

Modeling Point Defect Diffusion in Compound Semiconductor Alloys

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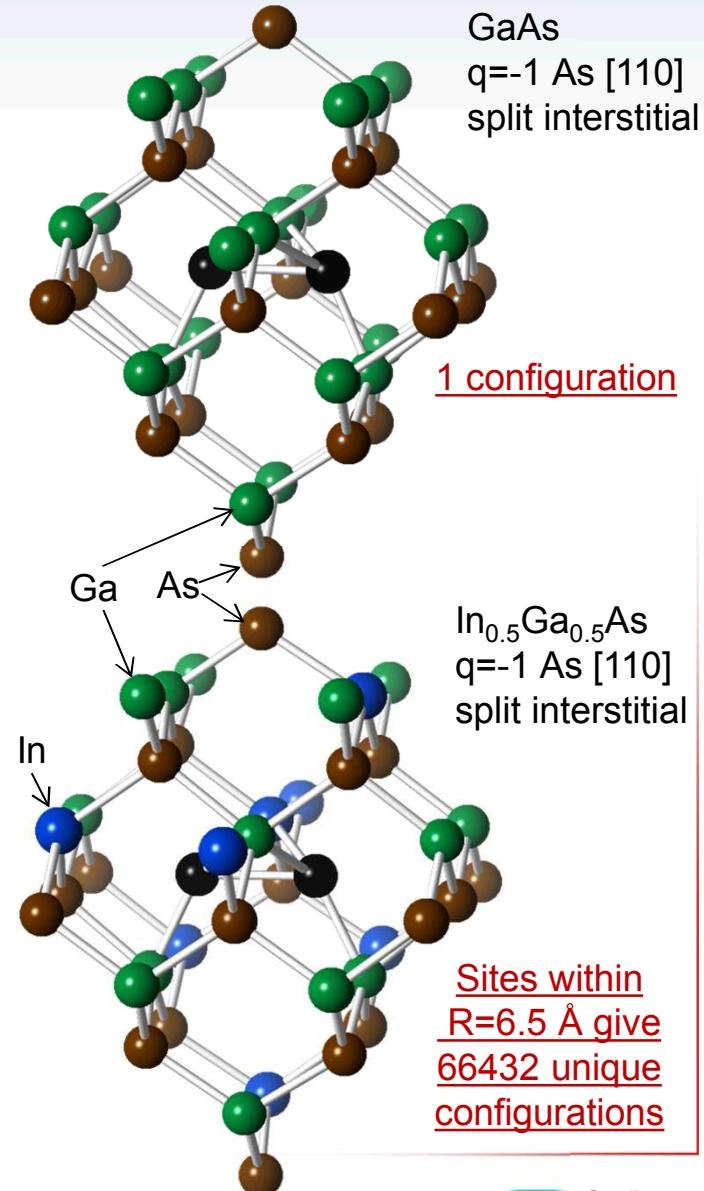
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Objective and Approach

Develop a new capability to simulate diffusion of point-defects in semiconductor alloys (InGaAs) with density-functional-theory accuracy

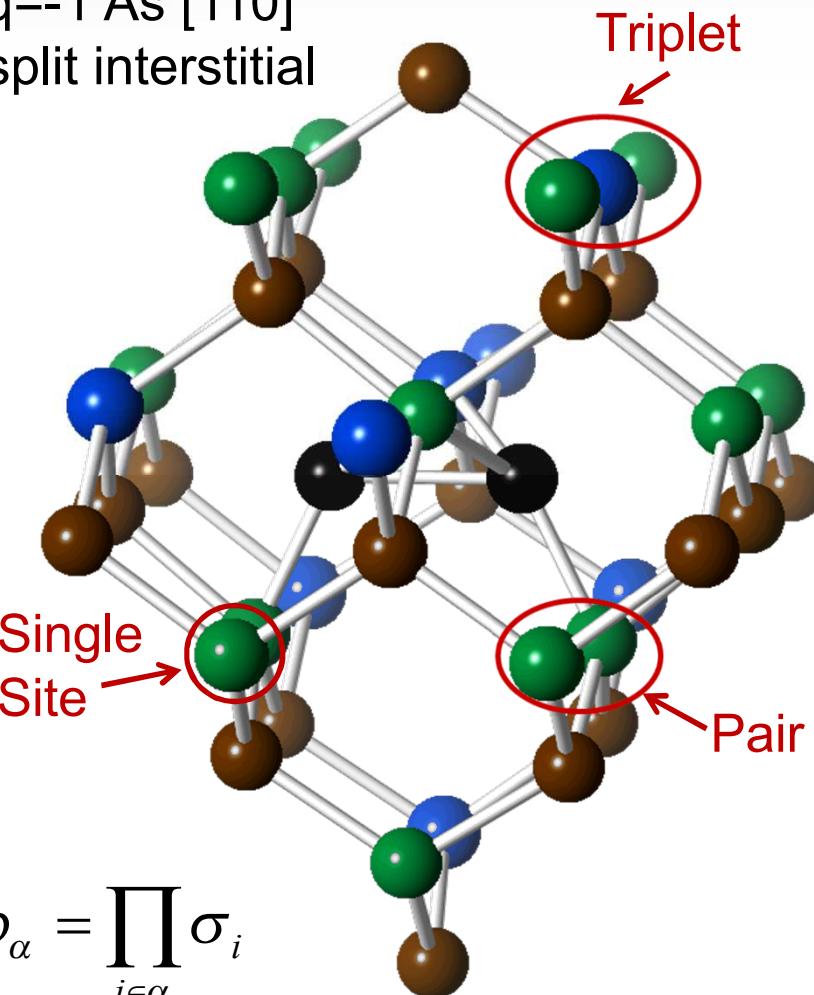
Why is this challenging? – Configurational complexity fundamentally alters defect energetics & behavior – Computational burden rises exponentially

