A Kinetic Monte Carlo Model for Material Aging:

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Second Phase Formation at Au/Bi_2Te_3 Junction in Oxygen Environment

X. W. Zhou, and N. Y. C. Yang

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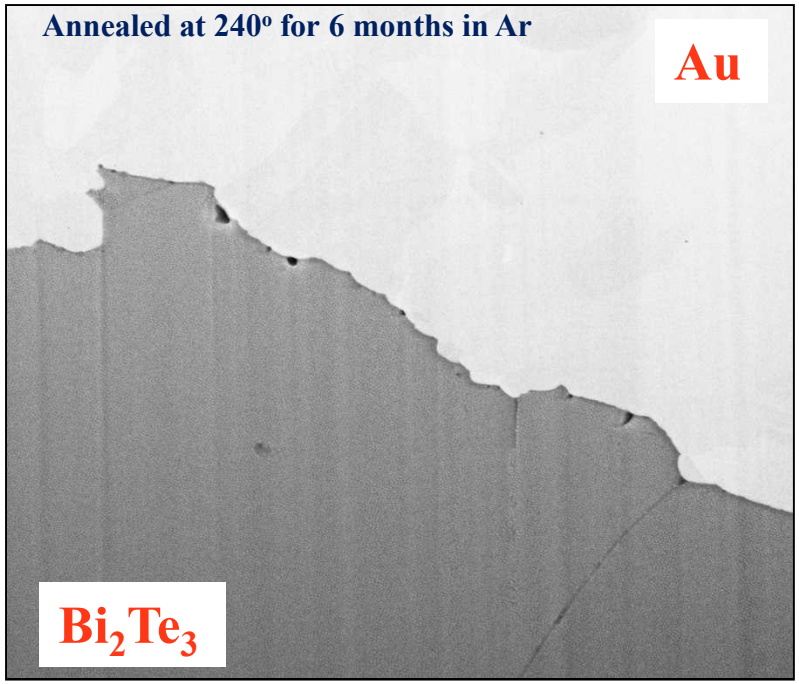
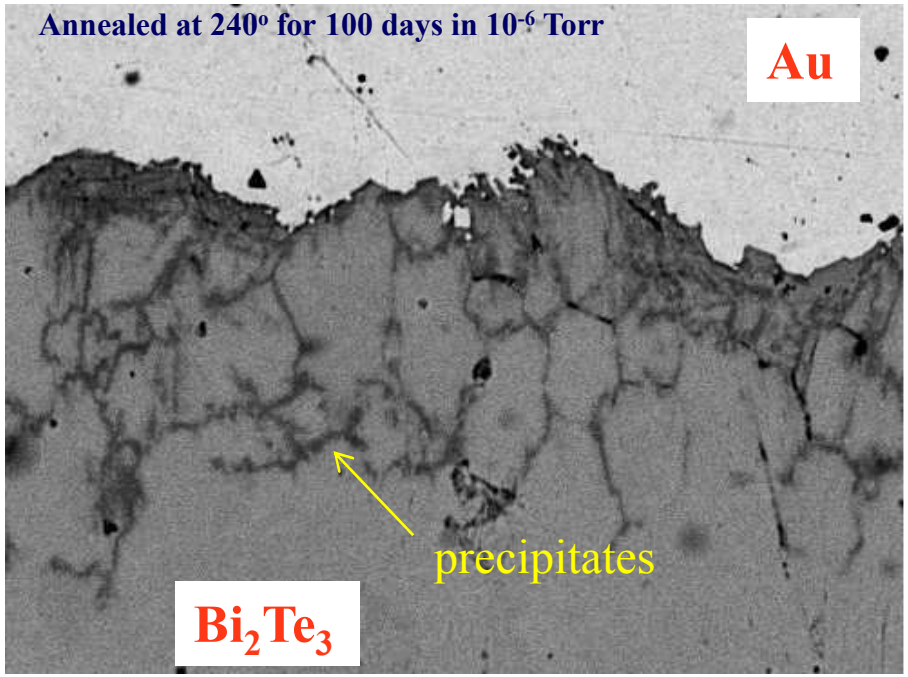
Motivation

(a) Bi_2Te_3 has the best known thermoelectric properties; (b) SEM analyses indicate interfacial second phase formation in electroplated Au/Bi_2Te_3 devices in oxygen environment.

