Growth Simulations of Single Crystal Perovskite Alloys

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1. **Why is this research interesting?**

   (Perovskite Crystals? $\rightarrow$ motivation)

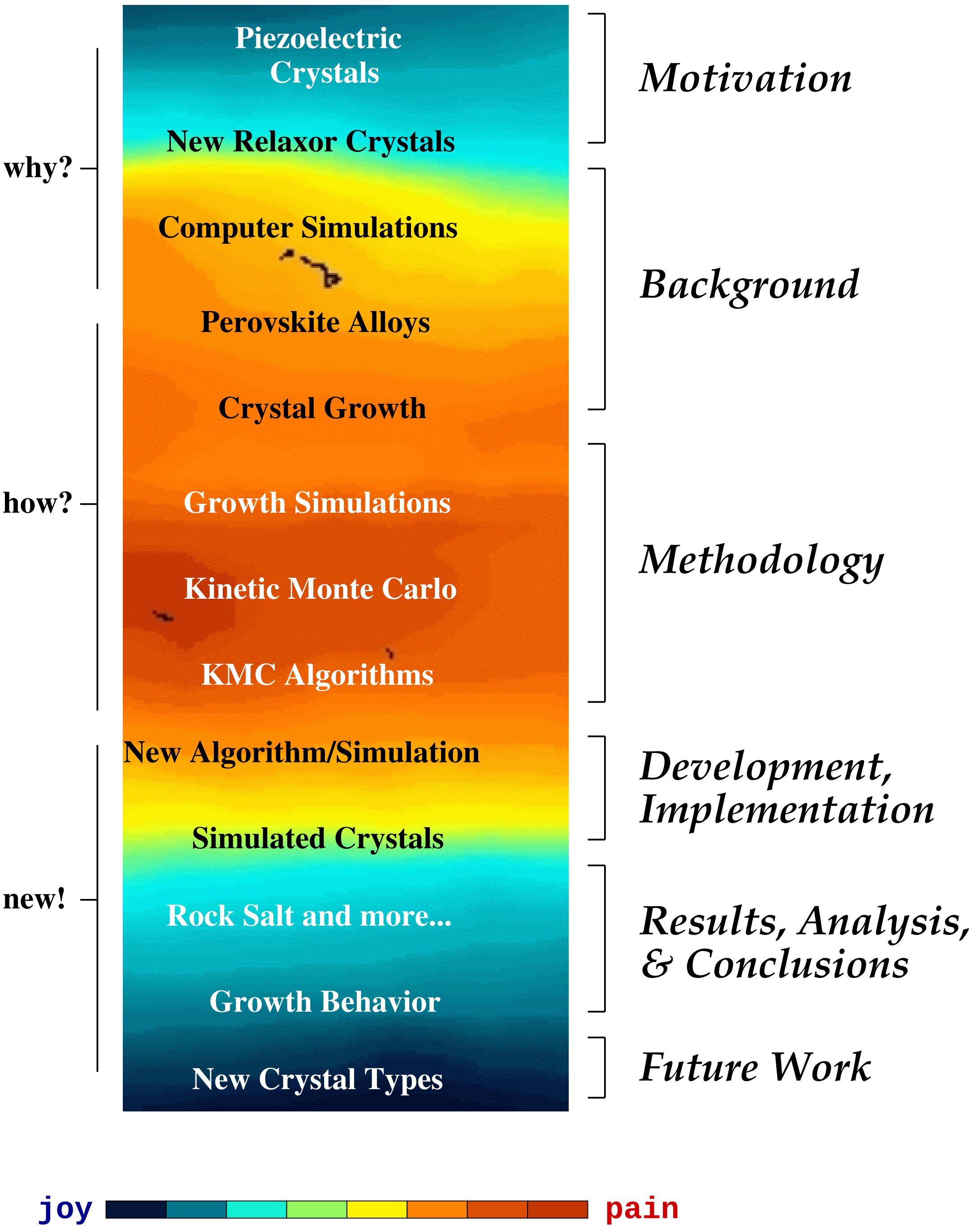
2. **How was it done?**

   (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



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,

     $\equiv$ **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).

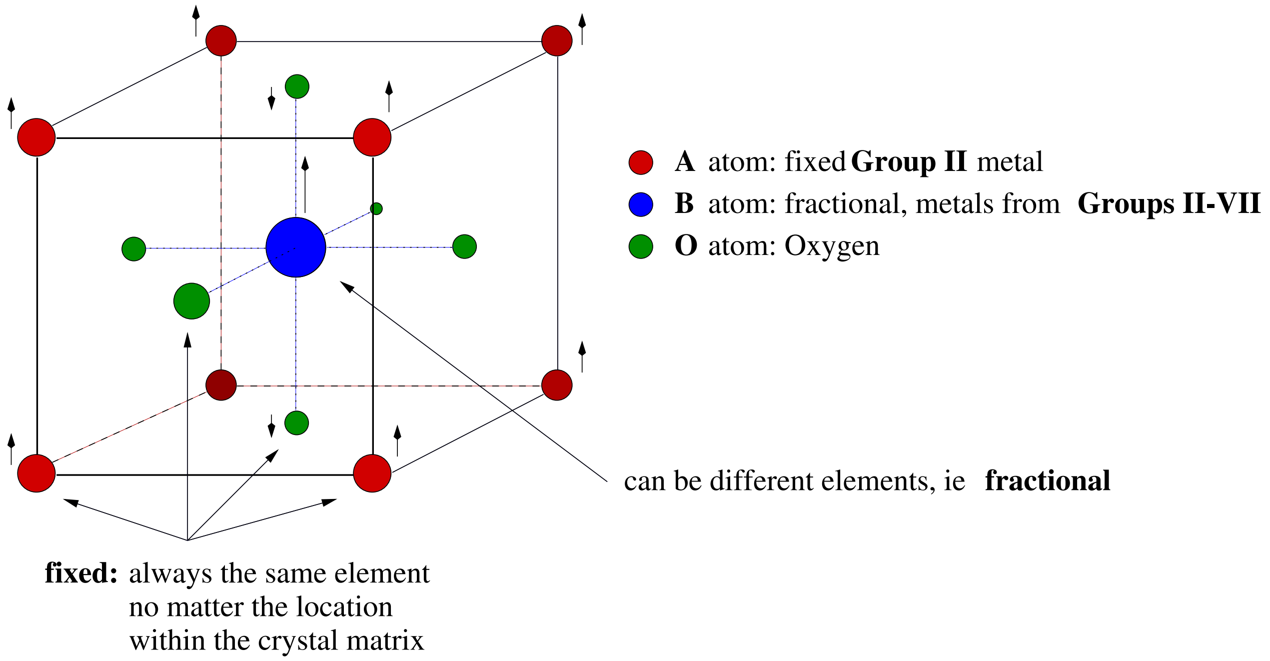
3. Develop an algorithm to realize—accurately—that model through time (the KMC method).

