compute these transport coefficients from atomic-scale data (jump mechanisms and jump rates)

If we compute transport coefficients once, we can have the flux for any driving force. But transport coefficients depend on temperature and local composition…

KineCluE = Kinetic Cluster Expansion

In ***dilute alloys***, at any time, we can split the system into isolated sub-systems which we call ***clusters*** using some interaction range which we call ***kinetic range***



$$L_{ij} = \sum_{c} [c] L_{ij}(c)$$

This way we decouple the thermodynamic calculation (cluster concentrations) from the kinetic calculation (cluster transport coefficients)

Each KineCluE calculation allows to compute one cluster transport coefficient $L_{ij}(c)$

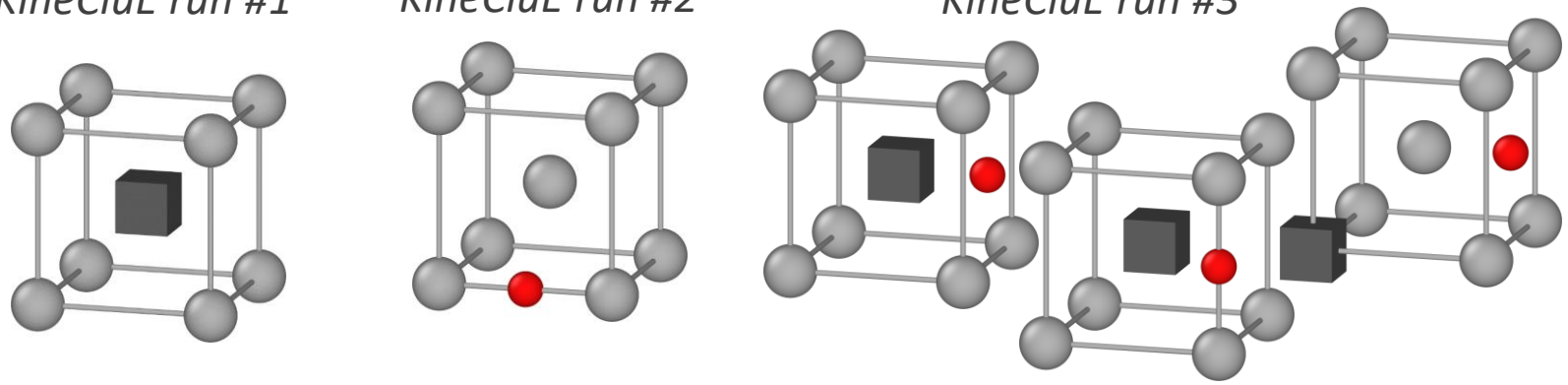
Example : Vacancy-oxygen interaction in BCC Fe

The Fe matrix is not accounted for explicitely. If vacancy and oxygen atoms are dilute we can apply our formalism to this system. Today we will consider the following clusters :

- Fe-vacancy monomer (V)
- Interstitial oxygen monomer (O)
- Fe-vacancy + interstitial oxygen pair (VO)

Cluster concentrations calculation (low-temperature expansion, cluster dynamics…)

$$\begin{pmatrix} J_{\mathrm{V}} \\ J_{\mathrm{O}} \end{pmatrix} = -\left[[\mathrm{V}] \underbrace{\begin{pmatrix} L_{\mathrm{VV}}(\mathrm{V}) & 0 \\ 0 & 0 \end{pmatrix}}_{\text{KineCluE run \#1}} + [\mathrm{O}] \underbrace{\begin{pmatrix} 0 & 0 \\ 0 & L_{\mathrm{OO}}(\mathrm{O}) \end{pmatrix}}_{\text{KineCluE run \#2}} + [\mathrm{VO}] \underbrace{\begin{pmatrix} L_{\mathrm{VV}}(\mathrm{VO}) & L_{\mathrm{VO}}(\mathrm{VO}) \\ L_{\mathrm{OV}}(\mathrm{VO}) & L_{\mathrm{OO}}(\mathrm{VO}) \end{pmatrix}}_{\text{KineCluE run \#3}} \right] \begin{pmatrix} \nabla \mu_{\mathrm{V}} \\ \nabla \mu_{\mathrm{O}} \end{pmatrix}$$



Example of solving for cluster concentrations at equilibrium

Mass-balance equations for each species

$$\begin{cases} [\mathrm{V}]_{\mathrm{tot}} = [\mathrm{V}] + [\mathrm{VO}] = Y_{\mathrm{V}} + Y_{\mathrm{V}} Y_{\mathrm{O}} Z_{\mathrm{VO}} \\ [\mathrm{O}]_{\mathrm{tot}} = [\mathrm{O}] + [\mathrm{VO}] = 3Y_{\mathrm{O}} + Y_{\mathrm{V}} Y_{\mathrm{O}} Z_{\mathrm{VO}} \end{cases}$$

Variables of these equations

$$Y_\alpha = \exp\left(\frac{\mu_\alpha}{k_B T}\right)$$

Pair partition function (total interaction probability)

$$Z_{\mathrm{VO}} = \sum_{i \in \mathrm{VO}} g_i \exp\left(\frac{E_b(i)}{k_B T}\right)$$

Rewriting the first equation we get

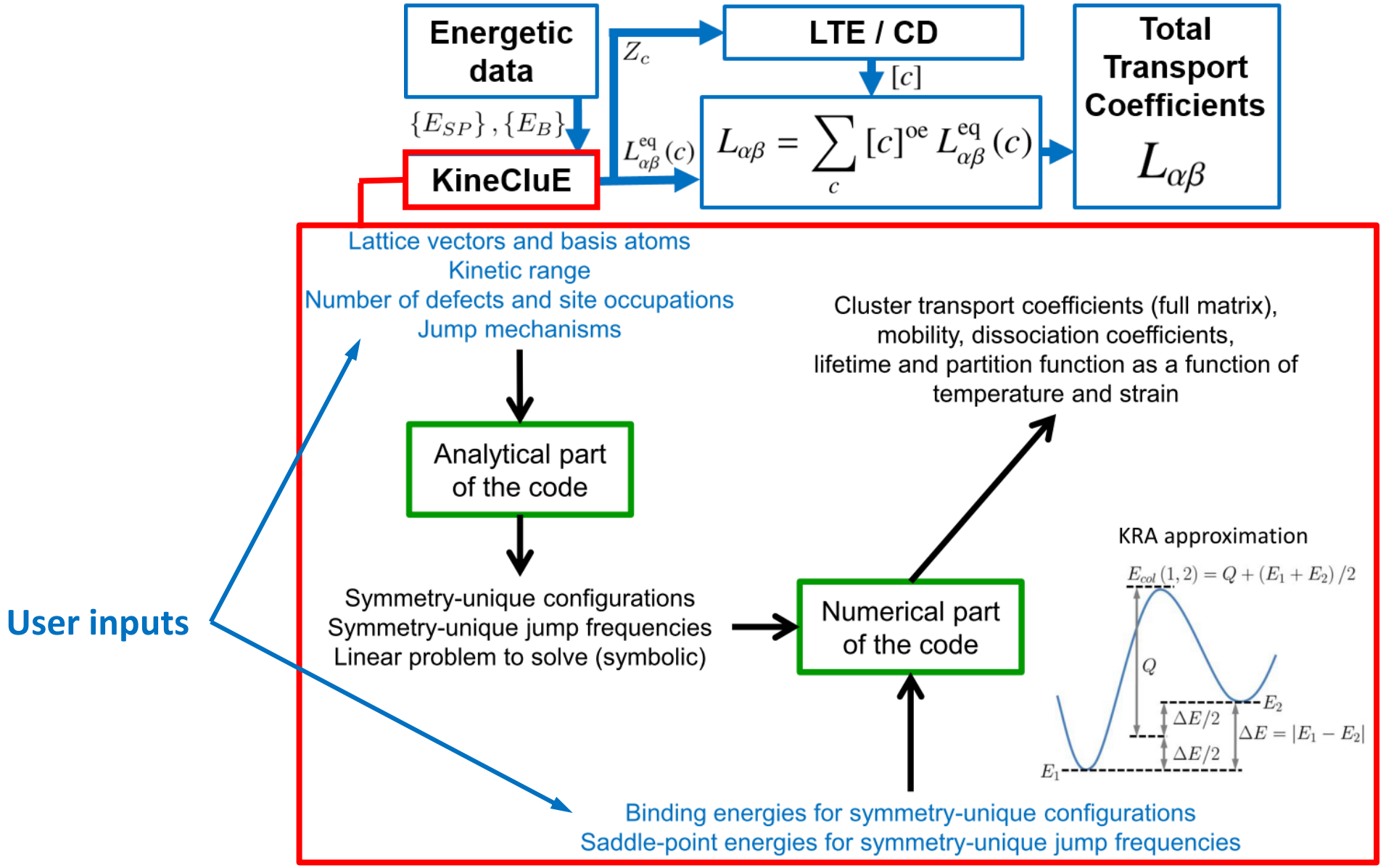
$$Y_{\mathrm{V}} = \frac{[\mathrm{V}]_{\mathrm{tot}}}{1 + Y_{\mathrm{O}} Z_{\mathrm{VO}}}$$

Replacing Y_V in the second equation we get a second order equation for Y_O and the solution reads

$$Y_{\mathrm{O}} = \frac{3 + Z_{\mathrm{VO}}\left([\mathrm{V}]_{\mathrm{tot}} - [\mathrm{O}]_{\mathrm{tot}}\right)}{6 Z_{\mathrm{VO}}} \left(-1 + \sqrt{1 + \frac{12 Z_{\mathrm{VO}} [\mathrm{O}]_{\mathrm{tot}}}{\left[3 + Z_{\mathrm{VO}}\left([\mathrm{V}]_{\mathrm{tot}} - [\mathrm{O}]_{\mathrm{tot}}\right)\right]^2}}\right)$$

The open-source KineCluE code

Schuler, Messina, Nastar, Comp. Mat. Sci. 172 109191 (2020)



Ex. 1: vacancy in BCC Fe, minimal input for the analytical part

There are **two input files** to write : one for the analytical part of the code, and one for the numerical part

Each input file is a text file containing **keywords** spotted by the « **&** » symbol

