Entropy-Driven Microstructure Evolution Calculated with the Steepest-Entropy-Ascent Quantum Thermodynamic Framework

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A Potts model and the Replica Exchange Wang-Landau algorithm are used to construct an energy landscape for a crystalline solid containing surfaces and grain boundaries. The energy landscape is applied to an equation of motion from the steepest-entropy-ascent quantum thermodynamic (SEAQT) framework to explore the kinetics of three distinct kinds of microstructural evolution: polycrystalline sintering, precipitate coarsening, and grain growth. The steepest entropy ascent postulate predicts unique kinetic paths for these non-equilibrium processes without needing any detailed information about the underlying physical mechanisms of the processes. A method is also proposed for associating the kinetic path in state space to a set of smoothly evolving microstructural descriptors. The SEAQT-predicted kinetics agree well with available experimental kinetics for ZrO$_2$ sintering, Al$_3$Li precipitate coarsening, and grain growth in nanocrystalline Pd. The computational cost associated with calculating the energy landscape needed by the approach is comparable to a Monte Carlo simulation. However, the subsequent kinetic calculations from the SEAQT equation of motion are quite modest and save considerable computational resources by obviating the need for averaging multiple kinetic Monte Carlo runs.

I. INTRODUCTION

The impetus for microstructural evolution lies in one of Clausius’s seminal statements of the second law of thermodynamics: the entropy of an isolated system at constant energy tends to a maximum. Historically, this maximum entropy principle was rarely used in materials science because it is impossible to relate entropy directly to measurable microstructural parameters. Instead, changes during processes like particle sintering, grain growth, and grain coarsening were typically modeled by the conjugate principle of minimizing energy at constant entropy. The kinetics of these processes were expressed as a linear function of a driving force typically taken to be a local free-energy change associated with reducing the area of surfaces and grain boundaries.

In contrast to such kinetic descriptions, the steepest-entropy-ascent quantum thermodynamic (SEAQT) framework provides a practical vehicle for applying Clausius’s maximum entropy principle. The framework identifies unique kinetic paths to stable equilibrium without the need for the usual near- and local-equilibrium assumptions. The SEAQT approach is based upon entropy calculated directly from a discrete energy landscape that covers all possible microstructures of a system. The energy landscape is determined from an appropriate model that depends upon the nature of the physical system [1][2][3]. The model can either be quantum mechanically-based or quantum mechanically-inspired (e.g., solid-state, Ising, Heisenberg, or Potts models).

The contribution presented here applies the SEAQT framework to an energy landscape to describe the kinetics of three kinds of microstructural evolution to demonstrate the generality and flexibility of the approach. The energy landscape is based on a Potts model, which is developed using the Replica Exchange Wang-Landau algorithm [4][5][6] with a Hamiltonian defined for a solid with surfaces and grain boundaries. The algorithm is used to numerically generate the energy landscape and corresponding density of states for the system. The state of the system is expressed as a probability density distribution at each instant of time over the energy levels of the system’s energy landscape [7], and expected values of the energy and entropy are calculated directly from these time-dependent probabilities. The probability density distributions are uniquely predicted by the SEAQT equation of motion, which provides the time evolution of the probabilities that describe the occupancy of the energy levels of the landscape and, thus, the non-equilibrium state of the system in time.

Different starting points or initial conditions on the energy landscape give rise to qualitatively and quantitatively different kinetic paths along which the system evolves. The results for three different initial conditions are given here to demonstrate the phenomenological behavior corresponding to polycrystalline sintering, precipitate coarsening (or Ostwald ripening), and grain growth. The results include time evolutions of the system microstructure as well as the microstructure’s average grain size, the number of grain boundaries and surface boundaries, and the relative density. Even though the three evolutions involve distinctly different phenomenological behaviors, they are obtained with a single model and a single energy landscape without reference to kinetic mechanisms or assumed limiting rates; state evolution in each case is driven simply by the principle of steepest entropy ascent. This principle has been postulated as a fundamental law of nature [8] and is used by the SEAQT equation of motion to maximize the entropy production at each instant along the non-equilibrium path the system takes through state space [9].
The remainder of the paper is organized as follows. Section II A describes the energy landscape and the Replica Exchange Wang-Landau method for developing this landscape. Section II B presents the SEAQT equation of motion and discusses how it is formulated for this application, and Section II C outlines how the system’s state space is linked to the system’s microstructure. Sections II A, II B, and II C present the results of the models for sintering, precipitate coarsening, and grain growth, respectively, and Section IV provides some summary conclusions.