- Kinetic Monte Carlo (KMC) simulations of point-defect diffusion in an alloy require rapid evaluation of defect energies at all relevant locations in the alloy
- Density-functional-theory (DFT) defect energies are sufficiently accurate to produce physically realistic simulations, but the computation time needed for DFT is orders of magnitude too large for direct use
- Cluster Expansions (CE) allow rapid evaluation of defect energies in an arbitrary local alloy environment
- We obtain the CE coefficients by fitting to a training set of defect energies calculated using DFT



Cluster Expansions For Defects In Alloys

$q=-1$ As [110]
split interstitial



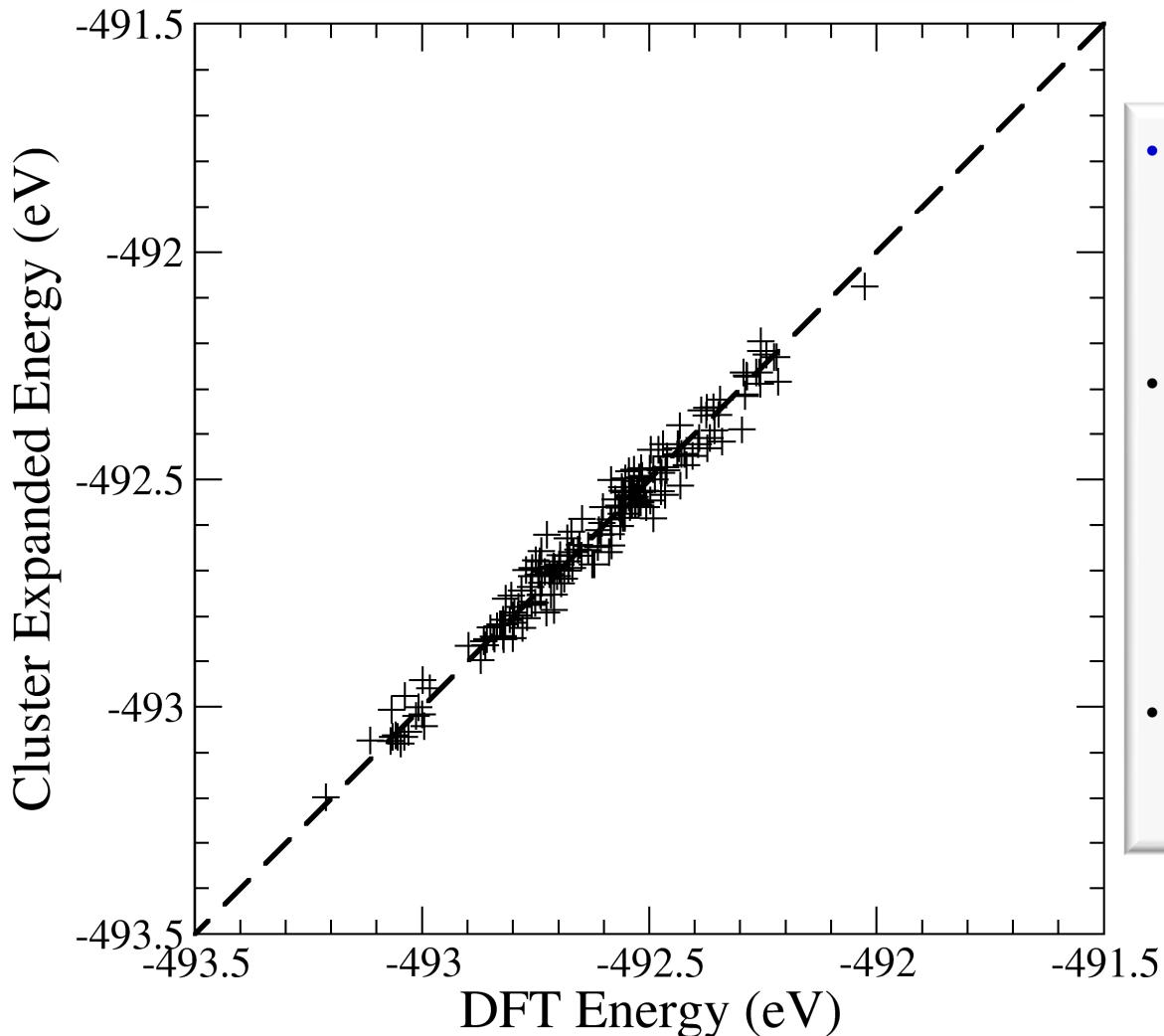
$$\varphi_\alpha = \prod_{i \in \alpha} \sigma_i$$