For each keyword there is a given number of **arguments** to provide

```
& CRYSTAL bcc                    ← Crystal name
+0.5 +0.5 -0.5                   ← First cell vector
+0.5 -0.5 +0.5                   ← Second cell vector
-0.5 +0.5 +0.5                   ← Third cell vector

& KINETICRANGE 1                 ← Kinetic interaction radius in the same units as above

& UNIQUEPOS 1                    ← Number of symmetry-unique lattice sites used by all cluster components
o 0 0 0                          ← Coordinates of the site

& SPECIES 1                      ← Number of explicit species (defects, solutes…)
1 1 vacancy                      ← List of site occupation numbers (0/1, one number for each UNIQUEPOS) + species name

& JUMPMECH
%% 1 vacjump                     ← Number of constraints in this jump + jump name
s 1 0 0 0 > 1 1 0 0              ← Initial {species + coordinates} > Final {species + coordinates}
                                   Note: {s 1 +1 +0 +0} is equivalent to {o 1 +0.5 +0.5 -0.5 }
```

Number of components belonging to this species in the cluster

Coordinate system
o: orthonormal
s: supercell (relative)

New jump mechanism

Ex. 1: output log from the analytical part (1/3)

```
 _____________________________________________________
 |                                                   |
 |          KineCluE v1.0 - 13/09/2018               |
 |        T. Schuler, L. Messina, M. Nastar          |
 |___________________________________________________|
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You are required to cite the following paper when using KineCluE or part of KineCluE:
T. Schuler, L. Messina and M. Nastar, Computational Materials Science (2019) [doi: https://doi.org/10.1016.j.commatsci.2019.109191]

Calculation date: 2021-04-09 15:43
Working in directory:  ./CALC/
Kinetic range is set to 1.01 lattice parameters
Thermodynamic range is set to 1.01 lattice parameters
!! Bravais lattice because (BASIS keyword not found)
Creating 3D crystal bcc
Searching for symmetry operations in crystal without strain...
  Found 48 symmetry operations (48 point group op. and 0 space groups op.)
!! Unstrained calculation (STRAIN keyword not found)
!! Setting default CPG direction as [1,0,0] in supercell basis. Might not be optimal (CPG keyword not found)
CPG direction (supercell, cartesian) [ 1.155  0.000  0.000] ; [ 0.577  0.577 -0.577]
!! Cluster transport coefficients are computed along the cpg direction only (NORMAL keyword not found)
```

Ex. 1: output log from the analytical part (2/3)

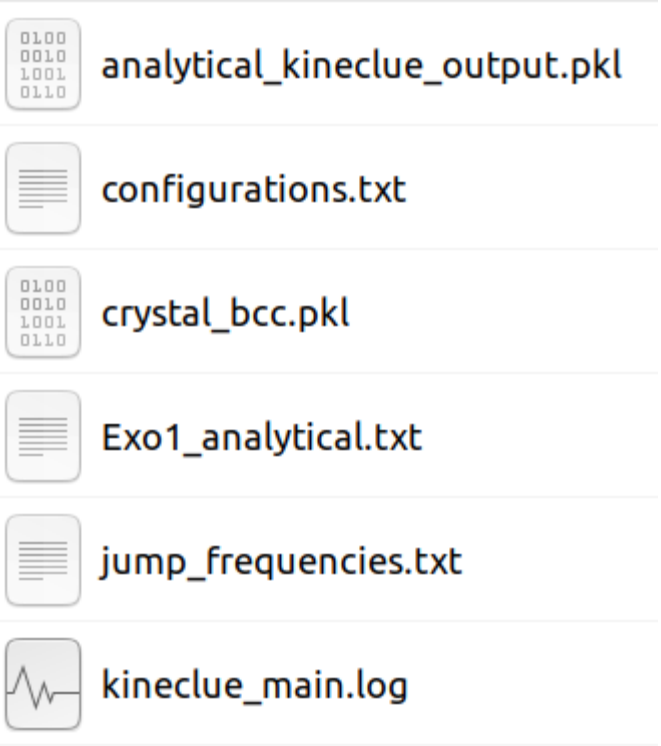
```
Searching for symmetry operations valid for the cpg...
  Found 12 symmetries that include the cpg.
Creating list of species and components, starting at 1.131 s
  Defect 0 on sublattice [0. 0. 0.] has 1 symmetry equivalent.
  Species 1 is a vacancy and can be in sublattices [0]
    Component 0 is a vacancy
Creating list of jumps, starting at 1.134 s
  Found 1 jump mechanisms
    Found 8 symmetry equivalent jump mechanisms for vacjump
Computing jump symmetry equivalent and average species displacements.. (starts at 1.138 s)
Checking if exploration space is connected.. (starts at 1.240 s)
Setting up initial configuration.. (starts at 1.240 s)
!! Automatically generating the initial configuration, starting at 1.240 s
New initial configuration (orthonormal coordinates):
  ['vacancy: [  0.0000   0.0000   0.0000]']
8 valid jumps from initial configuration (orthonormal coordinates)
  vacjump  [  0.5000   0.5000  -0.5000]
  vacjump  [ -0.5000  -0.5000   0.5000]
  vacjump  [ -0.5000  -0.5000  -0.5000]
  vacjump  [ -0.5000   0.5000  -0.5000]
  vacjump  [ -0.5000   0.5000   0.5000]
  vacjump  [  0.5000  -0.5000  -0.5000]
  vacjump  [  0.5000  -0.5000   0.5000]
  vacjump  [  0.5000   0.5000   0.5000]
```

Ex. 1: output log from the analytical part (3/3)

```
Creating configuration space (starts at 1.242 s)
  Found 1 configurations
  Found 1 thermodynamic interaction classes (including 0 dissociated)
  Found 0 kinetic interaction classes (and 0 site interactions)
!! Thermodynamic interaction range not specified or equal to or larger than the kinetic range
Searching for jump frequencies (starts at 1.244 s)
  Found 1 jump frequencies
!! Will not be able to perform the convergence study (KIRALOOP keyword not found)
Writing symbolic equations (starts at 1.249 s)
  T matrix contains 0 non-zero elements
Computing non-correlated matrix (starts at 1.249 s)
Computing partition function (starts at 1.249 s)
Writing configuration values file (starts at 1.250 s)
Writing jump frequency values file (starts at 1.250 s)
Saving objects to file (starts at 1.250 s)
Execution time: 1.251 s.
Peak memory usage: 95.695 MB.
```

Ex. 1: Files created by the analytical part of the code

In CALC folder (default)



- *Calculation results (unreadable) to be used by the numerical part of the code*
- *List of symmetry unique cluster configurations*
- *Crystal object (unreadable) to be reused*
- *Copy of the input file used for this calculation*
- *List of symmetry unique cluster jump frequencies between cluster configurations*
- *Copy of the output log*

Ex. 1: vacancy in BCC Fe, minimal input for the numerical part of the code

There are three ways to provide numerical data to KineCluE *(in order of priority)*

1) D**irectly fill-in** configuration.txt and jump_frequency.txt files (!! CAUTION !! These files are overwritten each time the analytical part of the code runs)
2) Use a separate **INTERACTIONMODEL** file with a list of configuration and jump frequencies. KineCluE will try to relate these to the ones found in the analytical part of the code
3) Rely on the **KRAACTIVATION** keyword which provides a default value to all jump frequencies

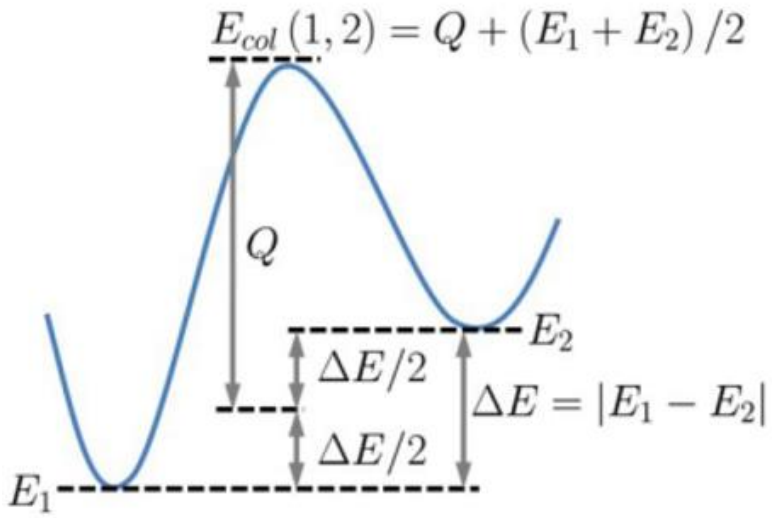
Must match jump names in the analytical input

& KRAACTIVATION

vacjump 1 0.0 ← *Prefactor, activation energy (Q)*

& TEMPERATURES 300 700 200 ← *Min, max, step*

KRA approximation



Ex. 1: output log from the numerical part (1/2)

```
 _____________________________________________________
|                                                     |
|          KineCluE v1.0 - 13/09/2018                 |
|        T. Schuler, L. Messina, M. Nastar            |
|_____________________________________________________|

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T. Schuler, L. Messina and M. Nastar, Computational Materials Science (2019) [doi:
https://doi.org/10.1016.j.commatsci.2019.109191]

Calculation date: 2021-04-12 09:17
Working in directory:  ./CALC/
Read numerical input file (starts at 0.002 s)
Reading output file from analytical results (starts at 0.002 s)
Will print results with 6 decimal digits.
The cluster contains:
  1 vacancy
!! Will not perform automatic convergence study (KIRALOOP keyword not found in the numerical input)
Lambdify matrices (starts at 0.004 s)
Reading configuration file (starts at 0.007 s)
```

Ex. 1: output log from the numerical part (2/2)

```
Reading jump frequency values from the file (starts at 0.008 s)
Lambdify jump frequencies and configuration probabilities (starts at 0.044 s)
Cluster transport coefficients are output in units of m2/s
Total number of configurations  Z0 = 1.0
Computing Onsager matrices (starts at 0.047 s)
  Computing cluster transport coefficients...

Temperature =  300.0 K - Strain =    0.000 %
  Z=1.000E+00   D=0.000E+00   t=   INF

      [  9.99999999999999e-09  ]

Temperature =  500.0 K - Strain =    0.000 %
  Z=1.000E+00   D=0.000E+00   t=   INF

      [  9.99999999999999e-09  ]

Temperature =  700.0 K - Strain =    0.000 %
  Z=1.000E+00   D=0.000E+00   t=   INF

      [  9.99999999999999e-09  ]

Execution time: 0.055 s.
Peak memory usage: 133.190 MB.
```

