

Growth Simulations of Single Crystal Perovskite Alloys

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1. Why is this research interesting?

(Perovskite Crystals? → motivation)

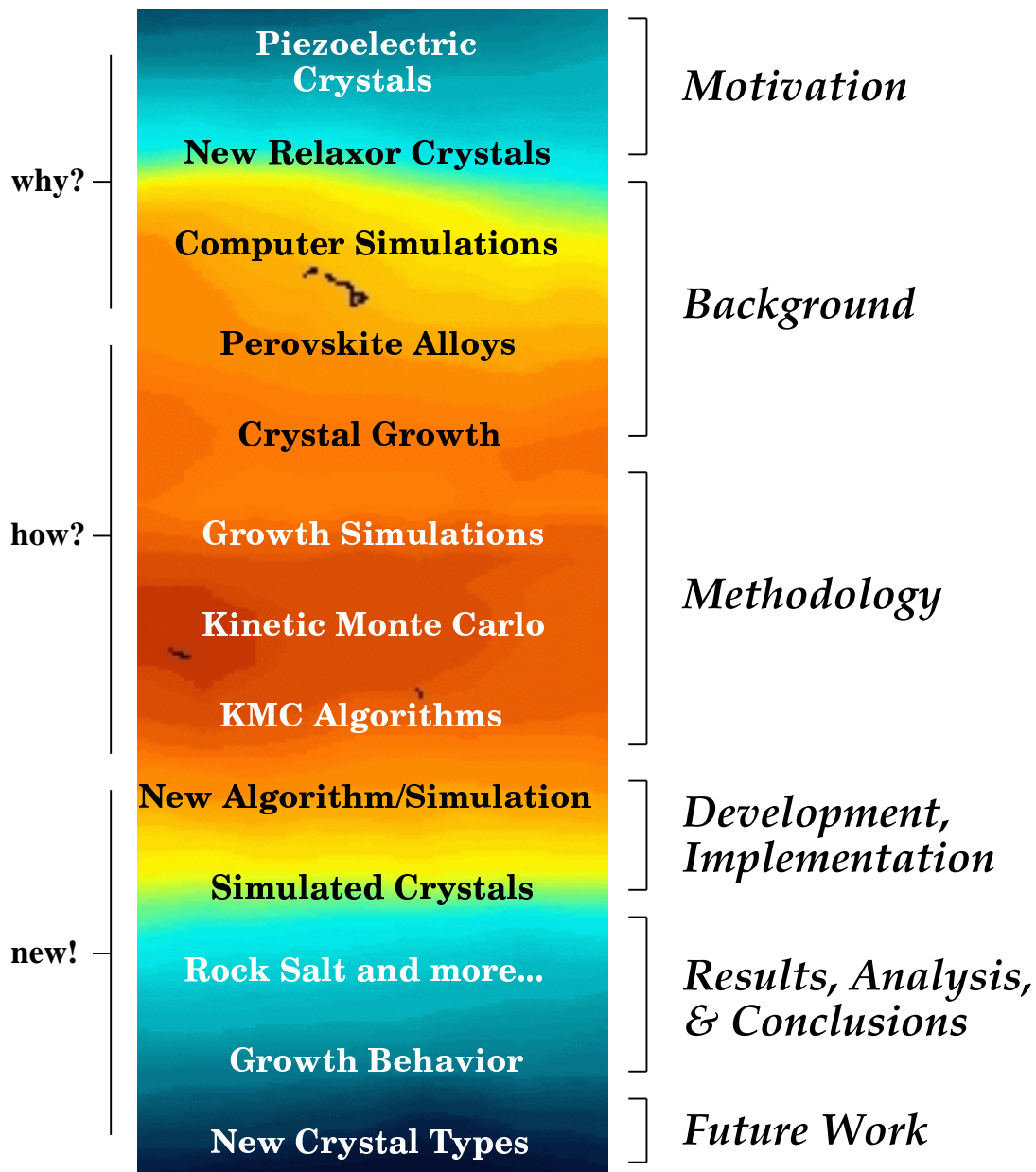
2. How was it done?

(Background: Computer Simulations, Materials, Methods)

3. What new things have I contributed?

(New method, algorithm, simulation, and results.)

T-PLOTT: Tahan Pain-Level-of-Talk Topography



joy  pain

Impetus: New Piezoelectric Crystals

1. Piezoelectric crystals are examples of **electromechanical actuators**.
2. A “new” class of actuating crystals was discovered by Park and Shrout at Penn State (1997):
 - **single crystal perovskite alloys** including **PMN-PT**, **PZN-PT** (“Relaxor-PTs”),
 - **piezoelectric properties** ten times better than the best today,
 - ≡ **E-field to strain ratios** exceeding 1%.
3. Truly remarkable with many possible applications.

However,

4. Difficult to grow big with the best possible piezoelectric properties.
5. Crystal growth theory/**simulations** may provide experimental guidance and further understanding.

Motivation of This Research

- **Kinetic Monte Carlo** (KMC) computational methods have been **applied successfully to crystal growth simulations**.
- Kinetic Monte Carlo seeks to **simulate the relaxation processes of physical systems away from equilibrium**, e.g. growth processes.
- **Traditional KMC crystal growth models/simulations are inadequate in simulating these new crystals:**
 - they do not incorporate **electrostatic interactions** between ions in the crystal,
 - they only consider **short-range (nearest-neighbor) interactions**.
- **We:**
 1. **incorporate long-range electrostatic interactions** into the formalism of KMC,
 2. **develop a new algorithm** to realize our enhanced model,
 3. **implement this algorithm in a long-range, ionic crystal growth simulation**.

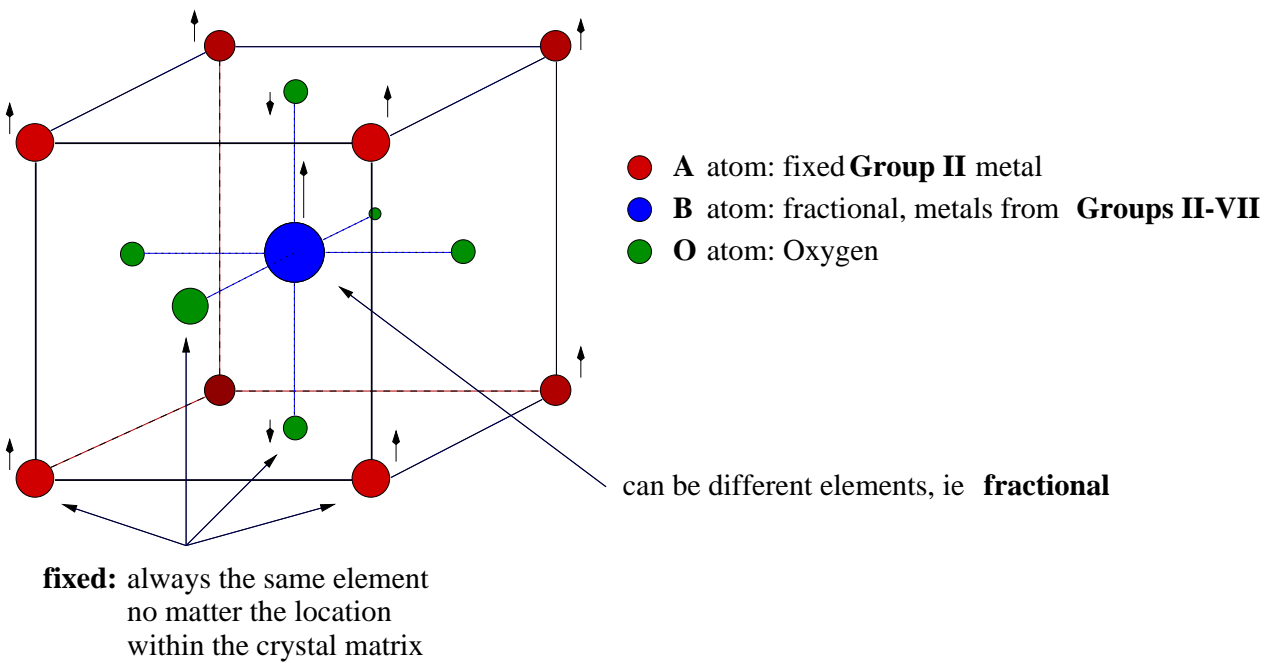
Steps to a Growth Simulation

1. **Understand the materials** to be simulated (crystals to be grown).
2. **Create a mathematical model** which captures the physics of the system (as much as possible).
3. **Develop an algorithm** to realize—accurately—that model through time (the KMC method).
4. **Implement it in a simulation** environment.