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

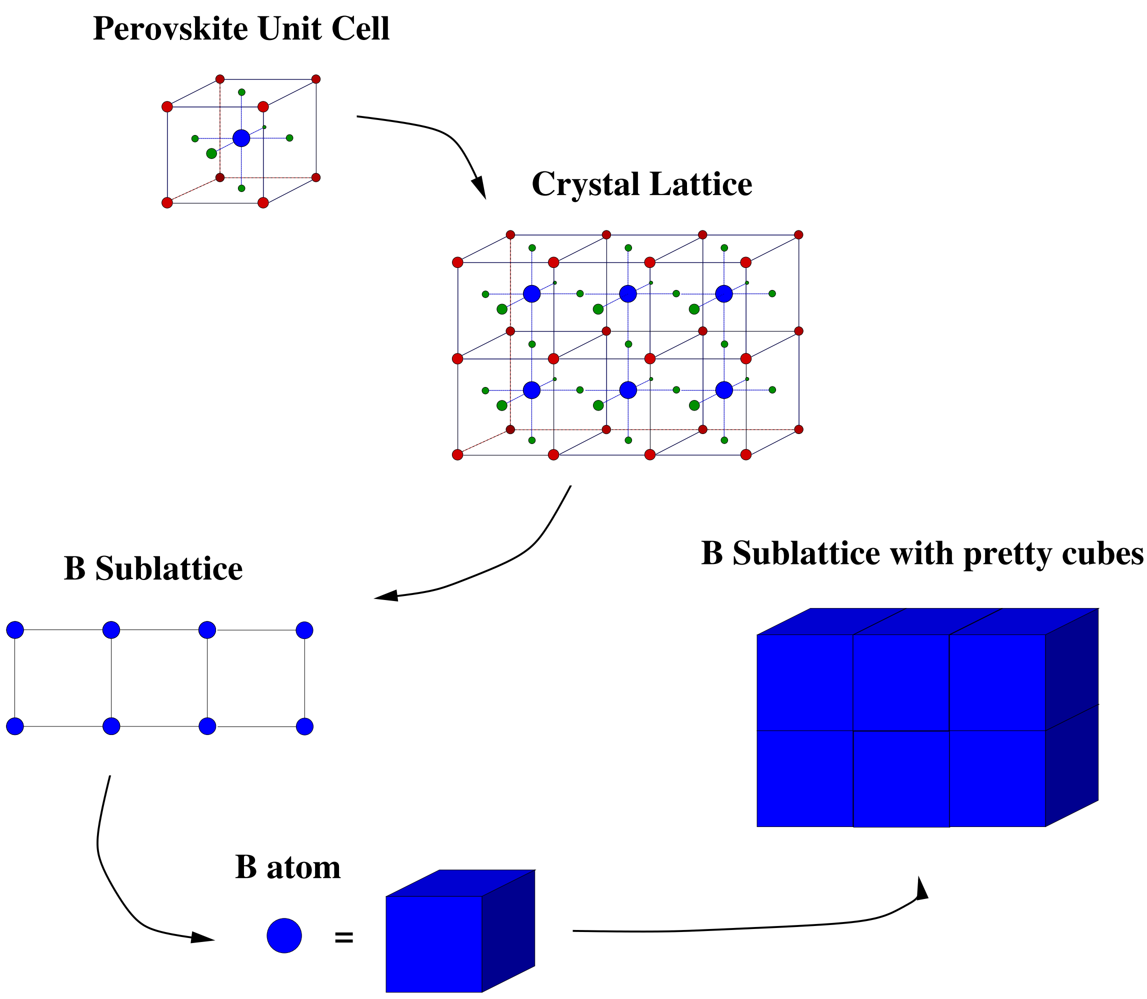


Fractional B-sites?

$$A^{2+} \underbrace{B^{4+}}_{B_{1-x}B'_x} O_3^{6-}$$

e.g.: $Pb(\underbrace{Mg_{1/3}Nb_{2/3}}_{II_{1/3}V_{2/3}})O_3$ (PMN) or $Pb(\underbrace{Sc_{1/2}Ta_{1/2}}_{III_{1/2}V_{1/2}})O_3$

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.

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

where Δq_l is the charge of a B site ion, and $\mathbf{l}$ is the vector to that ion.

• Success in predicting the B-site ordering behavior of perovskite alloys observed experimentally.