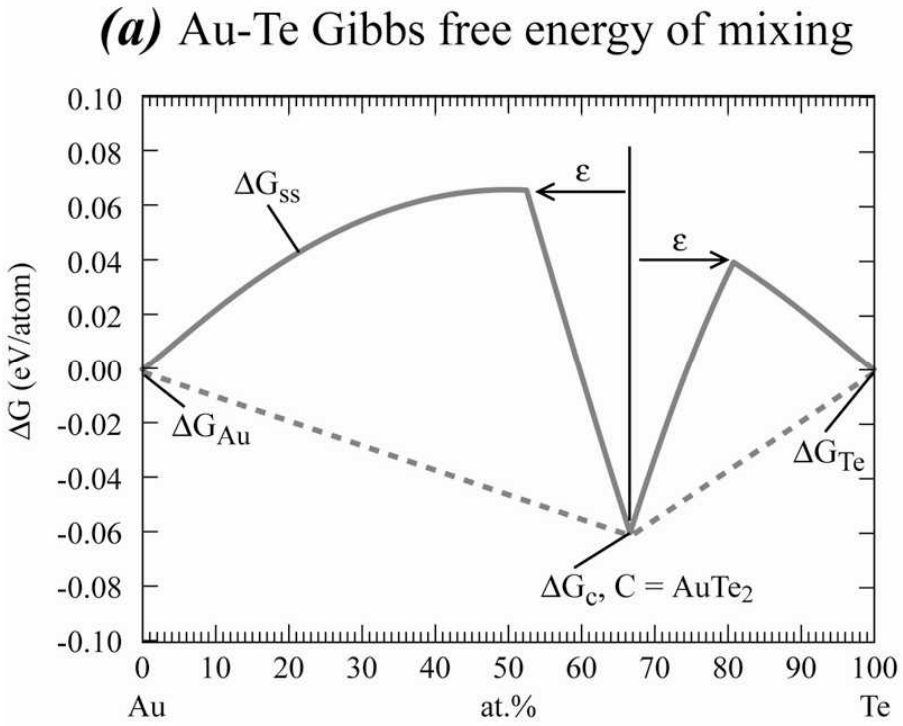


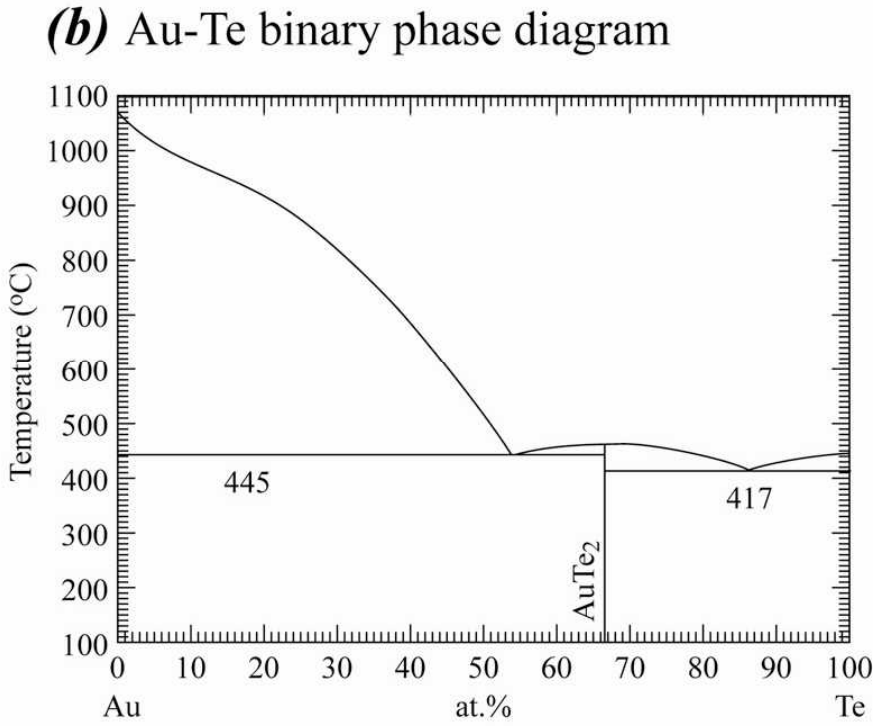


An Ideal Model must:

1. Accurately predicts aging as a function of time and oxygen tolerance;
2. Covers many species (Au, Bi, Te, O, …) with phase diagrams validation;
3. Addresses temperature and interfacial effects;
4. Allows engineering scales by using parallel kinetic Monte Carlo capability SPPARKS.

Key: Phase Diagram Incorporation





1. **Gibbs free energy for compounds:** $\Delta G_c = \sum_{i=0}^{4} b_0 \cdot T^i$

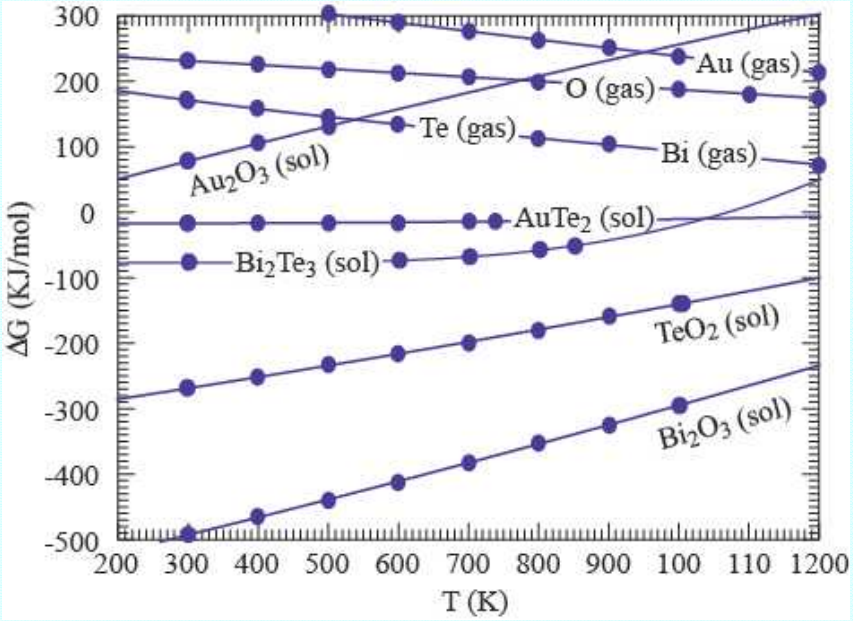
2. **Gibbs free energy for solid solution*:** $\Delta G_{ss} = kT \cdot \sum_{i=0}^{N} x_i \cdot \ln(x_i) + \sum_{i=1}^{N-1} \sum_{j>i}^{N} c_{ij} \cdot x_i \cdot x_j + \ldots$

3. **Near compound composition (<ε), ΔG is a linear combination of ΔG_c and ΔG_{ss}.**

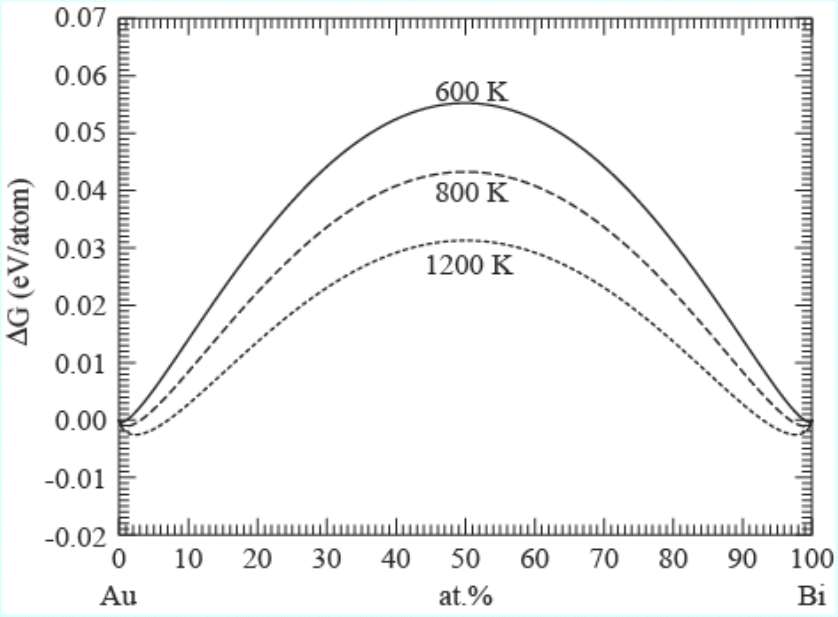
*: O. Redlich Kister, Ind. Eng. Chem., 40, 345 (1948)].