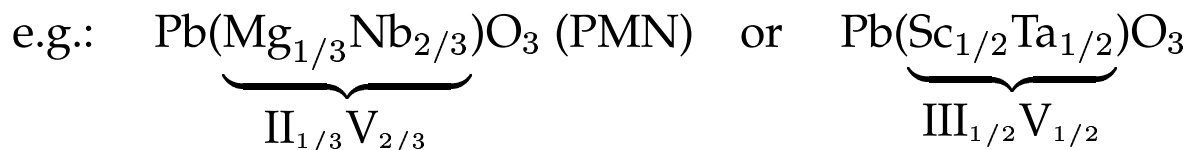
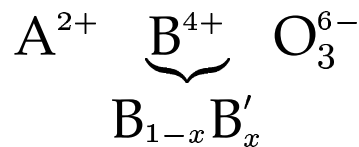
Single Crystal Perovskite Alloys

- **perovskite alloys:** oxide compounds usually containing a mixture of alkaline and transition metals.
- Just stack the unit cells together to get a **single crystal**.

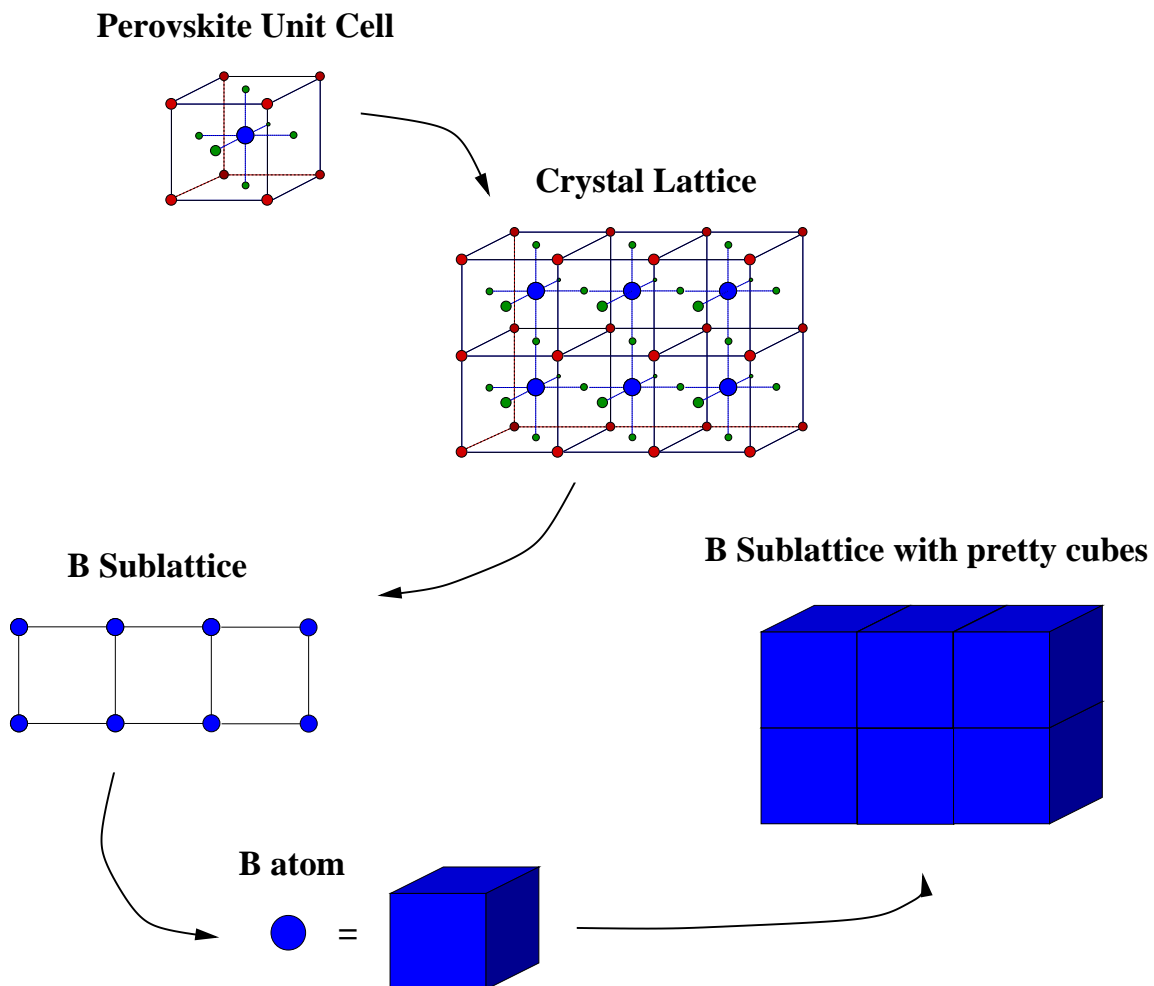
Unit Cell, Perovskite Alloy - ABO_3



Fractional B-sites?



Reduction to B Sublattice



- Since the A-site atoms and Oxygen atoms are constant throughout the crystal, we can remove them (gaining a constant energy term).

Bellaiche and Vanderbilt (BV) Model of Atomic Ordering

- Reduce system to a **B sublattice**.
- Assume long-range Coulomb interactions between ions are dominant ordering mechanism.

$$E_B = \text{electrostatic energy of B sublattice} = C \sum_{l \neq l'} \frac{\Delta q_l \Delta q_{l'}}{|l - l'|}$$

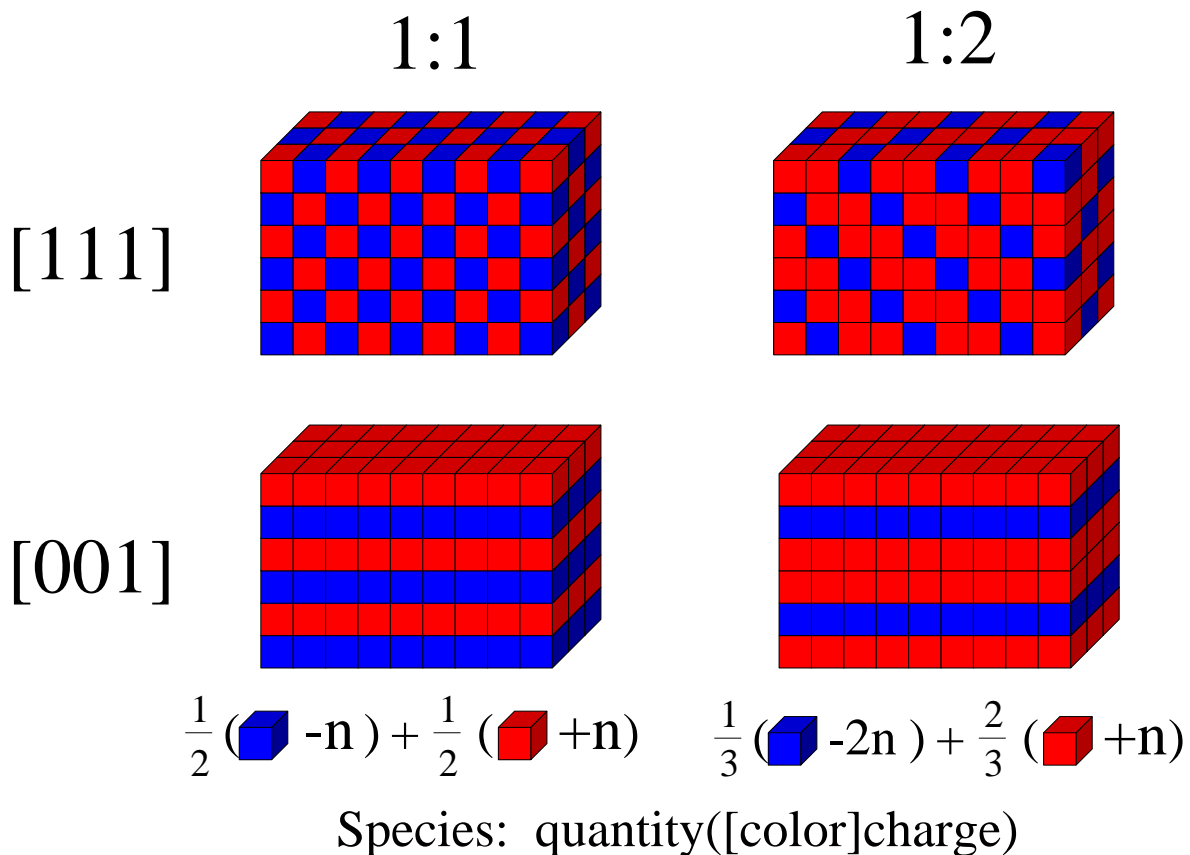
where Δq_l is the charge of a B site ion, and l is the vector to that ion.

