Kinetic Monte Carlo Simulations of Crystal Growth in Ferroelectric materials

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Abstract. We study the growth process of ferroelectric materials by kinetic Monte Carlo simulations. An ionic model with long-range Coulomb interactions is used to model the relaxor single crystals. The growth is characterized by thermodynamic processes involving adsorption and evaporation, with solid-on-solid restrictions. An algorithm is developed in order to simulate growth under such a model, for which existing formalism of the kinetic Monte Carlo algorithm is inadequate. We study the growth rates and the order structure of the grown crystals as a function of temperature, chemical composition, and growth orientation. Tests of our algorithm on NaCl gave good results. Preliminary results on growth in Ba-based heterovalent binaries showed 1:2 ordering along the [111] direction over limited scales.

I INTRODUCTION

The discovery of ultra-large coupling piezoelectrics [1] has intensified the theoretical interest in these remarkable materials. In addition to understanding equilibrium properties, where calculations by density-functional theory methods coupled with effective Hamiltonians have shown great promise [2], understanding how to grow large single crystals is clearly of key importance. In this paper, we explore theoretical approaches to study the crystal growth process of ferroelectric materials.

We use a "second-principles" procedure which simulates the growth process with kinetic Monte Carlo based on a simple model Hamiltonian. The model was proposed by Bellaiche and Vanderbilt [3] in 1998 for the perovskite alloys. It reduces the system to only the B-sites and assumes that the long-range Coulomb interactions between ions at these lattice sites are the driving mechanism for ordering. This simple electrostatic model successfully reproduced most of the B-site compositional long-range orders in equilibrium Monte Carlo simulations.

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Using this electrostatic model for the perovskite alloys, we study the crystal growth process by kinetic Monte Carlo (KMC) simulations [4]. KMC methods have seen various applications to study growth and kinetic processes in Ising-like lattice models. In particular, a sampling algorithm introduced by Bortz, Kalos, and Lebowitz (BKL) [5] works efficiently for the short-range interactions present in these systems. For the electrostatic model here, however, an enhanced sampling algorithm, which we develop below, is needed in order to treat long-range Coulomb interactions efficiently.

In this paper, we describe our theoretical and computational approach for growth simulations of ferroelectric crystals, and present preliminary results. The rest of the paper is organized as follows. In Section II, we discuss the electrostatic model, standard KMC, our new sampling algorithm to implement KMC for this model, and additional technical issues to treat the long-range Coulomb interactions in a growth simulation with a finite-sized simulation cell. In Section III, we show results on the growth processes of rock-salt type crystals. We conclude in Section IV with some remarks on future directions.

II   APPROACH

A   The model

The electrostatic model of Bellaiche and Vanderbilt [3] is a simple but remarkably successful ionic model of perovskite alloys. In this model, the electrostatic energy due to point-charge ions in the ideal cubic structure is assumed to be the dominant factor for the observed B-site ordering. For an $A(BB')O_3$ compound, the total electrostatic energy can be written as

$$E_t(C) = \sum_{(l\tau, l'\tau')} \frac{Q_{l\tau}Q_{l'\tau'}}{\epsilon |\mathbf{R}_{l\tau} - \mathbf{R}_{l'\tau'}|}, \tag{1}$$

where $\mathbf{R}_{l\tau}$ is the position of the ion on site τ ($\tau = \{A, B, O_1, O_2, O_3\}$) of cell l and ϵ is the dielectric constant. Because charges at the A-sites and O-sites have fixed values, it can be shown that, up to a constant, the configurationally averaged electrostatic energy depends only on the B-site charges

$$E_B(C) = \frac{1}{\epsilon a} \sum_{(l,l')} \frac{q_l q_{l'}}{|\mathbf{l} - \mathbf{l}'|}, \tag{2}$$

where a is the cubic lattice constant, $\mathbf{R}_{lB} = \mathbf{l}a$, and $q_l \equiv Q_{lB} - 4e$ for compounds whose A-sites are occupied by Pb or Ba.

Different classes of alloys can be conveniently described using this electrostatic model for the B-sites. For example, $IV_x IV'_{1-x}$ denotes a homovalent binary alloy having tetravalent B-atoms, e.g., $Pb(ZrTi)O_3$, while $II_{(1-x)/3}IV_x V_{2(1-x)/3}$ indicates a heterovalent ternary such as $(1-x)Ba(MgNb)O_3 + xBaZrO_3$.