Thermodynamics Data

Experimental ΔG is available for all elements and compound of interest[1].



Experimental ΔG for solid solutions can be fitted from phase diagrams[2].



1. I. Barin, O. Knacke, and O. Kubaschewski, Thermochemical Properties of Inorganic Compounds (Springer-Verlag, Berlin, 1977).
2. Redlich, and A. T. Kister, Ind. Eng. Chem., 40, 345 (1948); C. Servant, E. Zoro, B. Legendre, Comp. Coup. Phase Diag. Thermochem., 30, 443 (2006).

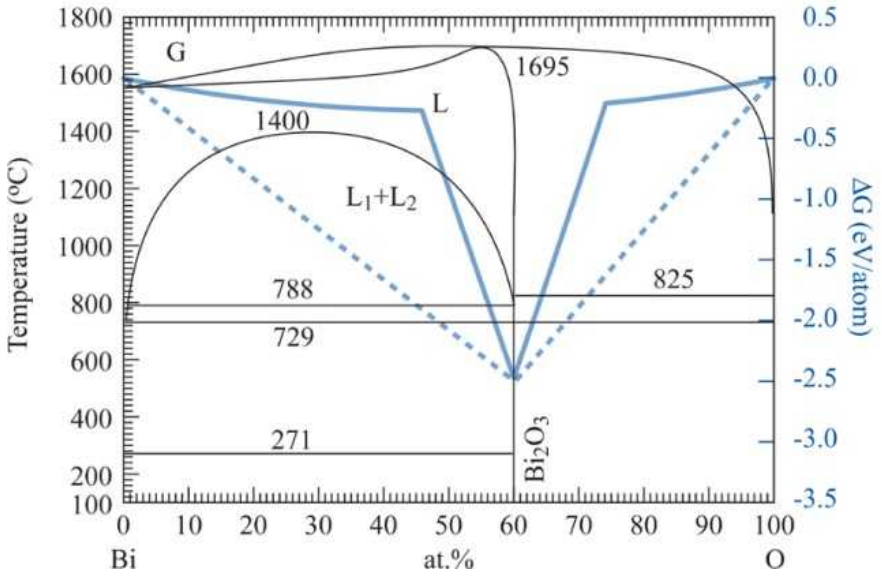
Phase Diagram Validations

$$\varepsilon_{AuTe_2} = 0.20, \varepsilon_{Au_2Bi} = 0.10, \varepsilon_{Au_2O_3} = 0.10, \varepsilon_{Bi_2Te_3} = 0.10, \varepsilon_{TeO_2} = 0.10, \varepsilon_{Bi_2O_3} = 0.20$$

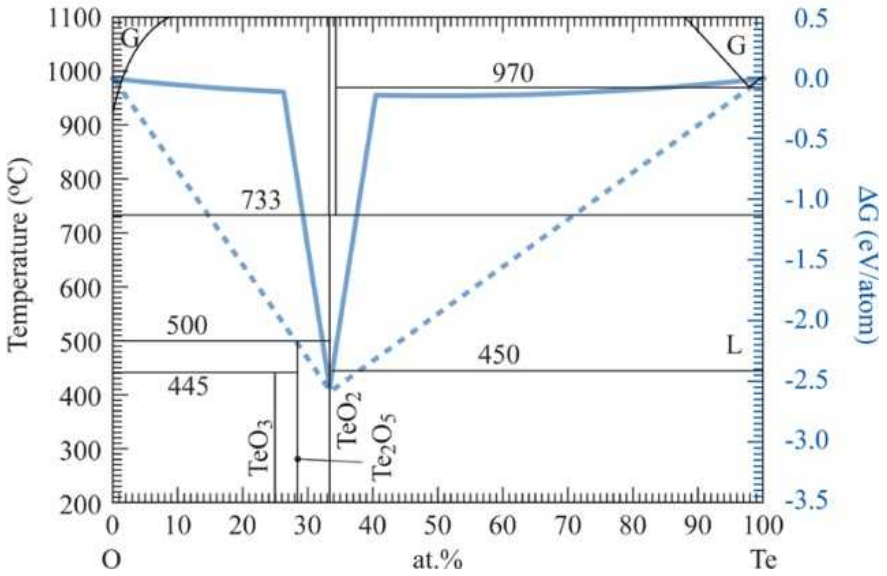
$$c_{AuBi} = 0.4353^{1,2}, c_{AuTe} = 0.333, c_{AuO} = 0.5, c_{TeBi} = -0.1, c_{TeO} = -0.5, c_{BiO} = -1.0$$

All superimposed binary Gibbs free energy of mixing curves, shown in blue, are at 25°C

