Derivation of TTT diagrams with kinetic Monte-Carlo simulations

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TTT-Diagram : Blueprint for heat treatment

Al-based Alloys

Precipitation hardening

Heat Treatment

Solid solution annealing

Precipitation Kinetics

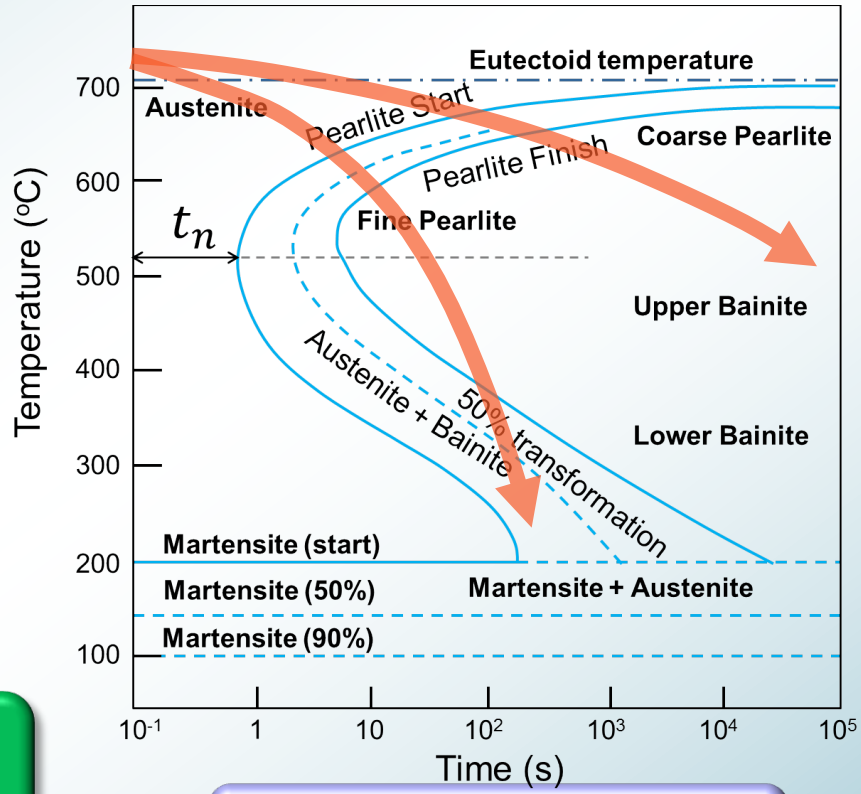
Precipitation

Finer precipitates

Coarse precipitates

Resulting Microstructure

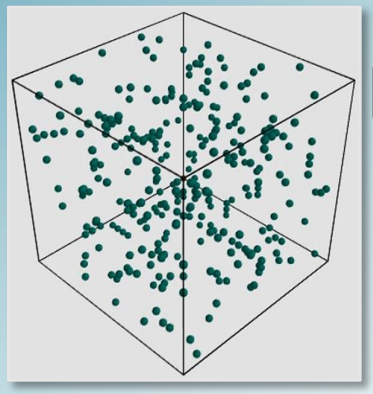
Sketch: Fe-C TTT-diagram



TTT-Diagrams

Final Product

kMC Methodology



Starting configuration

List all the possible jumps

Assign a transition rate *r* to each jump

Harmonic Transition State Theory

$$r^{\mathrm{hTST}} = \Gamma_0 \, e^{(-E_b/k_B T)}$$

Choose a jump *k*

$$R = \sum_{n=1}^{N} r_n$$

$$\sum_{n=1}^{k-1} r_n \leq \rho_1 R \leq \sum_{n=1}^{k} r_n$$