II. METHOD

A. Energy Landscape

The system microstructure is described by a 2-dimensional grid of pixels [22–26] whose energy is given by a q-state Potts model. This model defines a variable, $q$, that monitors the phase at each pixel in the system. The $q$ integers can range from 0 to several hundred, depending upon what physical entity the $q$ phases represent. In this work, each location has an associated integer $q$ value which represents either a void (when $q = 0$) or grain orientation ($q \geq 1$). The larger the maximum number of $q$ values is, the larger the number of allowed grain orientations. Surface energy arises when a void pixel is adjacent to a solid pixel (i.e., when a pixel with $q = 0$ is adjacent to a pixel with $q \geq 1$). Grain boundary energy arises between pixels with different positive $q$ values.

The system is represented by a square $L \times L$ lattice where $L$ is the linear size in pixels. The total energy, $E$, of the system is the sum of the energies of all the surface and grain boundaries and is represented mathematically by the following Potts model interaction Hamiltonian [22–26]:

$$E = \frac{1}{2} \sum_{n=1}^{N} \sum_{z=1}^{Z} J (1 - \delta(q_n, q_z))$$  \hspace{1cm} (1)

In this equation, $E$ is determined by summing over the number of lattice sites (pixels), $N (= L^2)$, and the number of neighbors to each site, $Z$. The Potts coupling constant or interaction energy, $J$, switches between a surface energy, $\gamma_s$, and a grain boundary energy, $\gamma_{gb}$, depending upon the identities of $q_n$ and $q_z$. The $\delta$ on the right side represents the Kronecker delta which returns a value of 1 if the neighboring $z^{th}$ grain to $n$ is of the same orientation (i.e., $q_n = q_z$), or 0 if it is not ($q_n \neq q_z$) [22–26]. Thus, the only contributions to the total energy come from boundaries in the system.

Equation (1) gives the energy of any arbitrary configuration or state of solid grains bounded by surfaces and/or grain boundaries. The energy landscape, or energy eigenstructure, represents all the energies of all possible system configurations. For lattices of appreciable size, many of these configurations have the same energy; stated conversely, most energy levels are degenerate. In order to calculate system properties like the entropy, it is essential to know the degeneracy of each energy level. This information is typically represented as a density of states for each level.

The density of states for the system can be obtained from the Wang-Landau method [27, 28]. The Wang-Landau method is a non-Markovian approach for estimating the degeneracies from a flat histogram generated via a Monte Carlo walk through all the possible energy levels of the system. The algorithm estimates the degeneracies from the fact that Monte Carlo transitions between individual energy levels occur with a probability given by $1/g(E_j)$, where $g(E_j)$ is the estimated degeneracy of the $E_j$ energy level. Repeated Monte Carlo sweeps through the energy spectrum refines the accuracy of the estimates. The “replica exchange” [17, 18] variant of the Wang-Landau method greatly accelerates the algorithm by subdividing the energy spectrum into multiple windows, utilizing multiple Monte Carlo walkers over the energy windows, and passing information among them. The basis of the Replica Exchange Wang-Landau code employed here is given in Vogel, Li, and Landau [29].

The density of states calculated with the Replica Exchange Wang-Landau algorithm for an $L \times L$ lattice with $L = 34$ and 50% solid is shown in Figure 1. The plot represents the natural log of the number of states or configurations as a function of the state energy. For this energy landscape, the surface energy and the grain boundary energy are assumed to be isotropic, and there are a maximum of 50 distinct grain orientations. This figure represents all the energies of all the possible states (configurations) of the physical system and the degeneracy of each energy level.