(a) Bi-O binary phase diagram



(b) O-Te binary phase diagram



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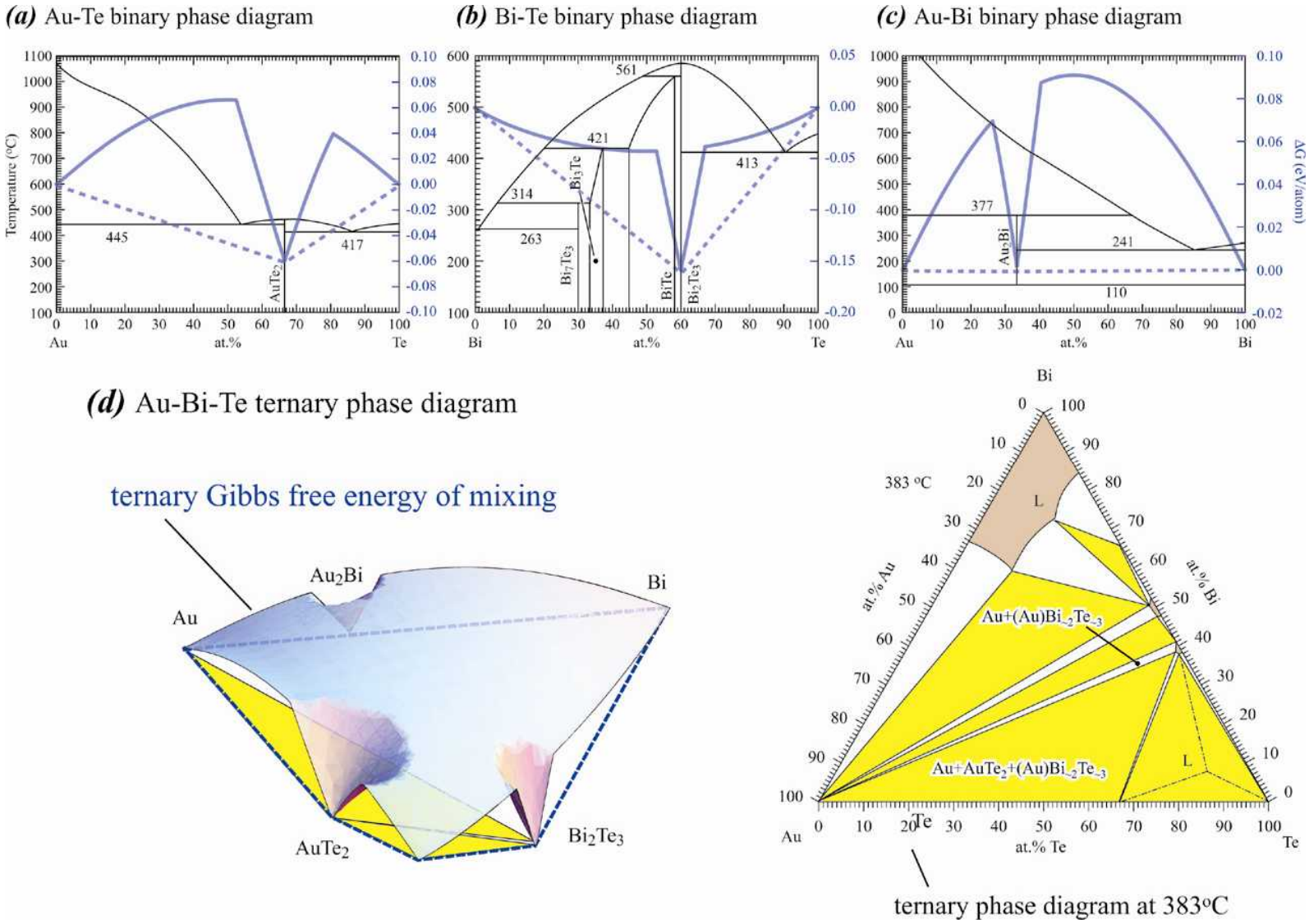
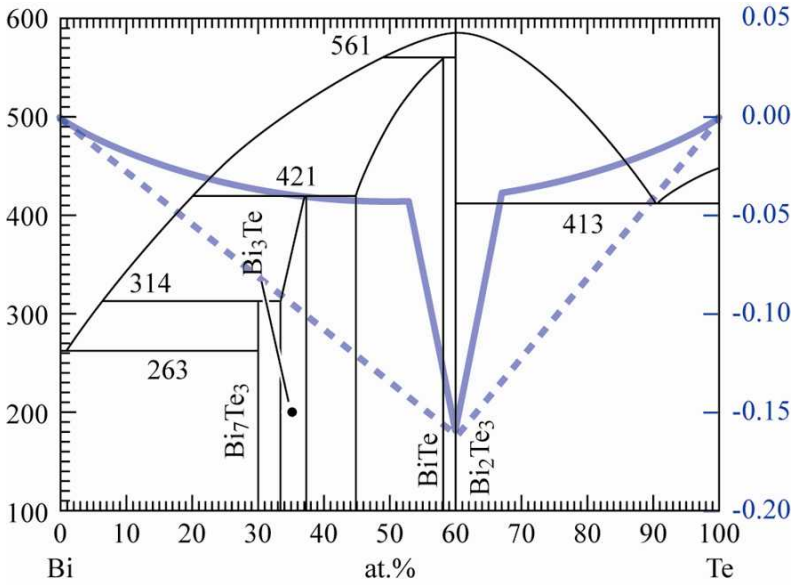
Phase Diagram Validations - continue

All superimposed binary Gibbs free energy of mixing curves, shown in blue, are at 25°C