Execute and update configuration

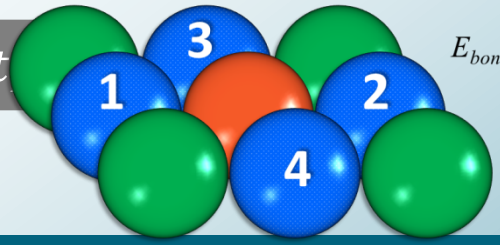
$$E_b = E_0 + n\,E_{\mathrm{bond}}$$

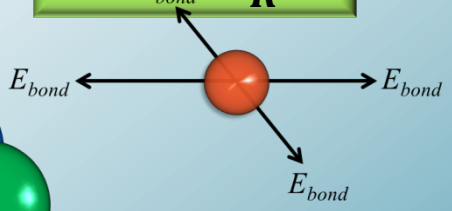
Linear Bond-Cutting Model

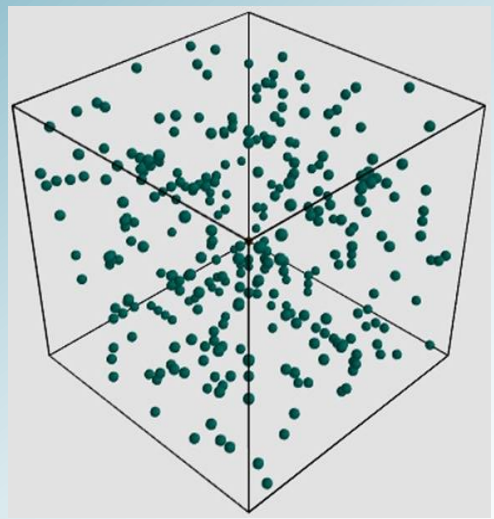
e simulation time $t = t + \Delta t$

$$\Delta t = -\frac{\ln(\rho_2)}{R}$$

While $t < t$



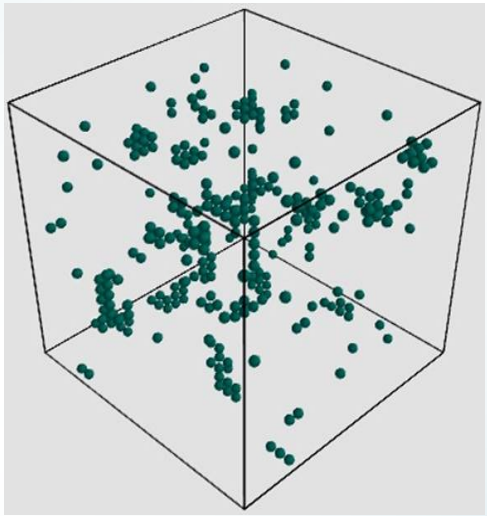




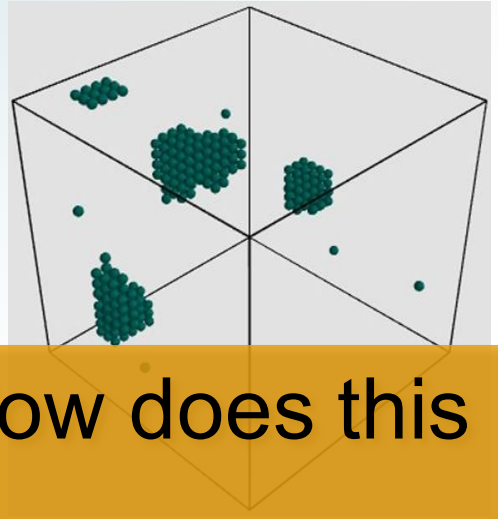
t_1

$t_1 = 0$

t_2



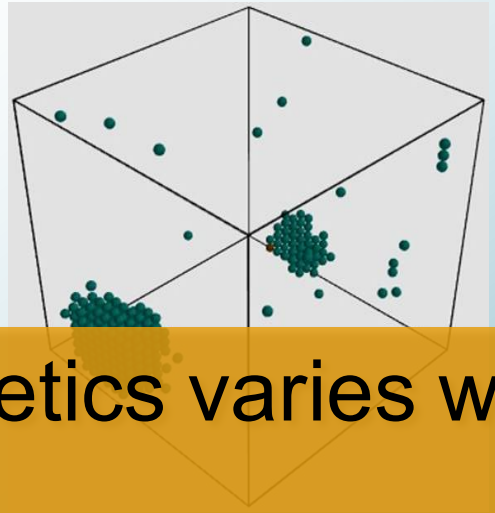
$t_2 \approx 0.1\ \mu s$



t_3

$t_3 \approx 1\ \mu s$

t_4

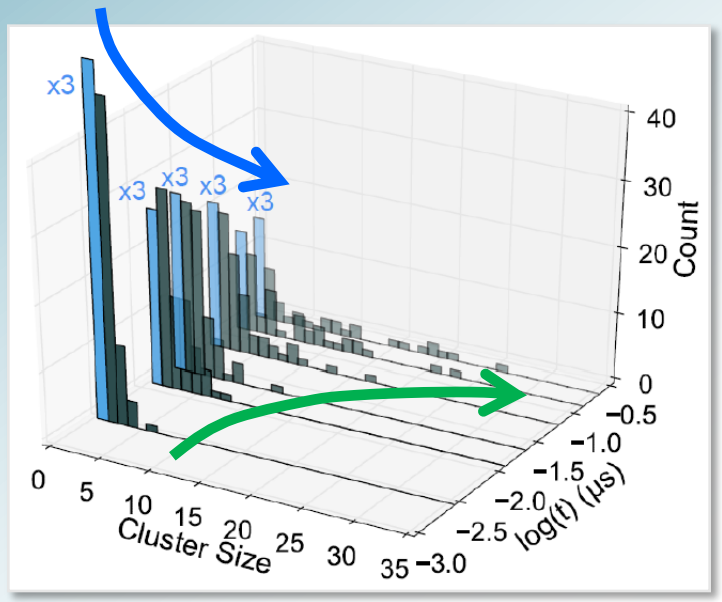


$t_4 \approx 3\ \mu s$

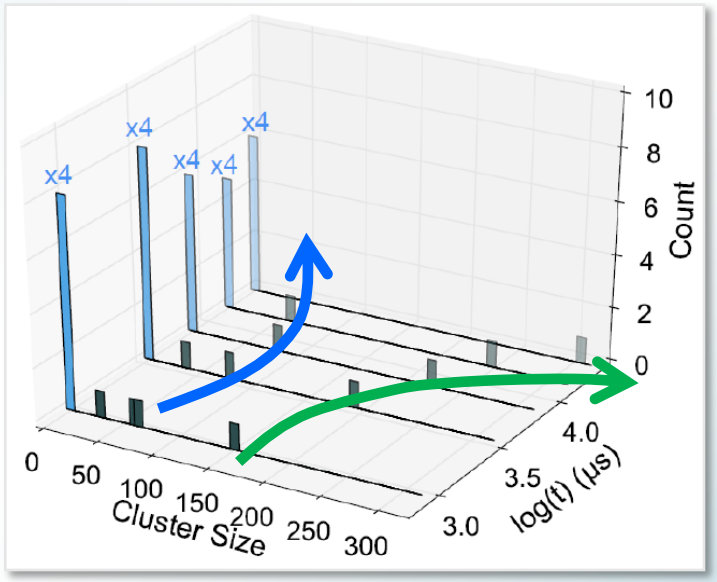
How does this precipitation kinetics varies with temperature?

Size distribution of precipitates (Low T)