- Success in predicting the B-site ordering behavior of perovskite alloys observed experimentally.
- BV \rightarrow equilibrium MC simulation \rightarrow no growth information.
- Our starting point.

What do we mean by ordering anyway?

B Sublattice Ordering

- B site charge (Q_B), on average, must equal +4.
- If we subtract this from the individual B elements, then we get **relative charges**, $\Delta q_B = Q_B - 4$.
- e.g.: $Q_{Mg} = +2 \rightarrow \Delta q_{Mg} = -2$
- B-site elements tend to exhibit **Long Range Order (LRO)**:



- Notice that the **B sublattice of relativized charges must be charge neutral**.

Crystal Growth from the Melt

◇ Laboratory Growth

- The high temperature flux technique.

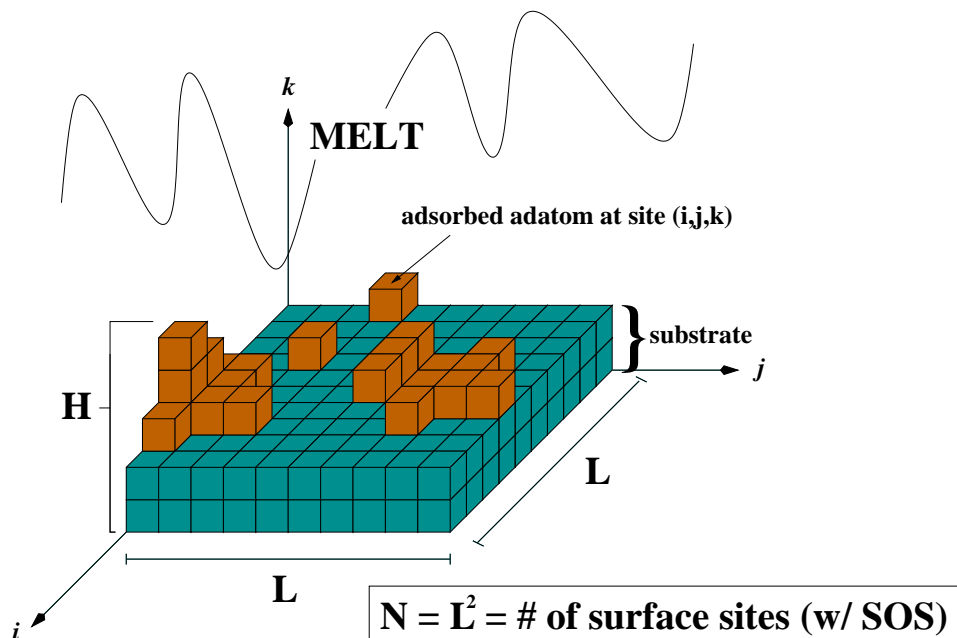
◇ Crystal Growth Simulations

- environmental parameters: **temperature (T)** and $\Delta\mu = \mu_s - \mu_l$, the **chemical potential difference** between the solid and liquid states.

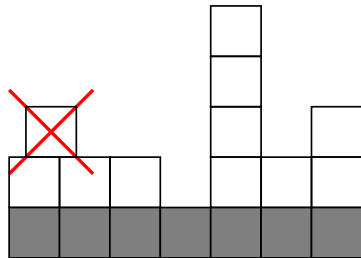
- **adatom**: simulation lingo for an atom or molecule.

- Three processes define crystal growth:

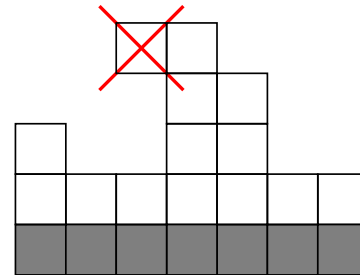
- 1] **adsorption**: adatom sticks to surface.
- 2] **evaporation**: adatom desorbs from surface.
- 3] **surface migration**: adatom travels across surface.



Simulation Restrictions

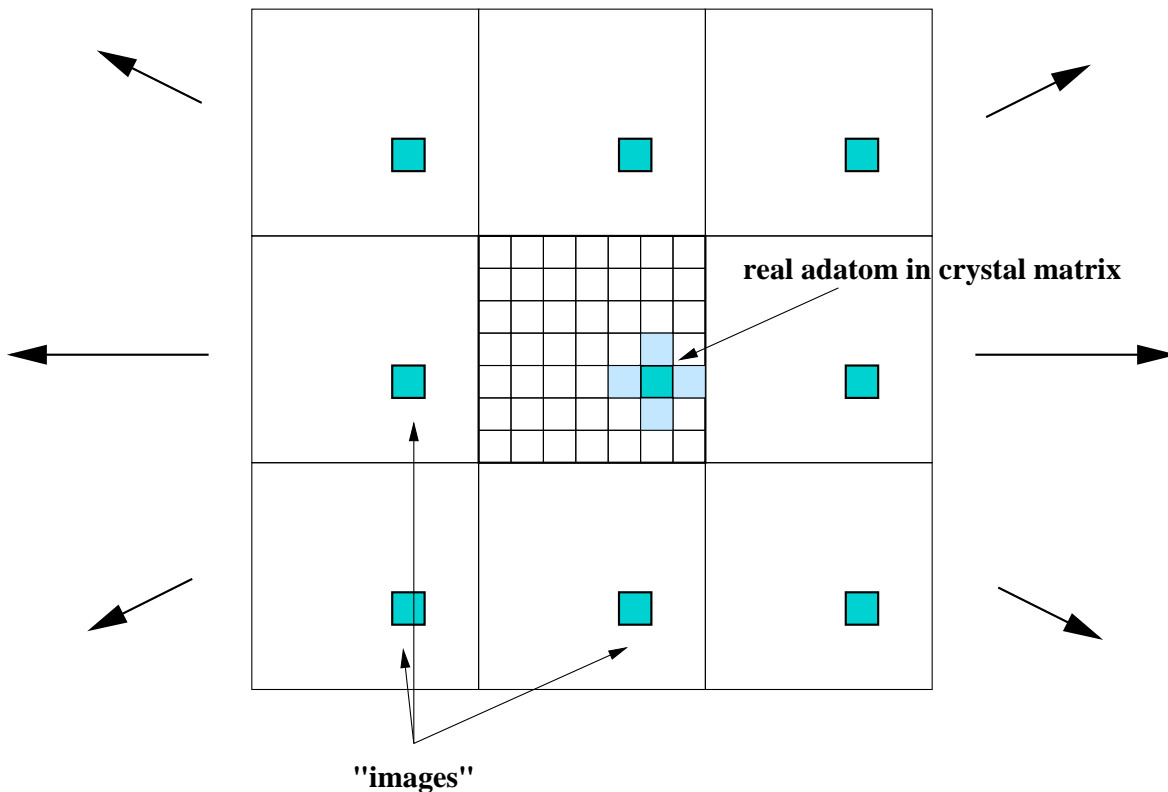


Only discrete placement on our perfect 3-d lattice.