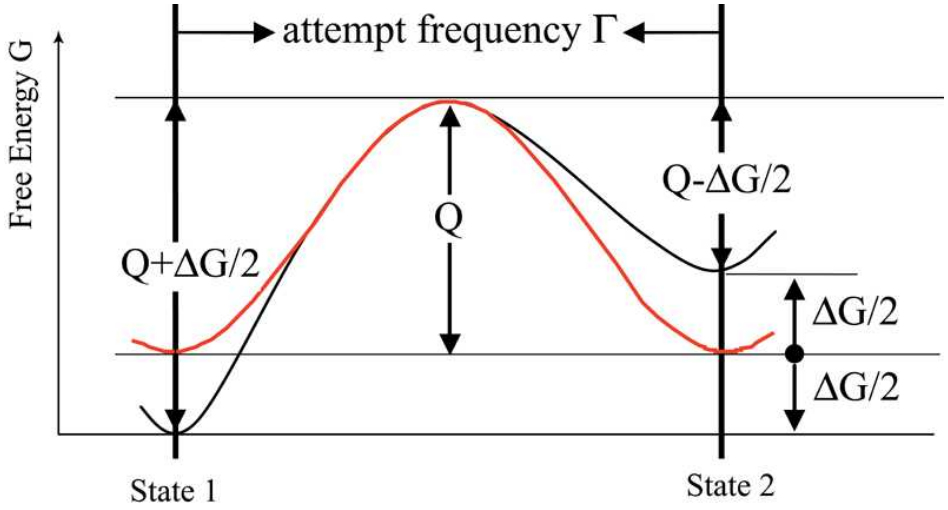


Thermodynamics + Kinetics Model



Thermodynamics

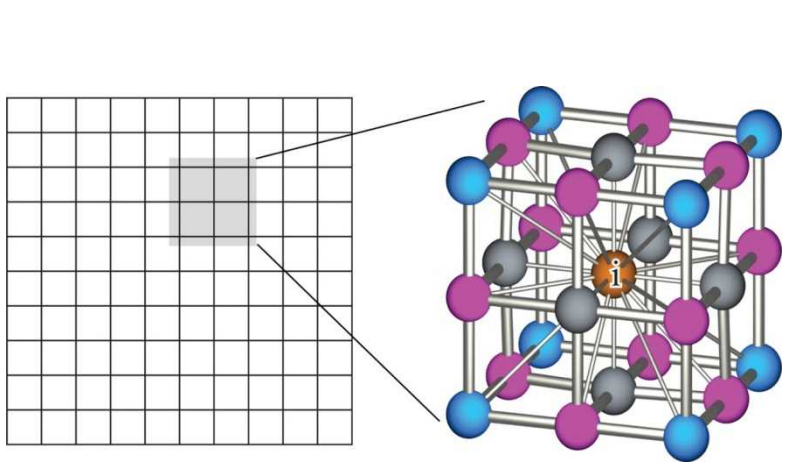
1. Our thermodynamics model (e.g., left figure) defines free energies (G) of different phases as functions of composition;
2. This model is validated against experimental Au-Bi, Au-Te, Bi-Te, Bi-O, Te-O binary and Au-Bi-Te ternary phases diagrams;
3. It allows calculation of Gibbs free energy change ΔG for any phase transition.

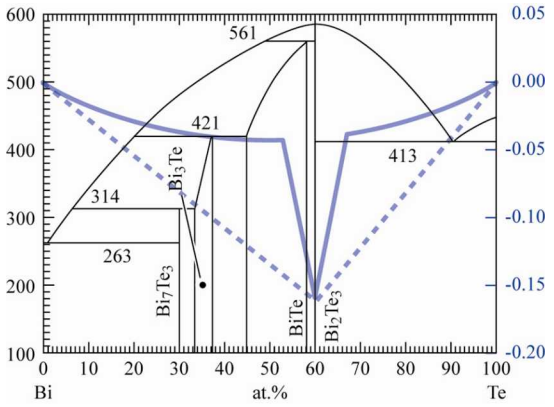


Kinetics

1. Our kinetics model (left figure) defines an energy barrier Q for phase transition;
2. Combining thermodynamics and kinetics models then defines forward/backward energy barriers (Q-ΔG/2)/(Q+ΔG/2);
3. Arrhenius equation can then be used to simulate phase evolution.

Kinetic Monte Carlo (kMC) Phase Transformation Simulation



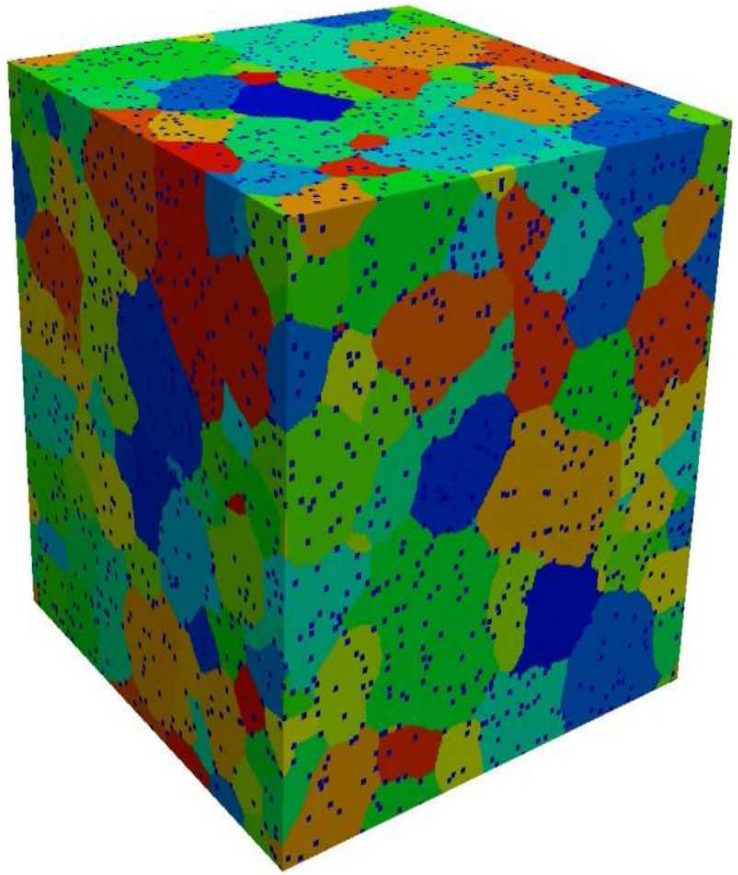


$$\Gamma = \nu \cdot \exp\left(-\frac{Q + 0.5\Delta G}{kT}\right)$$

1. Divide material into a lattice (simple cubic lattice assumption);
2. Assign atoms to each lattice sites;
3. Calculate compositions at lattice sites;
4. Define events (e.g., switch atoms between neighboring sites);
5. Calculate Gibbs free energy change due to each event;
6. Executes events according to the rates from Arrhenius equation;
7. March the clock accordingly (e.g., average time per event for the system).