$$N(t) = (N_1, N_2, N_3, \ldots, N_i, \ldots, N_N)$$



Initial stage of transformation



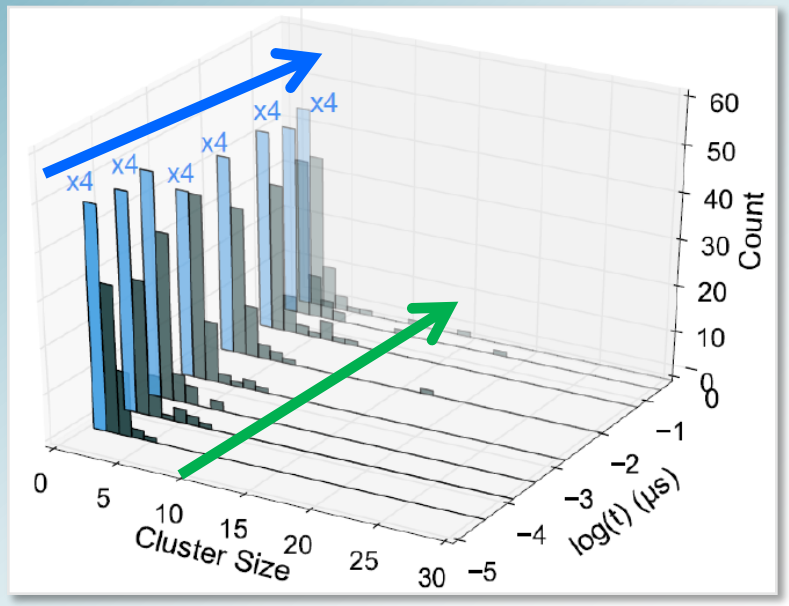
Later stage of transformation

- Decrease in gas phase concentration
- Smearing towards larger particle sizes

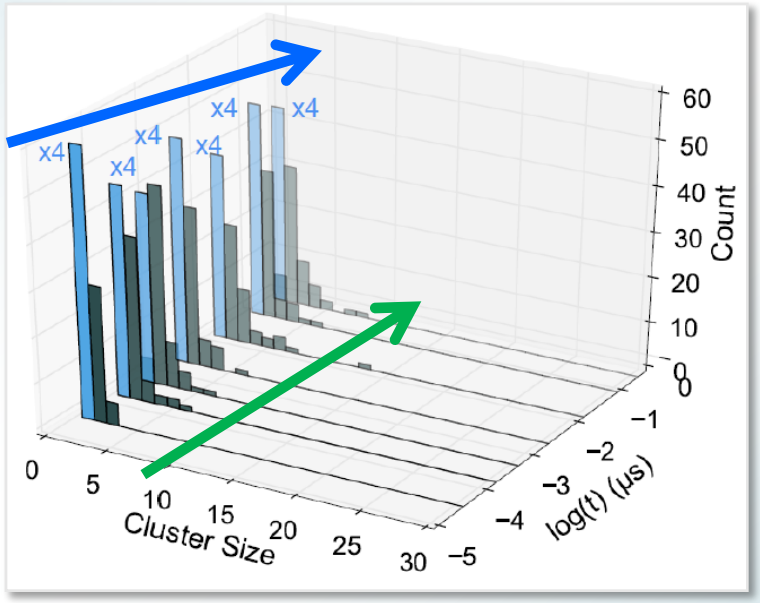
- Smaller precipitates dissolves and leads to the growth of large precipitate
- Ostwald ripening

Simulation Parameters: 400 K, 25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV

Size distribution of precipitates (High T)



