Kinetic lattice Monte Carlo simulations of diffusion processes in Si and SiGe alloys

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Multiscale Modeling Hierarchy

Configuration energies and transition rates.

Induced strains, binding/migration energies.

Ab-initio

MD

KLMC

Continuum

Calibration/testing of empirical potentials

Configuration energies and transition rates

Behavior during regrowth, atomistic vs. global stress

KLMC Flow Chart

Start

Initialize rates k_{ij}

Generate r_1, select transition

Perform transition

Generate r_2, advance time by $t = -\ln(r_2)/k_{tot}$

Conditions Satisfied?

No → Update rates k_{ij} → Generate r_1, select transition

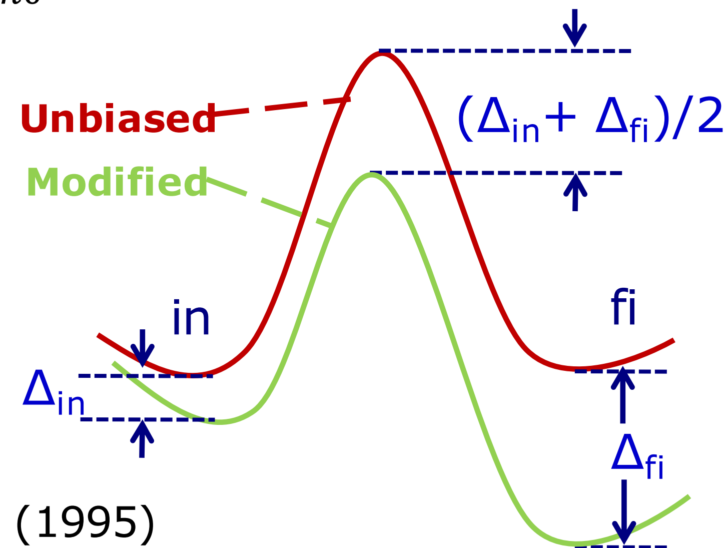
Yes → Terminate

Building the rate catalogue

- Task: find migration barriers for all allowed transitions at each step
- Surrounding conditions modify migration barriers
  - Presence of other defects (binding energy)
  - Presence of strain (additional strain energy)
- Solution:
  - Store an unbiased energy barrier E_{m0}
  - Calculate change of barriers due to change of formation energies of initial and final states.
  - Assume transition state scales linearly with initial and final state

$$E_m = E_{m0} + \frac{1}{2}(\Delta E_{\mathrm{fi}} - \Delta E_{\mathrm{in}})$$

Dunham *et al.*, *J. Appl. Phys.* **78**, 2362 (1995)



Outline

- *Interstitial-mediated self-diffusion in Si*
- Vacancy mediated inter-diffusion in SiGe

Silicon Self Diffusion

- Mediated by point defects (V, I)

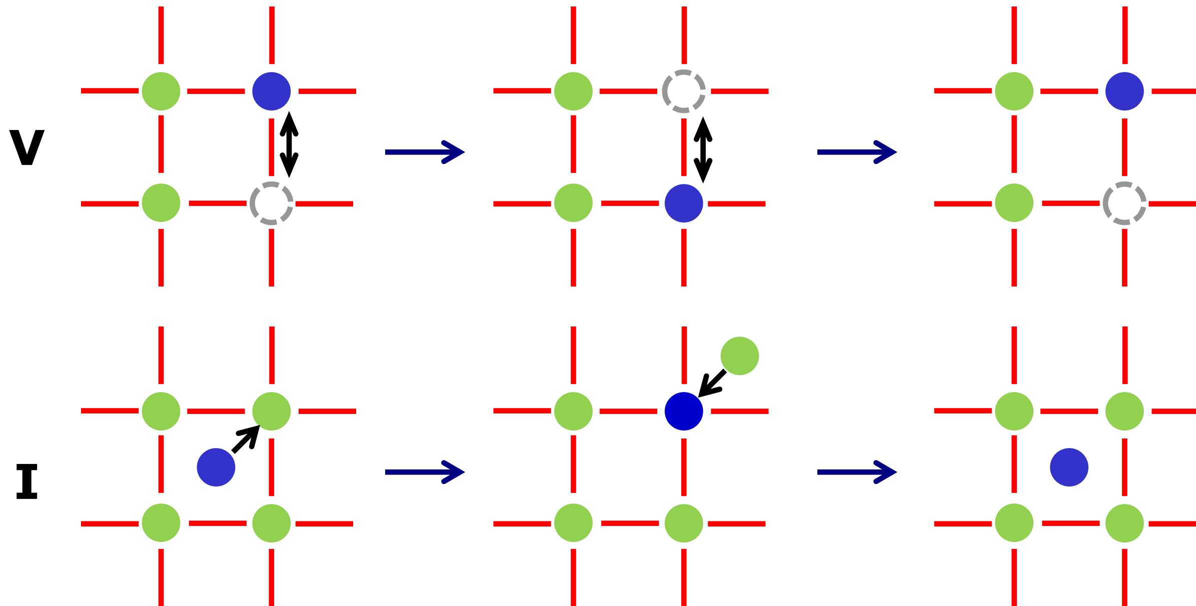
- One of the few directly measurable point defect properties.
- Quantified by diffusion of an isotropic tracer (T)