B. SEAQT Equation of Motion

The SEAQT equation of motion is used to predict the non-equilibrium thermodynamic behavior of the system. This equation requires no a priori knowledge of the kinetic mechanisms involved since it predicts the evolution of system properties on the principle of steepest entropy ascent. For the case of a simple quantum system, this equation of motion is expressed as [30, 32]

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{\rho}, \hat{H}] + \frac{1}{\tau(\hat{\rho})} \hat{D}(\hat{\rho})$$  \hspace{1cm} (2)

In this expression, $t$ is time, $\hbar$ the modified Planck constant, $\hat{H}$ the Hamiltonian operator, $\hat{D}$ the dissipation operator, $\tau$ the relaxation parameter, and $\hat{\rho}$ the density operator, which represents the thermodynamic state of the system (i.e., the distribution of eigenstates that comprise the thermodynamic state) at each instant of time. Note that $[,]$ represents the Poisson bracket. The term on the left-hand side of the equation and the first
FIG. 1. Density of states calculated with the Replica Exchange, Wang-Landau algorithm for a 34 × 34 system consisting of 50% solid with surfaces and grain boundaries. There are 629,997 discrete energy levels for the system. The horizontal axis is scaled by the energy of the maximum level, and the vertical axis is the natural log of the degeneracy of the $E_j$ energy level. a) shows the entire energy landscape; the individual energy levels are represented by points that are too close to differentiate and the density of states appears like a solid, continuous region. b) is a greatly enlarged segment of a) that reveals the individual energy levels. Aligned arcs of points at this magnification correspond to states with the same grain boundary area and the same surface area.
term on the right side, the so-called symplectic term, constitute the time-dependent part of the von Neumann form of the Schrödinger equation of motion used in quantum mechanics to predict the reversible evolution of pure states (i.e., zero-entropy states). The second term on the right is there to capture evolutions involving the non-zero-entropy states of irreversible processes.

Now, since the energy landscape considered here is only quantum-inspired and as a result contains no quantum information, the density operator reduces to a probability density distribution and the symplectic term is zero (because there are no quantum correlations) and, thus, $\hat{H}$ and $\hat{\rho}$, which is diagonal in the energy eigenvalue basis of the Hamiltonian, commute [1, 2, 4, 30–32]. Furthermore, $\hat{D}$, which was originally postulated by Beretta [25, 44], can be derived via a variational principle that preserves the energy and occupational probabilities by a constrained-gradient-descent in Hilbert space along the direction of steepest entropy ascent at each instant of time. For the case considered here when the only two generators of the motion are the Hamiltonian and the identity operators, the equation of motion (Eq. 2) reduces to [30, 32]:

$$\frac{dp_j}{dt} = \frac{1}{\tau} \left[ \begin{array}{c} -p_j \ln \frac{p_j}{g_j} \\ \langle S \rangle \\ \langle E \rangle \\ \langle E^2 \rangle \\ \langle ES \rangle \\ \langle E \rangle \langle E^2 \rangle \end{array} \right]$$

(3)

Here, $p_j$ represents the occupation probability of the $j^{th}$ energy eigenlevel, $E_j$, and $g_j$ its associated degeneracy. The degeneracy is the number of possible system configurations for a given energy eigenvalue. In the SEAQT framework, the von Neumann form for entropy, $S_j = -p_j \ln \frac{p_j}{g_j}$, is used because it satisfies the necessary characteristics for the entropy required by thermodynamics [35] and it provides a simple means of directly calculating the entropy of the system in any of its possible states. Additionally, $\langle \cdot \rangle$ represents the expectation value of a property of the system such as the energy, $E$, the entropy, $S$, the energy squared, $E^2$, or the product of the energy and entropy [30, 32], e.g.,

$$\langle E^2 \rangle = \sum_j E_j^2 p_j$$

(4)

$$\langle ES \rangle = \sum_j E_j p_j \ln \frac{p_j}{g_j}$$

(5)

Although the equation of motion is only applicable to an isolated system, any set of systems may be treated as an isolated composite of subsystems. This enables interactions — such as the exchange of heat and mass — among subsystems to be taken into account. For example, the equation of motion for an isolated composite of two subsystems $A$ and $B$ experiencing a heat interaction is given by [1]:

$$\frac{dp_j}{dt^*} = p_j^A \left( -\ln \frac{p_j^A}{g_j^A} - \frac{C_A^2}{C_1} - E_j^A \right)$$

(6)

$$\frac{dp_j}{dt^*} = p_j^B \left( -\ln \frac{p_j^B}{g_j^B} - \frac{C_B^2}{C_1} - E_j^B \right)$$

(7)

where the dimensionless time $t^* = \int_0^t \frac{1}{\tau(R)} dt'$ is used to replace $t$ and $\tau$. In this definition for the dimensionless time, the dissipation parameter, $\tau$, is taken to be a function of the time-dependent occupation probabilities $p_j$ represented as the vector $\vec{p}^c$.