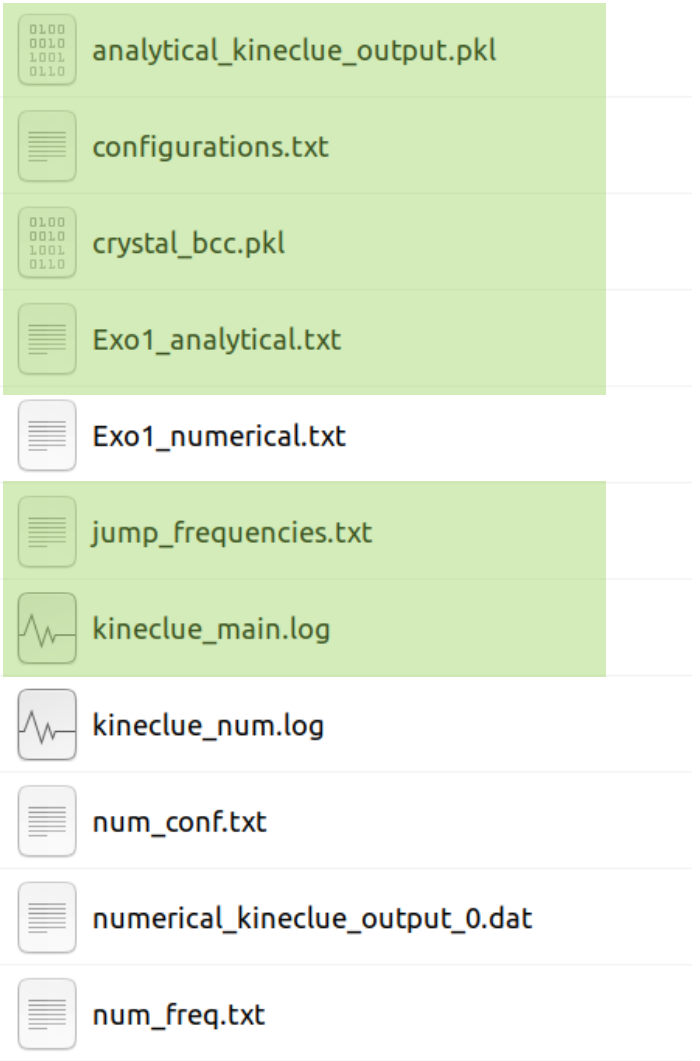
Z: cluster partition function
D: cluster dissociation rate
t: cluster lifetime (1/D)

Cluster Onsager matrix

Note: cluster transport coefficients are proportional to lattice parameter squared (default 1ang) times attempt freqency (default 1 THz)

Ex. 1: Files created by the numerical part of the code

In CALC folder (default)



- Exo1_numerical.txt ← *Copy of the input file used for this calculation*
- kineclue_num.log ← *Copy of the output log*
- num_conf.txt ← *List of the numerical values used for each cluster configuration*
- numerical_kineclue_output_0.dat ← *Results (cluster transport coefficients, partition function)*
- num_freq.txt ← *List of the numerical values used for each cluster jump frequency*

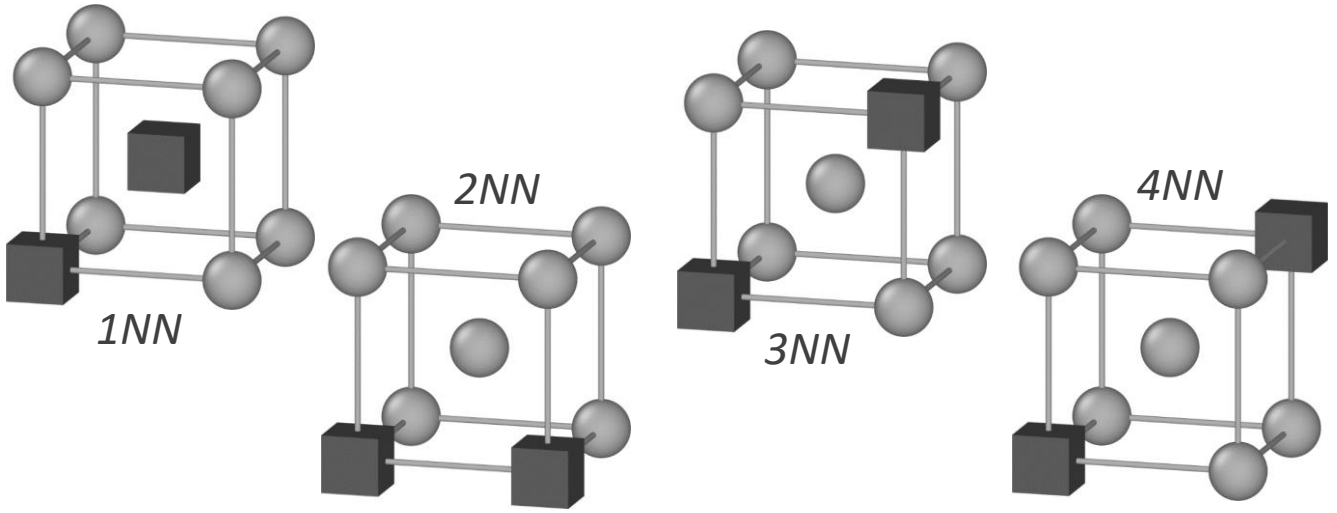
Ex. 2: divacancy in BCC Fe, input for the analytical part of the code

```
& CRYSTAL bcc
+0.5 +0.5 -0.5
+0.5 -0.5 +0.5
-0.5 +0.5 +0.5

& KINETICRANGE 1.8

& UNIQUEPOS 1
o 0 0 0

& SPECIES 1
2 1 vacancy

& JUMPMECH
%% 1 vacjump
s 1 0 0 0 > 1 1 0 0

& DIRECTORY V2

& CPG o 1 0 0
```

```
[…]
Working in directory:  V2/
Kinetic range is set to 1.81 lattice parameters
Thermodynamic range is set to 1.81 lattice parameters
[…]
Searching for symmetry operations valid for the cpg...
 Found 16 symmetries that include the cpg.
[…]
 Species 1 is a vacancy and can be in sublattices [0]
  Component 0 is a vacancy
  Component 1 is a vacancy
[…]
New initial configuration (orthonormal coordinates):
 ['vacancy: [  0.0000   0.0000   0.0000]', 'vacancy: [ -0.5000  -0.5000   0.5000]']
16 valid jumps from initial configuration (orthonormal coordinates)
[…]
Creating configuration space (starts at 1.249 s)
 Found 31 configurations
 Found 7 thermodynamic interaction classes (including 1 dissociated)
 Found 0 kinetic interaction classes (and 0 site interactions)
!! Thermodynamic interaction range not specified or equal to or larger than the kinetic range
Searching for jump frequencies (starts at 1.290 s)
 Found 10 jump frequencies
[…]
```

Ex. 2: divacancy in BCC Fe, configurations.txt

1) *Configuration class;*
2) *Entropy prefactor (no units);*
3) *Binding energy (eV, >0 means attraction);*
4) *Dissociated;*
5) *Number of symmetry equivalents;*
6) *Position of each defect in orthonormal coordinates*

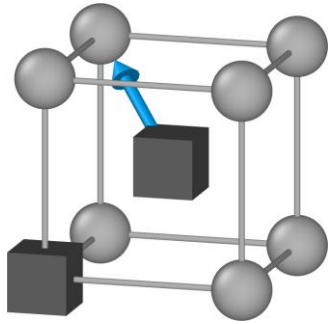


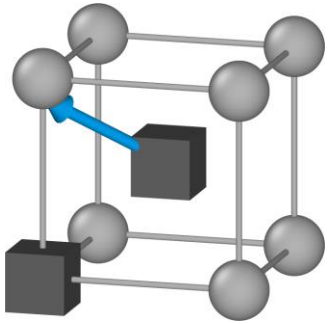

```
5    -1.000  0.000  d1|1    0 [+0.00 +0.00 +0.00] [-1.50 -1.50 +1.50]
0    -1.000  0.000  -        4 [+0.00 +0.00 +0.00] [-0.50 -0.50 +0.50]
1    -1.000  0.000  -        4 [+0.00 +0.00 +0.00] [-1.00 -1.00 +1.00]
2    -1.000  0.000  -        1 [+0.00 +0.00 +0.00] [+0.00 +0.00 +0.00]
3    -1.000  0.000  -        3 [+0.00 +0.00 +0.00] [+0.00 +0.00 -1.00]
4    -1.000  0.000  -        6 [+0.00 +0.00 +0.00] [-1.00 -1.00 +0.00]
6    -1.000  0.000  -       12 [+0.00 +0.00 +0.00] [-0.50 -0.50 +1.50]
```

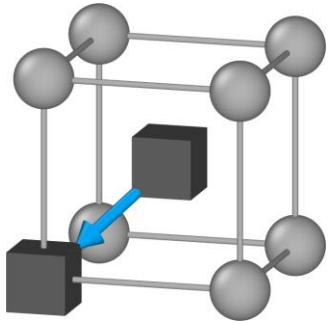
→ Dissociated (beyond kinetic range)
→ 1NN
→ 5NN
→ 0NN
→ 2NN
→ 3NN
→ 4NN

Ex. 2: divacancy in BCC Fe, jump_frequencies.txt

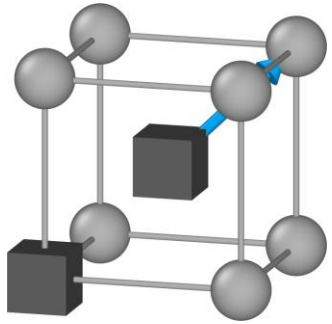
1) *Jump frequency number;*
2) *Jump prefactor (no units);*
3) *Saddle-point energy (eV);*
4) *Configuration class 1;*
5) *Configuration class 2;*
6) *Jump mechanism name;*
7) *Number of symmetry equivalent jumps*


1NN->3NN


1NN->2NN


1NN->0NN

?


