Diffusion in unstable phases
or
Can we calculate something that does not (and cannot) exist in nature?

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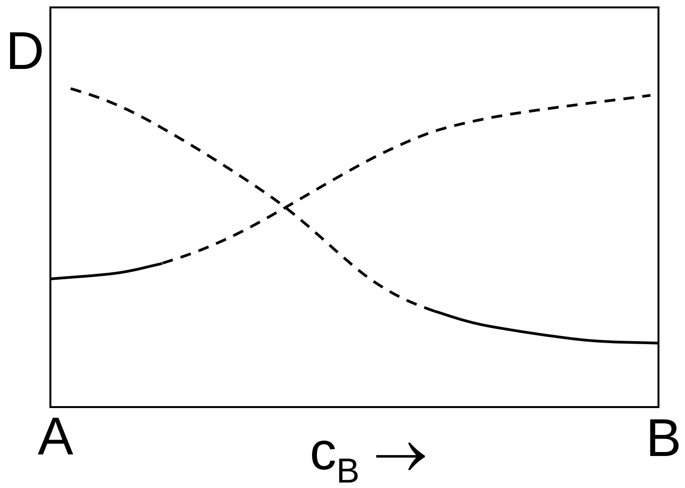
Problem formulation



How to find D_A at $c_B \rightarrow 1$ and D_B at $c_B \rightarrow 0$?

Main difficulty: Element A with the structure of B can be mechanically unstable, and vise versa.

Shear modulus (in GPa) of selected metals

	FCC	BCC
Cu	23.7	-6.8
Ni	43.3	-5.3
Al	26.1	-24.0

Computed with EAM potentials

$$C' = \frac{c_{11} - c_{12}}{2}$$

C’ < 0 $\rightarrow$ structure unstable against homogeneous shear deformation

Problem formulation (cont'd)

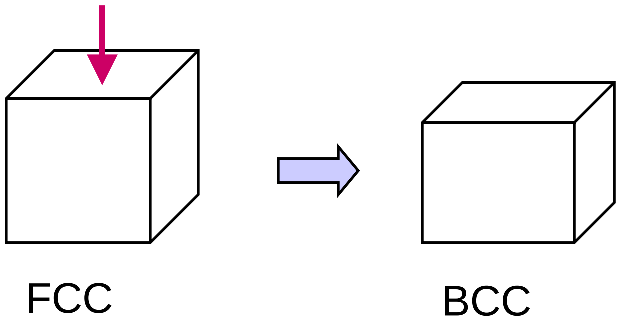
Diffusion calculation in stable phases:

- Vacancy formation energy E_v by molecular statics
- Vacancy formation entropy S_v in the harmonic approximation
- Saddle point search by the nudged elastic band (NEB) method - E_m
- Vacancy jump rate in the harmonic TST (Vineyard)

What does not (or may not) work in unstable phases:

- Static relaxation may trigger a transformation to the stable structure
- Some of the normal frequencies are imaginary $\rightarrow$ harmonic calculations do not work

For example:



(Bain path)

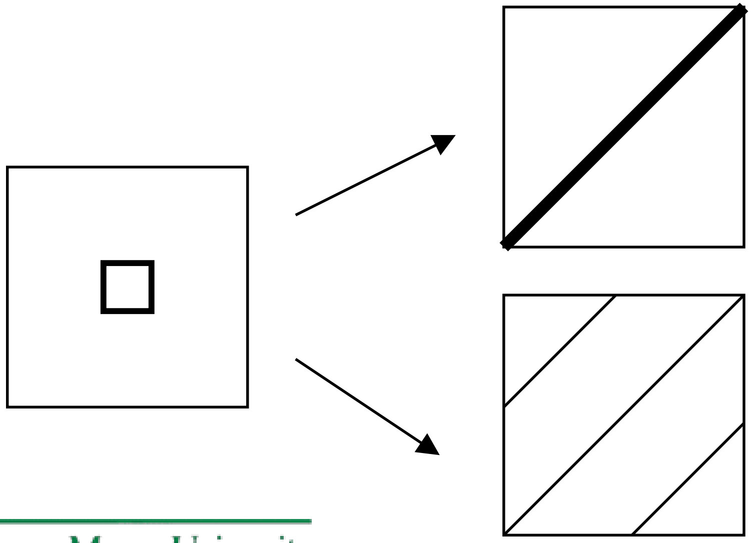
Approach 1: Constraint by periodic boundaries

Idea: Use cubic simulation cell with periodic boundary conditions. The boundary conditions will prevent homogeneous shear deformation.