$$E(\vec{\sigma}) = E_0 + \sum_{\alpha} V_{\alpha} \cdot \varphi(\vec{\sigma})$$

- Performed cluster-expansion for the formation energy of the $q=-1$ As [110] split interstitial
- Used a modified version of the *CHASM* code developed in Anton Van der Ven's group
- Calculated a 258 configuration training set using Socorro DFT software
- The occupations of 18 Group-III sites near the defect are represented by Ising-like variables
- Products of these Ising-like variables give terms in the cluster expansion
- Current CE includes 6 single-site terms, 7 pair terms, & 26 triplet terms
- The 18 site CE models 66432 unique local environments for the defect
- Hence, direct simulations by DFT would be nearly impossible

Accuracy of the $q=-1$ As Interstitial Cluster Expansion

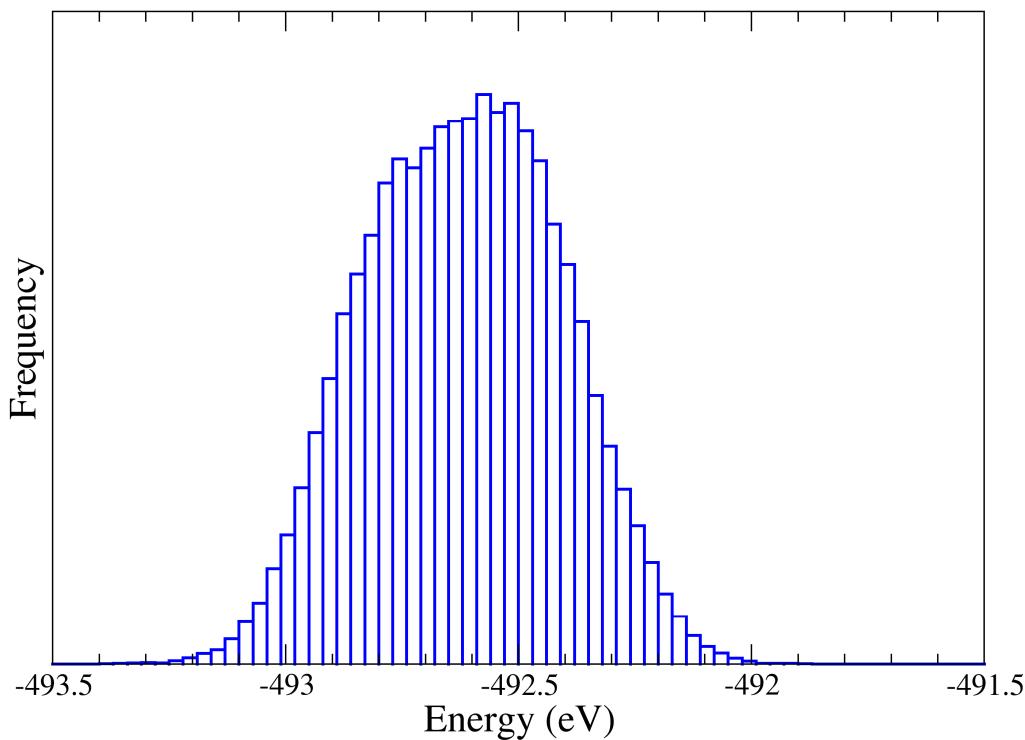
Comparison of CE and DFT for Fitting Set