1NN->5NN

0	-1.000	0.000	0	1	vacjump	4	→	**1NN -> 5NN**
1	-1.000	0.000	0	2	vacjump	4	→	**1NN -> 0NN**
2	-1.000	0.000	0	3	vacjump	12	→	**1NN -> 2NN**
3	-1.000	0.000	0	4	vacjump	12	→	**1NN -> 3NN**
4	-1.000	0.000	1	5	vacjump	4	→	**5NN -> dissociated**
5	-1.000	0.000	1	6	vacjump	12	→	**5NN -> 4NN**
6	-1.000	0.000	3	6	vacjump	12	→	**2NN -> 4NN**
7	-1.000	0.000	4	5	vacjump	12	→	**3NN -> dissociated**
8	-1.000	0.000	4	6	vacjump	24	→	**3NN -> 4NN**
9	-1.000	0.000	6	5	vacjump	12	→	**4NN -> dissociated**

From configuration.txt,
0=1NN
1=5NN
2=0NN
3=2NN
4=3NN
5=dissociated
6=4NN

Ex. 2b: divacancy in BCC Fe, input for the analytical part of the code

```
& CRYSTAL bcc
+0.5 +0.5 -0.5
+0.5 -0.5 +0.5
-0.5 +0.5 +0.5

& KINETICRANGE 1.8 1.0

& UNIQUEPOS 1
o 0 0 0

& SPECIES 1
2 1 vacancy

& JUMPMECH
%% 2 vacjump
s 1 0 0 0 > 1 1 0 0
s 0 1 0 0 > 0 0 0 0

& DIRECTORY V2
& CPG o 1 0 0
```

Thermal range

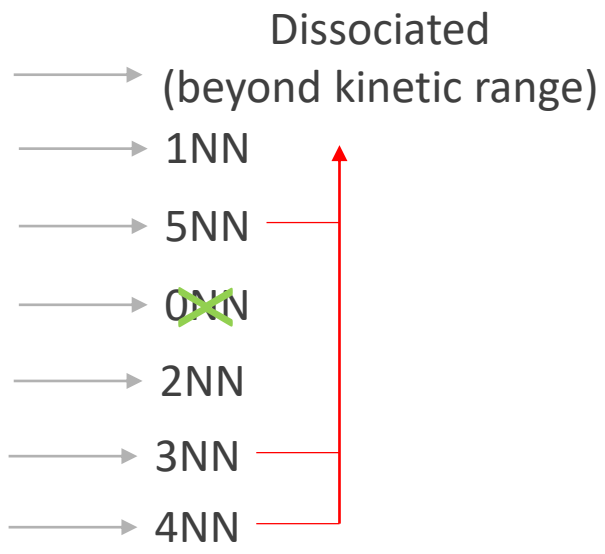
Additional jump constraint

[…]
Kinetic range is set to 1.81 lattice parameters
Thermodynamic range is set to **1.01** lattice parameters
[…]
Found 1 jump mechanisms
Found 8 symmetry equivalent jump mechanisms for vacjump
[…]
Creating configuration space (starts at 1.228 s)
Found **30** configurations
Found **6** thermodynamic interaction classes (including 1 dissociated)
Found 0 kinetic interaction classes (and 0 site interactions)
Using the thermodynamical range to reduce the number of variables (starts at 1.269 s)
Now **3** configuration variables are left
Searching for jump frequencies (starts at 1.269 s)
Found **5** jump frequencies
[…]

Ex. 2b: divacancy in BCC Fe, configurations.txt

Previous :

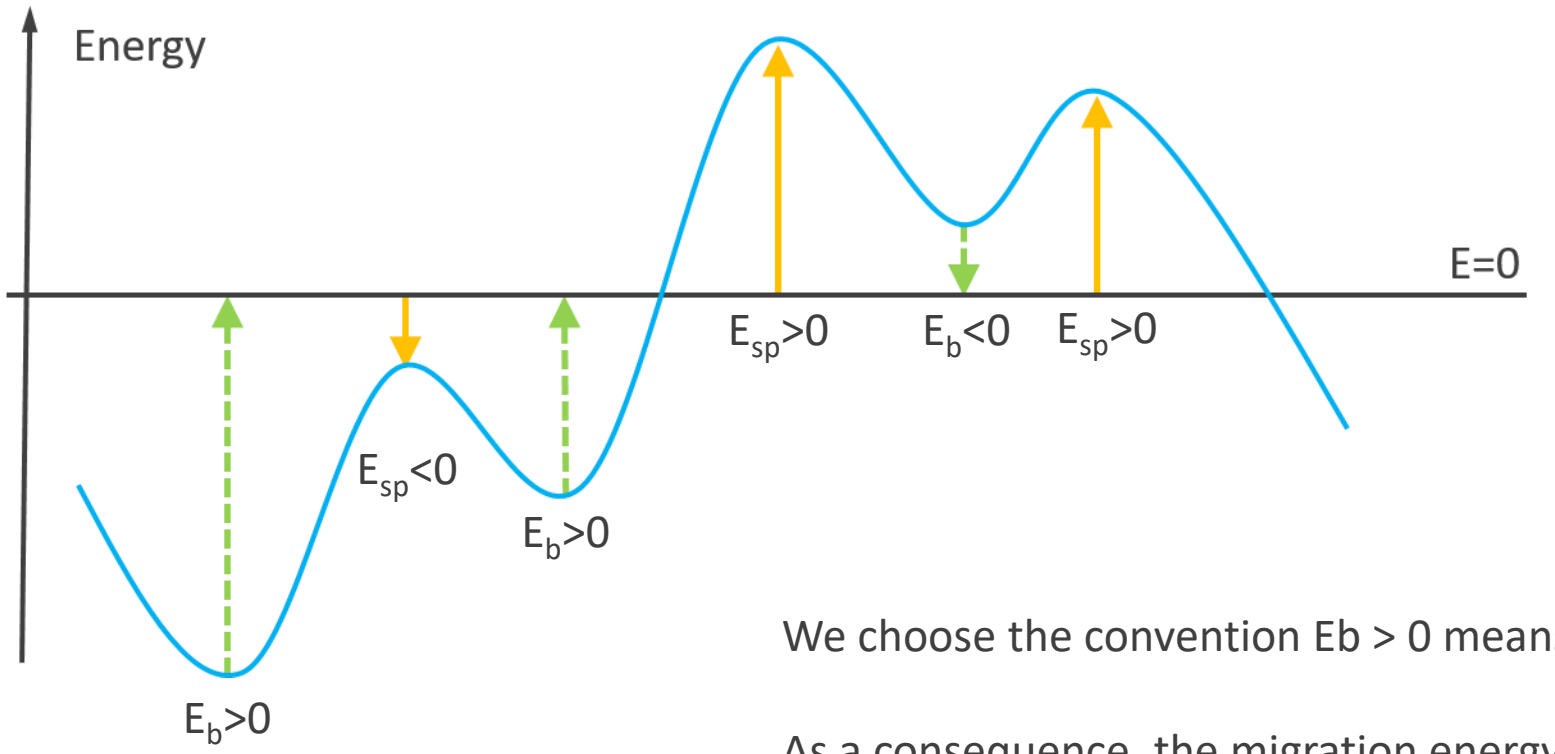
```
5    -1.000  0.000  d1|1    0 [+0.00 +0.00 +0.00] [-1.50 -1.50 +1.50]
0    -1.000  0.000  -        4 [+0.00 +0.00 +0.00] [-0.50 -0.50 +0.50]
1    -1.000  0.000  -        4 [+0.00 +0.00 +0.00] [-1.00 -1.00 +1.00]
2    -1.000  0.000  -        1 [+0.00 +0.00 +0.00] [+0.00 +0.00 +0.00]
3    -1.000  0.000  -        3 [+0.00 +0.00 +0.00] [+0.00 +0.00 -1.00]
4    -1.000  0.000  -        6 [+0.00 +0.00 +0.00] [-1.00 -1.00 +0.00]
6    -1.000  0.000  -       12 [+0.00 +0.00 +0.00] [-0.50 -0.50 +1.50]
```



New :

```
0    -1.000  0.000  d1|1   22 [+0.00 +0.00 +0.00] [-1.50 -1.50 +1.50]
1    -1.000  0.000  -        4 [+0.00 +0.00 +0.00] [-0.50 -0.50 +0.50]
2    -1.000  0.000  -        3 [+0.00 +0.00 +0.00] [+0.00 +0.00 -1.00]
```

A word on energies and energy reference



Energy reference configuration : ***all cluster components dissociated as monomers***.

Therefore the energy difference between any conference and the reference is a ***binding energy***.

We choose the convention Eb > 0 means attraction.

As a consequence, the migration energy reads E_{sp}+E_b and

- ***high energy saddle-points will have a large positive value***;
- ***high energy configurations will have a large negative value;***

Ex. 3 : O monomer in BCC Fe, input for the analytical

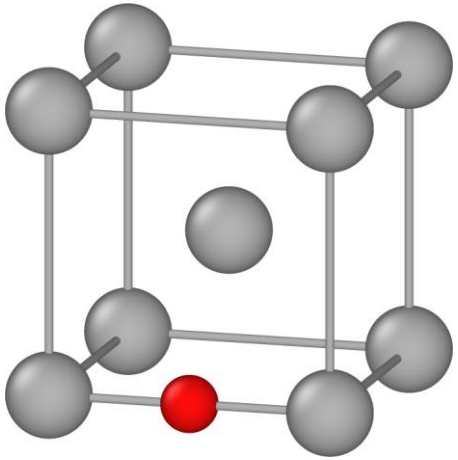
```
& CRYSTAL bcc
+0.5 +0.5 -0.5
+0.5 -0.5 +0.5
-0.5 +0.5 +0.5
& KINETICRANGE 1.8 1.0
& CPG o 1 0 0
& DIRECTORY O
& UNIQUEPOS 2
o 0 0 0
o 0.5 0 0
& SPECIES 2
0 1 0 vacancy
1 0 1 oxygen
& JUMPMECH
%% 2 vacjump
s 1 0 0 0 > 1 1 0 0
s 0 1 0 0 > 0 0 0 0
%% 2 ojump
o 2 0.5 0 0 > 2 0.5 0.5 0
o 0 0.5 0.5 0 > 0 0.5 0 0
```