If the size of subsystem $B$ is assumed to be significantly larger than $A$, subsystem $B$ can be treated as a reservoir, denoted by $R$, and the previous equation reduces to [1, 4]:

$$\frac{dp_j^A}{dt^*} = p_j^A \left( -\ln \frac{p_j^A}{g_j^A} - \frac{C_A^2}{C_1} - E_j^A \beta R \right)$$

(8)

where $\beta R = C_3/C_1$ reduces to $\frac{1}{T}$ with $T R$ representing the temperature of the reservoir. With this formulation, the constant-temperature kinetic processes can be simulated [1, 2].

To solve the system of equations represented by Eq. (8), an initial condition defined by a distribution of occupied energy levels is needed. Eigenstructure information was used to generate initial microstructures for the three types of microstructural evolution considered (sintering, coarsening, and grain growth). For sintering, the initial microstructure was chosen to be an agglomeration of un-sintered particles, for coarsening, it was a distribution of small precipitates within a single grain, and for grain growth the initial microstructure was a collection of small grains within a contiguous solid without voids. Partially canonical distributions along with a perturbation function are then used to calculate the initial probability distributions needed for the SEAQT equation of motion. The partially canonical probabilities of the initial condition, the $p_j^c$, are calculated from,
where \( \delta_j \) takes a value of 1 or 0 depending on whether or not it is assumed that the \( j^{th} \) energy eigenvalue is initially occupied or not and \( g_j \) and \( E_j \) are the degeneracy and energy eigenvalue of the \( j^{th} \) eigenvalue. In this equation, \( \beta_{\text{pe}} \) is an unknown determined by adding an energy constraint to the system of equations for the \( p^e_{j\text{pe}} \). Once the initial \( p^e_{j\text{pe}} \) are known, an initial non-equilibrium distribution (i.e., initial state) is found using a perturbation function that utilizes the partially canonical probabilities and those of a corresponding canonical distribution.

\[
p^e_{j\text{pe}} = \frac{\delta_j g_j \exp(-\beta_{\text{pe}} E_j)}{\sum_j \delta_j g_j \exp(-\beta_{\text{pe}} E_j)} \quad (9)
\]

C. Linking State Space to Microstructure

A distinguishing feature of the SEAQT framework is that it works in state space, i.e., Hilbert space or Fock space. The kinetic path is calculated from the component of the entropy gradient perpendicular to the manifold that conserves the generator of motion (e.g., the Hamiltonian and the identity operators). Consequently, it does not depend upon an actual mechanism or even a microstructure to determine how the system evolves. However, to extend its usefulness and help validate the SEAQT framework, the kinetic path information in state space must be connected to the physical microstructures of the evolving material. This is challenging because the degeneracies of some energy levels can be beyond enormous (Figure 1 indicates there are more than \( 10^{1300} \) configurations for some energy levels of the present energy landscape!) and the microstructures corresponding to a single energy level can be quite different from each other.

This situation poses two problems. The first is that it is impossible to store all the representative microstructures from such an astronomically large collection of possibilities, and the second is that even if one could, randomly selected microstructures along the smooth kinetic path would not necessarily be at all related to each other in time. However, it is possible to select representative microstructures that are consistent with a smooth evolution of microstructure by introducing one or more microstructural parameters in the description of the states. These descriptors can be used to select from among the many degenerate configurations only those that are consistent with a given initial state’s evolution to some final stable equilibrium state. Each microstructural descriptor is chosen to reflect an important physical characteristic. For example, relative density, grain boundary length, and surface length are appropriate descriptors to track sintering kinetics. In the cases of precipitate coarsening and grain growth, appropriate descriptors are the average precipitate size (area) and grain size (area), respectively.