- Identified key procedures to optimize the sites and interactions included in the CE and improve the accuracy of the CE
- The cluster expansion for the $q=-1$ As [110] split interstitial captures over 90% of the energy variance:
 - Training set rms error = 0.036 eV
 - Training set max error = 0.105 eV
 - Cross-validation error = 0.047 eV
- The errors introduced by the CE can be less than typical DFT errors for defects in semiconductors

Defect Properties Strongly Dependent on Local Alloy Environment

Histogram of Defect Energies
Obtained from the Cluster Expansion

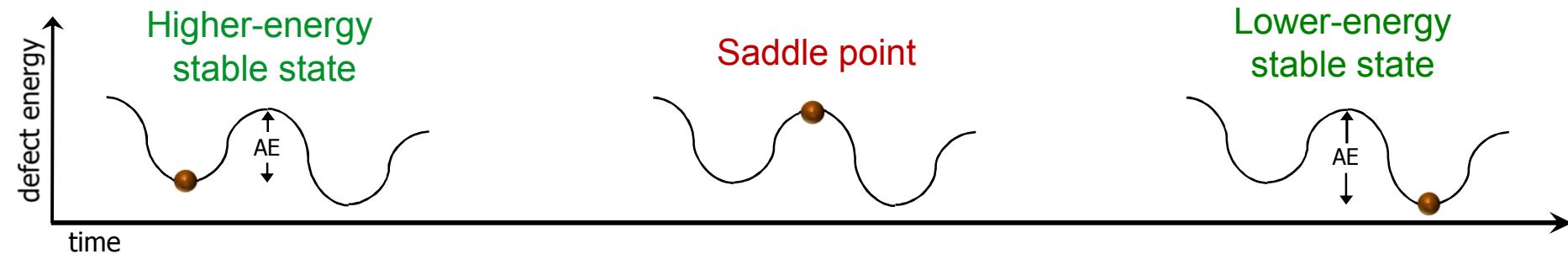


The range of predicted formation energies for the $q=-1$ As [110] split interstitial energies exceeds 1 eV!

- In the alloy, the energy of the defect depends strongly on position
- This energy variation is larger than the diffusion barrier in GaAs and thus should have a major impact on diffusion
- The virtual crystal approximation cannot capture these effects
- In order to explore these effects, we have incorporated our CE into a Kinetic Monte Carlo (KMC) model of diffusion

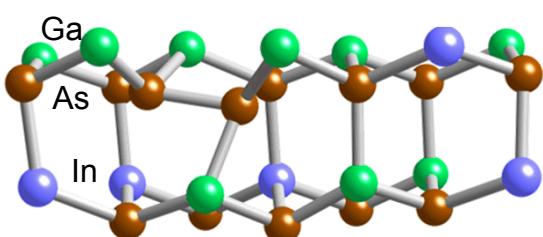
Thermal Diffusion of the $q=-1$ As Interstitial

Thermal-diffusion with a site-dependent energy (AE = Activation Energy)