Solid-on-Solid (SOS) restriction for adatom placement on the crystal surface.

Periodic Boundary Conditions (PBC)



Revised Model Describing our Crystal

We define the total energy of our crystal (\mathcal{C}) as

$$\mathcal{H}(\mathcal{C}) = \underbrace{E(\mathcal{C})}_{\text{total electrostatic energy}}^{BV \text{ model}} + \Delta\mu \underbrace{\sum_{(ij)} h_{ij}}_{\text{all adsorptions}}.$$

where h_{ij} is the height of an adatom “stack” in the crystal at (i, j) .

Kinetic Monte Carlo

- Crystal growth is a direct outcome of the competing processes of adsorption and evaporation (we ignore diffusion).
- Crystal growth is a *stochastic process* governed by the laws of thermodynamics.
- A KMC simulation, unlike equilibrium MC, aims to faithfully reproduce the time evolution of the system.

Defining the Process Rates

- Adatoms “stick” to the crystal surface with some constant rate w_{adsorb} dependent on the chemical potential difference, $\Delta\mu$, between the solid-liquid interface and the temperature.

We choose this rate of adsorption to be

$$w_{adsorb} = e^{\Delta\mu/kT}$$

- Adatoms evaporate from the surface with some rate w_{evap} dependent on their binding energy, ΔE , and on the temperature.

The rate of evaporation is calculated relative to the adsorption rate using the equilibrium condition given by the Boltzmann distribution, $Z^{-1} \exp\left[\frac{-\mathcal{H}(c)}{kT}\right]$, giving

$$w_{evap} = e^{-\Delta E/kT}$$

ΔE is situation specific and is calculated differently for short-range or long-range interactions.

Nearest-Neighbor vs. Long-Range Interactions

old *new*

Their difference manifests itself in the calculation of ΔE :

$$\Delta E = \mathcal{V}_o = \begin{cases} C \sum_{\langle l' \neq o \rangle} \Delta q_o \Delta q_{l'}, & \text{nearest neighbor} \\ C \sum_{(l' \neq o)} \Delta q_o \Delta q_{l'} \underbrace{v_{lr}(\mathbf{o} - \mathbf{l}')}_{\text{Ewald potential}}, & \text{long-range} \end{cases},$$

where \mathbf{o} and Δq_o ($o = (i, j, k)$) define the position and charge of the **surface adatom considered for evaporation**.

!!! The **long-range summation** over all adatoms in the infinite crystal lattice (PBC) is **ill-defined** and **conditionally convergent**.

- The **Ewald Summation technique** allows for consistent binding energy calculations and incorporates the charge neutrality of the system.
- **T.J. Walls** solved this problem last year. From him, **we have an equation for the Ewald potentials as a function of the distance between two adatoms within the crystal matrix: $v_{lr}(\mathbf{o} - \mathbf{l}')$** .

KMC Algorithms

- Our **process rate equations** coupled with choices for kT and $\Delta\mu$ completely define the evolution of our physical system.
- A **KMC algorithm** allows us to turn these into a **full-blown crystal growth simulation**.

BKL (Traditional) Algorithm

- (i) Randomly select an (i, j) pair from the L^2 possible surface sites;
- (ii) Generate a list, E , of possible events at (i, j) .
In our case, $E = \{adsorption, evaporation, no\ event\}$;
- (iii) Define the probability each event will occur by normalizing the event rates relative to the maximum possible rates.
- (iv) Generate a random number $r \in [0, 1)$ and choose the first event E_i such that $\sum_i^n P_i \geq r$;
- (v) Generate new configuration \mathcal{C} based on chosen event E_i ;

+ The maximum possible rate is determined by the maximum magnitude of $|\Delta E|$.

+ For nearest-neighbor interactions, $|\Delta E|_{max}$ is **constant**;
for long-range interactions, $|\Delta E|_{max}$ depends on $L^2 \times H$.)

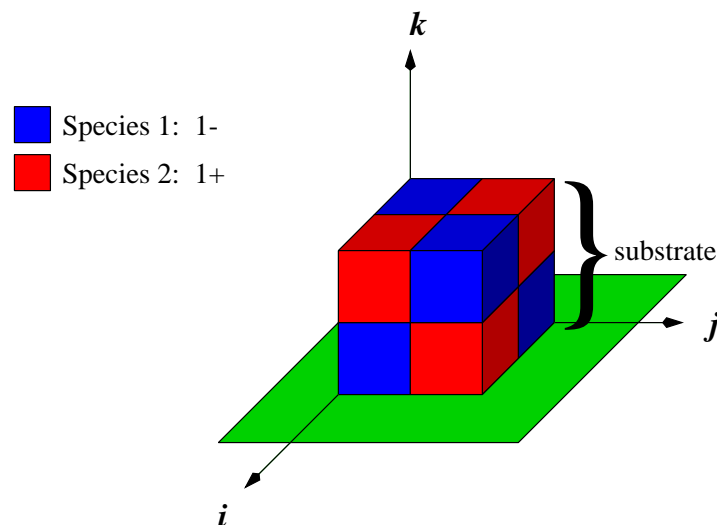
- **BKL breaks down for long-range model with increasing lattice size. Nothing ever happens!**

New Algorithm

- (i) Generate a list, E , of all possible events per time step; There are $2N$ possible events: an evaporation or an adsorption could happen on each of the $N = L^2$ surface sites;
 - (ii) Calculate the rates (w) of adsorption and evaporation for each site on the surface ($2N$ rates);
 - (iii) Normalize these $2N$ rates, giving probabilities, P_i , for evaporation/adsorption on site 1, on site 2, ... on site N , which all add to unity;
 - (iv) Generate a random number $r \in [0, 1)$ and choose the first event E_i such that $\sum_i^n P_i \geq r$. An event will always be chosen;
 - (v) Generate new configuration C based on chosen event E_i .
-
- **An adsorption or evaporation happens at every time step, guaranteed.**
 - No need to calculate $|\Delta E|_{max}$.
 - Necessitates more data structures—much harder to program.
 - **MC time step = L^2 algorithm iterations.**

Long-Range 2×2 Walk Through

The Crystal at $t = 0$



The Surface Potential Array, U

- Holds the potential or binding energy (ΔE) of the $\mathbf{N} = \mathbf{L}^2$ surface adatoms that can evaporate.

$$U_{ij} \equiv U_{\mathbf{o}} = \sum_{(\mathbf{o} \neq \mathbf{l}')} \Delta q_{\mathbf{o}} \Delta q_{\mathbf{l}'} V_{|\mathbf{o}-\mathbf{l}'|}$$

$$U(0) = \begin{pmatrix} -1.682327 & -1.682327 \\ -1.682327 & -1.682327 \end{pmatrix}$$

The Probability Event List, P

- Holds the normalized probabilities of the $2N$ possible events (N adsorptions, N evaporations).

$$P_{m=1\dots 2N} = \frac{w_m}{\sum_m w_m}$$

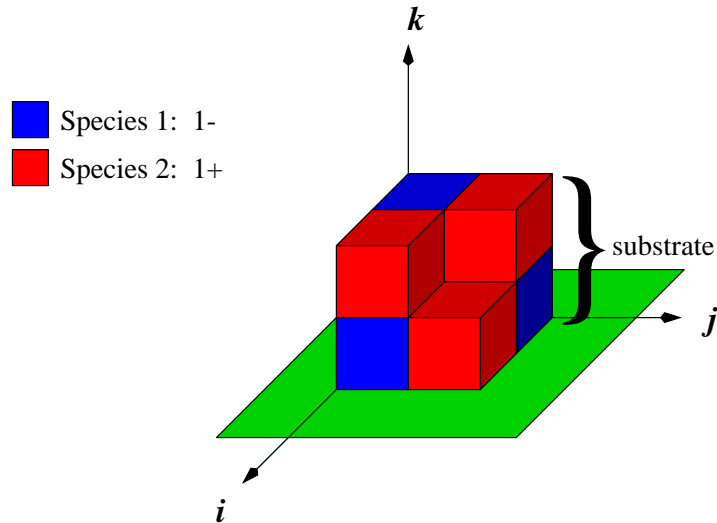
where, if you'll remember,

$$w_m = \text{rate of event } m = \begin{cases} e^{\Delta\mu/kT}, & \text{if } m \text{ is even} \\ e^{U_{ij}/kT}, & \text{if } m \text{ is odd} \end{cases}$$