700 K

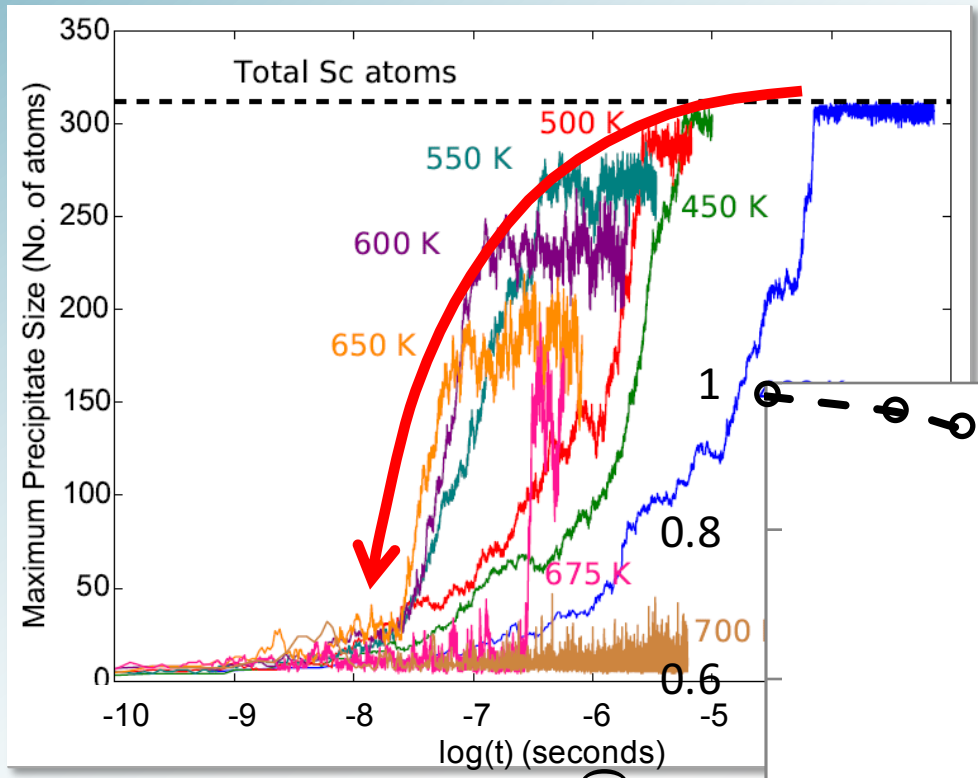


750 K

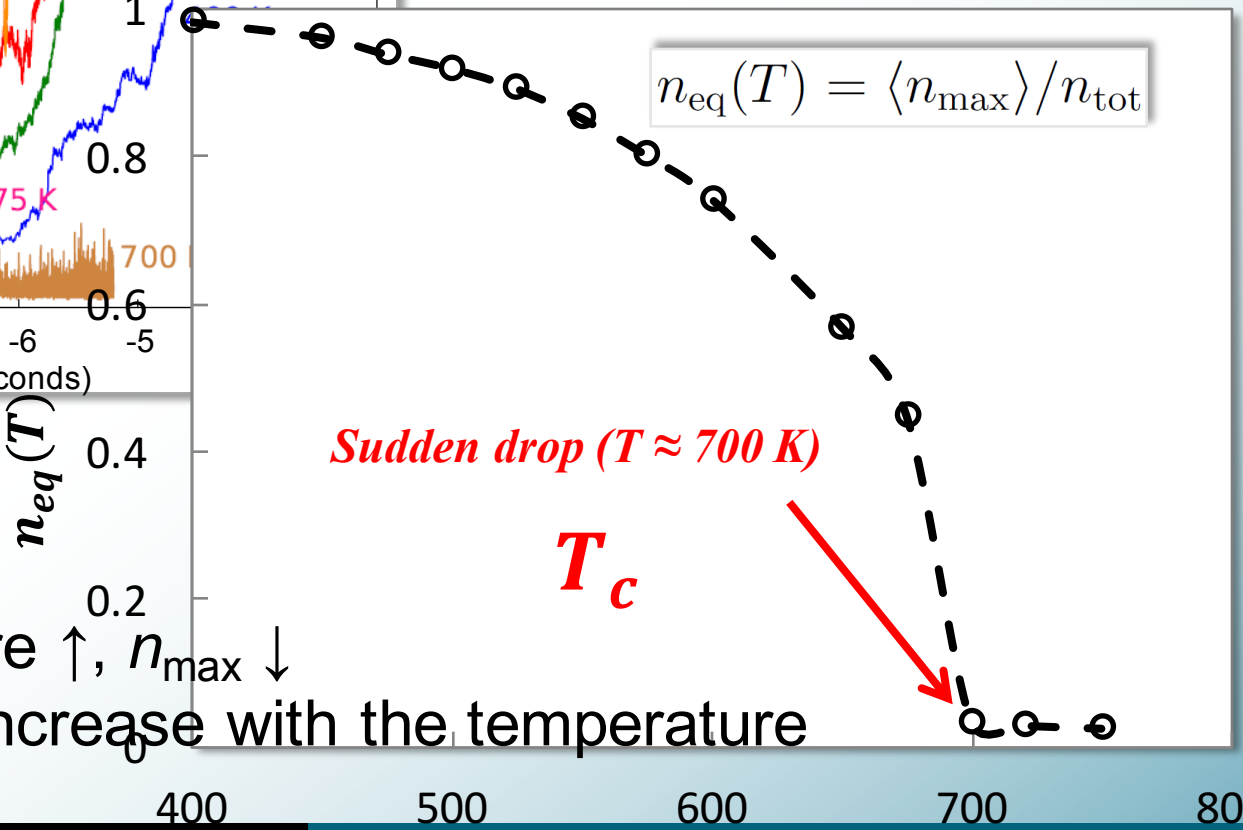
- Gas phase concentration remains constant
- No precipitate growth observed

How does this transition from low to high T varies?

Evolution of largest precipitate (n_{max})

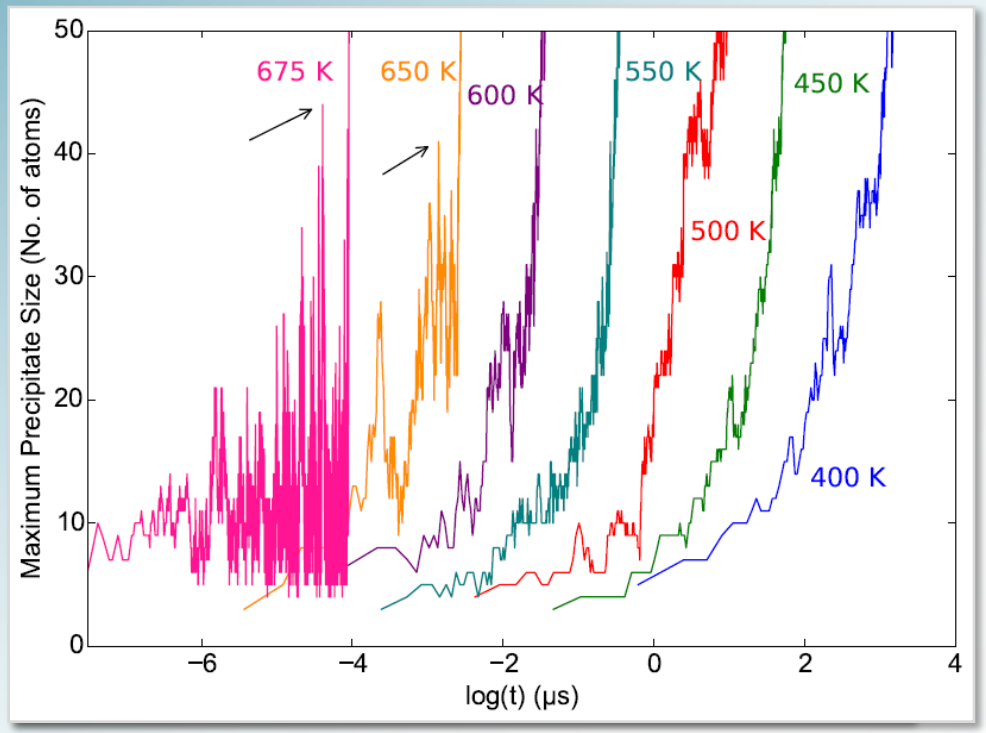


Simulation Parameters:
25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV



- As the temperature ↑, n_{max} ↓
- The fluctuations increase with the temperature