$$D_T = f_I D_I \frac{C_I^*}{C_s} + f_V D_V \frac{C_V^*}{C_s}$$

- f_I, f_V: correlation factors
- Point defects perform uncorrelated random walks.
- Tracer atoms perform correlated random walks.

Correlation of Self Diffusion

- **Tracer atoms perform correlated random walk**
  - The previous direction affects the direction of the next step



A tracer, once exchanges with a V, has a higher probability of re-exchange with the V.

A tracer, once kicks an atom out, has a higher probability of being kicked back.

- **Correlation of interstitial diffusion (f_I) via indirect process depends on mechanism/hopping network**

Methodology

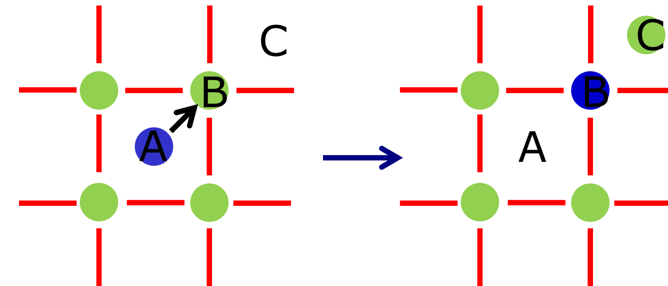
➢ Interstitial self diffusion on diamond lattice:

- KLMC: Simulates diffusion of various hopping mechanisms on different lattice networks, find f_I by:

$$f_I = \frac{\langle \Delta r^2 / N \rangle^{\text{tracer}}}{\langle \Delta r^2 / N \rangle^{\text{interstitial}}}$$

  - N: number of steps
  - Δr^2: square displacement

Compaan *et al.*, Trans. Faraday Soc. 1956

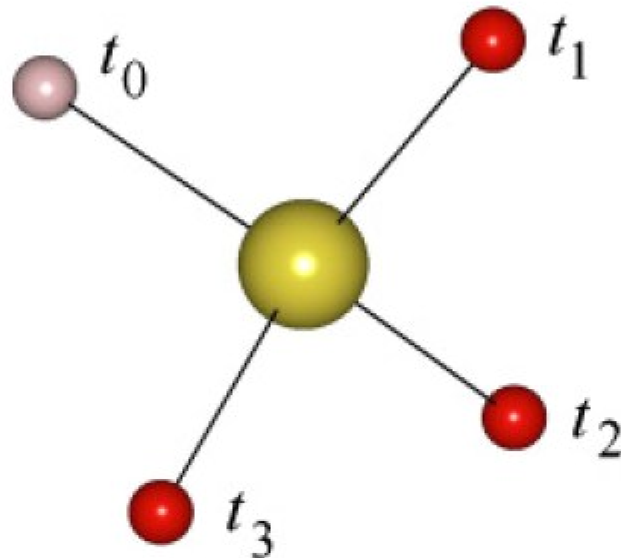


➢ Interstitial self diffusion in silicon

- DFT: Find dominant hopping mechanisms
- KLMC: Simulates diffusion in Si and find f_I.