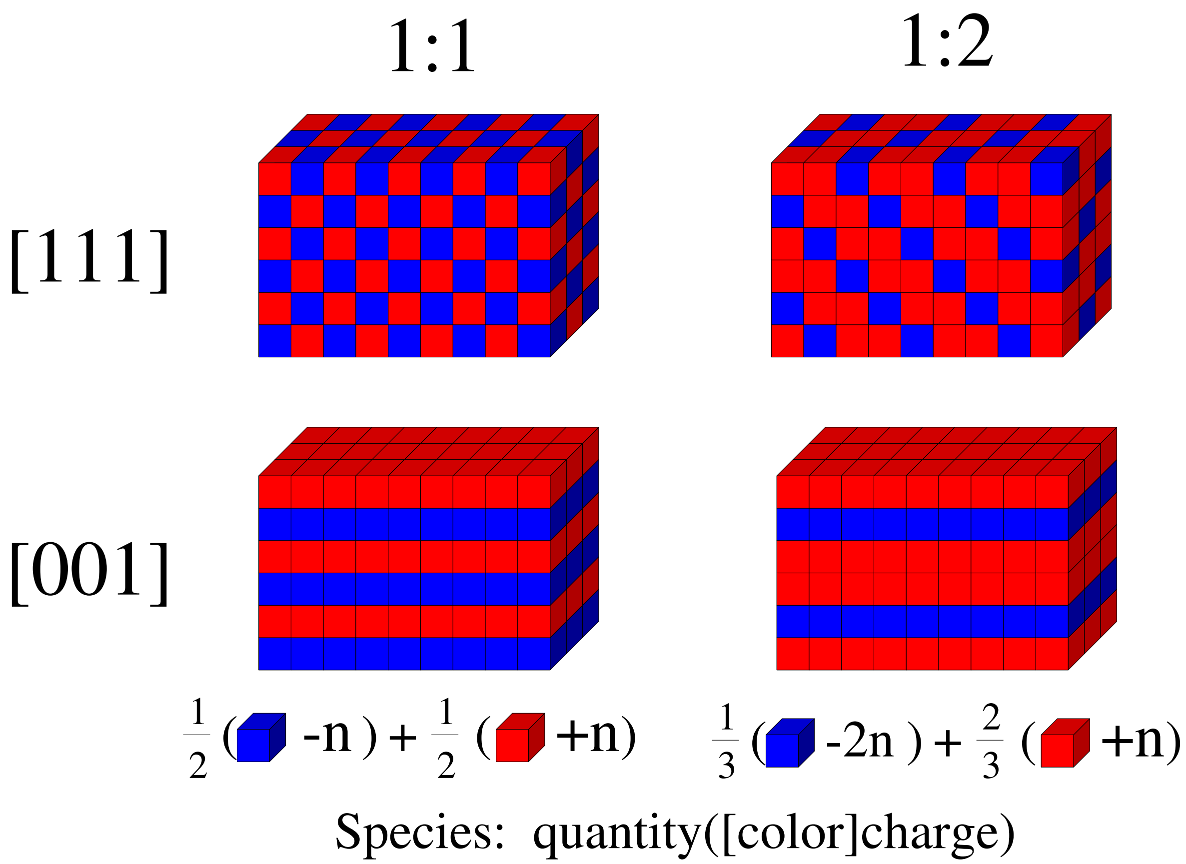
• BV $\rightarrow$ equilibrium MC simulation $\rightarrow$ no growth information.

• 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.: $Q_{Mg} = +2 \quad \rightarrow \quad \Delta q_{Mg} = -2$
- 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.

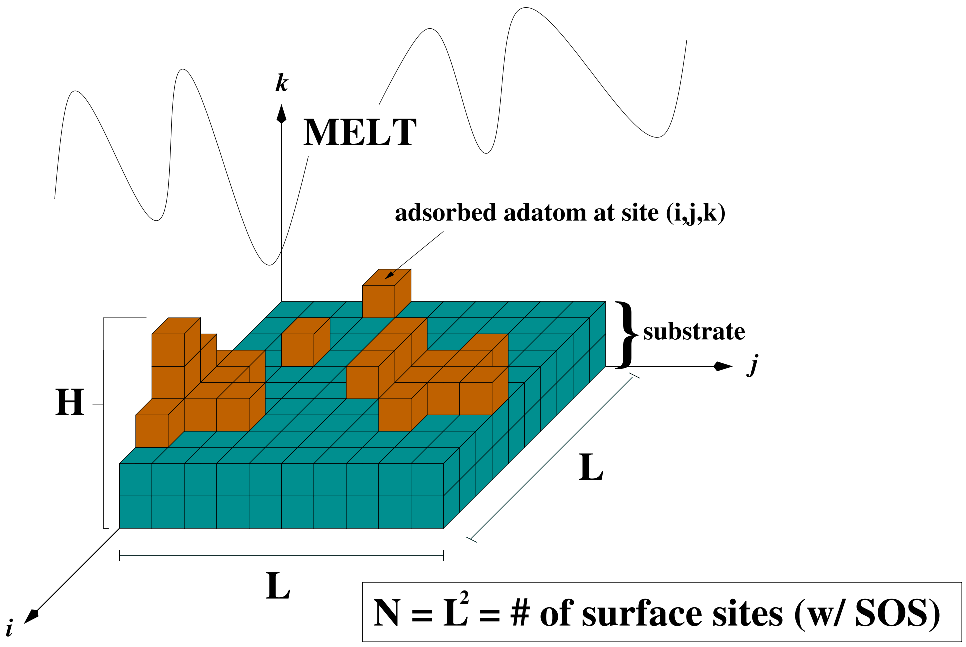
◇ **Crystal Growth Simulations**

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

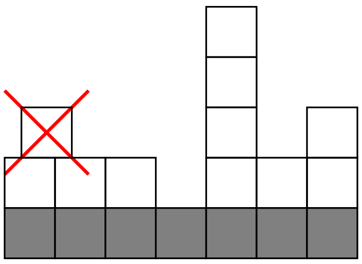
- **adatom:** simulation lingo for an atom or molecule.

- Three processes define crystal growth:

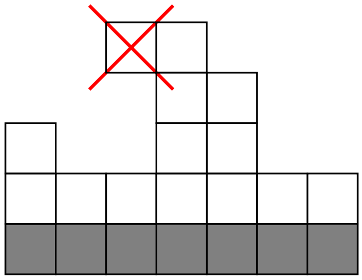
1] **adsorption:** adatom sticks to surface.
2] **evaporation:** adatom desorbs from surface.
3] **surface migration:** adatom travels across surface.