The model of Eq. (2) leads to the following Hamiltonian for our system,

$$\mathcal{H}(C) = E_B(C) + \Delta\mu N, \tag{3}$$

where N is the total number of occupied sites, i.e., the total number of ions in the grown crystal. The second part of the Hamiltonian accounts for the chemical potential difference between the crystal and the melt. The magnitude of $\Delta\mu$ controls the "sticking" rate from the melt.

B Kinetic Monte Carlo (KMC) method

The kinetic Monte Carlo (KMC) method is one of several simulation techniques used to simulate the relaxation processes of systems away from equilibrium (e.g. growth processes). It has been applied successfully to crystal growth and surface/interface phenomena [4,6], mostly in the context of kinetic Ising models. Our growth simulation uses the general approach of KMC, although significant enhancement to the algorithm must be introduced to make it practical for the long-range electrostatic interactions.

The objective of the growth simulation is to create a model that describes the dynamics of crystal growth as stochastic processes such as adsorption, evaporation, and surface migration. Our simulations presently include the first two only, namely the adsorption and evaporation of the adatoms. The adatoms represent the B-site ions in the single crystal perovskite alloy, characterized entirely by their charge and interacting with each other through the potentials that we discuss in Section II.D. The structure of the simulation is a three-dimensional lattice where adatoms can individually and singularly occupy lattice sites.

We carry out our growth simulations in an $L \times L \times \infty$ cell on an ideal cubic lattice. Periodic boundary conditions (PBC) are imposed in the x-y plane. The z-direction is free and is the growth direction. We start our growth simulations with an $L \times L \times H_0$ substrate which serves as the growth seed. The crystal configuration C at any time is specified by the sites which are occupied and the charge q_l at each occupied site $l = (i, j, k)$.

In our simulations, we impose a solid-on-solid (SOS) restriction, which does not permit the appearances of vacancies. The SOS restriction means that we can write H as

$$\mathcal{H}(C) = E_B(C) + \Delta\mu \sum_{(i,j)} h_{ij}, \tag{4}$$

where h_{ij} is the height of the present crystal configuration at position (i, j).

We now outline the basic theoretical background for the kinetic Monte Carlo method. The goal is to simulate the time evolution of the system through a Markov chain of configurations. We define $P(C, t)$ as a time-dependent distribution of configurations, C as the current crystal configuration, and C' as a crystal configuration

related to C by one time step. The transition rate from C to C' is denoted by $w(C \to C')$. The transition rate is to be chosen to simulate the physical system as realistically as possible.

We can then write down the following master equation

$$\frac{\partial P(C,t)}{\partial t} = -\sum_C w(C \to C')P(C,t) + \sum_{C'} w(C' \to C)P(C',t), \qquad (5)$$

where the first term on the right describes the loss because of transitions away from C, while the second term describes the gain because of transitions into C. In the equilibrium limit (as $t \to \infty$), the Boltzmann distribution

$$P_{eq} = Z^{-1} \exp\left[\frac{-\mathcal{H}(C)}{kT}\right] \qquad (6)$$

is reached. We require that detailed balance be satisfied:

$$\frac{w(C \to C')}{w(C' \to C)} = \frac{P_{eq}(C')}{P_{eq}(C)} = \exp\left[-\frac{\mathcal{H}(C') - \mathcal{H}(C)}{kT}\right]. \qquad (7)$$

The KMC technique can be viewed as a method of solving equation (5). We adopt the following choice of transition rates $w(C \to C')$

$$w_{\mathrm{a}} = \exp\left(\Delta\mu/kT\right) \qquad (8)$$
$$w_{\mathrm{e}} = \exp\left(-\Delta E_B(C)/kT\right), \qquad (9)$$

where w_a and w_e are the rates for adsorption and evaporation, respectively, of an adatom. In this choice, the adsorption rate is a constant, while the evaporation rate depends on the change in total potential energy in the crystal when an adatom evaporates from the surface: $\Delta E_B(C) \equiv E_B(C') - E_B(C)$.