Kick-out Mechanism

Tetrahedral network:

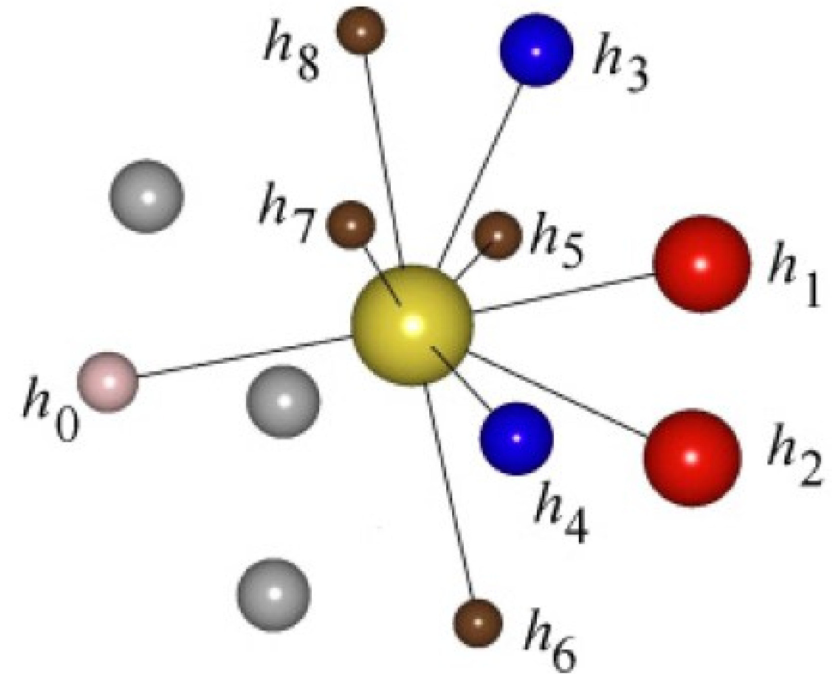


$$I_{tet} \leftrightarrow I_{tet}$$

$$f_I = 0.7276 \pm 0.0001$$

c.f. 0.7273 [Compaan et. al.]

Hexagonal network:



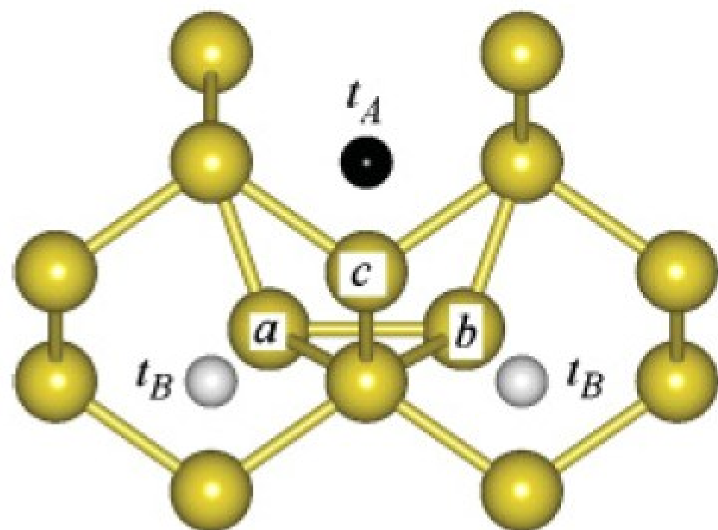
$$I_{hex} \leftrightarrow I_{hex}$$

$$f_I = 0.4690 \pm 0.0001$$

Stable-split Mechanism

- **Assuming the split configuration is stable**

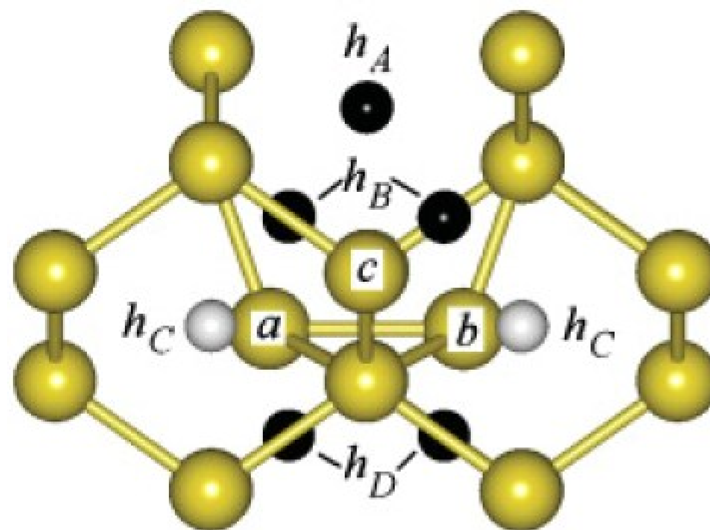
Tetrahedral network:



$$I_{tet} \leftrightarrow I_{sp} \leftrightarrow I_{tet}$$

$$f = 0.7275 \pm 0.0001$$

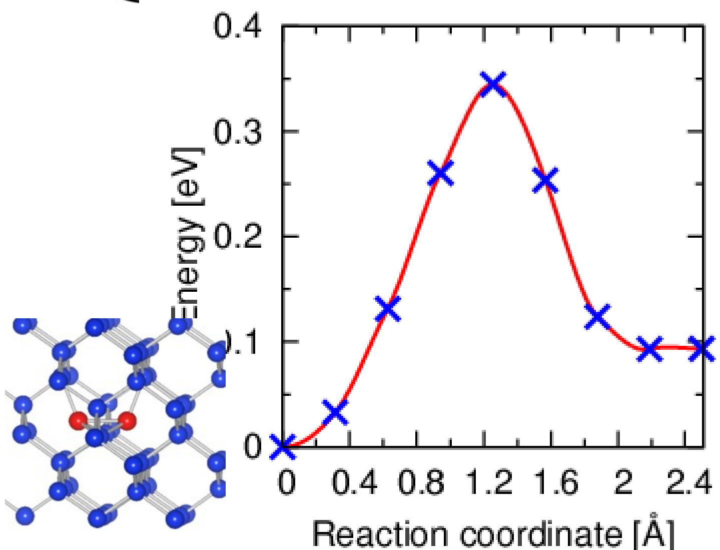
Hexagonal network:

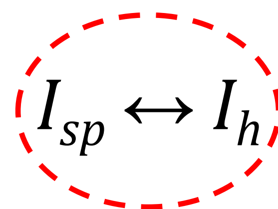


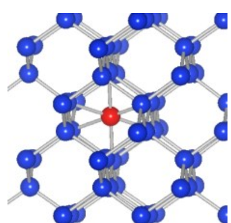
$$I_{hex} \leftrightarrow I_{sp} \leftrightarrow I_{hex}$$

