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Combining DFT, Cluster Expansions, and KMC to Model Point Defect Diffusion in Alloys

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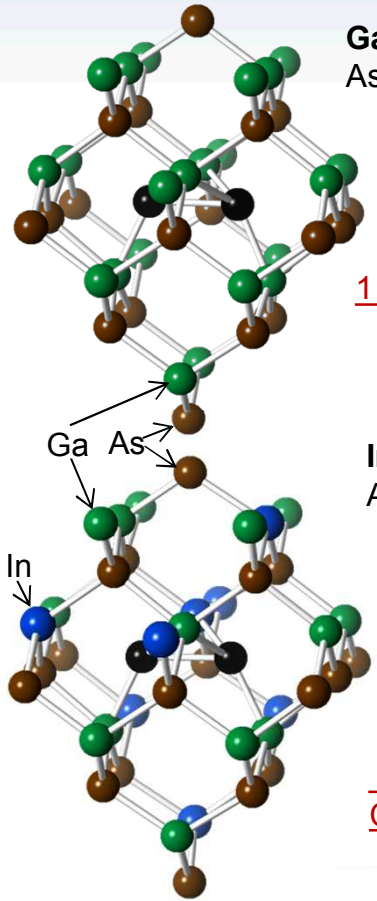
Objective and Approach

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

Why is this challenging? – Defect energies and behavior depend on local alloy environment – Computational burden rises exponentially

- Kinetic Monte Carlo (KMC) simulations of defect diffusion in an alloy require rapid evaluation of defect energies in each alloy environment
- Density-functional-theory (DFT) defect energies are sufficiently accurate to produce realistic simulations, but the computation time is orders-of-magnitude too large for direct use in KMC
- Cluster Expansions (CE) are fit to a training set of DFT energies and then allow rapid evaluation of defect energies in an arbitrary alloy environment



GaAs:
As split interstitial

1 Configuration

$In_{0.5}Ga_{0.5}As$:
As split interstitial

66432 Unique Configurations

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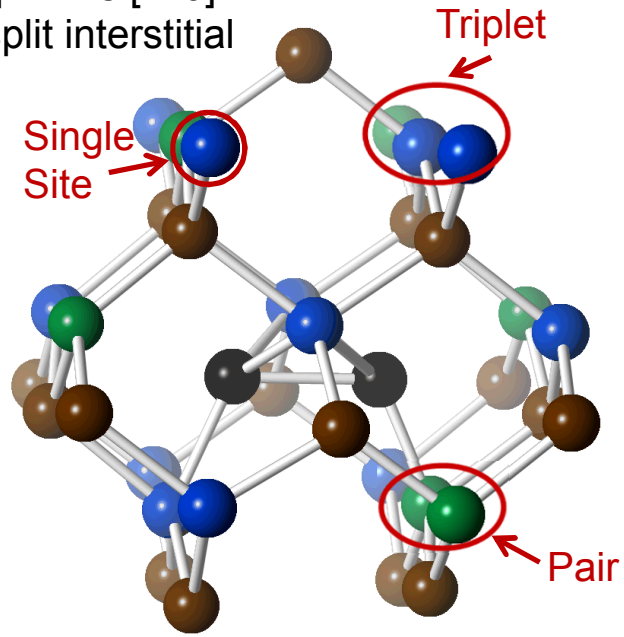
Cluster Expansions For Defects In Alloys

q=-1 As [110] split interstitial



$$E(\vec{\sigma}) = E_0 + \sum_{\alpha} V_{\alpha}\varphi_{\alpha}(\vec{\sigma}) \text{ where } \varphi_{\alpha} = \prod_{i \in \alpha} \sigma_i$$

- Performed cluster-expansion for the formation energy of the $q = -1$ As [110] split interstitial
- Used a modified version of the *CASM* 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, 6 pair terms, and no triplet terms
- The 18 site CE models 66432 unique local environments for the defect
- Hence, direct simulations by DFT would be nearly impossible