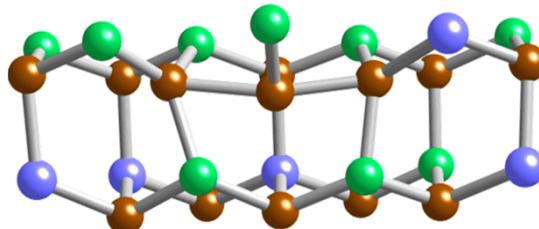


Atomistic configurations obtained from DFT

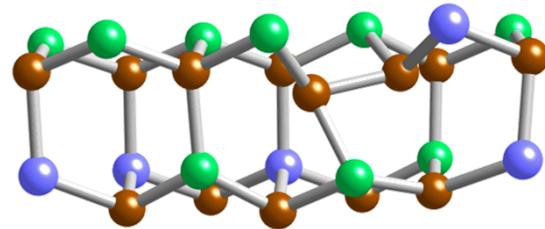
[110] split with local environment A



C_{2v} -001g saddle point with local environment A+B

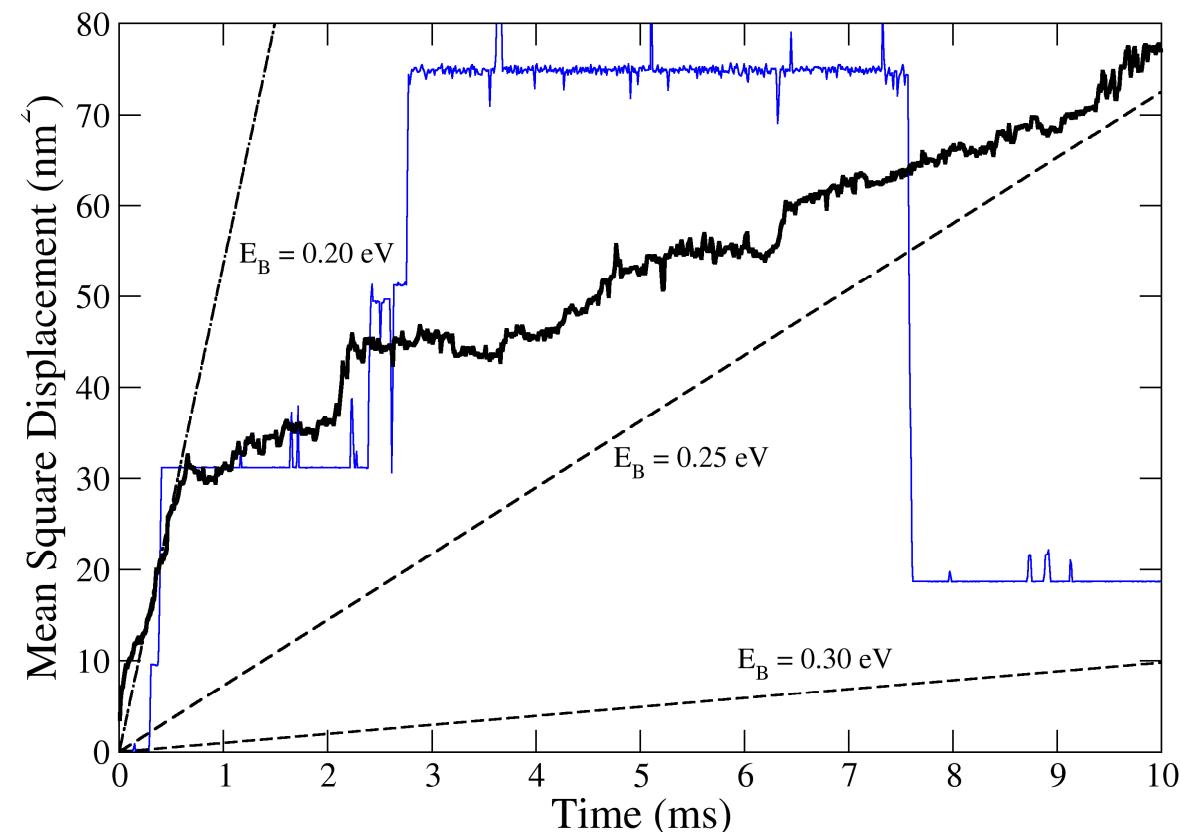


[110] split with local environment B



Kinetic Monte Carlo (KMC) for Thermal Diffusion

Defect Displacement vs Time

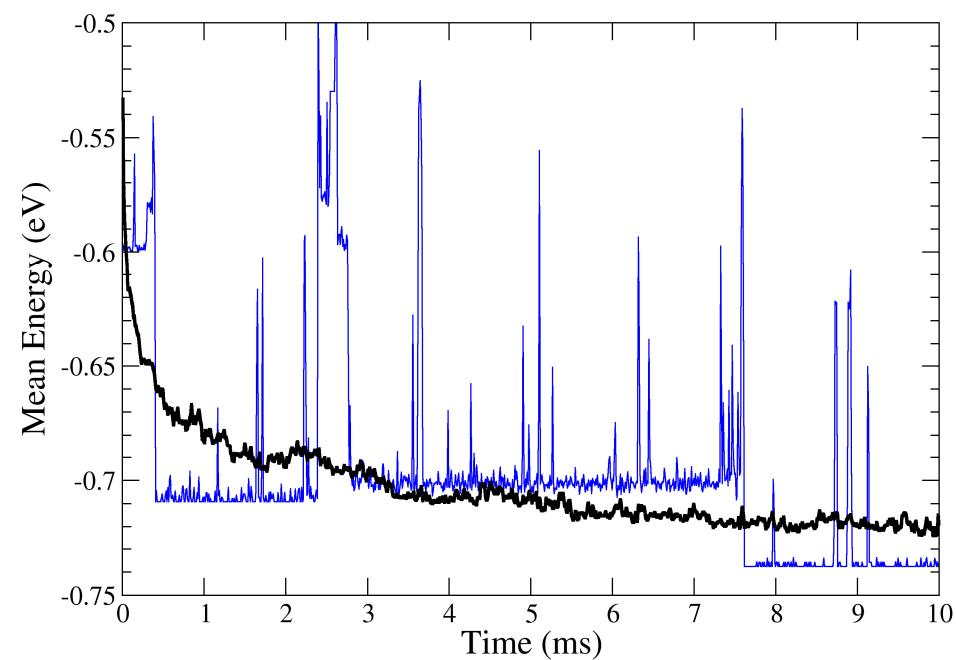


- KMC simulation of a single thermally diffusing $q = -1$ As interstitial in InGaA
- Use cluster expansion for position-dependent stable state energies
- Approximate saddle point energies chosen to give a small constant barrier for the higher energy stable state
- Room temperature simulation with an attempt rate of 10^9 s⁻¹
- Blue line is averaged over time bins for a single trajectory; Black line is averaged over time bins and 96 independent trajectories