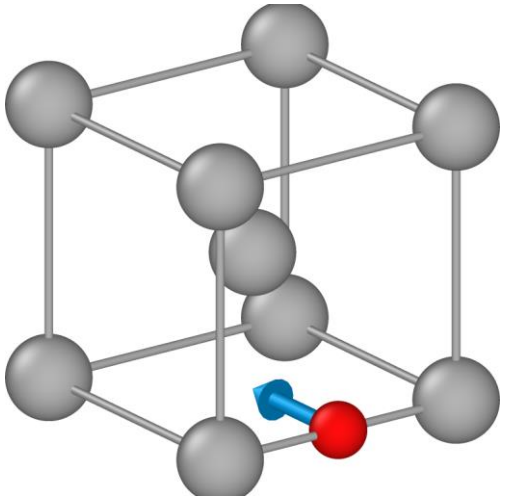
We are adding a second lattice position (interstitial octaedral sites in the BCC lattice). By symmetry, the code will automatically find all the equivalent sites (which you can check with keyword PRINTSYMEQS)

Removing the vacancy (setting the first number to 0) and adding a zero to say that the vacancy is not allowed to go on interstitial sites

Adding 1 oxygen atom to the cluster. It can go to interstitial sites but not to substitutional sites

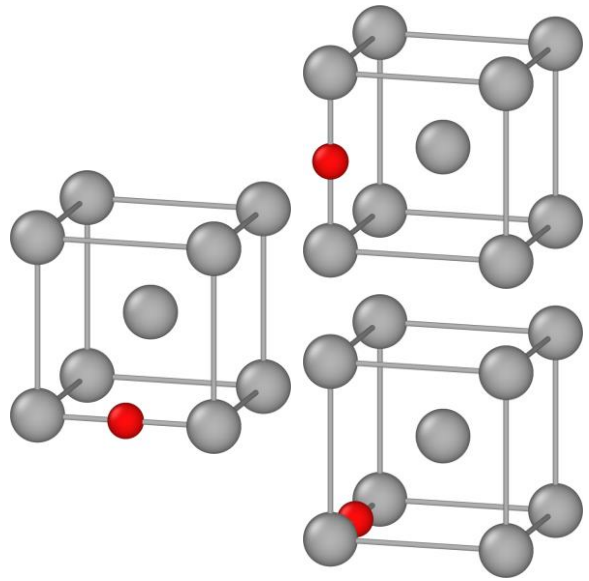
Adding the jump mechanism for oxygen atom, between two nearby interstitial octaedral sites. The equivalent jumps will be find automatically using crystal symmetries (again you can check with the keyword PRINTSYMEQS)

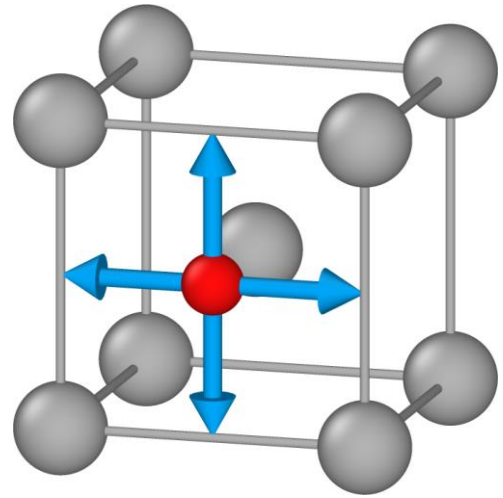




Ex. 3 : O monomer in BCC Fe, log from the analytical part

```
Creating list of species and components, starting at 1.069 s
  Defect 0 on sublattice [0. 0. 0.] has 1 symmetry equivalent.
  Defect 1 on sublattice [0.5 0.5 0. ] has 3 symmetry equivalent.
  Species 1 is a vacancy and can be in sublattices [0]
  Species 2 is a oxygen and can be in sublattices [1]
    Component 0 is a oxygen
Creating list of jumps, starting at 1.084 s
!! Jump vacjump is not taken into account because it requires components that are not part of the cluster
  Found 1 jump mechanisms
    Found 12 symmetry equivalent jump mechanisms for ojump
[…]
New initial configuration (orthonormal coordinates):
  ['oxygen: [  0.5000   0.0000   0.0000]']
4 valid jumps from initial configuration (orthonormal coordinates)
  ojump  [  0.5000   0.5000   0.0000]
  ojump  [  0.5000  -0.5000   0.0000]
  ojump  [  0.5000   0.0000  -0.5000]
  ojump  [  0.5000   0.0000   0.5000]
Creating configuration space (starts at 1.381 s)
  Found 3 configurations
  Found 1 thermodynamic interaction classes (including 0 dissociated)
[…]
  Found 1 jump frequencies
```





Ex. 4 : VO pair in BCC Fe, input and log for the analytical part

```
& CRYSTAL bcc
+0.5 +0.5 -0.5
+0.5 -0.5 +0.5
-0.5 +0.5 +0.5
& KINETICRANGE 1.8 1.0
& CPG o 1 0 0
& DIRECTORY VO
& UNIQUEPOS 2
o 0 0 0
o 0.5 0 0
& SPECIES 2
1 1 0 vacancy
1 0 1 oxygen
& JUMPMECH
%% 2 vacjump
s 1 0 0 0 > 1 1 0 0
s 0 1 0 0 > 0 0 0 0
%% 2 ojump
o 2 0.5 0 0 > 2 0.5 0.5 0
o 0 0.5 0.5 0 > 0 0.5 0 0
```

```
Species 1 is a vacancy and can be in sublattices [0]
  Component 0 is a vacancy
 Species 2 is a oxygen and can be in sublattices [1]
  Component 1 is a oxygen
Creating list of jumps, starting at 1.141 s
 Found 2 jump mechanisms
  Found 8 symmetry equivalent jump mechanisms for vacjump
  Found 12 symmetry equivalent jump mechanisms for ojump
[…]
New initial configuration (orthonormal coordinates):
 ['vacancy: [ 0.0000  0.0000  0.0000]', 'oxygen: [ 0.5000  0.0000  0.0000]']
12 valid jumps from initial configuration (orthonormal coordinates)
 vacjump [ 0.5000  0.5000 -0.5000 ,  0.5000  0.0000  0.0000]      x8
 ojump [ 0.0000  0.0000  0.0000 ,  0.5000  0.5000  0.0000]        x4
Creating configuration space (starts at 1.581 s)
 Found 145 configurations
 Found 9 thermodynamic interaction classes (including 1 dissociated)
 Found 13 kinetic interaction classes (and 0 site interactions)
Using the thermodynamical range to reduce the number of variables (starts at 1.642 s)
 Now 3 configuration variables are left
Searching for jump frequencies (starts at 1.643 s)
 Found 9 jump frequencies
```

→ **Correlations !**

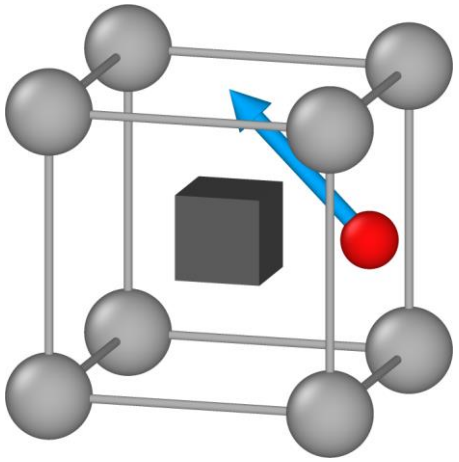
Ex. 4b : VO pair in BCC Fe, adding specific jumps

& JUMPMECH

%% 2 vacjump
s 1 0 0 0 > 1 1 0 0
s 0 1 0 0 > 0 0 0 0

%% 2 ojump
o 2 0.5 0 0 > 2 0.5 0.5 0
o 0 0.5 0.5 0 > 0 0.5 0 0

%% 3 ojump2nn
o 2 0.5 0 0 > 2 0 0.5 0
o 1 0 0 0 > 1 0 0 0
o 0 0 0.5 0 > 0 0.5 0 0



Found 3 jump mechanisms
  Found 8 symmetry equivalent jump mechanisms for vacjump
  Found 12 symmetry equivalent jump mechanisms for ojump
  Found 24 symmetry equivalent jump mechanisms for ojump2nn
[…]
16 valid jumps from initial configuration (orthonormal coordinates)
  vacjump [0.5000 0.5000 -0.5000 , 0.5000 0.0000 0.0000] **x8**
  ojump [0.0000 0.0000 0.0000 , 0.5000 0.5000 0.0000] **x4**
  ojump2nn [0.0000 0.0000 0.0000 , 0.0000 0.5000 0.0000]
  ojump2nn [0.0000 0.0000 0.0000 , 0.0000 -0.5000 0.0000]
  ojump2nn [0.0000 0.0000 0.0000 , 0.0000 0.0000 -0.5000]
  ojump2nn [0.0000 0.0000 0.0000 , 0.0000 0.0000 0.5000]
Creating configuration space (starts at 2.069 s)
  Found 145 configurations
  Found 9 thermodynamic interaction classes (including 1 dissociated)
  Found 13 kinetic interaction classes (and 0 site interactions)
Using the thermodynamical range to reduce the number of variables (starts at 2.132 s)
  Now 3 configuration variables are left
Searching for jump frequencies (starts at 2.132 s)
  Found 10 jump frequencies

Ex. 5: Kinetic Cluster Expansion with 3 clusters (V, O and VO): input for the numerical part of the code

The idea is to use the same input to run the numerical part of each cluster, changing only the working directory

& DIRECTORY VOb # choose a directory where an analytical calculation has already ran
& KRAACTIVATION # set activation energy for each jump mechanism for default value calculations
vacjump 0.67 # only one number: activation energy (i.e. prefactor set to 1.0)
ojump 0.149 0.56 # two numbers: prefactor then activation energy
ojump2nn 0.149 0.40
& TEMPERATURES 300 1000 20 # temperature loop
& UNITS cm2/s # change the units
& PREFACTOR 82 # jump frequency prefator common to all frequencies (in THz)
& LATTPARAM 2.856 # lattice parameter (in angstroms)
& MOB # cluster mobility (without dissociation) as in cluster dynamics
& OUTOPTIONS CF # output a file with a direct calculation of cluster correlation factors
& OUTPUT numout # base-name of the output files
& INTERACTIONMODEL fevo.txt # use an external file to provide numerical information

Ex. 5: Kinetic Cluster Expansion with 3 clusters (V, O and VO): interaction model file

The interaction model file is the easiest way to provide energetic data (for instance obtained using DFT calculations) to the code