Simulation Restrictions

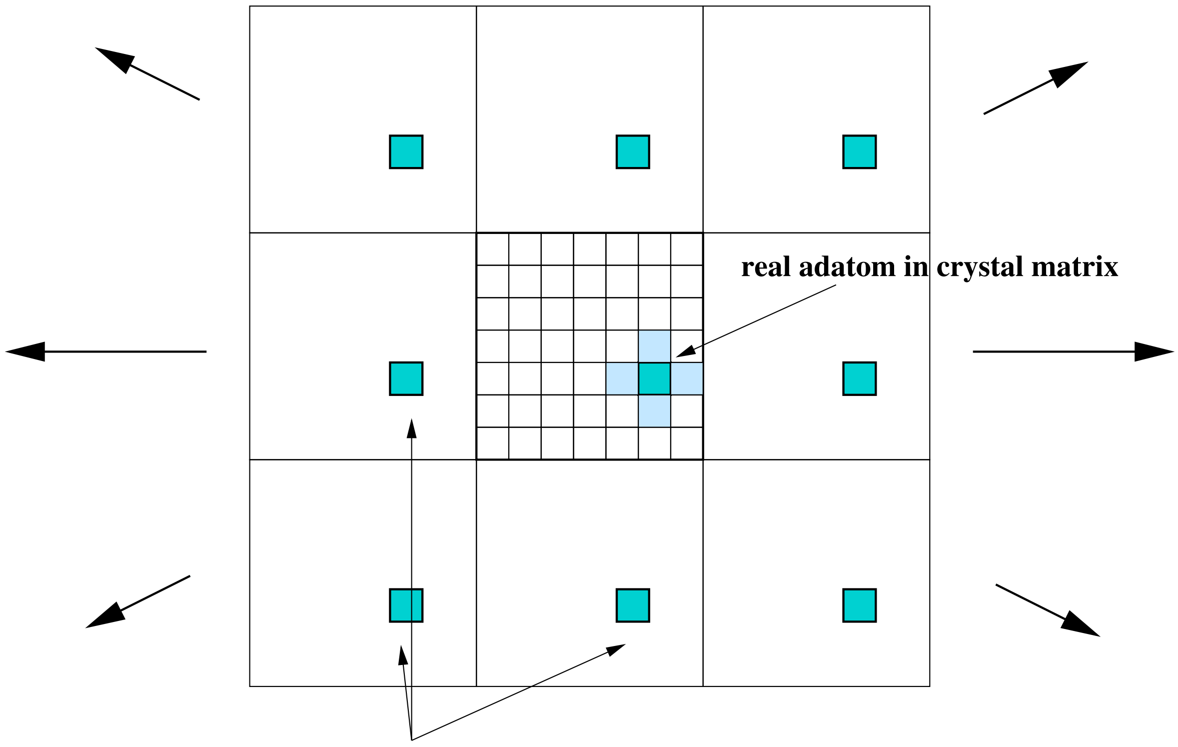


Only discrete placement on our perfect 3-d lattice.



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

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

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 the 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, $Z^{-1} exp\left[\frac{-\mathcal{H}(\mathcal{C})}{kT}\right]$, giving

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

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

$\underbrace{\textbf{Nearest-Neighbor}}_{old}$ vs. $\overbrace{\textbf{Long-Range}}^{new}$ Interactions

Their difference manifests itself in the calculation of ΔE:

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

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;

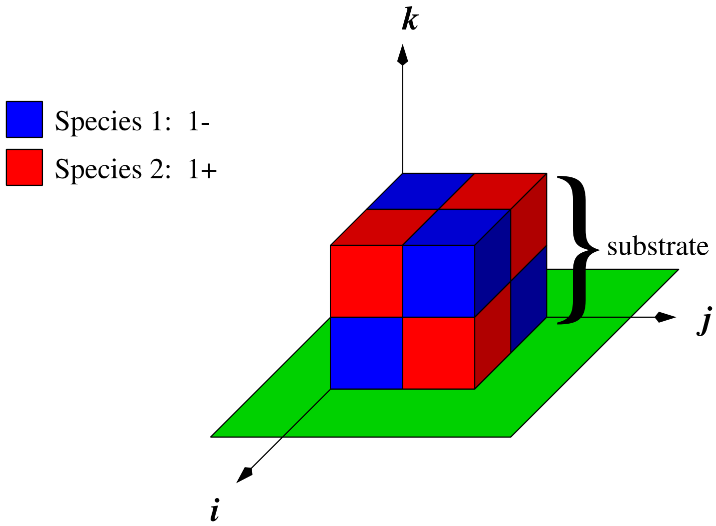
(iv) Generate a random number $r \in [0, 1)$ and choose the first event E_i such that $\sum_i^n P_i \geq r$. An event will always be chosen;

(v) Generate new configuration $\mathcal{C}$ 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.

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

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

The Probability Event List, P

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

$$P_{m=1\ldots 2N} = \frac{w_m}{\sum\limits_m w_m}$$

where, if you'll remember,

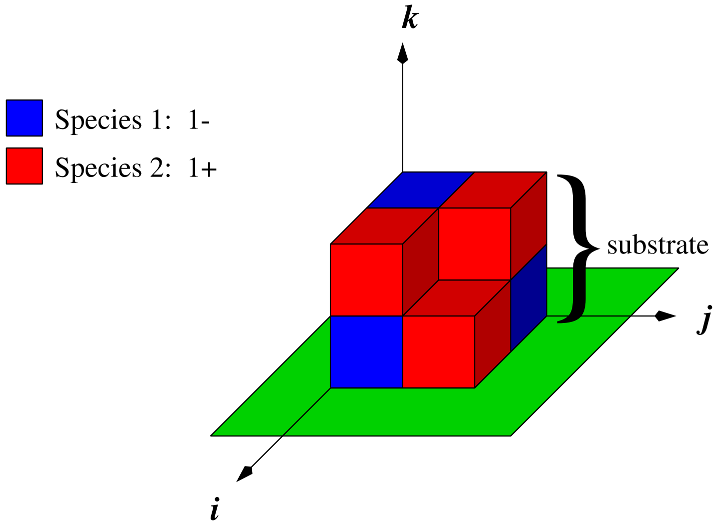
$$w_m = \text{rate of event } m = \begin{cases} e^{\Delta\mu/kT}, & \text{if } m \text{ is even} \\ e^{U_{ij}/kT}, & \text{if } m \text{ is odd} \end{cases}$$

$P(0) =$

m	(x,y,z)	$Type$	$Rate$	$Probability$	$Total$
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

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

The Crystal at t = 1



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

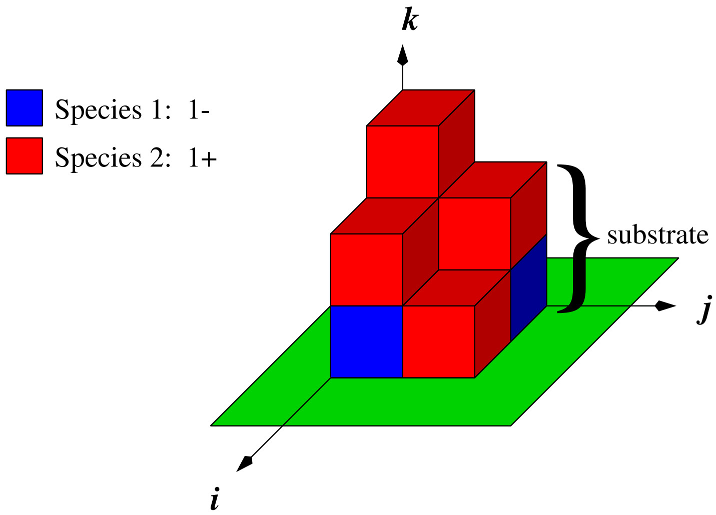
$$U(1) = \begin{pmatrix} -0.867998 & -1.181894 \\ -1.181894 & -2.000866 \end{pmatrix}$$

$P(1) =$

m	(x, y, z)	$Type$	$Rate$	$Probability$
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

- 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 $III_{1/2}V_{1/2}$ ($\Delta q = \pm 1$) and $II_{1/2}VI_{1/2}$ ($\Delta q = \pm 2$).