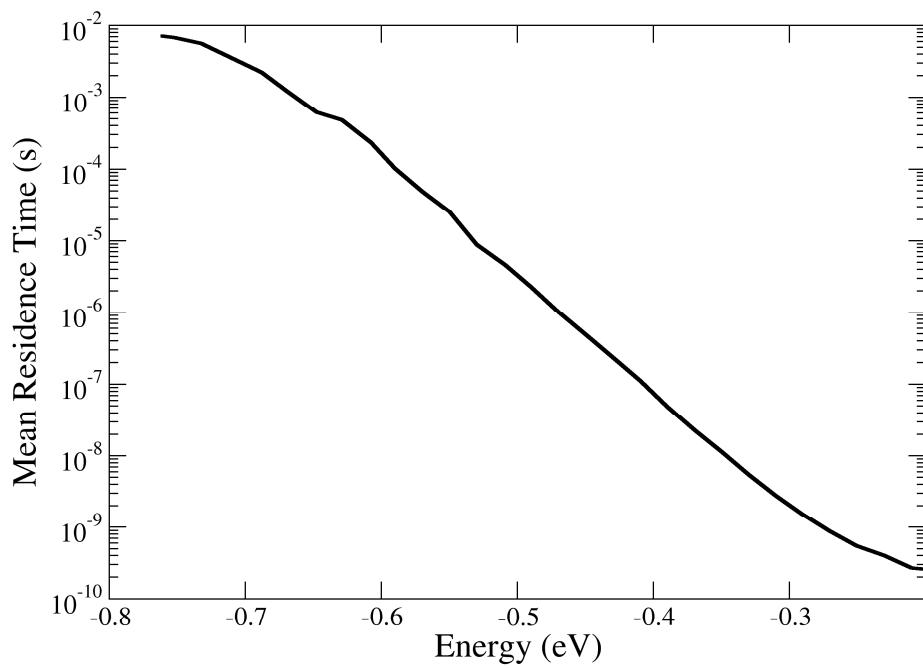
The rate of diffusion decreases dramatically with time!

Why Does Diffusion Slow Down?

Defect Energy vs Time

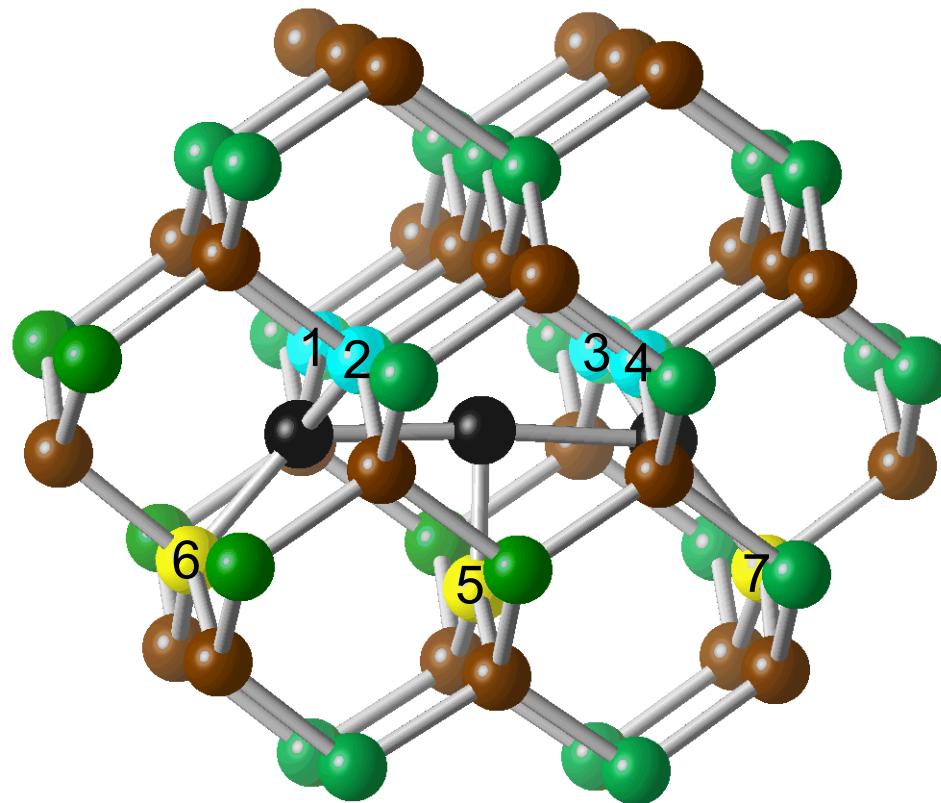


Residence Time vs Energy



- As the defect diffuses, it finds lower energy sites in the alloy.
- Lower energy sites trap the defect for (exponentially) longer times.