Tried for Cu, Ni and Al.

Result: Static relaxation of a vacancy leads to an infinite "crowdion" formation or trigger stacking-fault generation

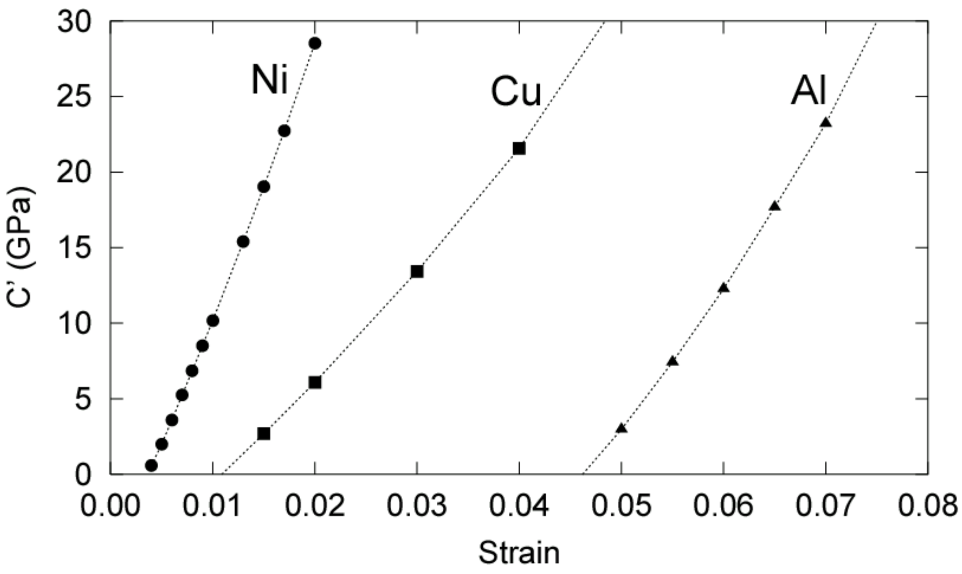
Conclusion: It does not work.



Approach 2: Extrapolation of high-pressure calculations

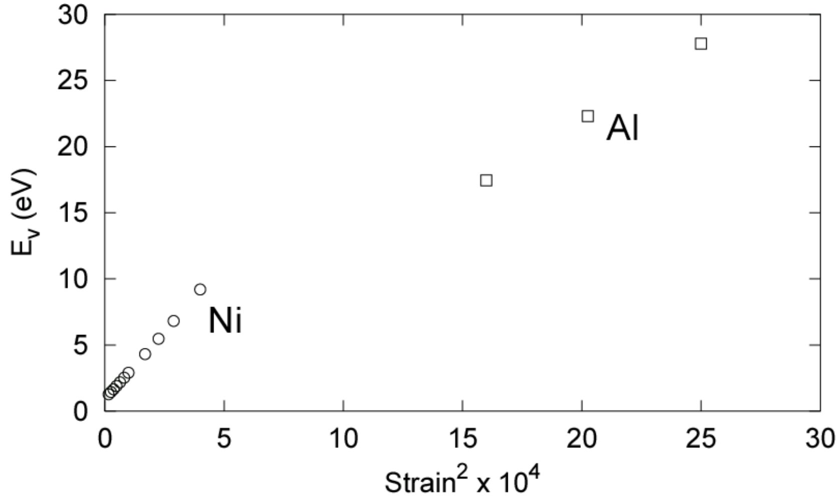
Idea: Reverse the sign of C' by applying a hydrostatic strain ε. Calculate D as a function of ε. Extrapolate to $\varepsilon \rightarrow 0$.