Nucleation stage

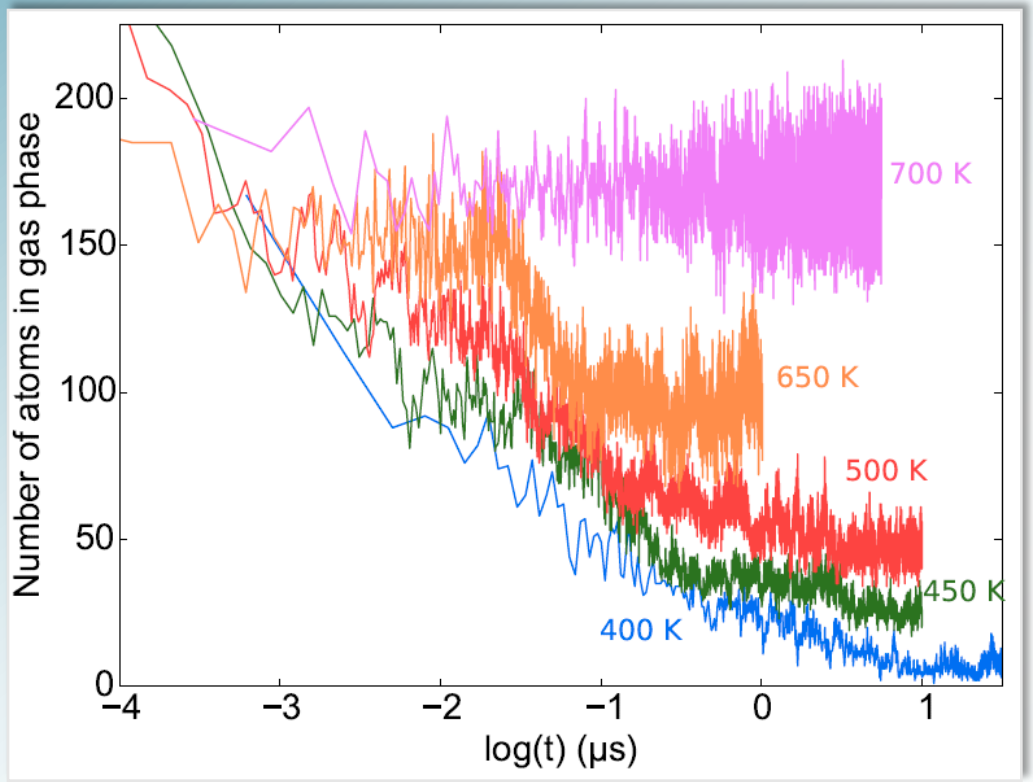


Simulation Parameters:
25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV

- As T increases:
  - the duration of nucleation stage increases.
  - the critical nuclei size increases.

We know precipitate size → remaining gas phase

Evolution of the gas phase



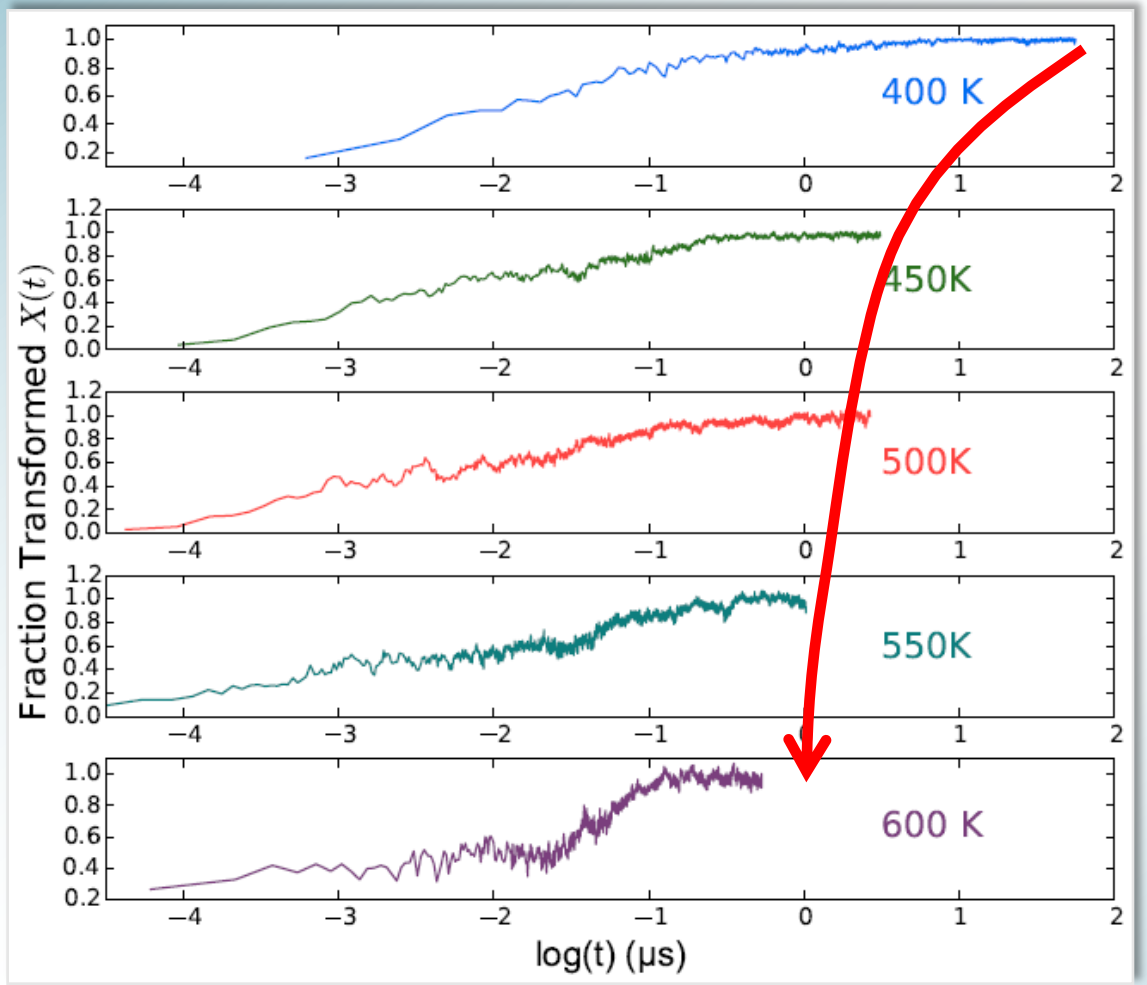
Simulation Parameters:
25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV

- With increasing temperature, gas phase amount increase
  → Entropy dominates at high temperatures
- Fluctuations increase with increasing temperature

Advancement Factor $X(t)$: Degree of Transformation

$$X(t) = \frac{c_m(t=0) - c_m(t)}{c_m(t=0) - c_m(t \to \infty)}$$

- $c_m(t=0)$ initial conc. of solute in the matrix
- $c_m(t)$ remaining solute conc. at time t
- $c_m(t \to \infty)$ equilibrium conc. of solute atoms



- X(t) = 1 means end of transformation process
- Equilibrium value of 1 is reached ∀ T.
- As T increases, total time for completion decreases → signifies the speed up with increasing temperature.