Once an appropriate set of descriptors are selected, state space is linked to the system’s microstructural evolution with the following procedure. First, the Replica Exchange Wang-Landau algorithm is run to establish the energy levels and the density of states for the energy landscape. At the same time, the values for one or more microstructure descriptors are calculated and recorded for a selected fraction of the times an energy level is visited by the algorithm (e.g., about 20% of the visits). Each energy level is characterized by arithmetically averaging the descriptor(s) over the recorded fraction of visits to the level. Second, an initial state on the energy landscape is selected and the SEAQT equation of motion is solved to find the kinetic path through state space. The energy levels along this path with non-zero occupation probabilities typically represent a very small subset of all the available energy levels; they are the only levels for which microstructure information need be stored. Third, the Replica Exchange Wang-Landau code is re-run to record representative microstructures only for this small subset of energy levels and that also have microstructural descriptor values close to the averaged value for the energy level. This subset of representative microstructures is indexed by energy level and one or more arithmetically-averaged descriptor value(s).

Lastly, at each moment of time along the SEAQT kinetic path, the occupation probabilities are used to calculate the system energy (an expectation value) and weight-averaged descriptor values. These values at each time are used to select the closest microstructure from the collection of stored representatives. The resulting time sequence of microstructures evolves smoothly and continuously along the kinetic path through state space. Additional properties such as the relative density and particle size distribution of the system microstructure can, of course, also be tracked in time.

To scale the results predicted by the SEAQT equation of motion to real time, the relaxation parameter, \( \tau \), from Equation \( \tau \) can be linked to experimental data or to some dynamical model of the phenomena involved. The former approach is used here. Thus, \( \tau \) as a function of the real time, \( t \), is determined from experimental data found in the literature.

Finally, grain area calculations for the individual energy levels are based upon the percolation algorithm found in [50]. The algorithm functions by assigning tags to individual pixels in the modeled domain. When particles of like orientation are checked the system assigns the smallest available tag to both grains and adds the counted area of the grains to this tag. This function allows for efficient calculation of grain size in a single pass of a given lattice.

III. RESULTS

A. Sintering

The evolution of microstructure during sintering is shown in Figure 2 which presents a time series of mi-
FIG. 2. Sequence of representative microstructures during sintering. Each image represents a weighted average of the expected states obtained from the SEAQT equation of motion and a descriptor that links the energy levels to the microstructure. The descriptor in this case is the average grain size. Panel a) is the initial state and panels b) through f) are example microstructures along the kinetic path to stable equilibrium.
crostructures of the material subsystem (the thermodynamic system is a composite system of the material plus the thermal reservoir of Equation 9). Part a) of the figure is the initial microstructure. Each pixel in the figure represents a powder particle 10 nm on a side. The pixel colors indicate crystal orientations, and gray pixels are voids. Different colors adjacent to each other indicate either two grains separated by a grain boundary or a grain with a surface. The maximum number of possible orientations is 50. The physical parameters chosen for the simulation correspond to sintered zirconia with a surface energy of 2.570 J/m² and grain boundary energy of 0.987 J/m² [37, 38].

Initially, the energy of the material subsystem is distributed over a narrow set of energy levels associated with many small powder particles. As the material subsystem in Figure 2 moves toward stable equilibrium, the steepest entropy ascent principle distributes the subsystem energy more uniformly over the available energy levels. Since the energy of the subsystem in this model arises only from surface and grain boundaries [39], the removal boundaries during sintering is accomplished by transferring heat from the material subsystem to the thermal reservoir. When the evolution of states predicted by SEAQT equation of motion are converted to microstructures, the common physical features of sintering and grain growth are evident. For example, the initial small, single-crystal powder particles agglomerate to form larger polycrystalline particles with necks between them (Figure 2f), and these polycrystalline particles gradually grow in size (Figures 2g–e). The smaller powder particles eventually disappear entirely as a single solid mass appears (Figure 2h). Also, the grains within each of the polycrystalline particles grow in size during the process (Figure 2i–d). Within the larger particles, one grain orientation eventually grows at the expense of all the others, and at stable equilibrium, the entire solid becomes a single-crystal with minimum surface area (the flat surfaces in Figure 2i result from periodic boundary conditions on the simulation domain).

The change in relative density associated with this microstructural evolution is shown in Figure 3. The relative density descriptor is calculated from averaged configurations of the thermodynamic states represented by the probability distributions predicted by the SEAQT equation of motion. The predicted relative density in Figure 3 deviates only slightly from the experimental results of [37]. The largest deviation, which occurs at later times for 700 MPa sintering (Figure 3a), suggests equilibrium was not reached during lower pressure sintering because the experimental relative density failed to reach 100%.