• **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:

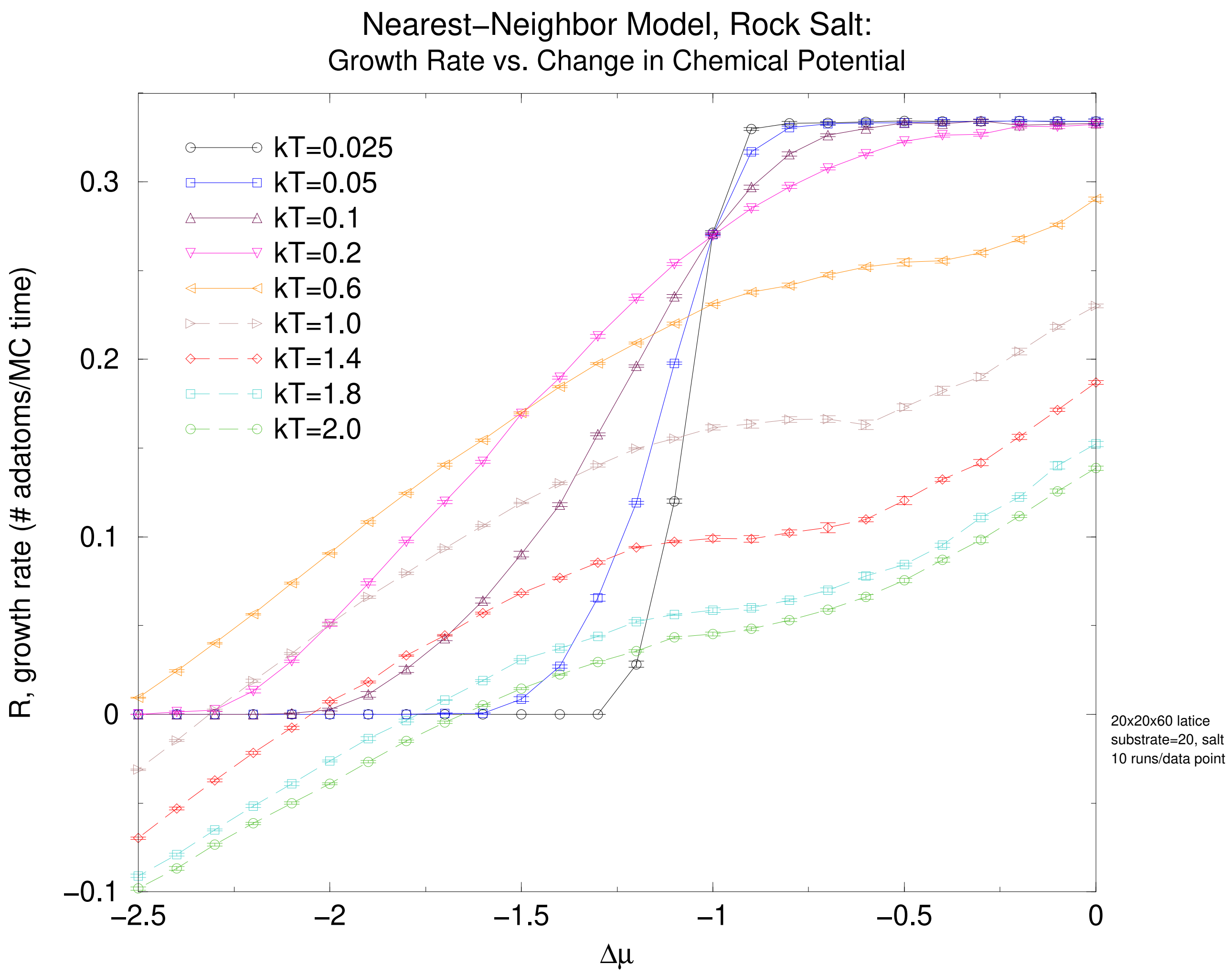
+ **layer-by-layer growth:** a crystal layer tends to be completed before a new layer is started above it;

+ **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.