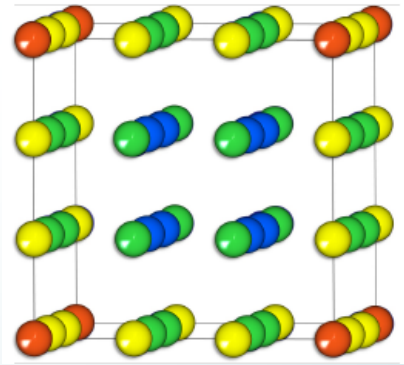
Gas Phase Concentration: Analytical vs Calculated

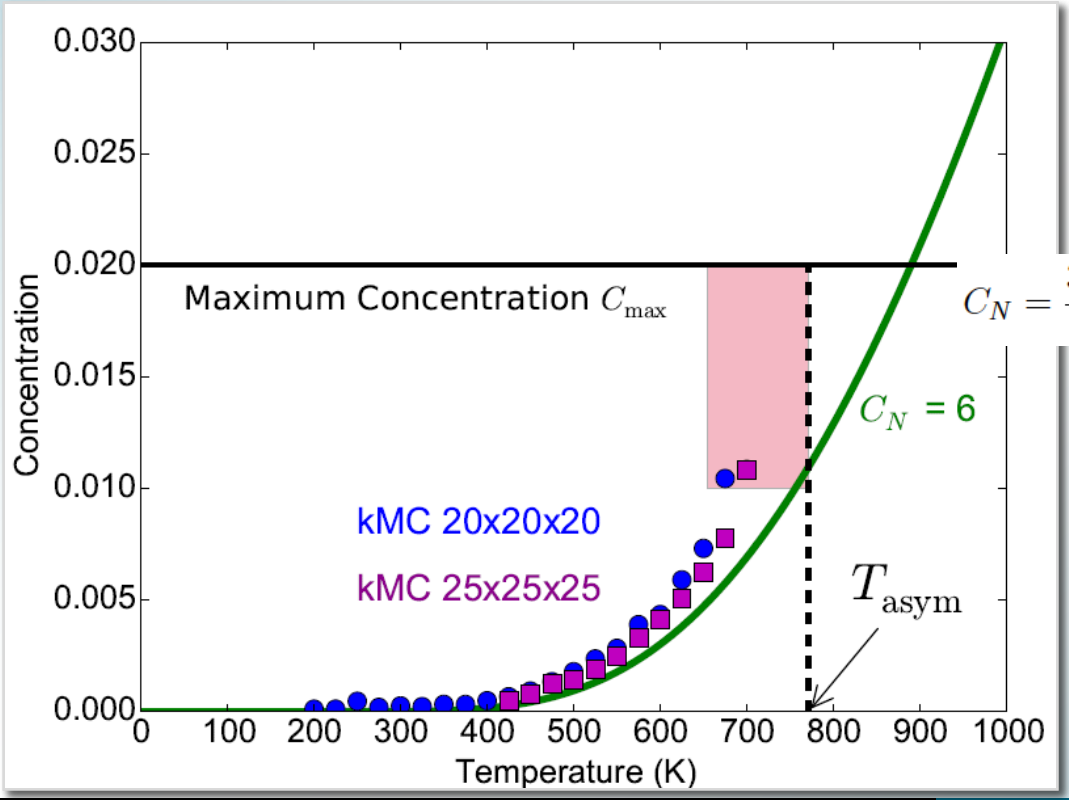
$$\mu_{\text{precipitate}} = C_N \frac{E_{\text{bond}}}{2} = \mu_{\text{gas}} = -k_B T \ln(c_{\text{gas}})$$

Equilibrium

$$\mu_{\text{gas}} = -k \quad c_{\text{gas}}(T) = \exp\left(-\frac{\mu_{\text{precipitate}}}{k_B T}\right)$$

Simulation Parameters:
25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV





$$C_N = \frac{3*8 + 4*12(N-2) + 5*6(N-2) + 6*(N-2)^3}{N^3}$$

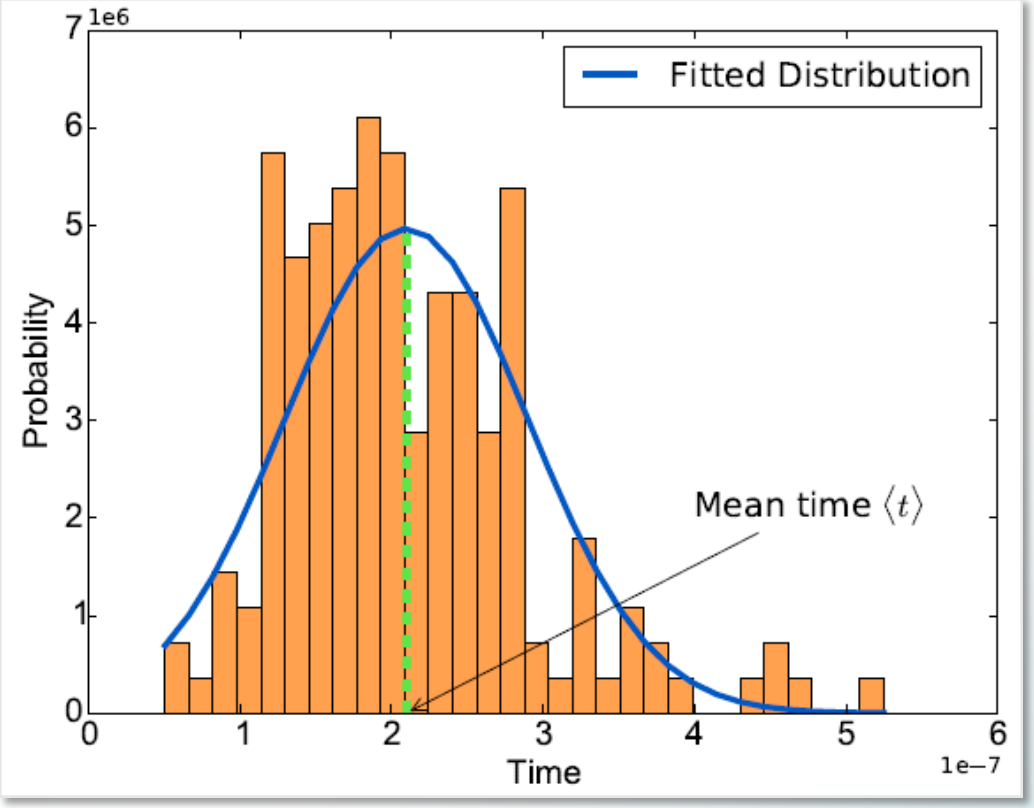
- Finite size effect observed (real system C_N = 6)
- Shaded area : no stable precipitates observed