For kinetic Ising models, the algorithm of BKL [5] allows an efficient stochastic realization of the kinetic process under the choice in Eq. (9). In this algorithm, a site (i,j) is selected randomly in each step. An event is then selected at (i,j) by Monte Carlo sampling [7] from the list of all three possible events, {*adsorption, evaporation, nothing*}. For Ising-like models, where the interaction is limited to near-neighbors, the energy difference $\Delta E_B(C)$ is completely determined by the *local* environment at site (i,j). The relative probabilities $\{P_a, P_e, P_n \equiv 1 - P_a - P_e\}$ can thus be easily obtained from the global maximum of w_e, i.e., the minimum possible $\Delta E_B(C)$ for any C.

C   KMC algorithm for long-range interactions

The electrostatic model of Eq. (2) means that the energy change needed in Eq. (9) depends on the *entire* configuration C. It is therefore difficult to determine the global minimum, $\Delta E_{\min} \equiv \min[\Delta E_B(C)]$. Furthermore, even if $\Delta E_{\min}$

could be identified, the energy change $\Delta E_B(C)$ for most configurations would be much greater than $\Delta E_{\min}$, which would cause P_n to approach unity, thereby driving evaporation and adsorption probabilities to zero and rendering the algorithm ineffective.

Our new algorithm goes a step beyond the standard KMC algorithm. [5] It considers all $N = L \times L$ surface sites *simultaneously* and creates an event list which includes every possible event for every possible surface site. The algorithm proceeds as below:

(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 $N = L \times L$ surface sites.

(ii) Calculate the rates (w) of adsorption and evaporation for each site on the surface ($2N$ rates). Denote the total rates by W, $W = \sum\limits_{i}^{2N} w_i$.

(iii) Normalize these $2N$ rates by W, giving probabilities, P_i, for adsorption and evaporation on sites $1, 2, \cdots, N$.

(iv) Generate a random number $r \in [0, 1)$ and choose the first event E_i such that $\sum\limits_{k=1}^{i} P_k \geq r$. An event will always be chosen.

(v) Generate the new configuration C based on chosen event E_i.

(vi) Assign a "real time" increment $\Delta t_{\text{real}} = -1/W \ln(r')$ to this MC step, where r' is another random number on $[0, 1)$.

The added complexity comes from the need to store and update an array of surface potentials, the calculation of an event list from these surface potentials, and finding the potential event in this list. The benefit comes in that an event is guaranteed to take place with each iteration of the algorithm and that the need for $\Delta E_{\min}$ is negated completely. Evaporation/adsorption rates for all possible sites are normalized; The sum of the probabilities that an adsorption or evaporation occurs at any site is unity.

We end the discussion of the algorithm with a comment on step (vi). The issue of time in a KMC simulation is a subtle one. Often the Monte Carlo (MC) time t_{MC} is used as a measure of the real time. This is approximate. We follow the same principle, but an adjustment is necessary because of our particular sampling algorithm. In our simulation, an event is forced to happen in each step regardless of the total rates W for the configuration at hand. We therefore rescale Δt_{MC} in each step to reflect the total normalization factor W.

D   The Coulomb interaction in a growth simulation

In addition to requiring a modified KMC sampling algorithm, the long-range Coulomb interactions themselves also require special treatment in a simulation

with a finite-sized simulation cell. In order to calculate the evaporation rate for a surface charge at $o = (i, j, k)$, we need to compute pair-wise interactions between this charge and every other charge in the present crystal configuration. Indeed, for each charge at $l \neq o$ inside the cell, the interactions between o and all the images of l from periodic boundary condition (PBC) also need to be included. A neutralizing background is then added to ensure that the total pair-wise interaction between o and l is finite. That is

$$V_{o-l} = \frac{q_o q_l}{|\mathbf{l} - \mathbf{o}|} + \sum_{l'} \frac{q_o q_l}{|\mathbf{l}' - \mathbf{o}|} - \sum_{o'} \frac{q_o q_l}{|\mathbf{o}' - \mathbf{o}|} \equiv q_o q_l \; v_{o-l}, \qquad (10)$$

where l' denotes the image positions of l due to PBC, and o' denotes those of o.