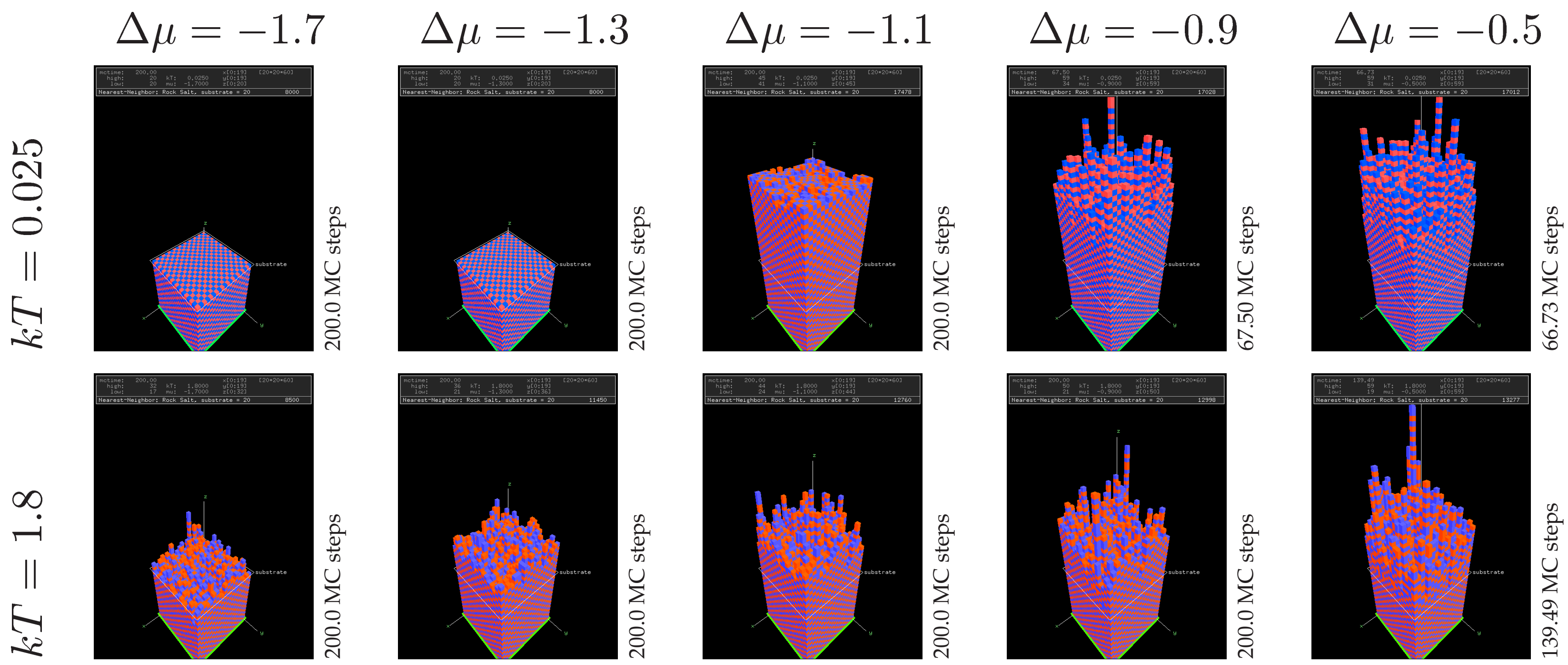
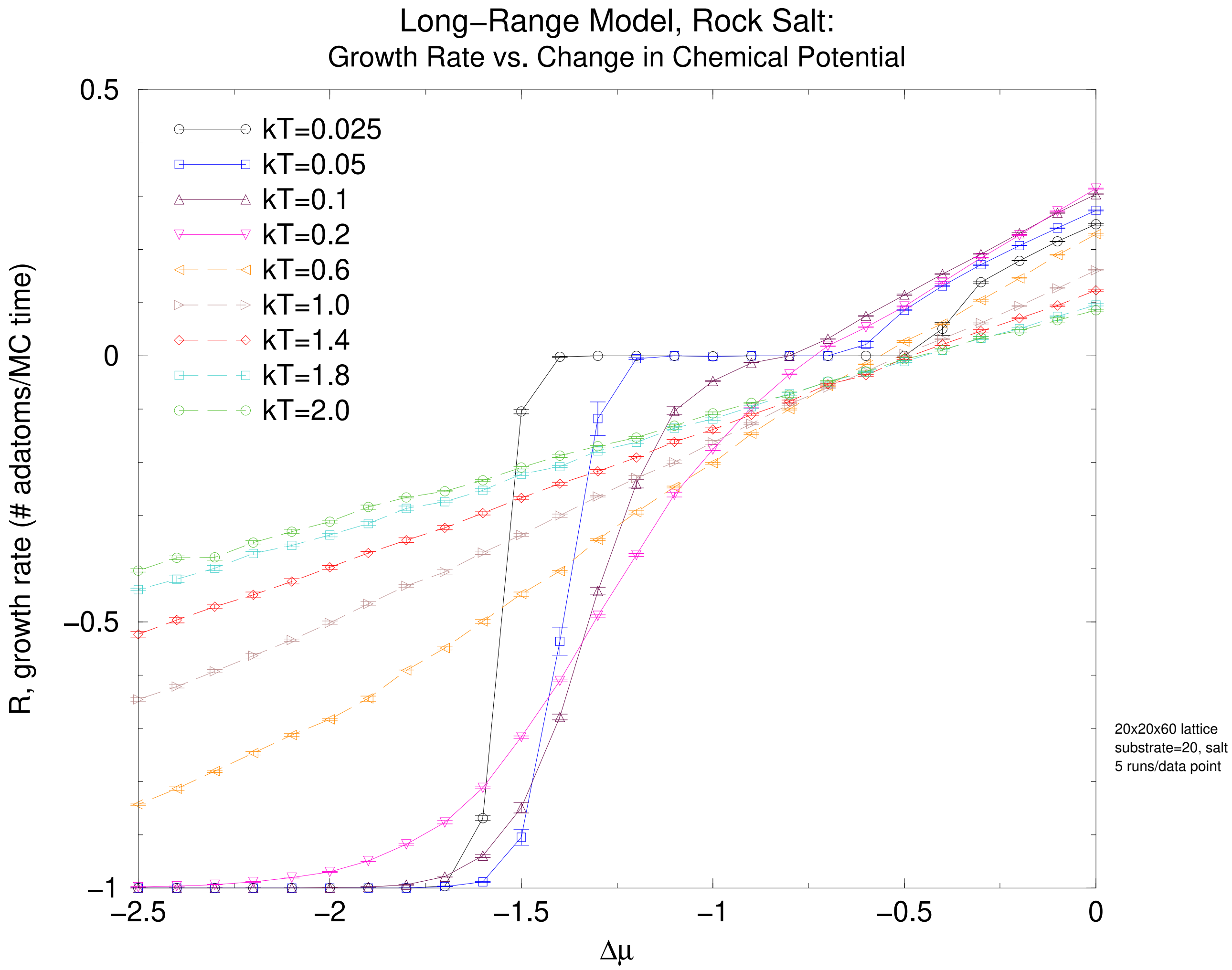