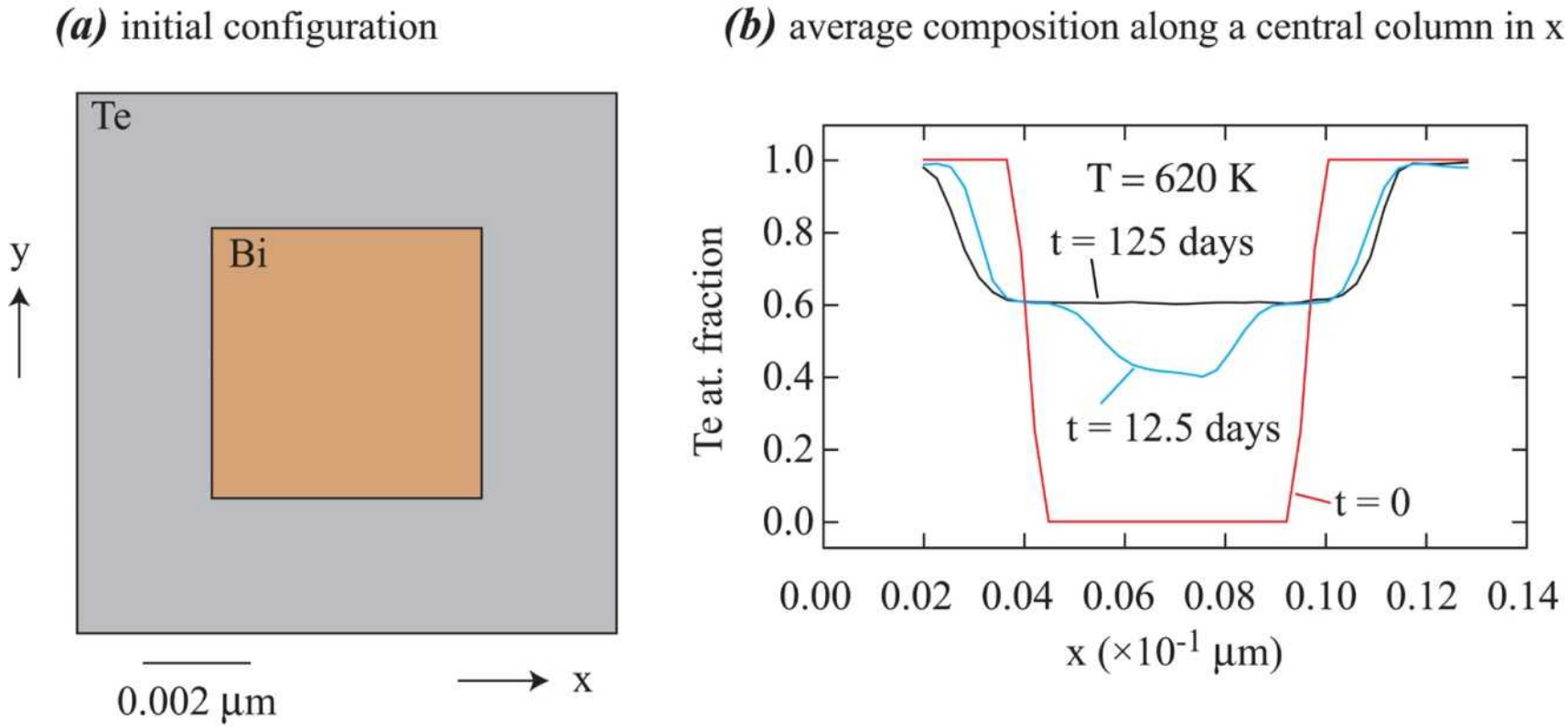
Towards Engineering Scales: Parallel Simulations

1. The Stochastic Parallel PARticle Kinetic Simulator (SPPARKS), developed at Sandia in recent years, is an ideal parallel kMC code for simulating phase transformation aging of the Au/Bi_2Te_3 system at the engineering scales;
2. The key to enable parallel kMC is to avoid different processors to operate on the same material regions at the same time. This is achieved by dividing the material domain of each processor into sectors, and all processors loop over these sectors sequentially;
3. SPPARKS allows users to develop applications specific to the problem of interest rapidly.



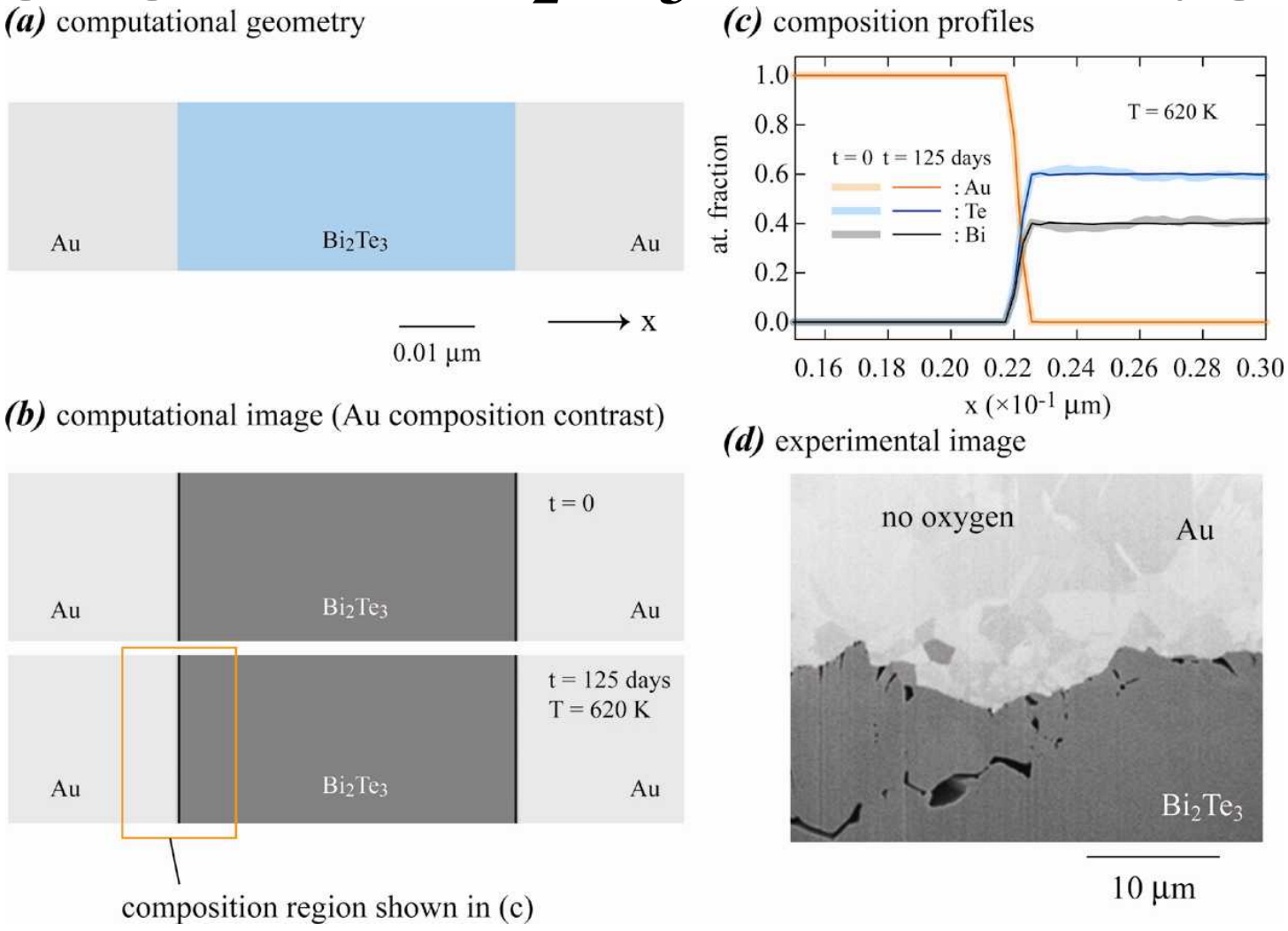
Our model has been implemented in SPPARKS.