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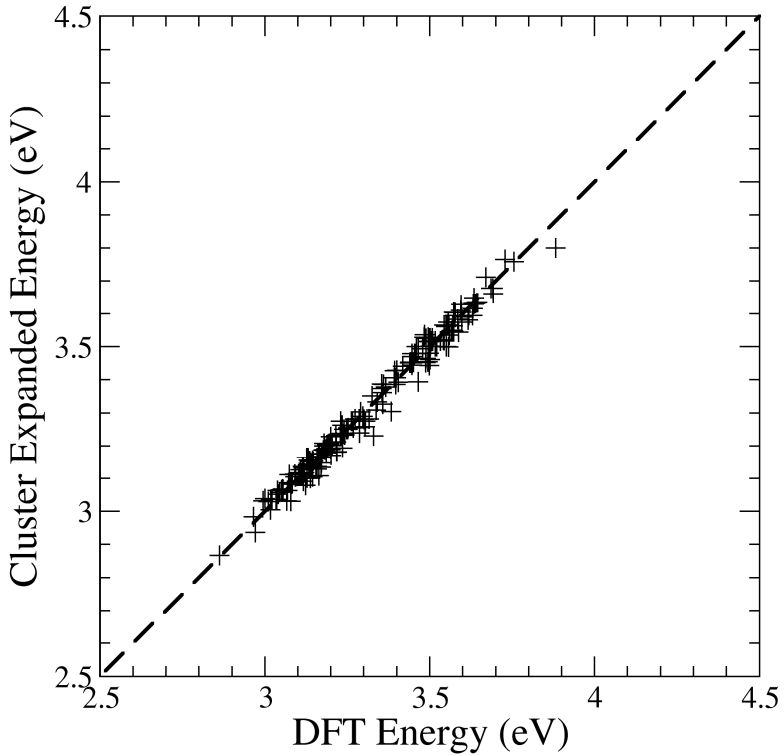
Accuracy of the $q = -1$ As Split Interstitial CE

Comparison of CE and DFT for the Training 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 = 0.024 eV
  - Training set max error = 0.100 eV
  - Cross-validation error = 0.025 eV
  - Independent-set error = 0.028 eV
- The errors introduced by the CE can be less than typical DFT errors for defects

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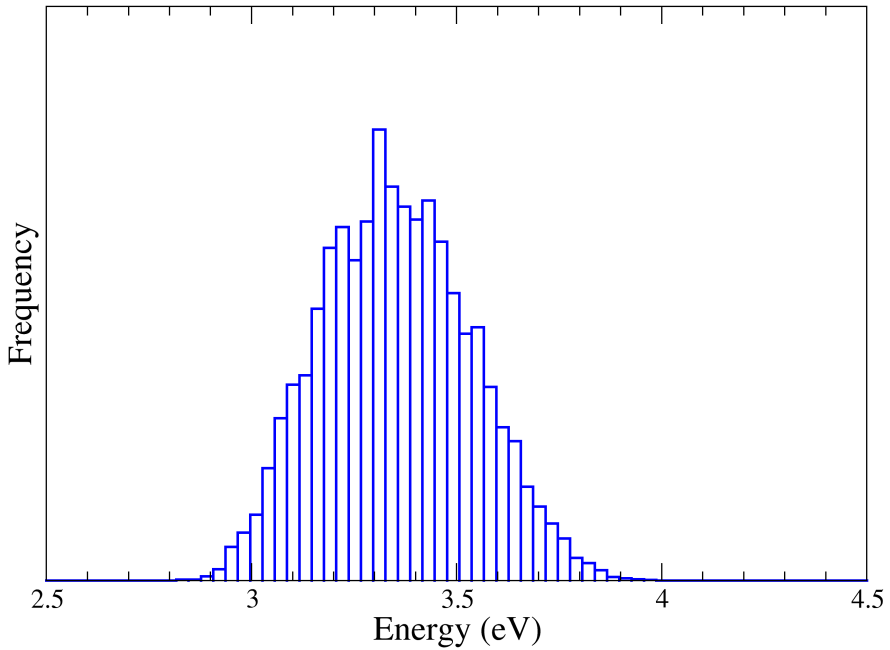
Strong Dependence of Defect Properties on the Local Alloy Environment

Histogram of Defect Energies
Obtained from the Cluster Expansion



The range of the predicted formation energies of the q = −1 As split interstitial energies exceeds 1 eV!