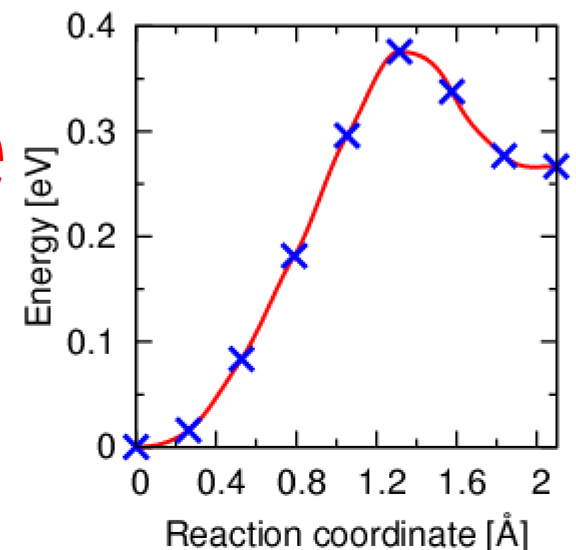
$$f = 0.6207 \pm 0.0001$$

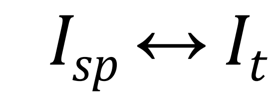
DFT: Migration Events

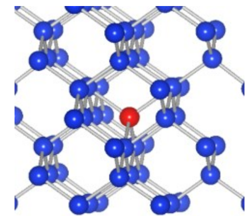


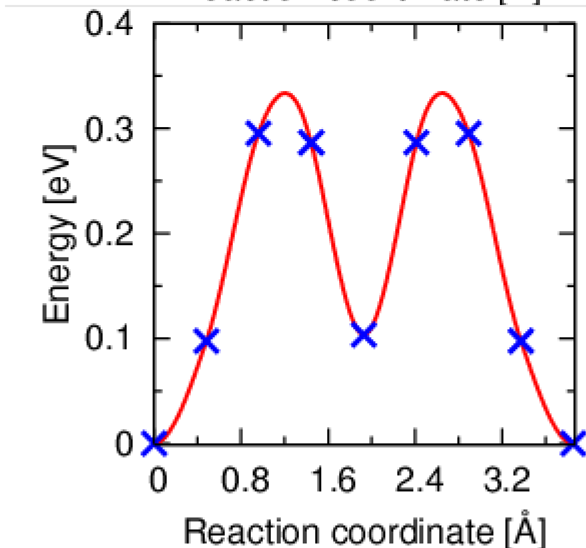


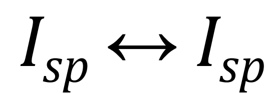


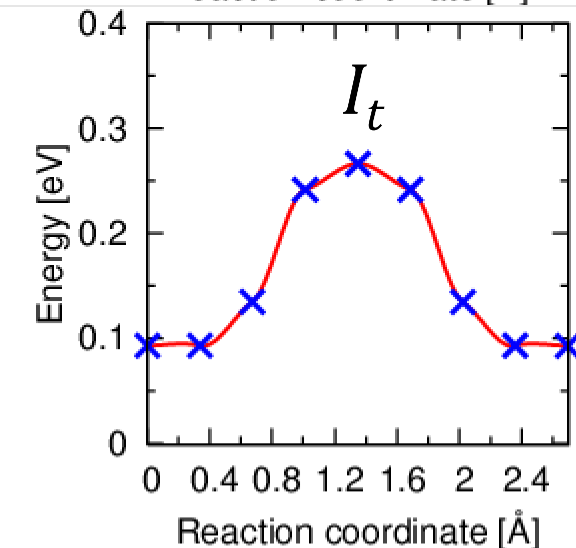


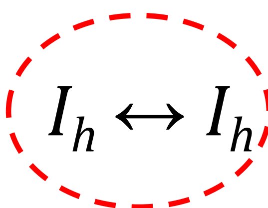












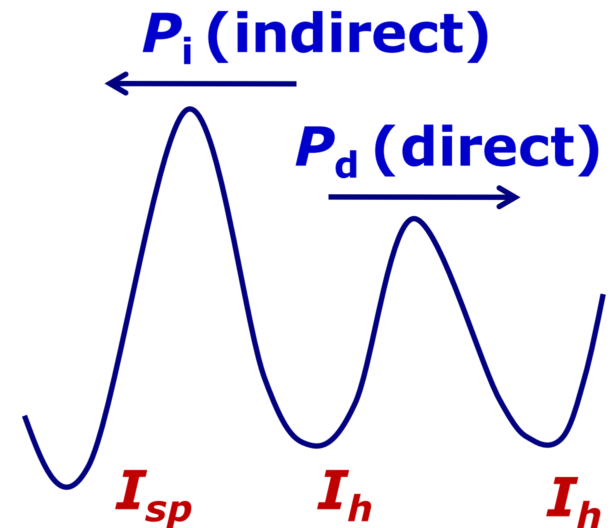
KLMC Simulations

Dominant mechanisms:

- The direct (uncorrelated) mechanism: $I_h \leftrightarrow I_h$ via I_t .
  Forward barrier:0.17 eV, reverse barrier: 0.17 eV.
- The indirect mechanism: $I_{sp} \leftrightarrow I_h$.
  Forward barrier:0.34 eV, reverse barrier: 0.25 eV.

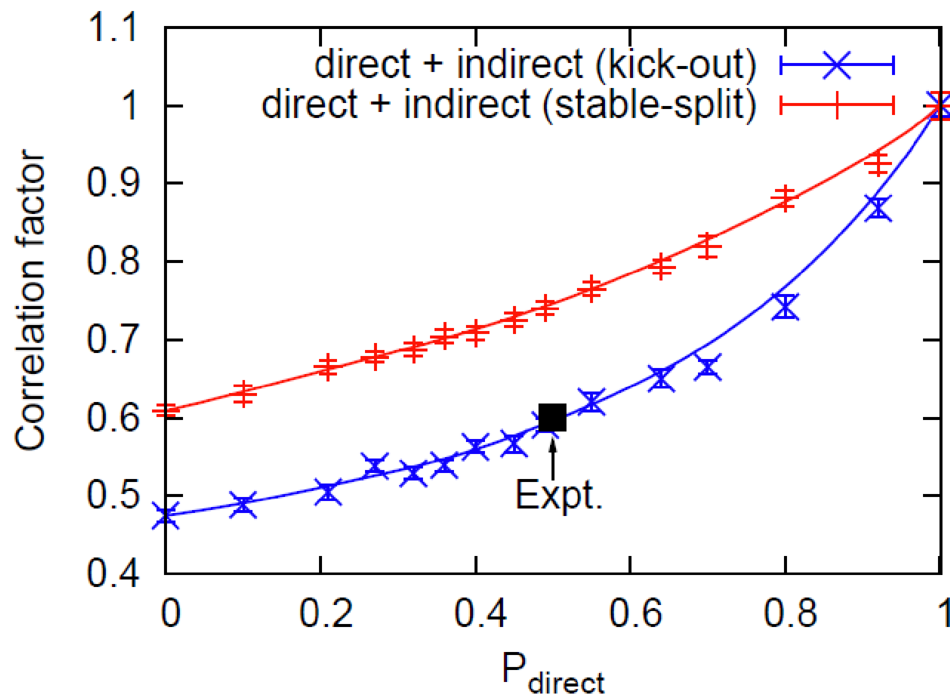
Probability to follow the direct path (P_d) depends on the barriers and temperature.