$$P(0) = \left\{ \begin{array}{c|cccc|c} m & (x, y, z) & Type & Rate & Probability & Total \\ \hline 1 & (1, 1, 3) & adsorb & 0.135335 & 0.105311 & 0.105 \\ 2 & (1, 2, 2) & evap & 0.185941 & 0.144689 & 0.250 \\ 3 & (2, 1, 3) & adsorb & 0.135335 & 0.105311 & 0.355 \\ 4 & (2, 1, 2) & evap & 0.185941 & 0.144689 & 0.500 \\ 5 & (1, 2, 3) & adsorb & 0.135335 & 0.105311 & 0.605 \\ 6 & (1, 2, 2) & evap & 0.185941 & 0.144689 & 0.750 \\ 7 & (2, 2, 3) & adsorb & 0.135335 & 0.105311 & 0.855 \\ 8 & (2, 2, 2) & evap & 0.185941 & 0.144689 & 1.000 \end{array} \right\}$$

- Select an event via a random number $r_0 = 0.885954$.

The Crystal at $t = 1$



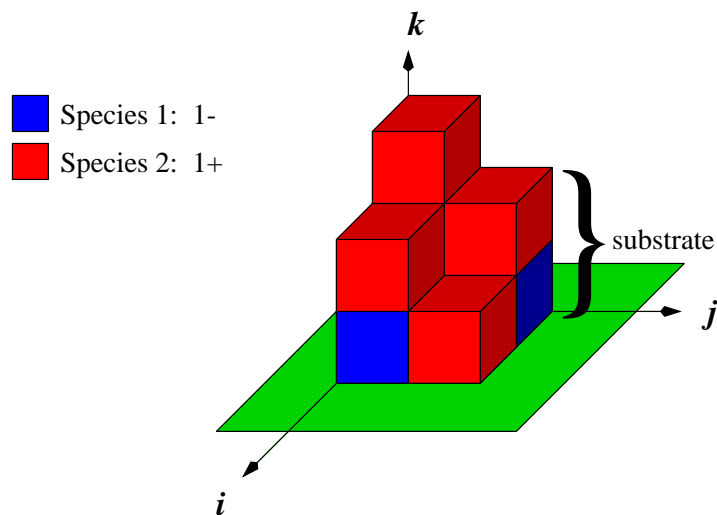
- Recompute U and P and generate $r_1 = 0.057315$:

$$U(1) = \begin{pmatrix} -0.867998 & -1.181894 \\ -1.181894 & -2.000866 \end{pmatrix}$$

$$P(1) = \left\{ \begin{array}{ccccc} m & (x, y, z) & Type & Rate & Probability \\ \hline 1 & (1, 1, 3) & adsorb & 0.135335 & 0.079156 \\ 2 & (1, 1, 2) & evap & 0.419791 & 0.245531 \\ 3 & (2, 1, 3) & adsorb & 0.135335 & 0.079156 \\ 4 & (2, 1, 2) & evap & 0.306679 & 0.179373 \\ 5 & (1, 2, 3) & adsorb & 0.135335 & 0.079156 \\ 6 & (1, 2, 2) & evap & 0.306697 & 0.179383 \\ 7 & (2, 2, 3) & adsorb & 0.135335 & 0.079156 \\ 8 & (2, 2, 2) & evap & 0.135218 & 0.079087 \end{array} \right\}$$

- This time an adsorption event was selected.
- We use another random number to determine which species will be adsorbed (relative to their quantities).

The Crystal at $t = 2$



- The crystal evolves in this manner...
- There are many tricks for speeding up the calculation of U and P and for searching through P ...
- Time complexity = $\mathcal{O}(N_T \approx L^2 \times H)$.
- But that's my problem, not yours. **On to the results!**

Verifying the Simulation

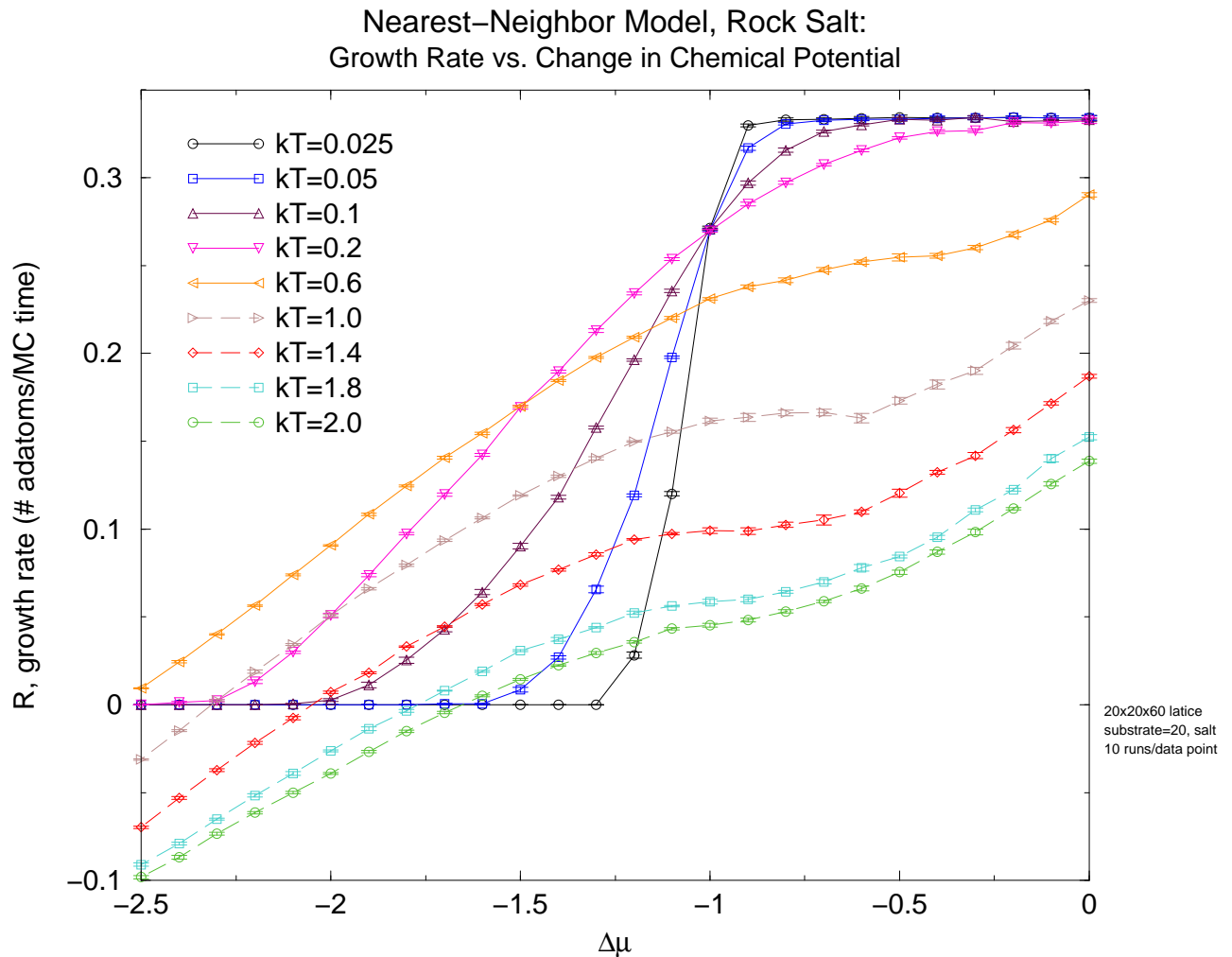
- Simplest crystal—good testbed: **Rock Salt** ($\Delta q = \pm 1$).
- (In our BV—B sublattice model, this includes groups of perovskite alloys such as $\text{III}_{1/2}\text{V}_{1/2}$ ($\Delta q = \pm 1$) and $\text{II}_{1/2}\text{VI}_{1/2}$ ($\Delta q = \pm 2$).
- **Nearest-Neighbor vs. Long-Range Comparison.**
- The right ordering should be produced: **$[111]_{1:1}$ order.**
- **Growth Rates:** should see reasonable **correlation with temperature and $\Delta\mu$** , phase transitions (solid to liquid).
- **Growth behavior** should match physical intuition and traditional Kinetic Monte Carlo results.