- In the alloy, the energy of the defect depends strongly on the alloy environment, and hence on position
- This energy variation is larger than the diffusion barrier in GaAs and thus should have a major impact on diffusion
- Simplified models (e.g., VCA or SQRS) cannot capture these effects
- In order to explore these effects, we have incorporated our CE into a KMC model of diffusion

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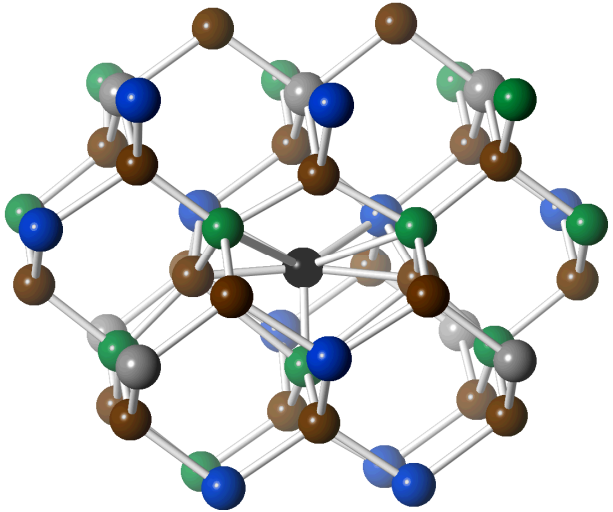
Cluster Expansions for Saddle Point Energies

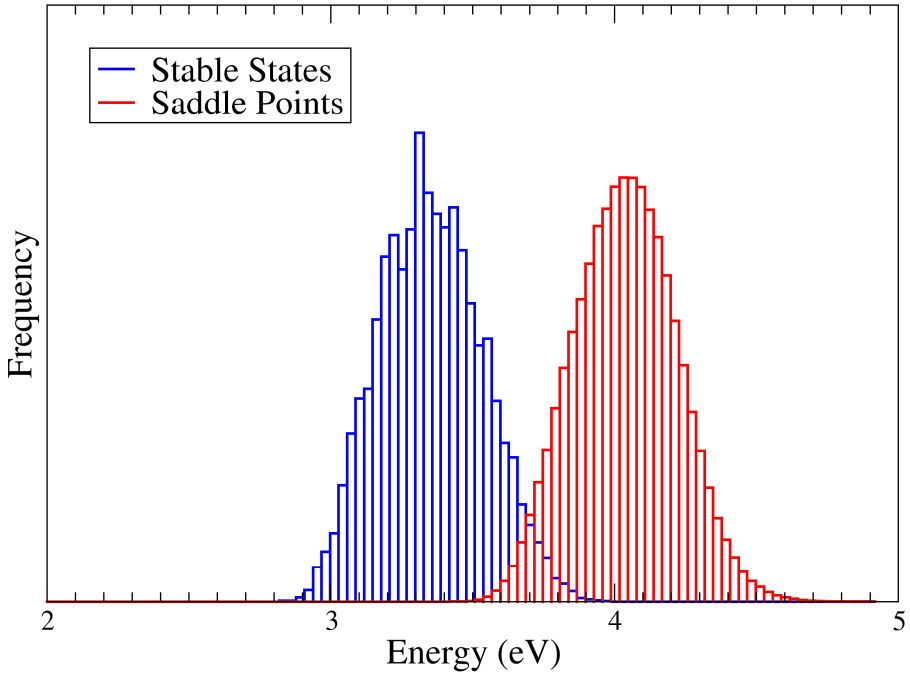
q=-1 As interstitial
C_{2v}-001g saddle point



- The dimer method is used to construct a training set of DFT saddle point energies
- In the q=-1 C_{2v}-001g saddle point cluster expansion, we used 8 single site terms (indicated by the green and blue spheres), 5 pair terms, and 3 triplet terms
  - Training set rms error = 0.027 eV
  - Training set max error = 0.088 eV
  - Cross-validation error = 0.029 eV

Results From Saddle Point Cluster Expansion

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)
- In the least favorable cases, variations in local alloy environment could almost triple the diffusion barrier