$$P_\mathrm{d} = \frac{\Omega_\mathrm{d}\exp(-\frac{E_\mathrm{d}^m}{kT})}{\Omega_\mathrm{d}\exp\left(-\frac{E_\mathrm{d}^m}{kT}\right)+\Omega_\mathrm{i}\exp(-\frac{E_\mathrm{i}^m}{kT})}$$



Effective correlation factor is temperature dependent

Correlation of Si Self Diffusion



Effective correlation factor as a function of the probability of the direct mechanism.

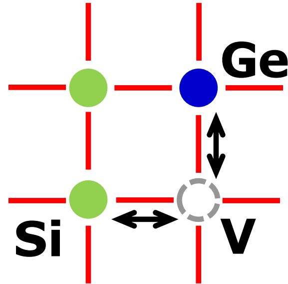
- *f* at 1000-1100°C calculated to be 0.6-0.8
- Experimental value is 0.6 [Voronkov et. al. 2005]
- Possible sources of inaccuracy:
  - Uncertainties of DFT predicted barriers
  - Neglect of entropy difference

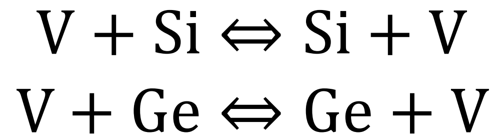
Outline

- Interstitial-mediated self-diffusion in Si
- *Vacancy mediated inter-diffusion in SiGe*

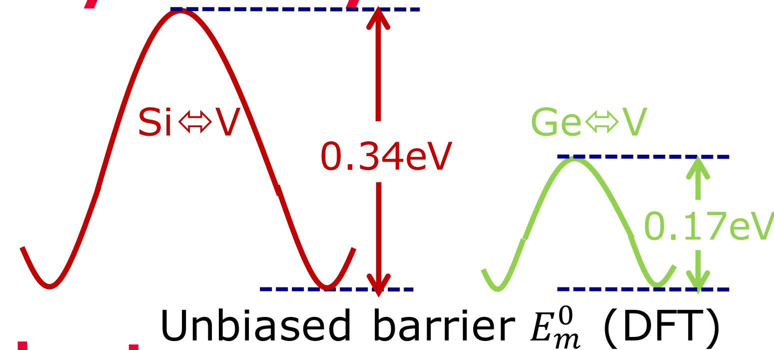
Simulational perspective

SiGe Inter-diffusion dominated by vacancy mechanism





$$V + Si \Leftrightarrow Si + V$$
$$V + Ge \Leftrightarrow Ge + V$$

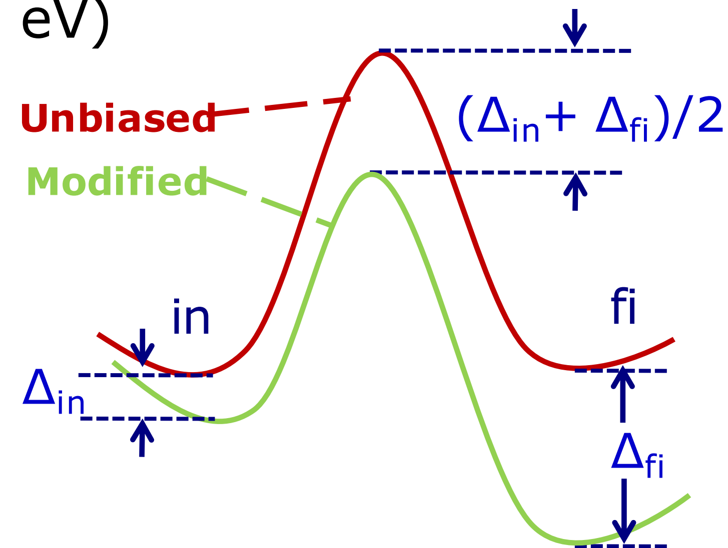


Change of formation energies due to

- Ge-V binding energy (DFT: 0.31 eV)
- Strain energy (determined by induced strains of defects)