& new entry

C or **J**: configuration or jump frequency

o or **s**: coordinate system

Number of constraints

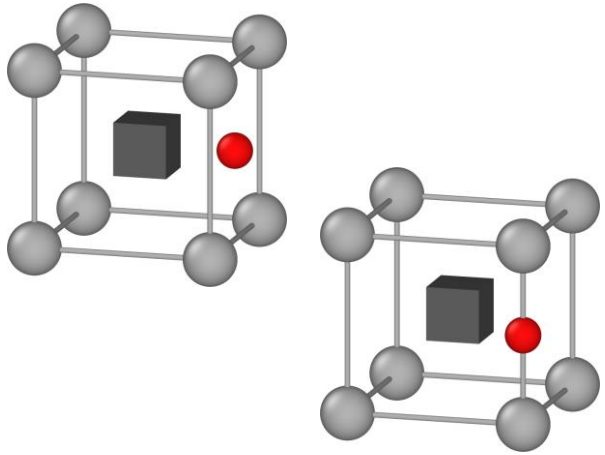
Prefactor, energy, elastic dipole

then 1 line per constraint with format

species position (for configuration) OR

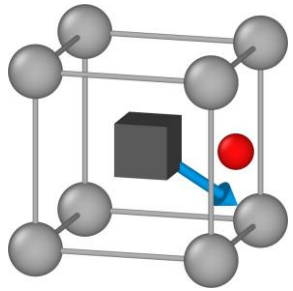
species initial position > final position (for jump)

```
& C o 2 1.33 # 1NN configuration
vacancy 0.0 0.0 0.0
oxygen  0.5 0.0 0.0
```

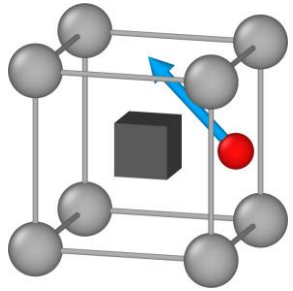


```
& C o 2 0.56 # 2NN configuration
vacancy 0.0 0.0 0.0
oxygen  0.5 0.5 0.0
```

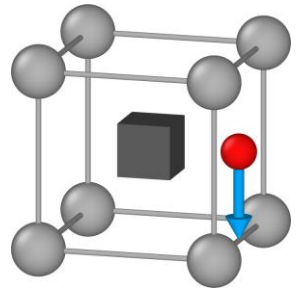
```
& J o 3 0.0 0.0 # 2NN to 1NN jump (vacancy jump), forbiden (prefactor=0)
vacancy 0.0 0.0 0.0 > 0.5 0.5 0.5
oxygen 0.5 0.5 0.0 > 0.5 0.5 0.0
bulk 0.5 0.5 0.5 > 0.0 0.0 0.0
```



```
& J o 3 -1.03 # 1NN to 1NN jump around V
vacancy 0.0 0.0 0.0 > 0.0 0.0 0.0
oxygen 0.5 0.0 0.0 > 0.0 0.0 0.5
bulk 0.0 0.0 0.5 > 0.5 0.0 0.0
```



```
& J o 3 -0.49 # 1NN to 2NN jump (oxygen jump)
vacancy 0.0 0.0 0.0 > 0.0 0.0 0.0
oxygen 0.5 0.0 0.0 > 0.5 0.5 0.0
bulk 0.5 0.5 0.0 > 0.5 0.0 0.0
```



Ex. 5: outputs for cluster VO

Pair cluster Onsager matrix
Diagonal coefficients must be positive, matrix must be symmetric

Temperature = 620.0 K - Strain = 0.000 %
Z=3.884E+11 D=4.535E+03 t=2.205E-04

[9.51837760928254e-16 7.74490791208072e-16]
[7.74490791208104e-16 8.70685251804943e-16]

Temperature = 640.0 K - Strain = 0.000 %
Z=1.784E+11 D=1.435E+04 t=6.967E-05

[2.63228254006413e-15 2.06514294966142e-15]
[2.06514294966153e-15 2.36572754184721e-15]

Temperature = 660.0 K - Strain = 0.000 %
Z=8.592E+10 D=4.240E+04 t=2.359E-05

[6.87221980097542e-15 5.18184793884052e-15]
[5.18184793884046e-15 6.05862622254524e-15]

The order of the coefficients depends on the order of the species. We defined V as the first species and O as the second species, therefore we are looking at the matrix

$$\begin{pmatrix} L_{VV}(VO) & L_{VO}(VO) \\ L_{OV}(VO) & L_{OO}(VO) \end{pmatrix}$$

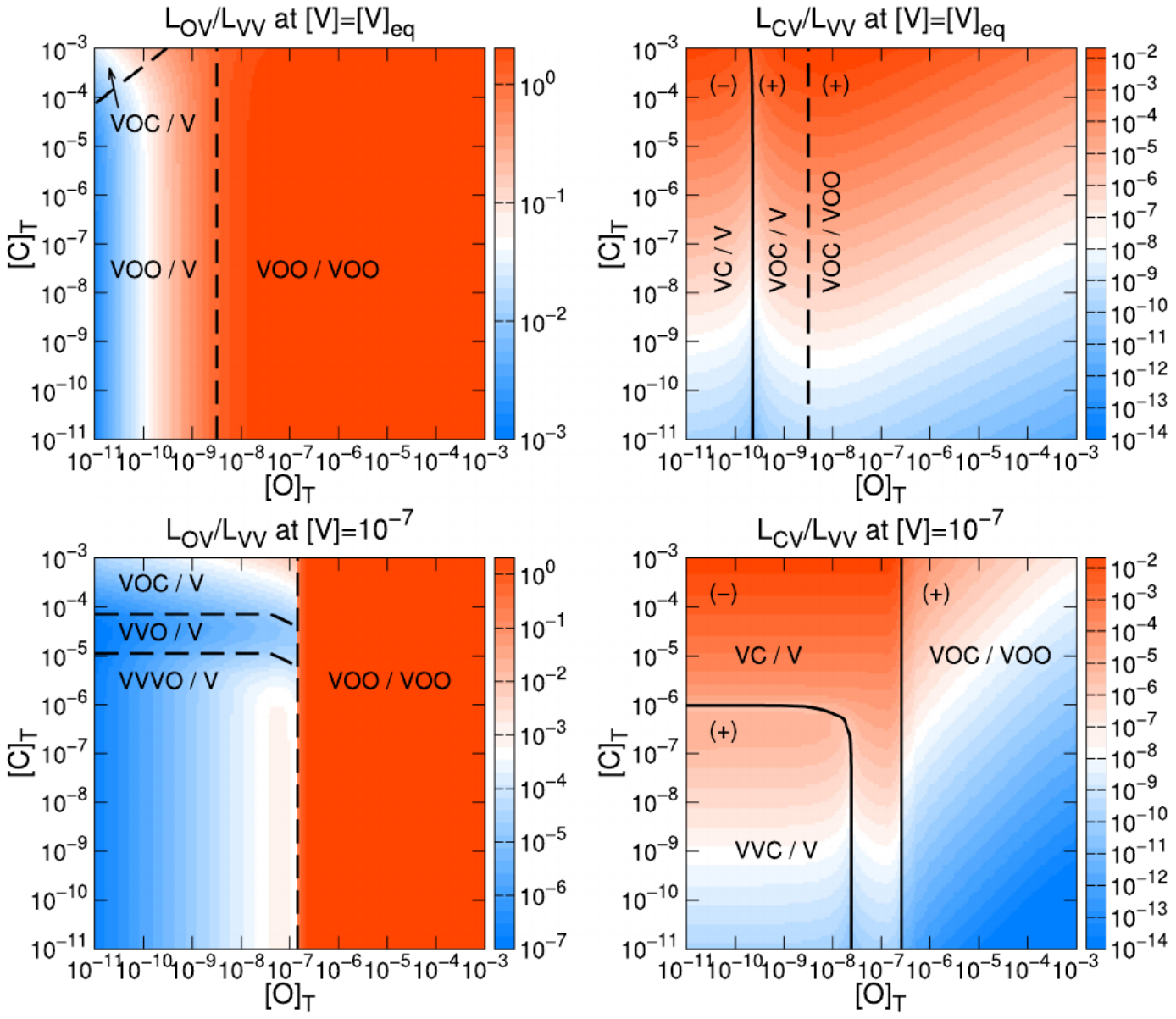
All these results are also written in numout_0.dat and numout_0CF.dat contains correlation factors

We now use the same input and change only the directory to get consistent results for V and O, and use the cluster concentrations to weigh each cluster contribution

Adding in more clusters…

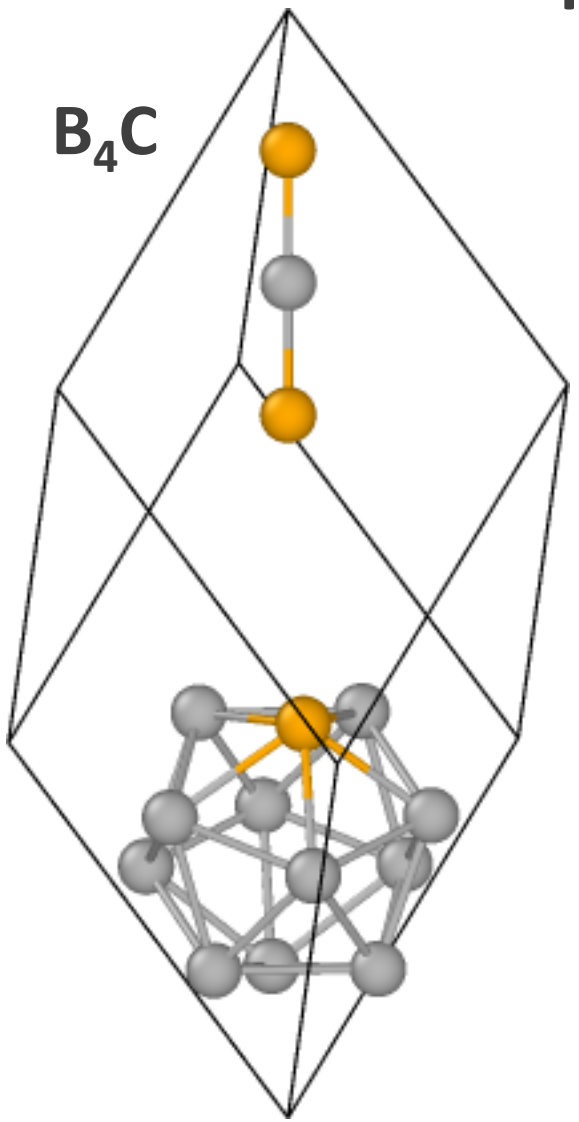
For instance, with 21 clusters in the FeVO system, you can get quantitative results on the effect of nominal concentration and vacancy concentration on the flux coupling properties in this system, and be able to tell which cluster drives the flux coupling…