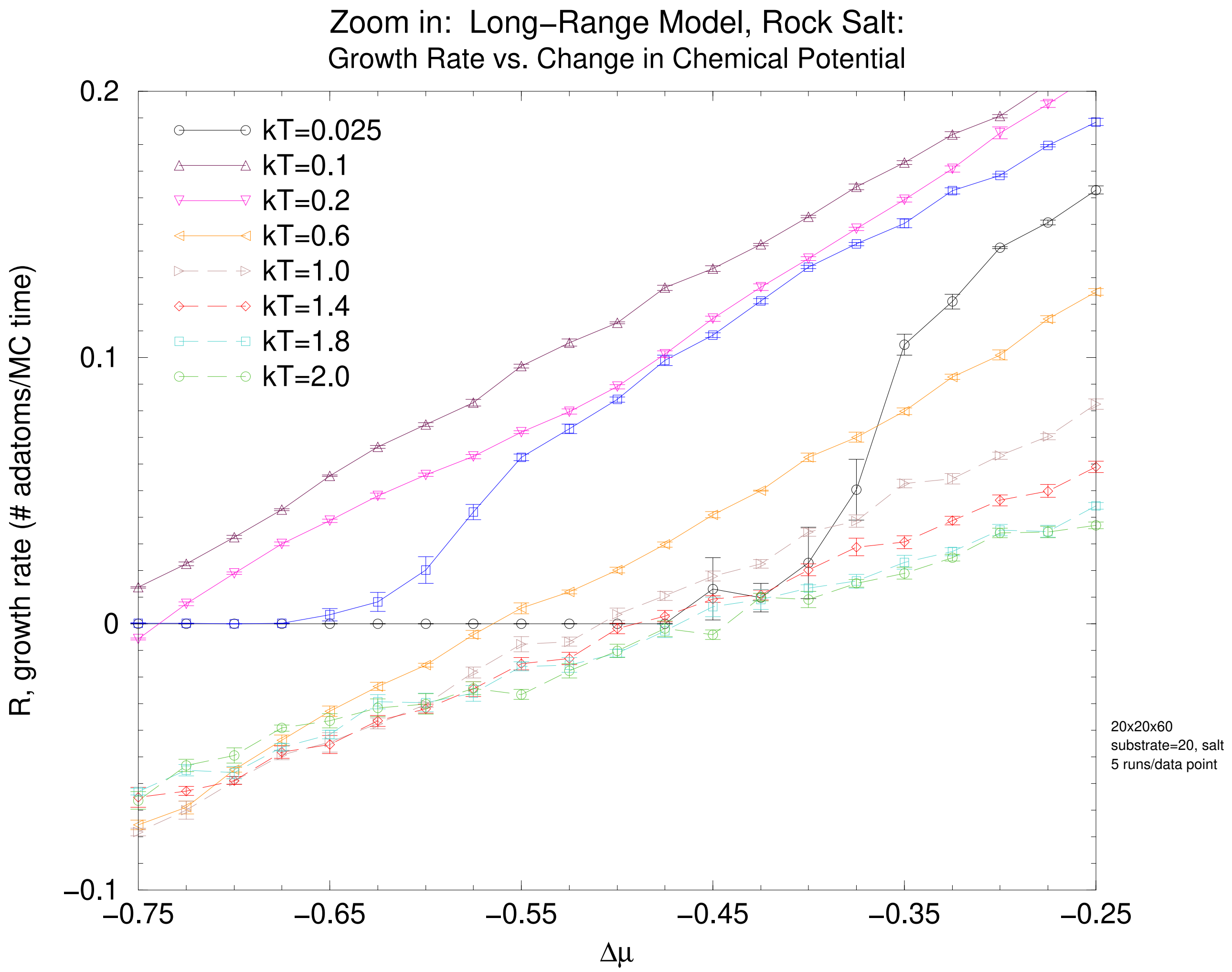
Figure 1: **Nearest-Neighbor** Simulations for Rock Salt, $20 \times 20 \times 60$ crystal matrix: from left to right $\Delta\mu$ increases from low to high; temperature increases going downward, from very low to very high.

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 ($>> 100$).

Results/Analysis

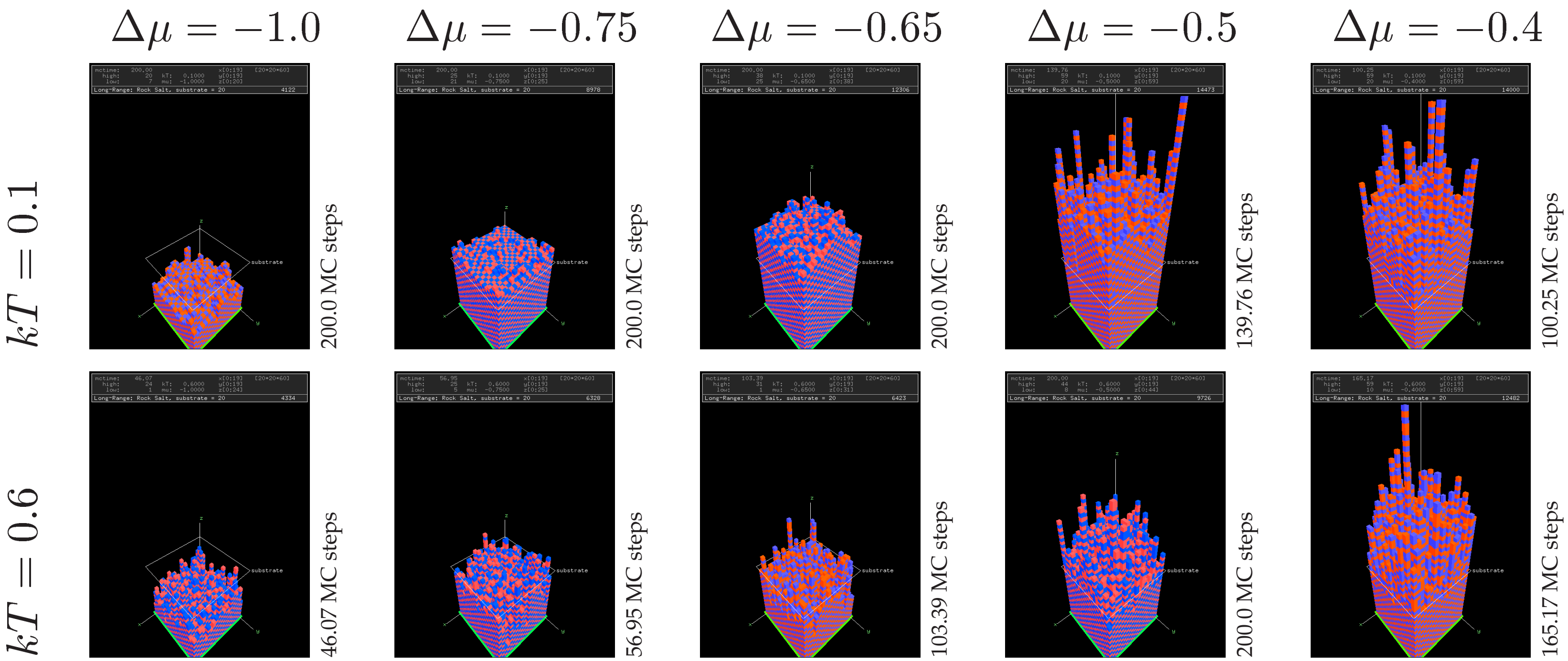
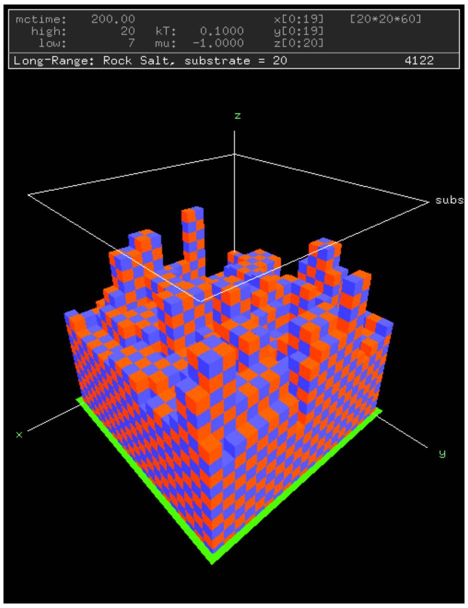


Figure 2: **Long-Range** Simulations for Rock Salt, $20 \times 20 \times 60$ crystal matrix: $\Delta\mu$ increases from left to right; temperature increases going downward.