Energy barrier scales as:

$$E_m = E_m^0 + \frac{1}{2}(\Delta E_f^{\mathrm{fi}} - \Delta E_f^{\mathrm{in}})$$



Determining Strain Energy

Hooke's Law $\quad \vec{\sigma} = C\vec{\varepsilon}$ (stress: $\vec{\sigma}$; strain: $\vec{\varepsilon}$)

$$\begin{pmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{pmatrix} = \begin{pmatrix}C_{11} & C_{12} & C_{13}\\ C_{12} & C_{22} & C_{23}\\ C_{13} & C_{23} & C_{33}\end{pmatrix}\begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\end{pmatrix}$$

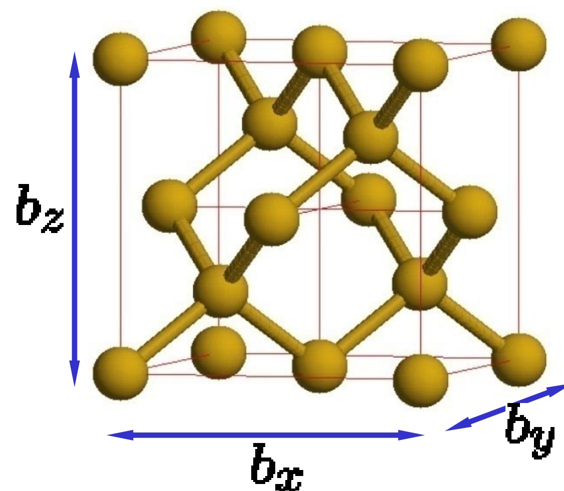
Strain energy $\quad E = \frac{1}{2}\vec{\sigma}\cdot\vec{\varepsilon}$

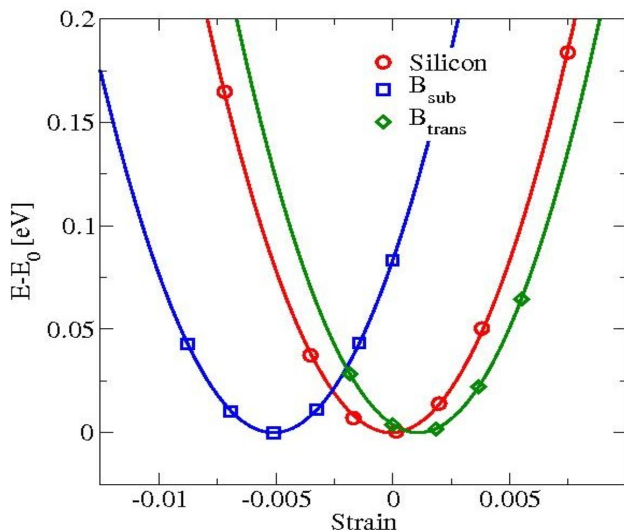
Strain dependence

$$E(\vec{\varepsilon}) = E_0 + \frac{1}{2}(\vec{\varepsilon} - x\Delta\vec{\varepsilon})^T C(\vec{\varepsilon} - x\Delta\vec{\varepsilon})$$