See « *Mass-transport properties of ternary Fe(C,O) alloys revealed by multicomponent cluster synergies* » *T. Schuler, M. Nastar, and L. Messina, Phys. Rev. Materials 4, 020401(R) –2020*

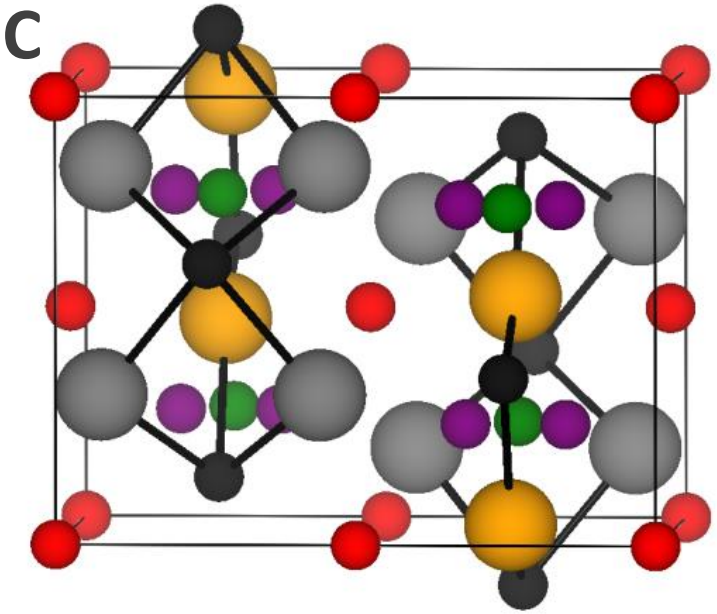


More complicated crystal structures

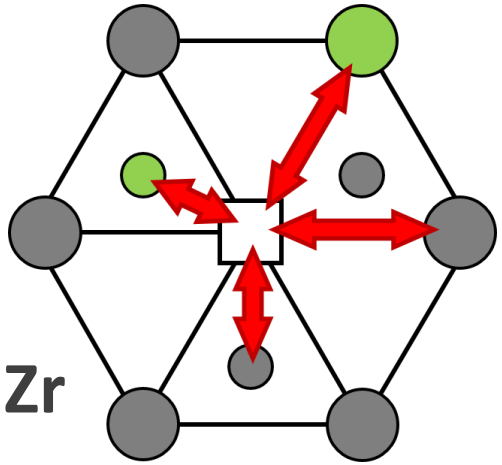
B_4C



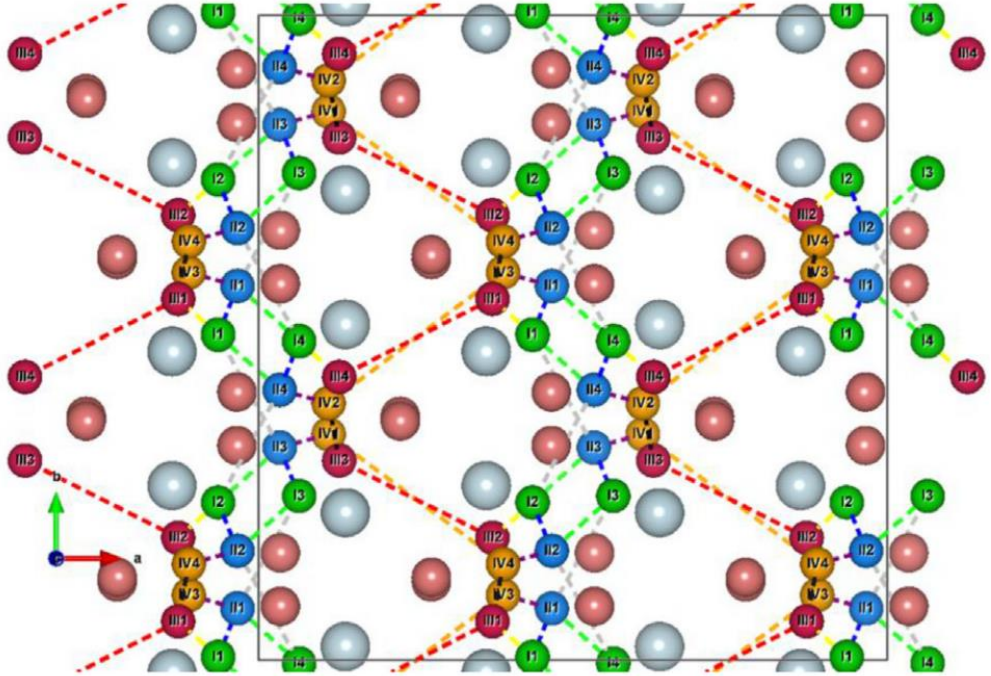
Fe_3C



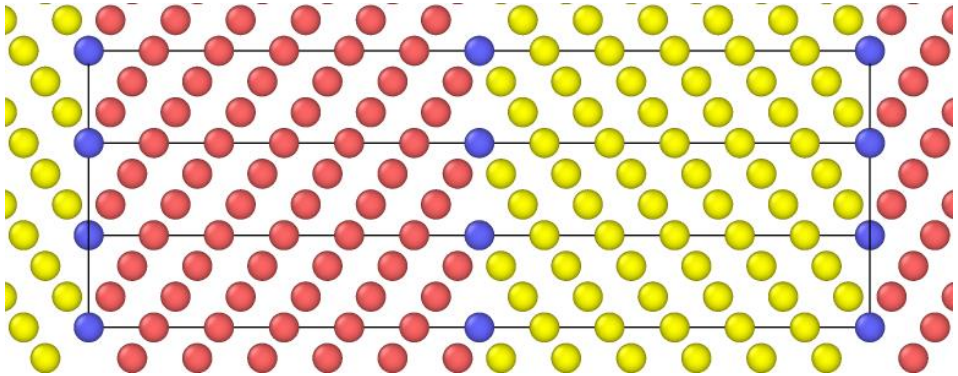
HCP Zr



H^+ in monoclinic zirconia

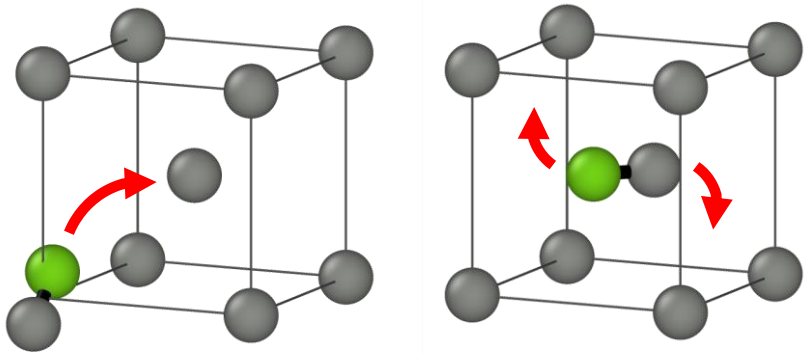


Symmetric tilt grain boundaries

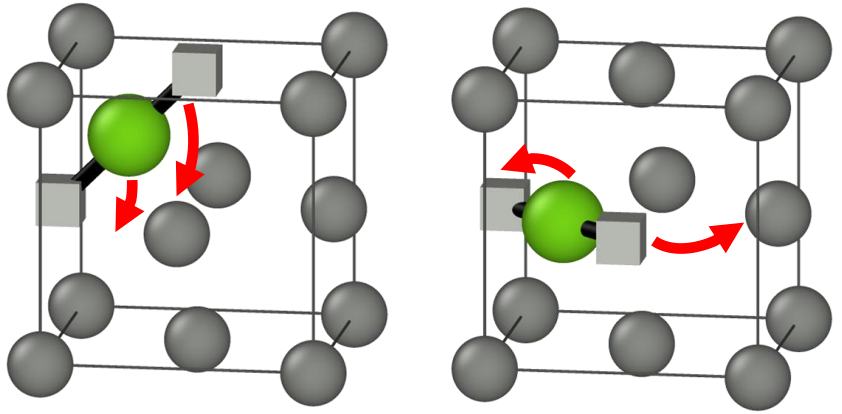


More complex jump mechanisms

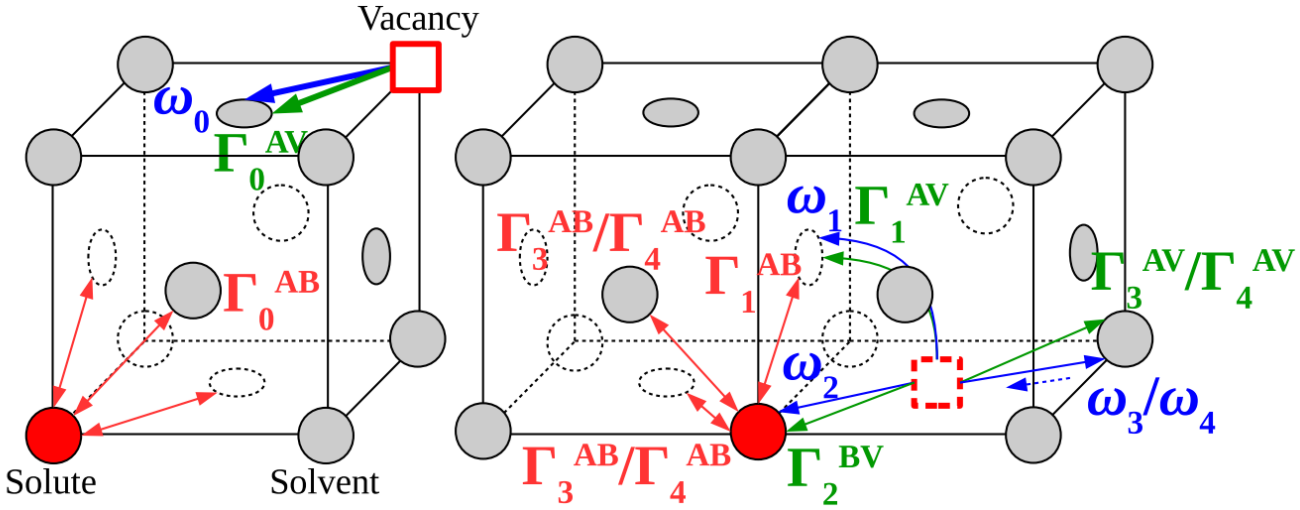
Dumbbell-solute in BCC structures



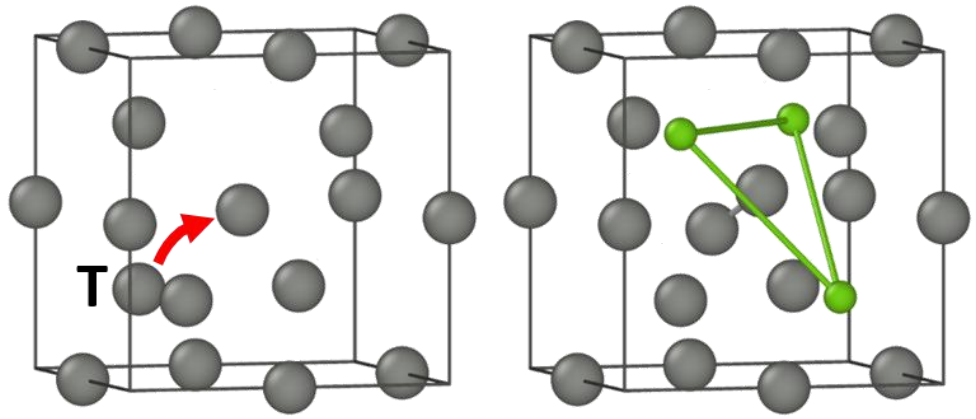
Vacancy-oversized solute in FCC structures



Ballistic mixing (no microscopic reversibility)



Interstitial kick-out mechanisms in diamond structures



Additional information

- The choice of the kinetic radius is important. It is done by looking at the convergence of the off-diagonal cluster transport coefficients. The KIRALOOP keyword automates this study

- A sensitivity study is available to identify the most important jump frequencies, i.e. those which should be computed as accurately as possible (DFT…)

- A batch calculation is available to see how various parameters affect cluster transport coefficients by efficiently sweeping through various values