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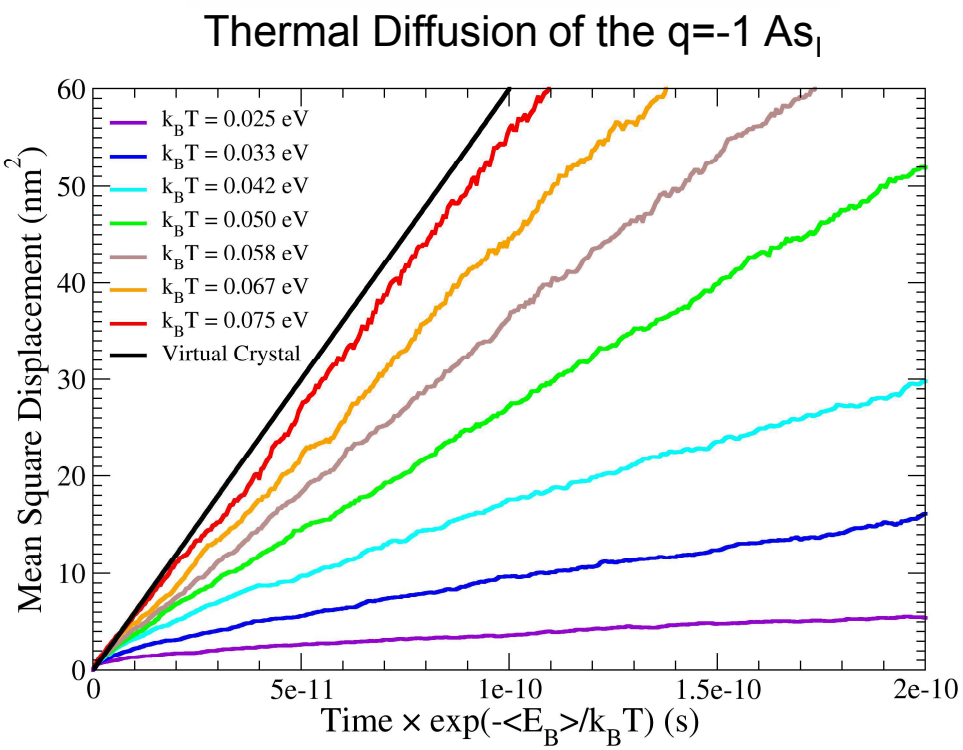
Kinetic Monte Carlo (KMC) for Thermal Diffusion



In a homogenous system, the rate of diffusion would be independent of time

Time has been rescaled so that all of the curves would collapse onto the black line for a fixed diffusion barrier <E_B>