Modes of Growth predicted by Traditional KMC:

- + **layer-by-layer growth:** a crystal layer tends to be completed before a new layer is started above it;
- + **rough growth:** many crystal layers grow at the same time, forming hillocks and cavities on the crystal surface;
- + Transitions from **negative growth** to **no growth** to **layer-by-layer** growth to **rough growth** as a function $\Delta\mu$ and kT .

Nearest-Neighbor Tests

- $20 \times 20 \times 60$ crystal matrix.
- Choice of parameters: kT and $\Delta\mu$.
- Growth rate, $R \equiv \#$ of adsorbed adatoms / MC time.



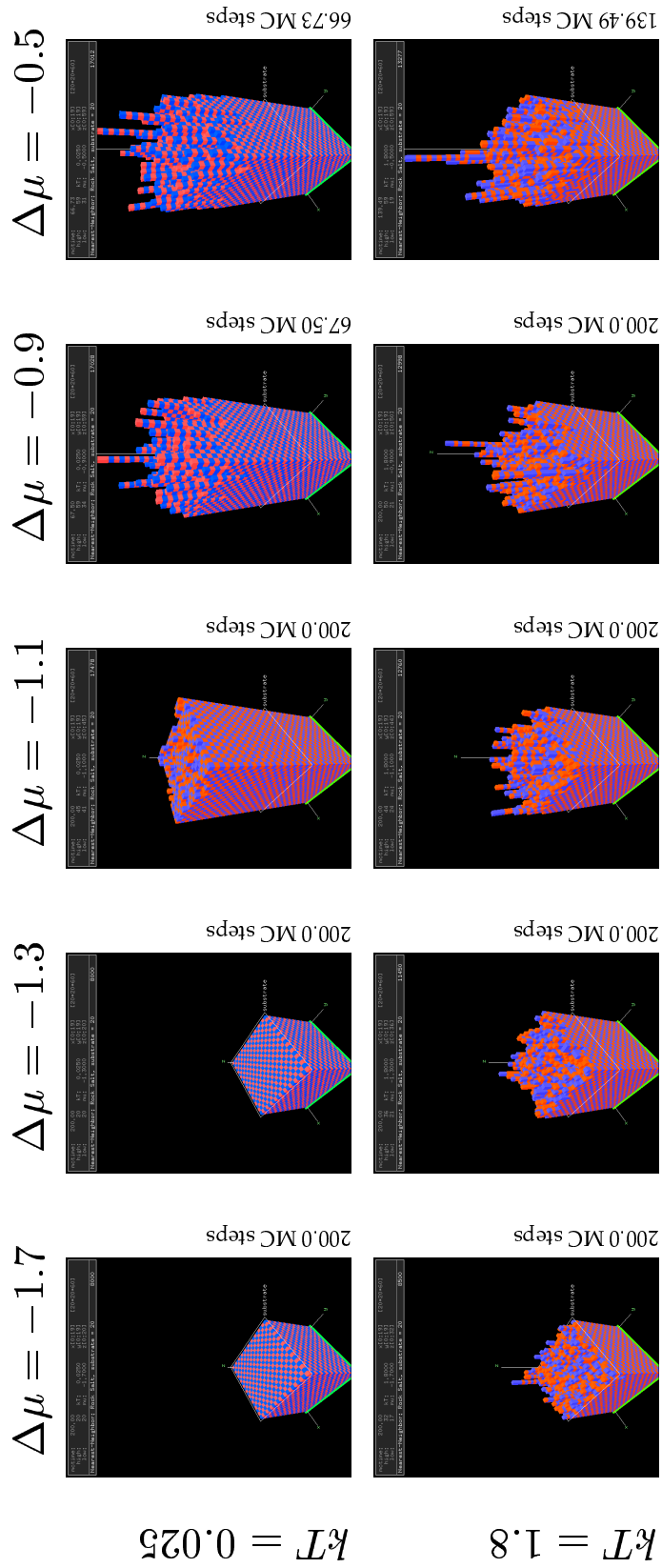
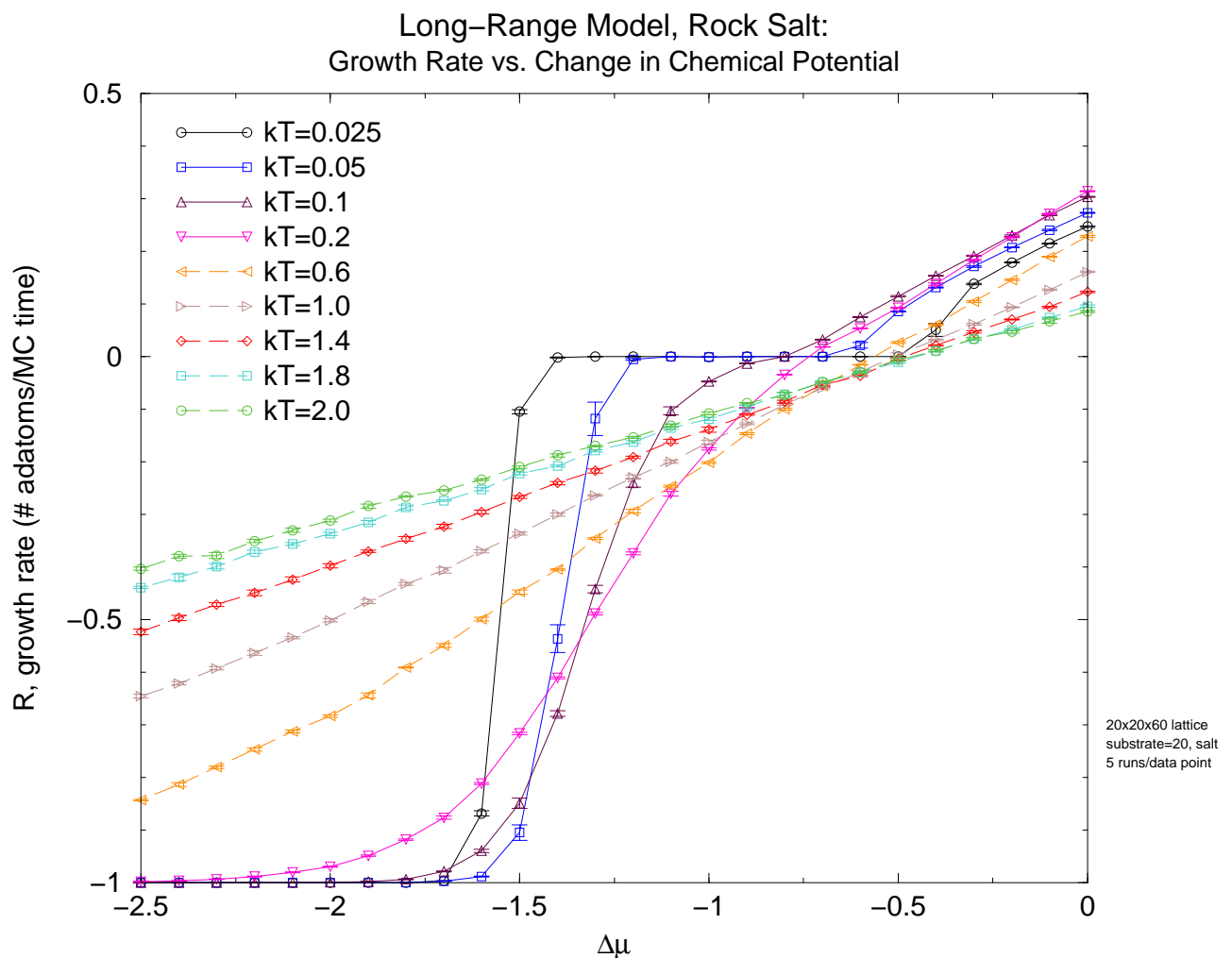