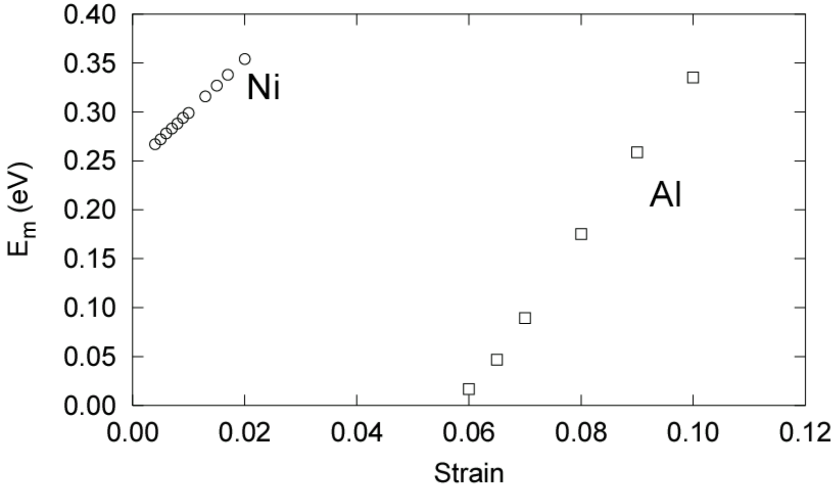
Tried for Cu, Ni and Al.



$\Rightarrow$ Strain stabilizes BCC

Vacancy formation and migration

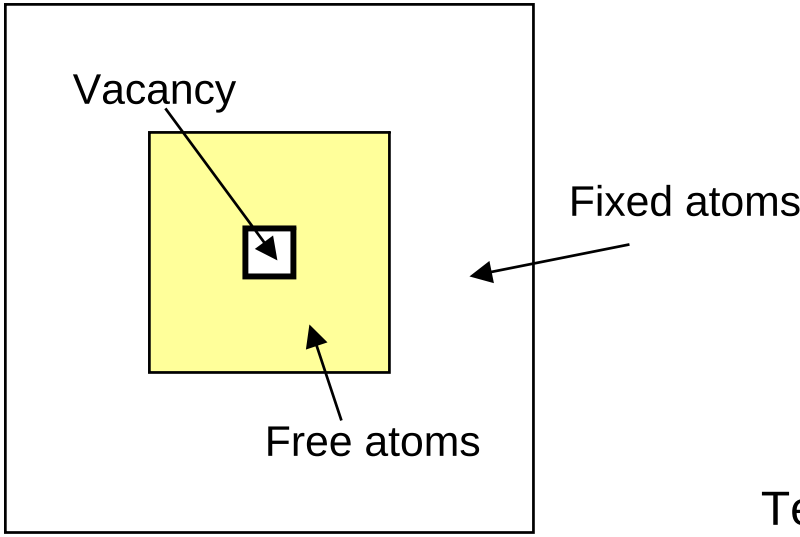




- Vacancy falls apart during relaxation **before** C’ turns to zero. Low-barrier effect?
- E_m can turns to zero when or before C’ turns to zero.
- Calculations are unstable

Conclusion: It does not work.

Approach 3: Constrained relaxation



- Number of free atoms must be small (54 in BCC; 32 in FCC)
- Fixed atoms should stabilize BCC
- Both E_v and E_m will be overestimated

Test: calculation for FCC structures

	Cu			Ni			Al		
	Exper	Exact	Approx	Exper	Exact	Approx	Exper	Exact	Approx
E_v (eV)	1.28	1.272	1.282	1.60	1.57	1.58	0.68	0.71	0.72
E_m (eV)	0.71	0.70	0.74	1.30	1.19	1.27	0.65	0.65	0.69