Validation: Dissolution of Bi in Te



The simulation successfully predicts the formation of a stoichiometric Bi_2Te_3 compound, validating the model.

Aging of Au/Bi_2Te_3 without Oxygen

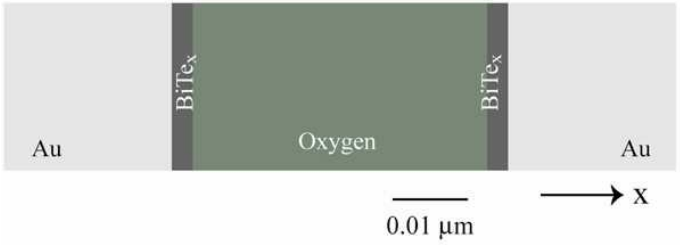


No second phase formation in both simulations and experiments.

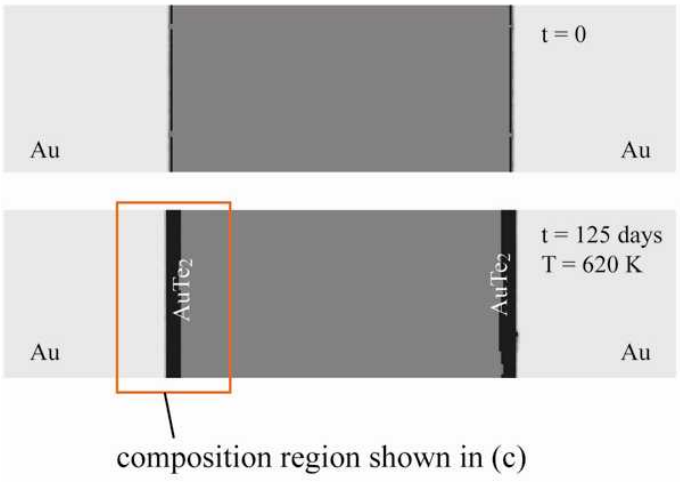
Experiment: electroplated Au on Bi_2Te_3, annealed at 240°C for 6 months in Ar, SEM backscattered electron image.

Aging of Au/Bi_2Te_3 with Oxygen

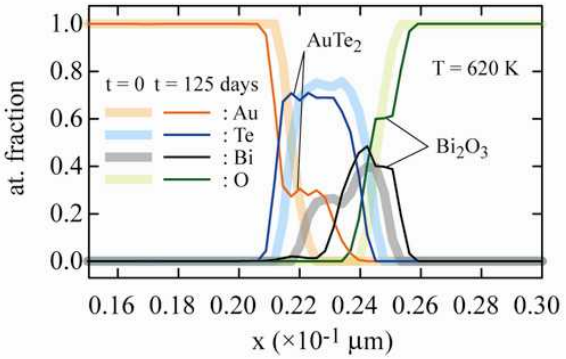
(a) computational geometry



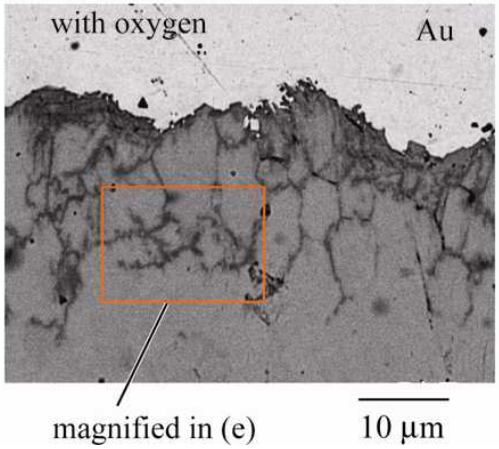
(b) computational image (Au composition contrast)



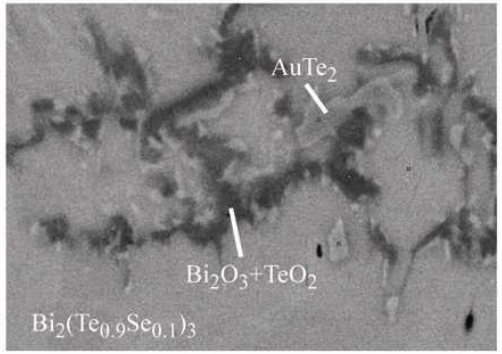
(c) composition profiles



(d) experimental image



(e) EDS analysis of experimental image



at.% measured from EDS spectra

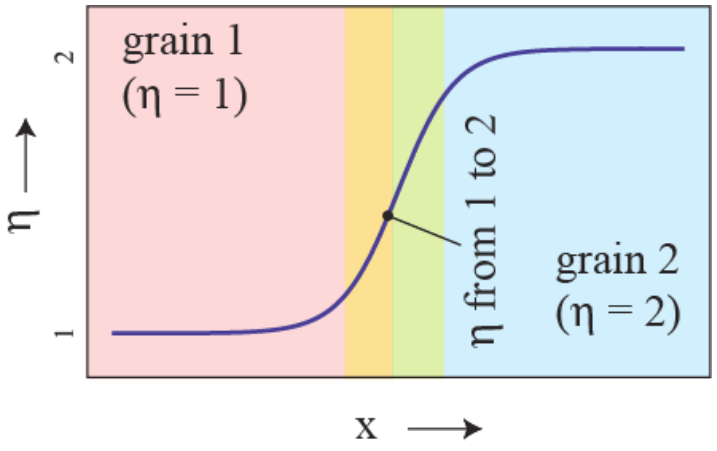
	O	Se	Te	Au	Bi
matrix	0	7	52	0	41
dark precipitates	63	0	15	1	20
light precipitates	0	2	61	29	9