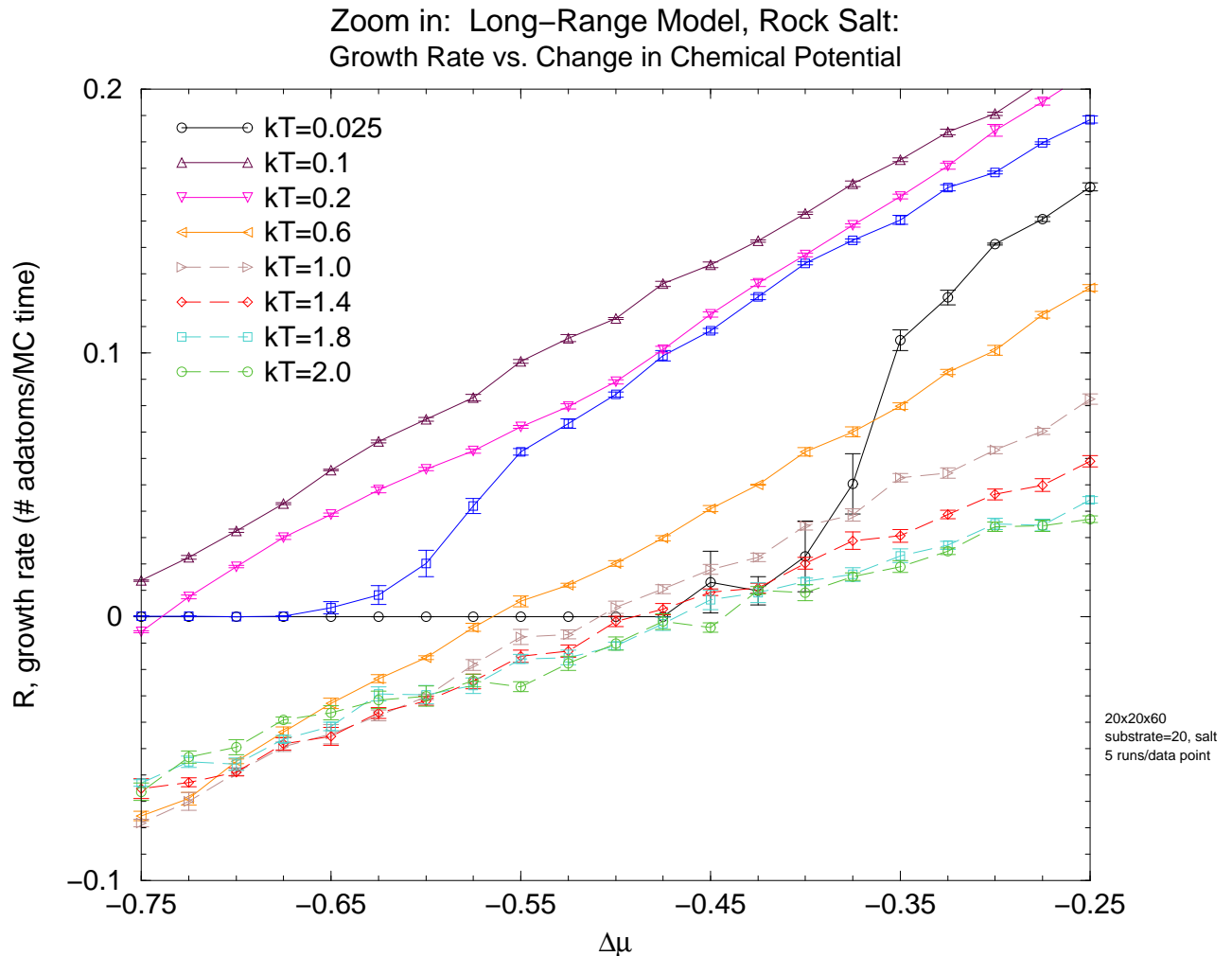
Figure 1: Nearest-Neighbor Simulations for Rock Salt, $20 \times 20 \times 60$ crystal matrix: from left to right $\Delta\mu$ increases from low to high; temperature increases going downward, from very low to very high.

Long-Range Model

- $20 \times 20 \times 60$ crystal matrix.
- Parameter range same as n-n.
- Where's the physics?



- Let's look at a range of growth rates comparable to the nearest-neighbor graph.



- Eventhough the crystal is charge neutral and the Ewald summation tries to ensure this, there is still a **finite size effect** across our range of lattice sizes.
- This lattice-size dependence of the parameters will go away with increasing lattice size ($\gg 100$).

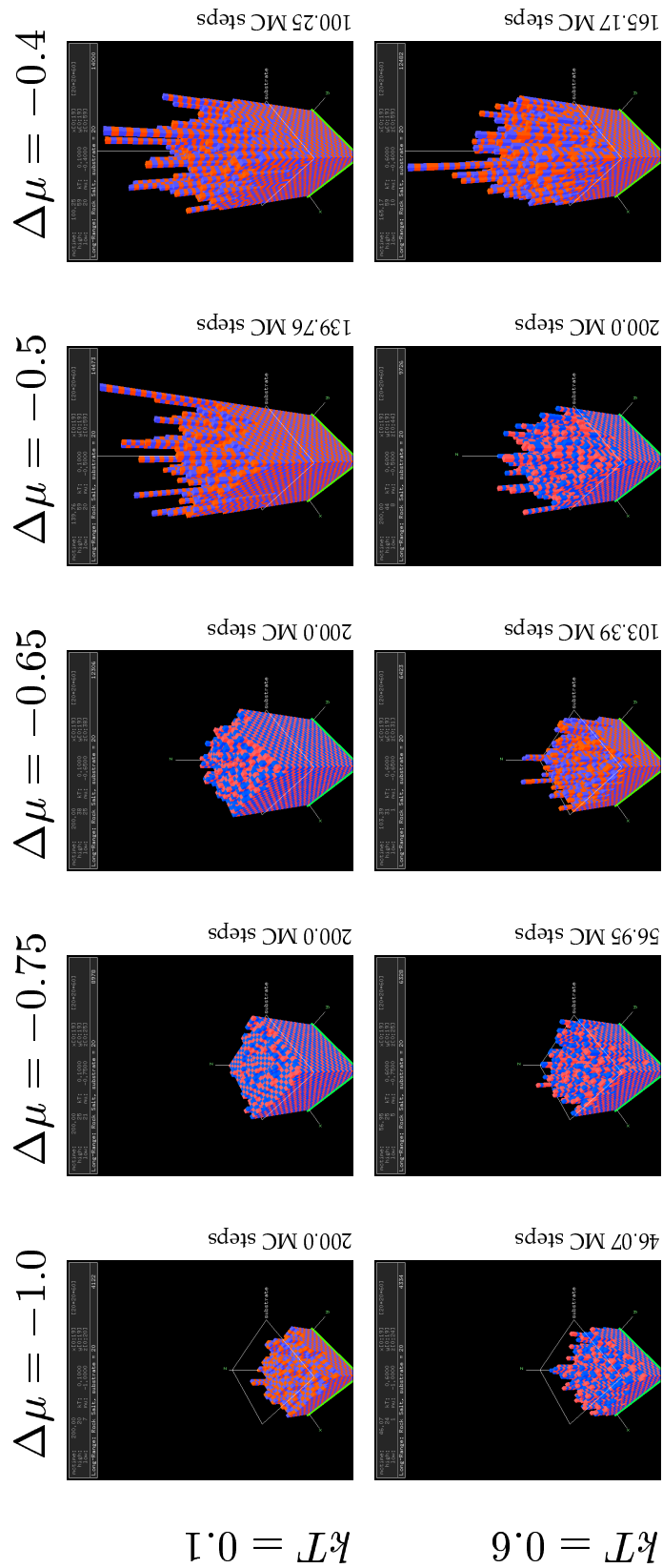
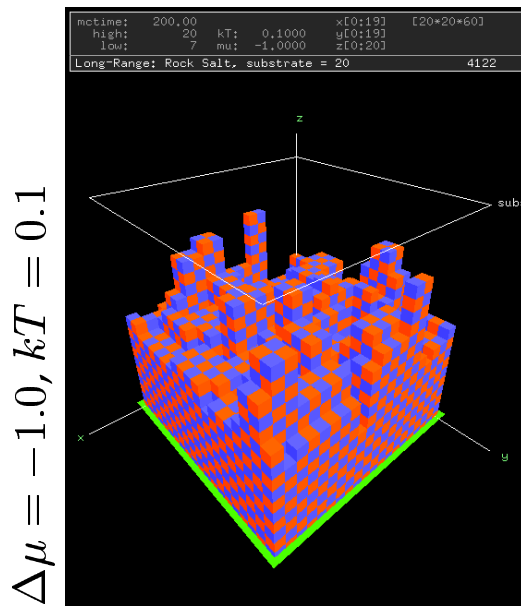