In an equilibrium simulations, PBC is implemented for the simulation cell in all directions. The formula indicated in Eq. (10) is the so-called Ewald method and evaluation of V_{o-l} is straightforward [8,9]. In our growth simulation, however, PBC is only in the x-y plane, while the z-direction is the direction of growth and is free. The sums in Eq. (10) are therefore restricted to two-dimensions. The sites o and l are in general not in the same x-y plane. We place all the images in the x-y plane of l. For l' this is natural. For o' we project o to the x-y plane of l along the growth direction, and then take the images of the projected position. In other words, the charges are in 3-D but the Ewald sum is limited to 2-D. A procedure for this "fractional-dimension" situation was developed to evaluate v_{o-l}. The energy change in Eq. (9) for evaporation of the charge at o is thus given by

$$\Delta E_B = -\frac{q_o}{\epsilon a} \sum_{l} q_l v_{o-l}, \qquad (11)$$

where the sum is over all sites l in the crystal inside the simulation cell. We use a look-up table for v_{o-l} in our simulation to improve computational efficiency.

III   RESULTS

Our results here will focus on the rock-salt structure, i.e., that of sodium chloride (NaCl). This structure is composed of alternating layers of Na^{1+} and Cl^{1-} in both the [111] and [$\bar{1}$11] directions. It typifies the crystal ordering of a wide variety of materials. Heterovalent binaries such as described by $II_{1/2}VI_{1/2}$ ($q_B = \pm 2$) or $III_{1/2}V_{1/2}$ ($q_B = \pm 1$) are good perovskite examples of rock salt type ordering. The rock-salt structure also represents the simplest crystal our ionic model can grow. It can also be modeled with Ising-like short-range interaction, for which various results are available for comparison and benchmark.

Our crystal growth simulation is a model of two parameters. The variation of the temperature of the system, T, and the chemical potential difference, $\Delta \mu$, will control the changing characteristics of the growing crystal. We choose $q_B = \pm 1$, i.e., the $II_{1/2}VI_{1/2}$ compound. Clearly, a trivial energy scale factor will allow us to convert the system to $III_{1/2}V_{1/2}$ compounds.

We define the growth rate of the crystal as the number of adatoms adsorbed divided by the total real MC time. The growth rates from the simulation, over a range of temperatures, are given in Figure 1 as a function of the chemical potential difference $\Delta\mu$. If we let $a \sim 8$a.u. and $\epsilon \sim 10$, our temperature scale is about 1000K, i.e., $kT = 1$ in the simulation corresponds to 1000K. We use an $L = 20$ crystal matrix. Each simulation ran for 100 MC steps or 100 crystal layers (including incomplete layers), whichever came first. (An MC step is defined as L^2 attempts at the procedure outlines in Section II.C.) The selected temperatures range from $kT = 0.025$ to $kT = 2.0$. Every data point represents the average growth rate value of ten separate crystal simulation runs. The error bars, which are the normal statistical error $(\sigma/\sqrt{n})$ in MC calculations, are smaller than symbol size in most cases.
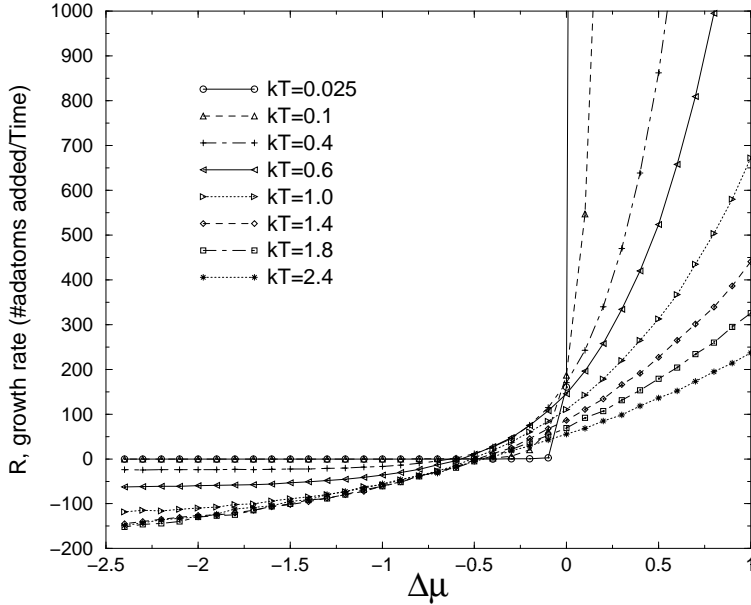

FIGURE 1. Growth rates for rock salt.