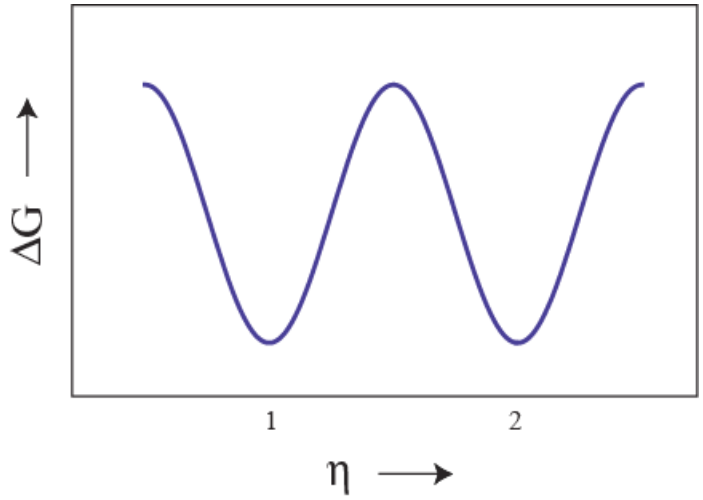
Extensive $AuTe_2$ formation in both simulations and experiments.

Experiment: electroplated Au on Bi_2Te_3, annealed at 240°C for 100 days in 10^{-6} Torr, SEM backscattered electron image.

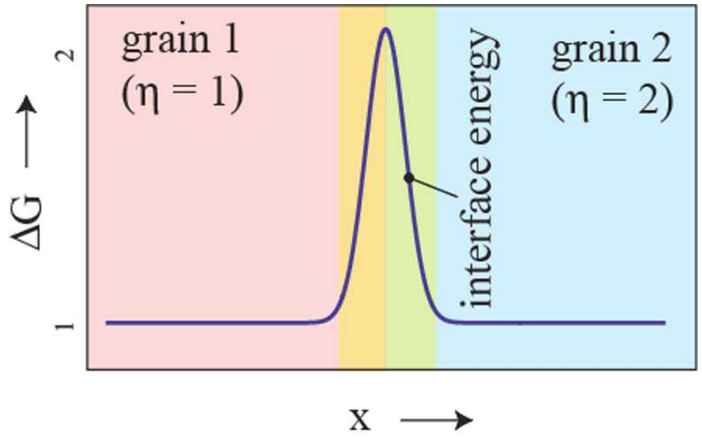
Grain Growth Model

Captures grain boundary energies to ensure accurate grain growth simulations.





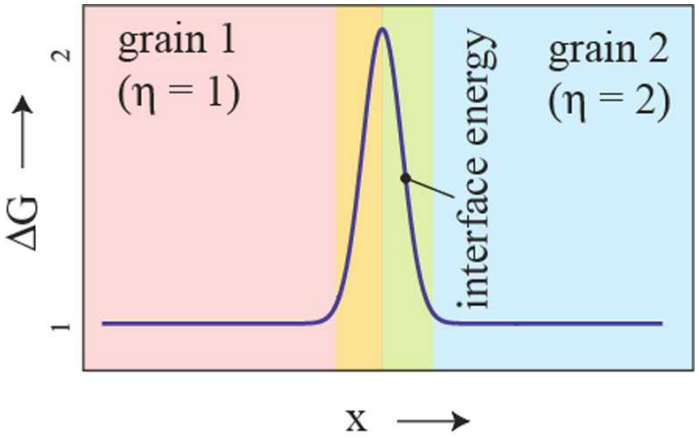
Grain growth is again based on
Q & ΔG calculation.



Physics ensures transformation towards lower energy, larger grain states.

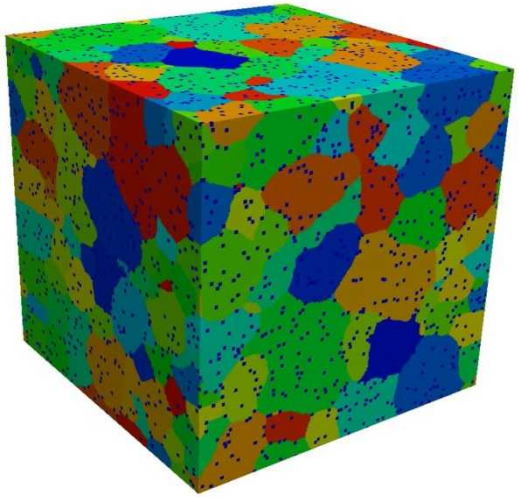
Ref. :X. W. Zhou, et al. , Acta Mater., 47, 1063 (1999).

Kinetic Monte Carlo (kMC) Grain Growth Simulation



$$\Gamma = \nu \cdot \exp\left(-\frac{Q + 0.5\Delta G}{kT}\right)$$

1. Divide material into grids;
2. Assign grain numbers (colors) to each grid;
3. Define possible events (e.g., flip the grain number);
4. Calculate Gibbs free energy changes due to each event;
5. Executes events according to the rates from Arrhenius equation;
6. March the clock accordingly (e.g., average time per event for the system).



Conclusions

1. Our SPPARKS model enable microstructure evolution to be accurately predicted at engineering scales. We found that for Au/Bi_2Te_3, oxygen environment can cause second phase formation at the interface;
2. Our model is based directly on experimental thermodynamics data, and has been validated from phase diagrams;
3. It can be easily extended to include more species (Au, Bi, Te, O, Sb, S, …);
4. Temperature and interfacial effects can be incorporated;
5. Can easily include other kinetic processes (SPS, extrusion, etc.);
6. Grain growth model is currently being added.