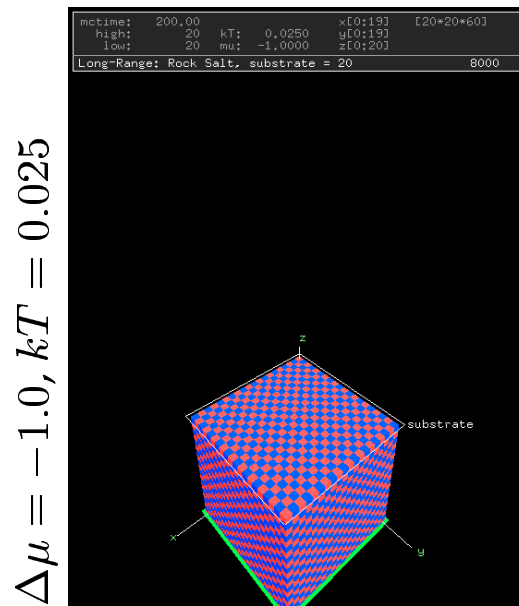
Figure 2: Long-Range Simulations for Rock Salt, $20 \times 20 \times 60$ crystal matrix: $\Delta\mu$ increases from left to right; temperature increases going downward.

Growth Mode Examples (Long-Range)

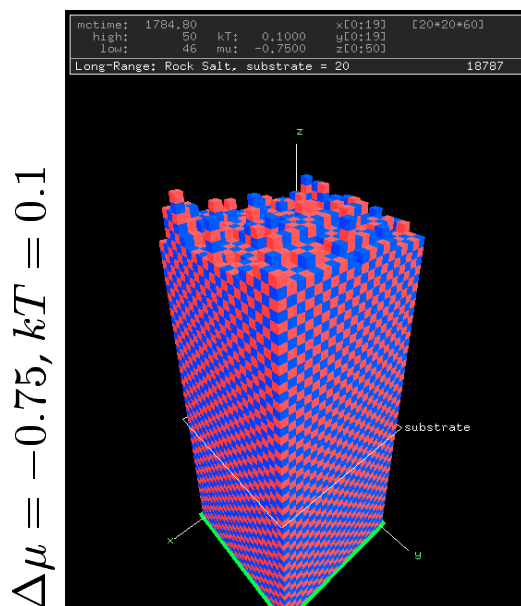
Negative Growth



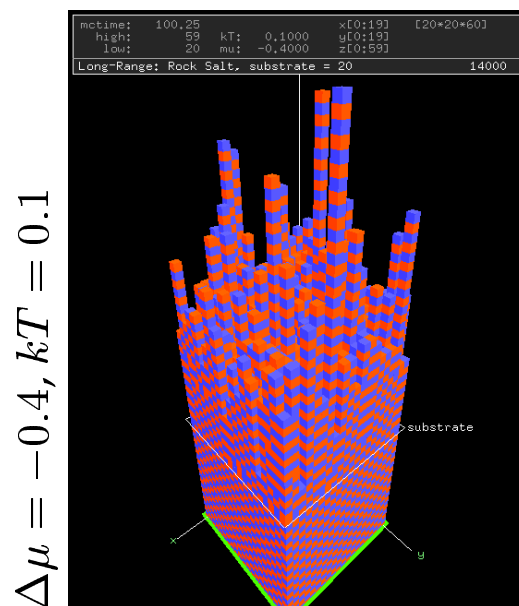
No Growth



Layer-by-Layer Growth



Very Rough Growth



Conclusions

- Preliminary success.
- Proper ordering and growth behavior observed for both nearest-neighbor and long-range interactions for rock salt type crystals.
- Bigger matrix sizes, wider parameter range, more runs are needed for confirmation.
- Simulation time to real time correlation function needed.
- Otherwise, we're pretty happy—now it gets exciting.

Other Crystal Types

$\text{II}_{1/3}\text{V}_{2/3}$, Heterovalent Binaries

- Includes the new relaxor crystals discovered by Park and Shrout (PMN, PZN).
- Really interesting behavior: $[\text{111}]_{1:2}$ order.
- Now we see the gross inadequacy of the nearest-neighbor model.

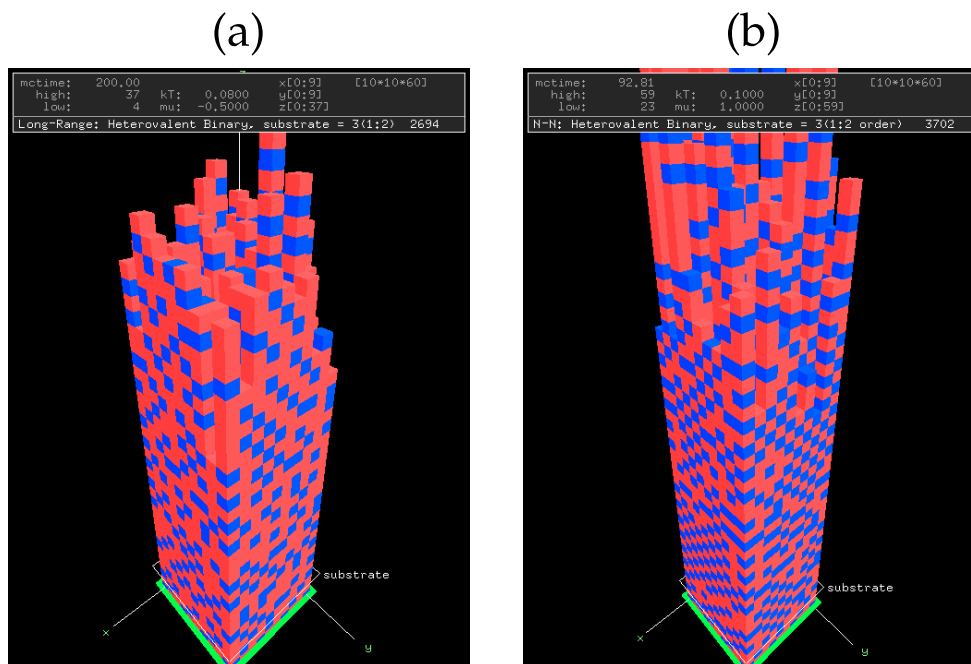


Figure 3: Long-Range and N-N Simulation for the Heterovalent Binary $\text{II}_{1/3}\text{V}_{2/3}$, $10 \times 10 \times 60$: notice that, although both systems show disorder, the long-range model has produced a charge neutral crystal whereas the nearest-neighbor model has not.

And the journey continues...

- Expand investigations to **other crystal types** including those that cover the Relaxor-PTs (heterovalent ternaries).
- Add diffusion? Get rid of SOS restriction?
- Include more B species and calculate the **charge-charge correlation functions** (which measure the degree of order).
- Look more closely at the growth. **Is there physics we're missing in our simple model?** (Are towers realistic?, ...)
- Vary kT over time throughout the simulation.
- **Look at [111] direction growth** (instead of [001]).
- Find a supercomputer.

Many thanks to:

my learned master: **Prof. Shiwei Zhang**,
my second learned master: **Prof. Henry Krakauer**,
Prof. Kossler for providing a desk/office space,
and my committee...