The qualitative features of these growth rate curves are consistent with the model and the expected behavior of crystal growth. As $\Delta\mu$ increases, an adatom is more likely to adsorb to the crystal surface. As kT decreases, the adsorption rate will increase but more importantly, the "selectiveness" of evaporation will increase. A lower kT will in effect increase the energy differences between competing config-urations. The direct result, as growth is concerned, will be that adatoms will increasingly have more neighbors instead of less (layer-by-layer growth vs. rough) and charge similar adatoms will seem even more repulsive. For very high $\Delta\mu$, adatoms will stick anywhere, no matter the location or ionic adversity, and the growth rate will be high. Alternatively, if the temperature becomes too high, the crystal will melt, the preferred phase becomes the liquid phase and result in the
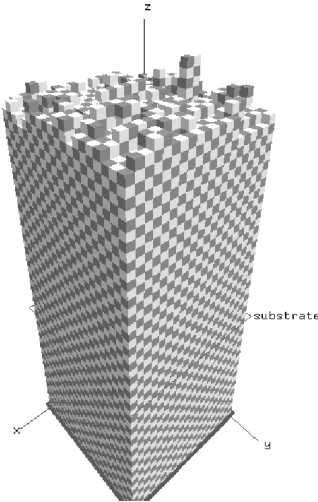
negative growth.

FIGURE 2. Long-Range Simulation for Rock Salt: layer-by-layer growth ($kT = 0.1$ and $\Delta\mu = -0.75$). Grey and white cubes represent the two different species. Initial substrate (seed) is indicated.

An interesting phenomena is the presence of "towers" when very rough growth occurs. At very high adsorption rates, crystal formations nucleate on the surface independent of one another and likely with several defects. As these initial formations grow, they will eventually meet and will not necessarily match up. That is, the alternation of charges will not fit the rock salt description. Since the crystal is growing so fast, there is not time to "correct for" these imperfections with evaporations and the most energy efficient alternative is the creation of individual towers of the correct crystal order. Since surface diffusion is not yet included in our simulation, it remains to be seen how robust these towers are in more realistic situations.

Simulations on heterovalent binaries of the form $II_{1/3}V_{2/3}$ are presently underway. The ground state crystal ordering of Ba-based materials is predicted (and confirmed by equilibrium MC [3]) to be $[111]_{1:2}$. In our model, $q_1 = -2$ and $q_2 = +1$, where the subscript on q is the species identifier of this two species system. In adsorption, the quantity of species one is therefore 1/3 and that of species 2 is 2/3, maintaining the charge neutrality of the B sublattice. Preliminary growth simulations in the [001] direction have shown 1:2 ordering along [111] over limited scales. We believe ordering over extended scales will be achieved as we move to direct simulations of growth along the [111] direction.

IV   SUMMARY AND DISCUSSIONS

In conclusion, we have presented an approach for growth simulations of ferroelectric materials. We use an ionic, long-range model and an enhanced kinetic
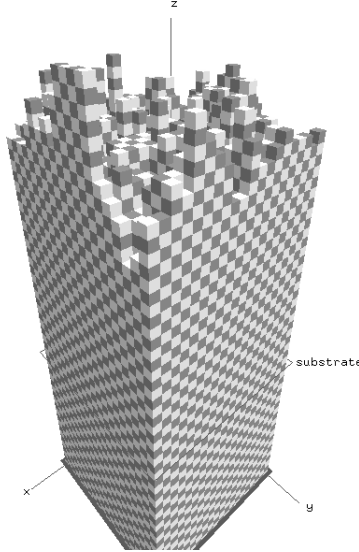
FIGURE 3. Long-Range Simulation for Rock Salt: rough growth with towers ($kT = 0.1$ and $\Delta\mu = -0.65$).

Monte Carlo formalism. Test results from our simulations on rock salt exhibit the expected growth and ordering behavior and are encouraging.

Clearly much progress would have to be made in theoretical and computational capabilities of growth simulations in order for them to contribute in a significant way to the understanding and control of the growth process of relaxor ferroelectric crystals, which has largely remained an experimental issue. Our goal here is a second-principles procedure to study growth processes which can be systematically enhanced. The two components of our approach are a model Hamiltonian and kinetic Monte Carlo. Either can be improved or even replaced eventually. For example, the electrostatic model could be modified to include charge transfer [10]. Within the framework of KMC, the effect of surface migration/diffusion could be incorporated. The impact of the solid-on-solid restriction should be explored. We are also studying growth along directions other than [100] in our simulations of heterovalent binaries.

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