Note that the SEAQT framework tracks system evolution through state space rather than through a microstructural space as is done with approaches like kinetic Monte Carlo (KMC). This creates important differences between the two methods, notably with regard to how representative configurations of the microstructure are selected and evolve. In KMC models, individual microstructures or snapshots are sequentially linked in time and are used to approximate material processes. Many KMC models also commonly begin with an idealized starting structure and may utilize algorithms to reduce the computational complexity [25, 40]. In contrast, the SEAQT framework utilizes state-based properties to track the kinetic path so that the selected microstructures are linked by evolving properties, i.e., energy and entropy, versus being explicitly linked in time. In addition, to maintain the generality of the model within the domain of the system, unconstrained particle exchange is allowed.

This difference means that greater microstructural variety may be present for a given state in the SEAQT framework, and the average morphology for a given energy level has the potential to differ significantly from a similar level visited in a KMC simulation. In other words, the average state-based morphology in the SEAQT framework possesses a greater number of similar permutations than a similar state visited in a KMC model. Thus, under KMC, a specific morphology may exert an inordinate influence on the state’s canonical properties. In addition, averaged state properties, such as grain size and particle size distribution, may vary for a KMC simulation, which visits the same energy level. This sampling problem makes it necessary to statistically average multiple KMC runs to obtain representative properties. This sampling problem is avoided in the SEAQT framework because all the evolving properties are expressed as time-dependent expected values.

An example of this difference is in the calculation of the relative density. In KMC, the relative density values are commonly calculated by selecting an inner region of the sintering mass and calculating the fraction of the occupied sites versus the number of occupiable sites within the selected region [22, 26, 40]. Additionally, KMC simulations often utilize processes to optimize the evolution of the sintering mass, which are not replicated with the SEAQT framework. Instead, the relative density is determined by selectively removing columns or rows from the simulated 2D domain, which contain the smallest number of individual grains. This process is successively iterated until > 95% of the original solid remains. This reduces the number of vacant sites in the system and creates similar bounds for the coarsening region. In this way, the relative density values and trends can be determined and compared with experimental data as is shown in Figure 3.

Overall, the experimental kinetics are described closely by the steepest entropy ascent principle. The predicted relative density in Figure 3 has an asymmetric S-shaped curve that reflects changing stages in the state of the subsystem and as well as the underlying microstructure evolution. The initial stage before significant grain growth corresponds to an initial incubation-like period of slow particle consolidation. Afterwards, the material transitions to a rapid densification stage with concurrent grain growth. This is followed by a final asymptotic stage.
FIG. 3. The relative density (a microstructural descriptor linked to energy levels) during sintering calculated from the SEAQT equation of motion. The two results model the evolution for simulated compacted Zirconia powder at pressures of 700MPA and 1000MPA. The differences in compaction pressures affect the starting relative density values and are modeled by averaging the relative density for 3000+ states at two separate initial probability evolution conditions.

FIG. 4. Scaling factor $\tau$ versus real time in minutes. The variance in the plotted values for $\tau$ effect the rapidity of certain phases in the microstructural evolution in the real system versus the initial simulation results.
during which the rate of property evolution decreases significantly. Microstructurally, this stage is characterized by a reorientation and agglomeration of the largest grains and a steady reduction of the remaining individual grains in the subsystem. As already mentioned above, these results correspond closely with yttria-stabilized zirconia sintering results used for comparison \[37\]. The relative density increase exhibits similar beginning and end lags and an intermediate stage of significant growth. However, the final stage of the experimental results for the yttria-stabilized zirconia still contains multiple grain boundaries not present in the SEAQT results. This can be attributed to the conformational freedom of the model; no constraints were placed on the model to prevent it from achieving stable (single-crystal) equilibrium.

The dissipation parameter, \( \tau \), in the SEAQT equation of motion can be adjusted to fit the predicted kinetics to experimental data. The values of \( \tau \) that were used to match the experimental sintering kinetics at 700 MPA and 1 GPa (Figure 3) are shown in Figure 4. Physically, these \( \tau \) values reflect how fast the system moves along the kinetic path in state space.