Obtaining Time Scale : Statistics

$$t_i(T, N_c) \equiv \{t_1, t_2, t_3, \ldots, t_n\}$$

***n* = 200, *T* = 400 K**
N_c = 30

Simulation Parameters:
25x25x25 supercell
E_{bond} = 0.1 eV, E_0 = 0.3 eV

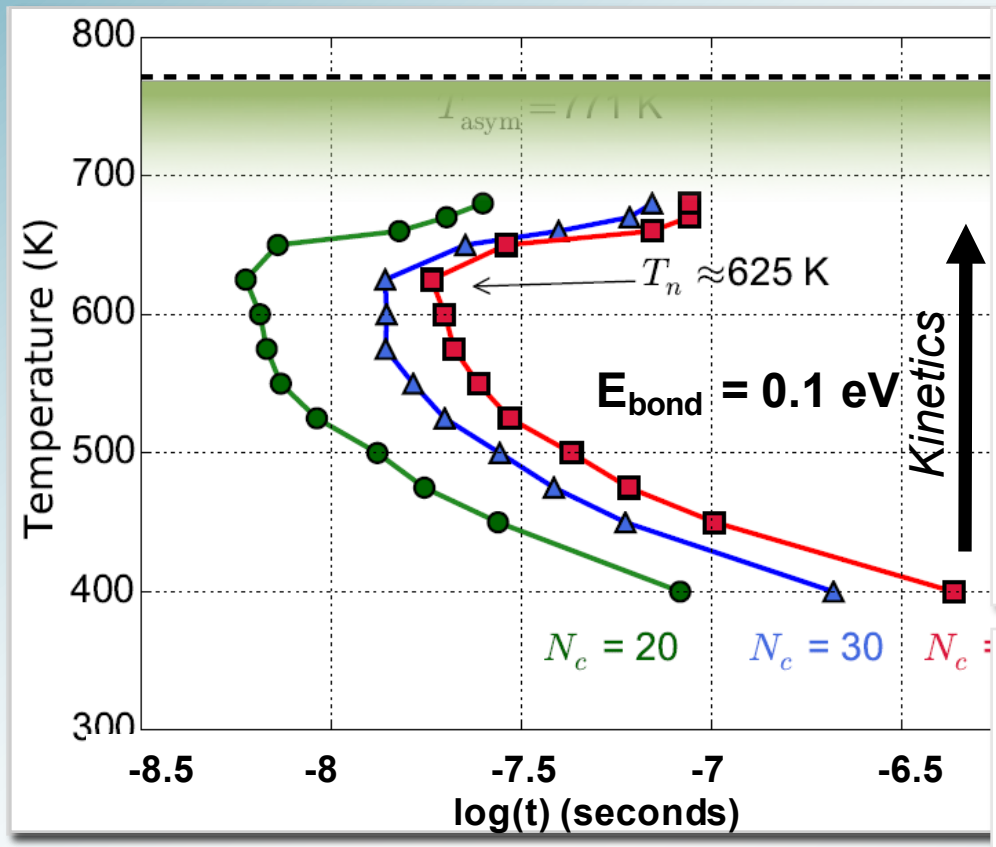


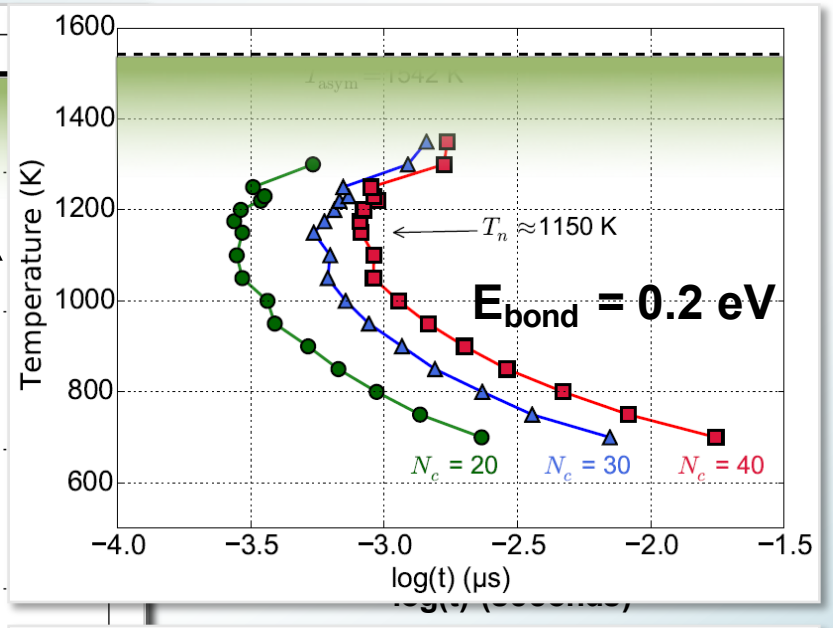
- Process repeated for different *T* and N_c.