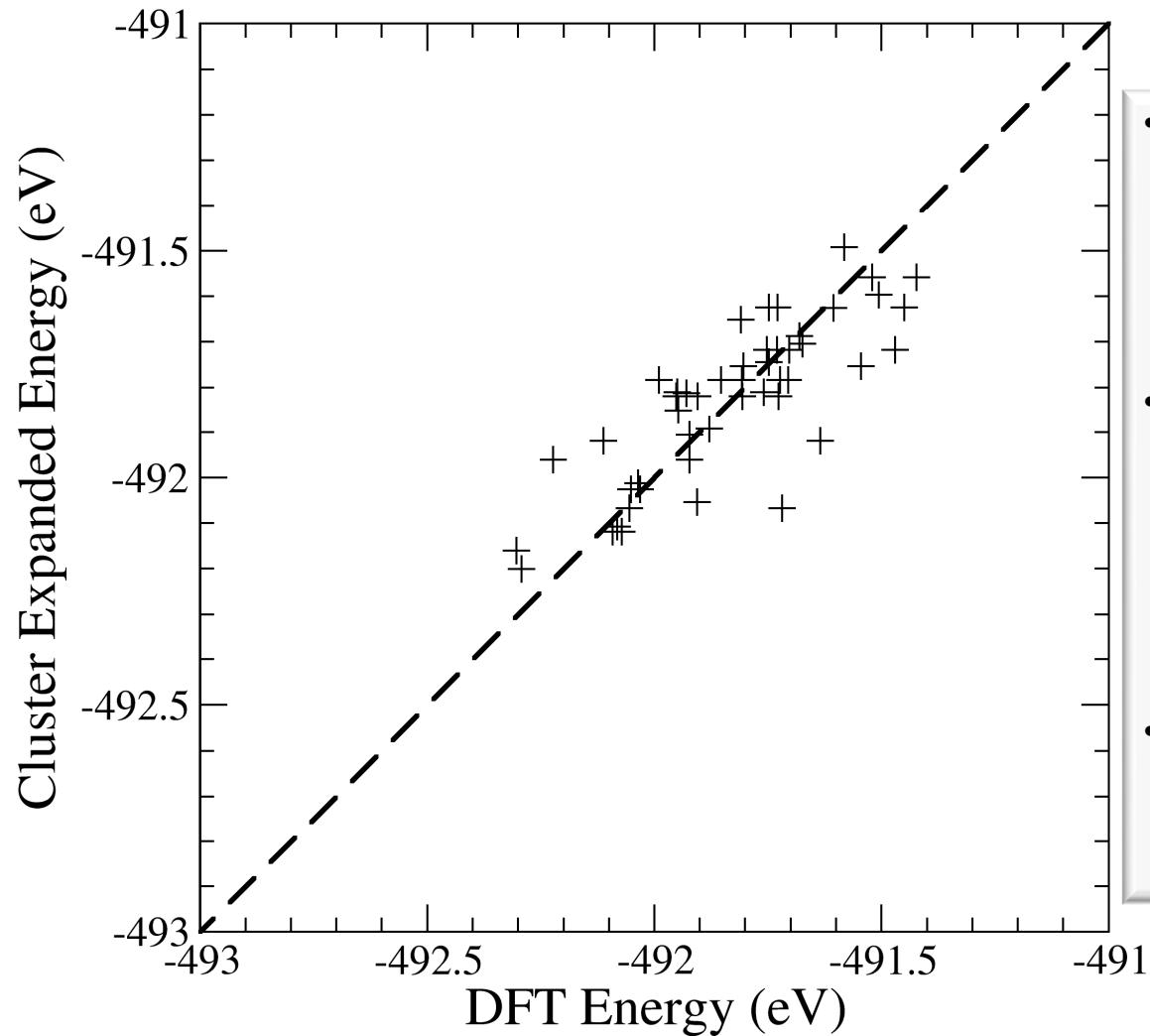
Preliminary Work on CE for Saddle Point Energies



- Saddle point structure has 7 nearest-neighbor sites and 31 next-nearest-neighbor sites
- We have constructed a 358-configuration training set using DFT and the dimer method
- Initial CE built using the 7 nearest neighbor sites and a 48 configuration training set