Growth Mode Examples (Long-Range)

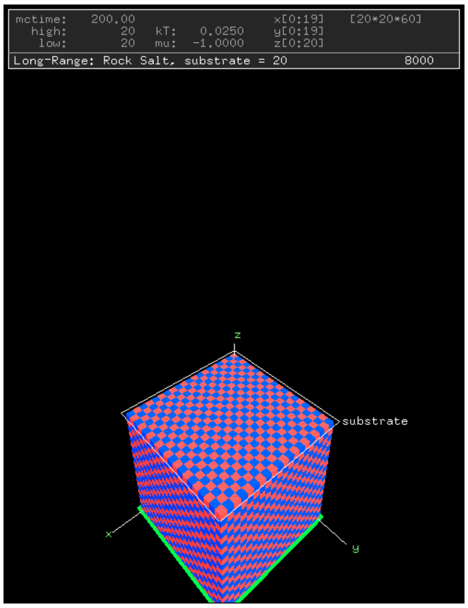
Negative Growth

$\Delta\mu = -1.0, kT = 0.1$



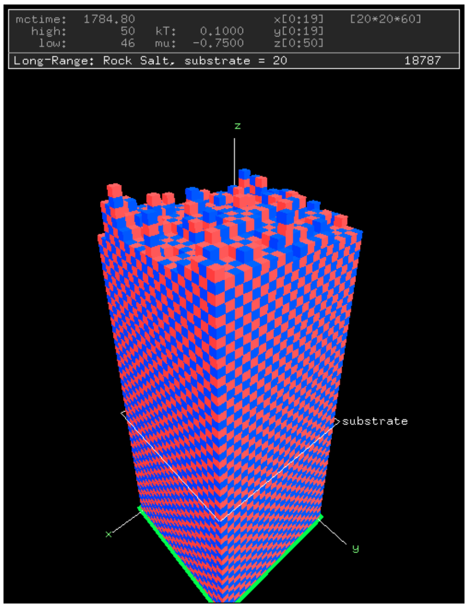
No Growth

$\Delta\mu = -1.0, kT = 0.025$



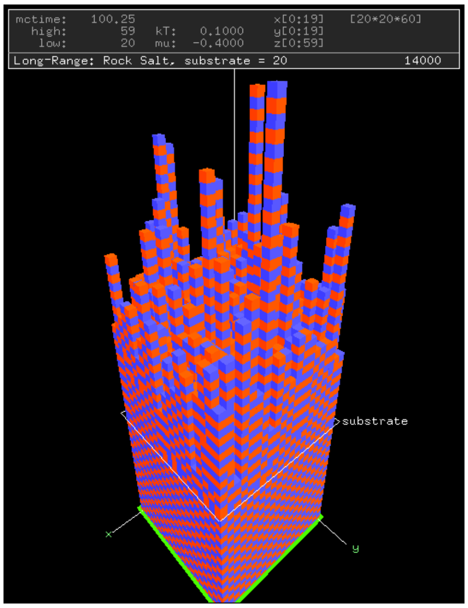
Layer-by-Layer Growth

$\Delta\mu = -0.75, kT = 0.1$



Very Rough Growth

$\Delta\mu = -0.4, kT = 0.1$



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

$II_{1/3}V_{2/3}$, Heterovalent Binaries

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

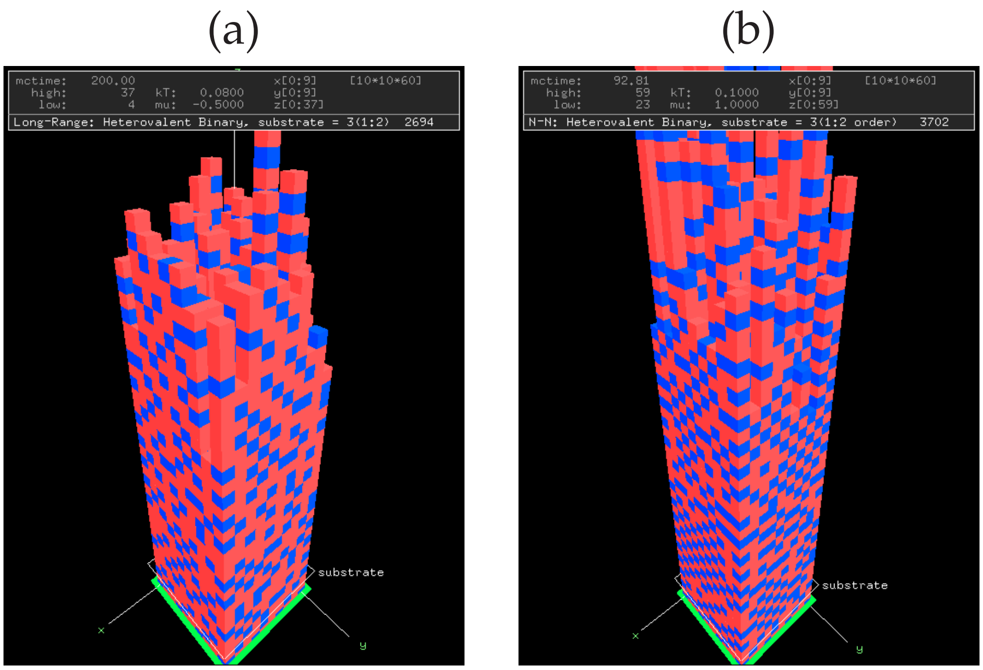


Figure 3: Long-Range and N-N Simulation for the Heterovalent Binary $II_{1/3}V_{2/3}$, $10 \times 10 \times 60$: notice that, although both systems show disorder, the long-range model has produced a charge neutral crystal whereas the nearest-neighbor model has not.

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:

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