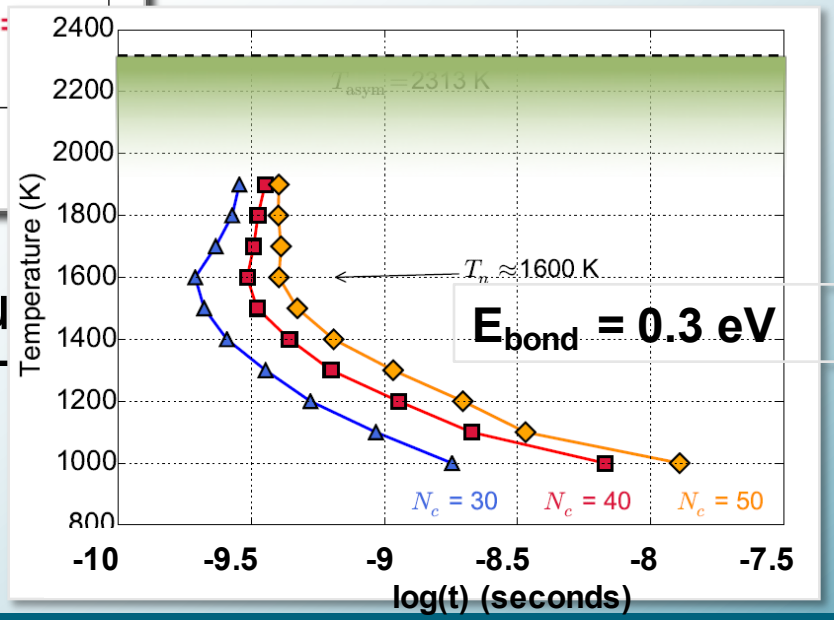
T* and *t

TTT Diagrams

Calculated TTT Diagrams

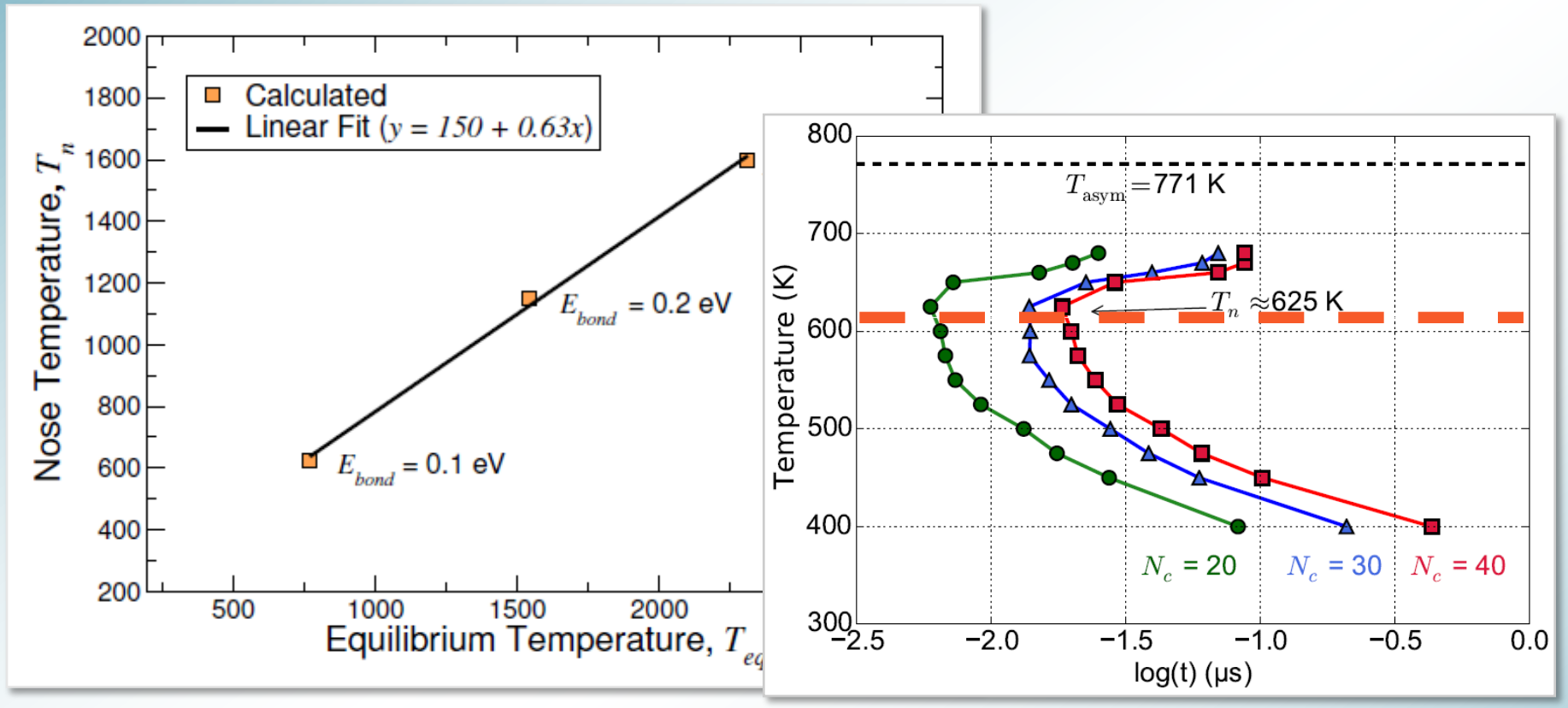






- No clusters observed at temperatu
- Is there a relation between Nose T and T_{asym} ?

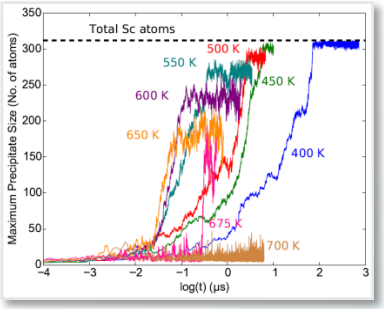
Relationship between nose temperature T_n and T_{asymp}

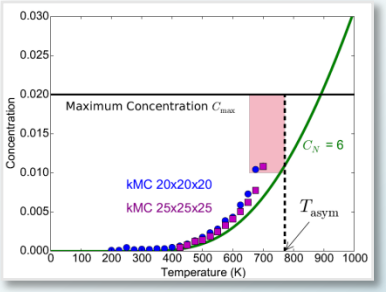


- Ignoring the intercept (150), $y = 0.63x$ reflects the asymmetric nature of C-shape of the TTT diagrams around the nose.
- Entropy only dominates at high temperatures which might explain this asymmetry

Conclusions

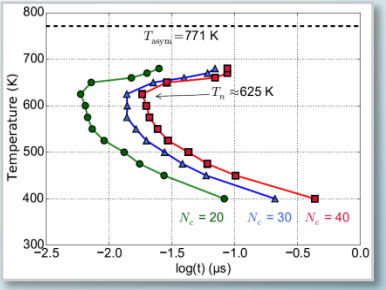
- Equilibrium size of the precipitate decreases with temperature due to entropy domination
- Finite-size effects observed
- Upper TTT curve challenging-no stable precipitates
- Relationship b/w nose and asymptotic temperature

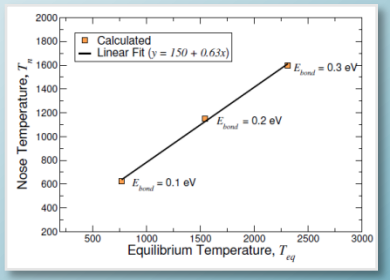




Outlook

- Extension to realistic binding energies and Al-Sc alloy
- Effect of strain on the precipitation kinetics within a combined EAM-cluster expansion-kMC formalism (in collaboration with Prof. Mark Asta, UC Berkeley)





THANK YOU FOR YOUR ATTENTION

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