Accuracy of Our Preliminary Cluster Expansion for the Saddle Points

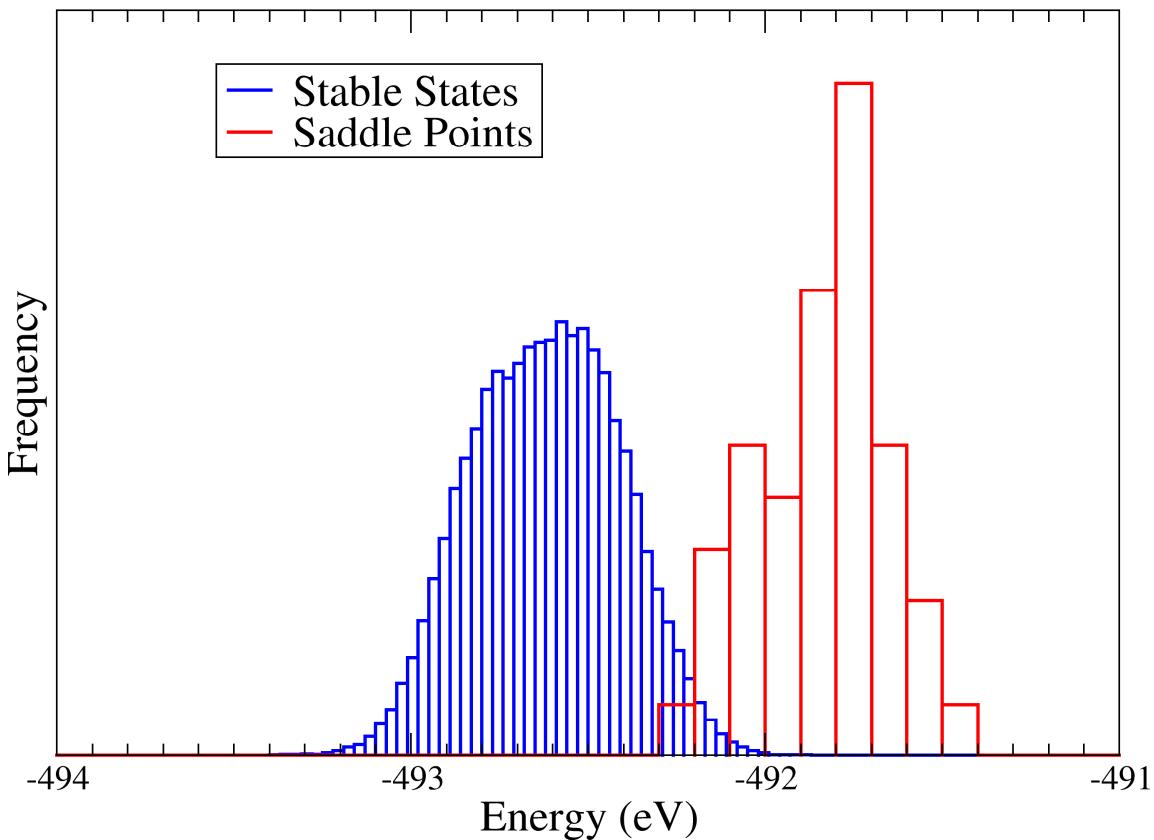
Comparison of CE and DFT



- Our initial cluster expansion for the saddle points is similar in accuracy to earlier cluster expansions for the stable states that used only nearest neighbors
- It is not as accurate as our final, optimized cluster expansion for the stable states:
 - Training set rms error = **0.123 eV**
 - Training set max error = **0.348 eV**
 - Cross-validation error = **0.143 eV**
- We will need to identify the most important next-neighbor sites and include them in the saddle point cluster expansion

Preliminary Analysis of Saddle Point Energies

Histograms of Saddle Point and Stable State Energies



- Similar distributions for saddle point and stable state energies
- The difference between the average saddle point and stable state energies is similar to the barrier in GaAs (0.7 eV)
- Correlations between stable state energies and saddle point energies will be critical in determining the effective barrier for diffusion



Conclusions

- We have combined DFT, Cluster Expansions, and KMC to simulate thermal diffusion of point defects in semiconductor alloys
- We have applied our approach to the $q=-1$ As interstitial in InGaAs
- The energy of a defect can vary dramatically ($> 1\text{eV}$) with position due to changes in the local environment
- Defects can become trapped in progressively lower energy sites leading to a slowing of defect diffusion with time
- In addition to improving our cluster expansion for the saddle points, we are working on other charge state of As, with the goal of treating both thermal and athermal (Bourgoin-Corbett-like) diffusion