$$\Delta\varepsilon_i = \frac{1}{x}\frac{a_i - a_0}{a_0}$$

x : defect concentration

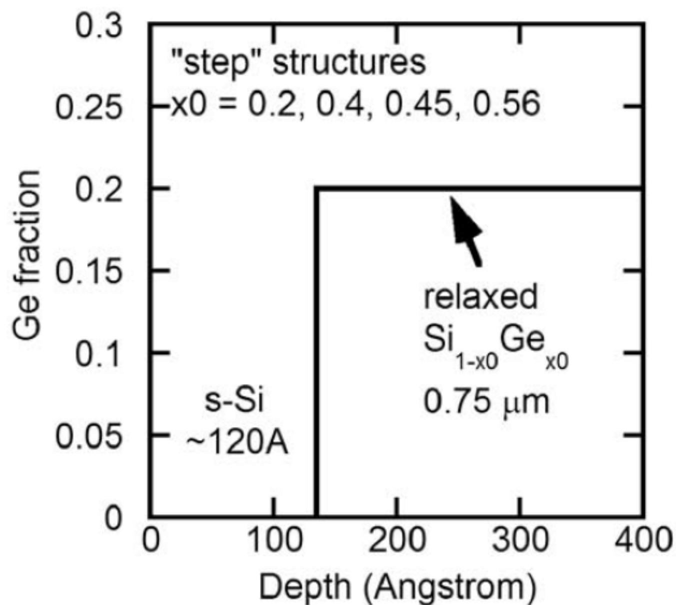




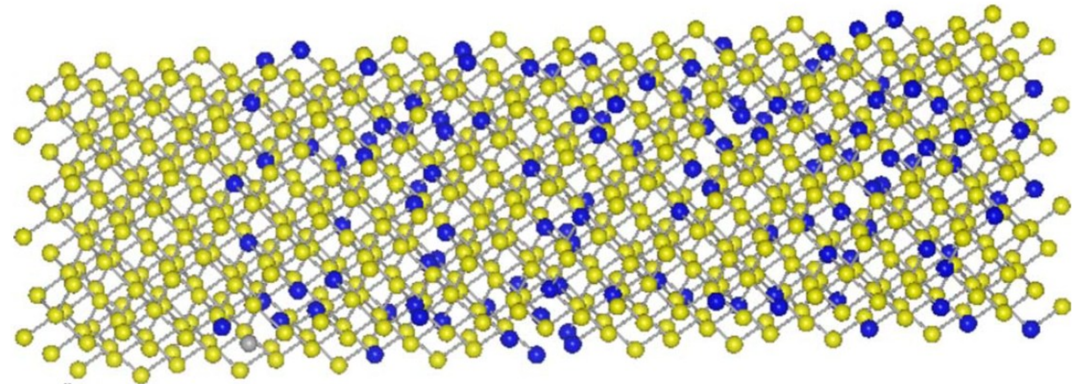
$\Rightarrow$ Induced strain ($\Delta\varepsilon$) and elastic stiffness tensor (**C**) can be extracted from DFT calculations for different strain conditions

Simulation Set-up

- Simulation set-ups are chosen to mimic experimental conditions (Si layers on relaxed $Si_{1-x}Ge_x$ layers, 920 °C).
- Simulation results scaled to the condition of equilibrium vacancy concentration



Experimental profile [Xia et al]



Simulation domain [Blue: Ge, Yellow: Si]

Extracting interdiffusivity

Ge affects inter-diffusivity via

- Stress effect: strain energy compensation of Ge and V
- Alloy effect: Ge-V binding lowers V formation energy.

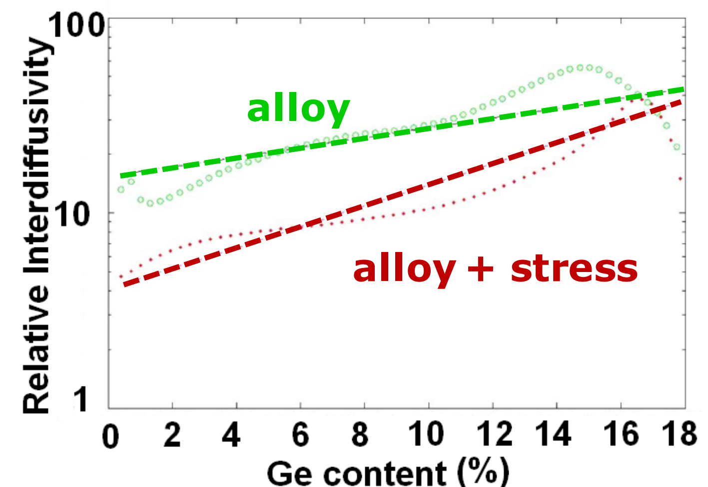
Interdiffusivity increases exponentially with Ge content

$$D(x_{\mathrm{Ge}}) \sim \exp(B x_{\mathrm{Ge}})$$

Extracting *B* from KLMC

B_{alloy}	5.8
B_{stress}	7.6
B_{total}	13.4
B_{total}(Expt*)	8.1

* [Xia et al]



Sources of error:

- Inaccurate parameters for diffusion and formation energies
- Small lateral dimension that results in large fluctuations
- Insufficient sampling of Monte Carlo simulations

Conclusion

- **KLMC combined with DFT calculations for**
  - Self diffusion in Si
  - Interdiffusion in SiGe

- **Future Research**
  - More accurate ways to calculate migration barriers based on local environment
  - Fully implement strain effect

Acknowledgements

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- Scott T. Dunham (Advisor)
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