In contrast, the rate of diffusion in the alloy slows dramatically with time

The amount by which the diffusion slows depends on temperature

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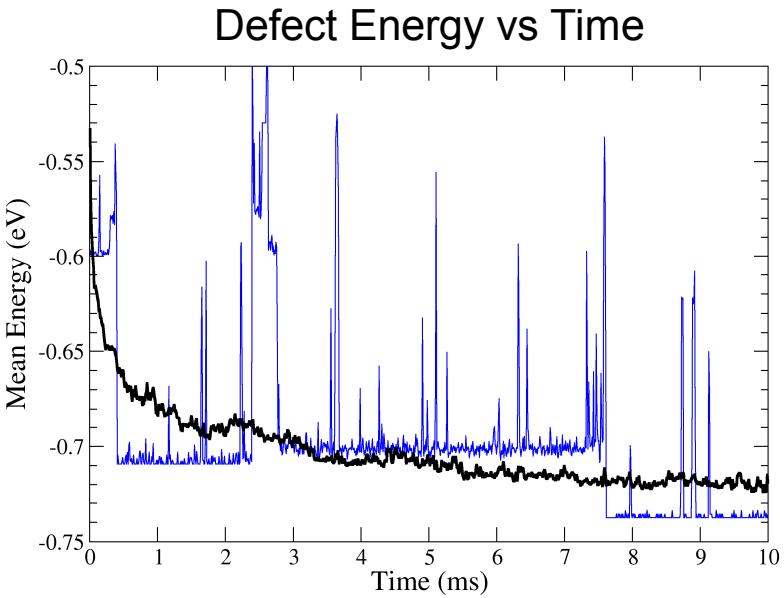
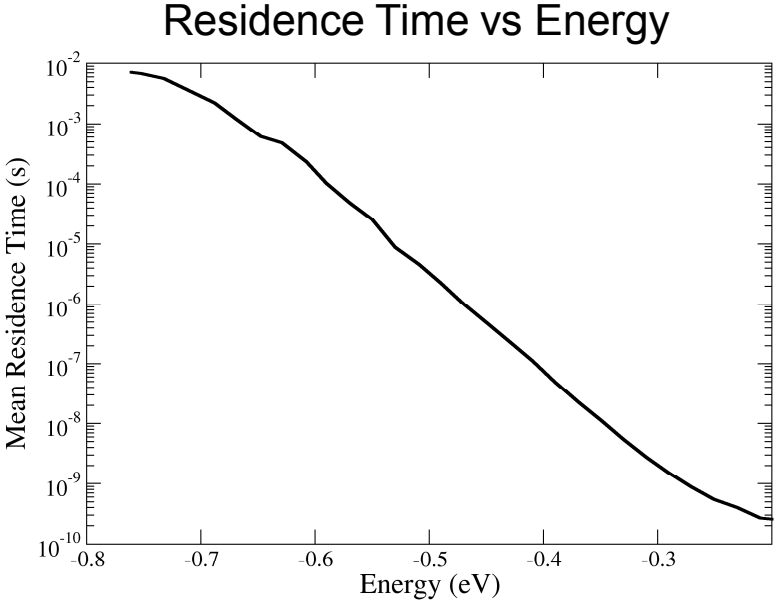
Why Does Diffusion Slow Down?





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

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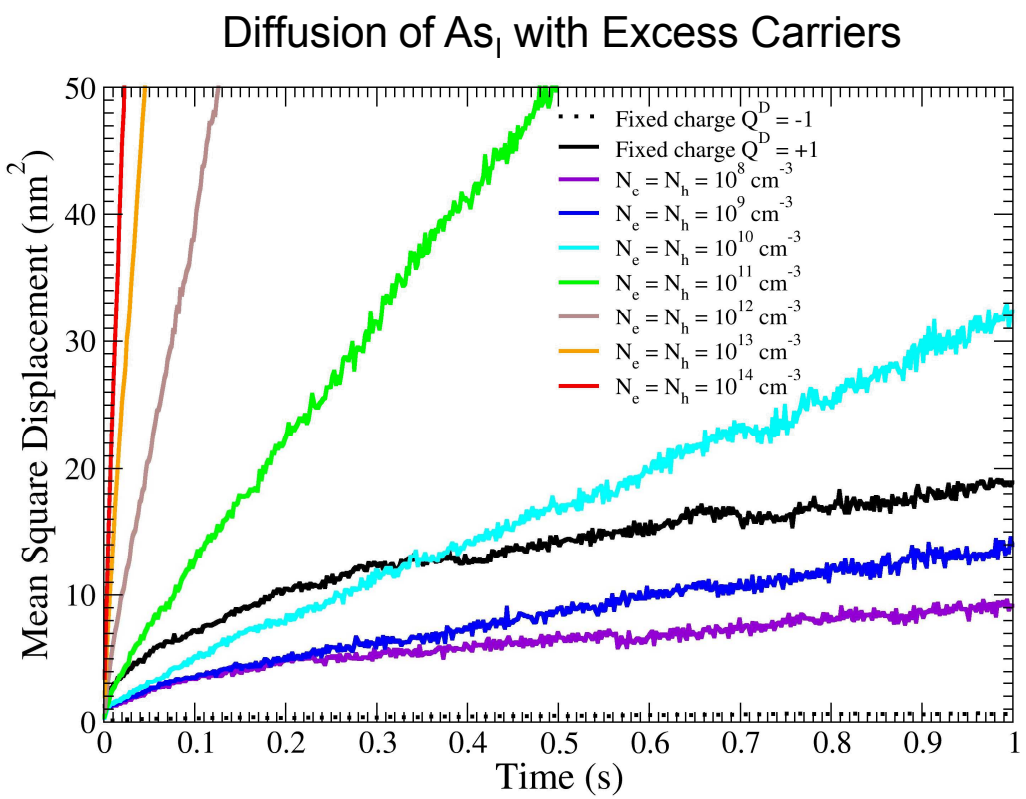
Kinetic Monte Carlo (KMC) for Combined Carrier-Induced and Thermal Diffusion