- Including strain effects is easily done with the STRAIN keyword and by adding elastic dipole tensor to the configurations and jump frequencies defined in the interaction model file.

Diffusion in strained systems: *Vacancy-mediated diffusion of Si in Ni*

Homogeneous stress/strain fields affect tranport coefficients because it modifies :

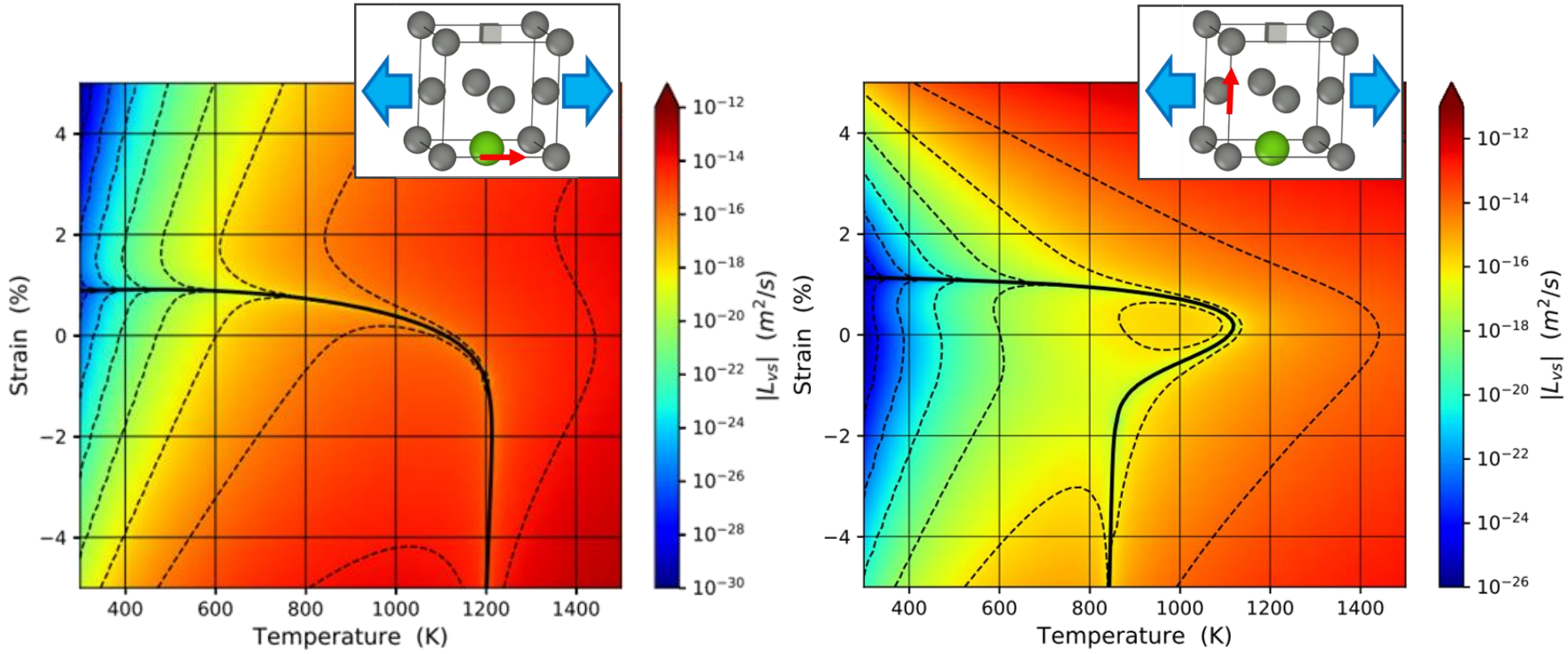
- The energetic landscape :
  Linear elasticity, elastic dipole approximation

$$E_i(\varepsilon) = E_i(0) - \mathbf{P_i} : \mathbf{S}$$

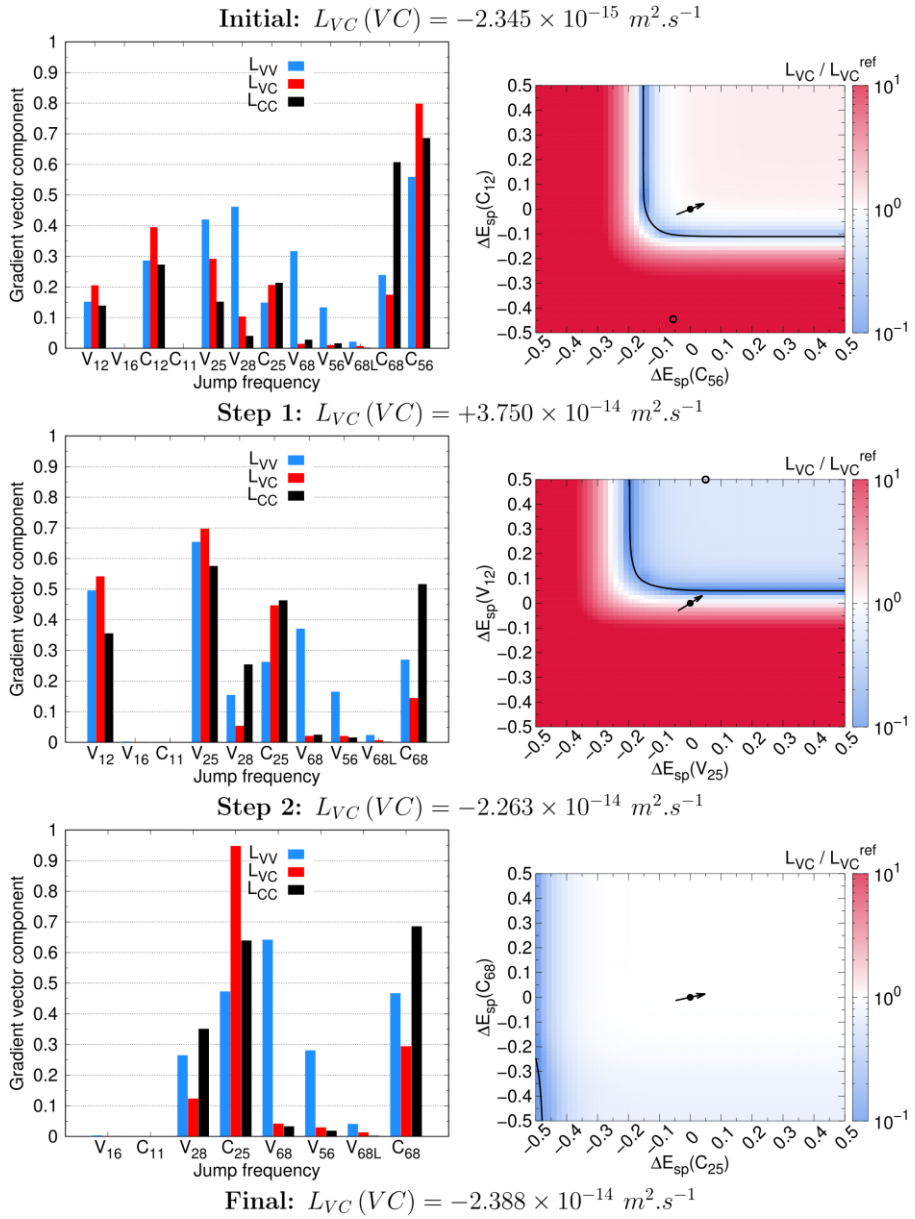
- Kinetic correlations
- Jump vectors orientation/length
  This may create normal diffusion, for instance under shear strain

$$\vec{v}(\varepsilon) = (\mathbf{I} + \mathbf{S})\,\vec{v}$$

- Relative cluster probabilities



Sensitivity analysis



Goal: identification of **key input parameters** (jump frequencies)

We compute the **gradient** of cluster transport coefficients in **jump frequency space** :

$$\nabla \mathbf{L}_d = \left(\frac{\partial \mathbf{L}_d}{\partial \omega_i}\bigg|_{\mathbf{W}_0} \right)$$

We have **analytic expressions** for this gradient => does not cost much computation time

Iterative process because the analysis is only local

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