Works well for FCC

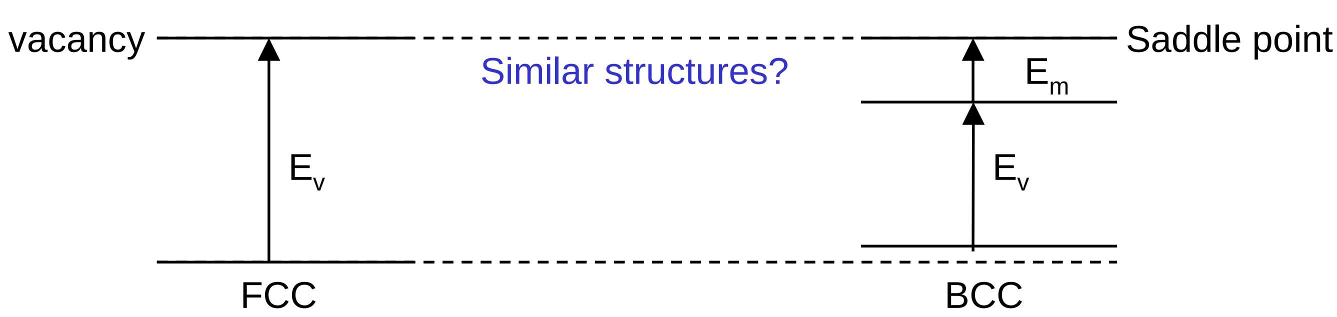
Does it work for BCC?

	Cu	Ni	Al
E_v (eV)	0.96	1.12	0.30
E_m (eV)	0.32	0.47	0.16
Q_{BCC} (eV)	1.28	1.59	0.46
Q_{FCC} (eV)	2.02	2.85	1.41
Q_{BCC} / Q_{FCC}	0.74	0.56	0.33

Conclusion: It has a potential. Further testing is needed (other metals, more accurate potentials,…).

As an aside:

For Cu and Ni, $Q_{BCC} \approx (E_v)_{FCC}$. Coincidence or…



Diffusion in ordered compounds

- We need to know diffusion mechanisms in ordered phases:
  - Predictive calculations
  - CALPHAD-type diffusion calculations
  - Interpretation of experiment
- History:
  - Diffusion mechanisms are complex
  - Experimental studies are difficult
  - Several mechanisms were proposed in 1970-80s (6-jump cycles, divacancy, etc.) but verification by simulations was impossible
  - Understanding is still poor
- New capabilities of atomistic simulations (accurate potentials, advanced saddle-point search, etc.). There is some progress in understanding: direct observation of 6-jump cycles, discovery of collective diffusive jumps, etc.
- New compounds become technologically important (e.g. silicides, etc.).
- **There has never been a better time to revisit the problem by theory and experiment**.

Creep in ordered compounds

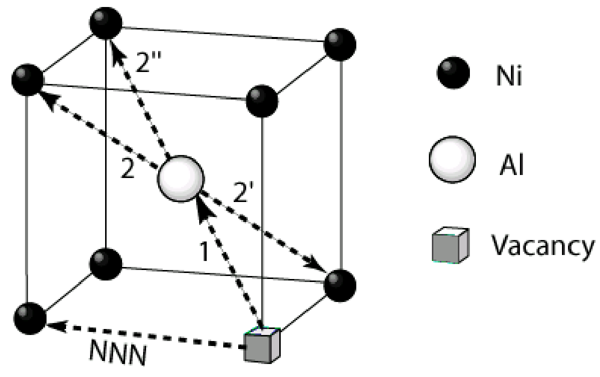
- Key question: What kind of diffusion coefficient (D_c) controls diffusion creep? [Generally, $D_c \neq D_{inter}$]

  Example: for a strongly ordered compound: $\frac{1}{D_c} = \frac{c_A}{D_A} + \frac{c_B}{D_B}$

  (similar to ambipolar diffusion in ionics)

- Creep in disordered alloys (de-alloying, slow species control, etc.)
- What happens in partially disordered compounds?

Diffusion in B2-NiAl



- Ni and Al isolated from each other
- NNN jumps on Ni sublattice
- NN vacancy jumps create mechanically unstable configurations
- Collective two-atom jumps
- Cyclic mechanisms

[110] cycle

[100] straight cycle

[100] bent cycle