Black curves show thermal diffusion for the q=-1 and q=+1 charge states of the As_I

The ratio of q=-1 (slow diffusion) to q=+1 (fast diffusion) changes with the concentration of carriers

However, for larger carrier densities and longer times, the rate of diffusion in enhanced relative to pure thermal diffusion

The presence of carriers seems to reduce the slowing of diffusion due to trapping

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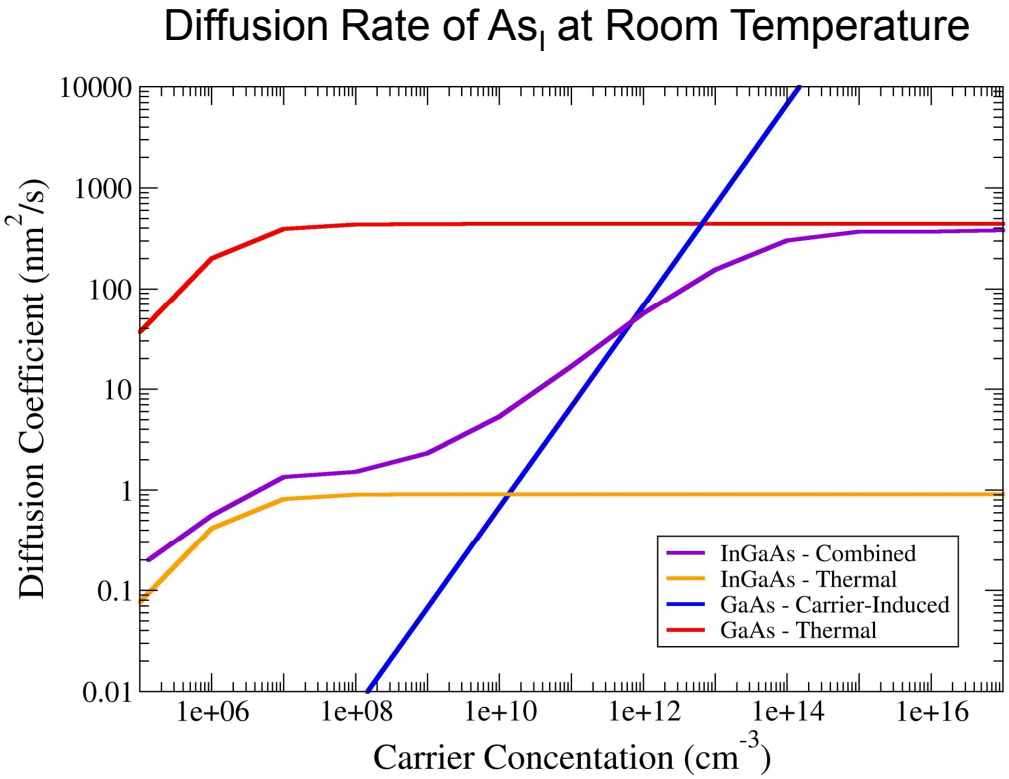
Effect of Carrier Concentration on Diffusion Rate



At low carrier concentrations, the calculated diffusion rate agrees with a weighted average of the q=-1 and q=+1 thermal diffusion rates in InGaAs

At high carrier concentrations, the calculated diffusion rate approaches the thermal diffusion rate in GaAs

The very large diffusion rates associated with the Bourgoin-Corbett mechanism at high carrier concentration are not observed

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Conclusions

- We have combined DFT, Cluster Expansions, and KMC to simulate thermal and carrier-induced diffusion of defects in semiconductor alloys
- We have applied our approach to the q=-1, 0, and +1 As_I in InGaAs
- Defect energies are found to vary dramatically (> 1eV) with location in the alloy due to changes in the local environment
- A diffusing defect becomes trapped in progressively lower energy sites leading to a slowing of thermal diffusion with time
- Excess carriers reduce the effects of trapping, but alloy effects seem to suppress ”pure” carrier-induced diffusion (at least in the current model)