Now, one of the distinct advantages of working in state space is that the steepest-entropy-ascent (or, equivalently, maximum entropy) principle is able to identify the unique kinetic path a system follows without any prior knowledge of the physical mechanisms involved. This is illustrated schematically in Figure 5, which represents a plot of the energy of the material subsystem as a function of its entropy. The solid bounding curve represents the set of equilibrium states; the ground state is the energy at the point \( S = 0 \). The two red points represent arbitrary non-equilibrium states. The information contained in the SEAQT equation of motion provides the unique path from an initial state to stable equilibrium (the dashed gray curve) that maximizes entropy ascent at each point in time. In the sintering case, the entropy of the material subsystem decreases from the initial state as surface and grain boundaries are removed from the solid and heat is transferred from the subsystem to the reservoir. However, the net entropy of the overall composite system (subsystem plus reservoir) increases along the path to equilibrium (see Figure 5b), and this entropy ascent spontaneously drives the sintering process. It is worth noting that most computational tools for finding stable states — like density functional theory, kinetic Monte Carlo methods, and molecular dynamics — all minimize system energy without regard to how energy is dissipated. Thus, these tools cannot predict the thermodynamic path between an arbitrary initial state and a stable equilibrium state. Perhaps most surprisingly, the SEAQT equation of motion predicts the microstructural evolution sequence (Figure 2) without any explicit assumptions about how the surfaces and grain boundaries physically behave during the sintering process.

B. Precipitate Coarsening

Appropriate regions of the energy landscape (Section II A and Figure 1) can be used to describe precipitate coarsening kinetics. Specifically, we represent a precipitate phase as a single grain orientation (one color or \( q \)-state of the Potts model) contained within a parent, or matrix, phase designated by a second orientation (color). Precipitate coarsening kinetics are simulated by choosing an initial state in a region of the energy landscape that has no surfaces and only two orientations. These two orientations can be interpreted as representing precipitate particles undergoing coarsening within a matrix phase.

The SEAQT predicted coarsening kinetics of a precipitate phase are compared against experimental data for the coarsening of \( \text{Al}_3\text{Li} \) precipitates (designated \( \delta' \)) in an \( \text{Al–Li} \) solid solution (the \( \alpha \) matrix) \[41–44\]. This alloy system is convenient because \( \delta' \) precipitates are nearly spherical and are thus comparable to the morphologies expected from the isotropic boundaries assumed in the model energy landscape. The representative microstructures calculated during grain growth are shown in Figure 6. The initial state is shown in Figure 6a.

In the actual alloy, the initial state for the coarsening process is a dispersion of small precipitates produced by nucleating \( \delta' \) precipitates within a supersaturated grain of \( \alpha \) \[41–44\]. Only one \( \alpha \) grain is considered, so there is only one matrix orientation. The energetics of nucleation in this system ensures that only one \( \delta' \) orientation appears within any particular \( \alpha \) grain, so the precipitate coarsening kinetics can be described with only two colors. In the model microstructure (Figure 6b), the \( \alpha \) phase is represented by the dark purple pixels and the \( \delta' \) phase by the yellow pixels. Rather than “grain” boundaries, the boundaries between purple and yellow pixels represent interphase boundaries. In the \( \text{Al–Li} \) system, the \( \delta' : \alpha \) boundary energy is quite small; it is assumed to be 0.005 \( \text{J/m}^2 \) for the SEAQT coarsening simulation \[45\].

In contrast to the sintering studies, precipitate coarsening is commonly characterized using precipitate size distributions. The precipitate size distribution is reported using normalized values for the precipitate size and frequency distributions. The normalized precipitate size is given by \( R/R' \) where \( R \) is the precipitate size of an individual precipitate crystal and \( R' \) is the average precipitate size. The frequency is normalized by the maximum frequency. The purpose of normalizing this way is to compare the system evolution with dimensionless values in time. The precipitate size distributions are commonly invariant with time.

In the SEAQT model, the precipitate size distribution is based upon the grain size normalized using the average of the distribution. Additionally, as in the sintering case, a cutoff of 10% of the largest grain size was used to reduce noise in the precipitate size statistics. The normalized precipitate size distributions at the initial state and final equilibrium state as well as at four intermediate non-
FIG. 5. (Left) A schematic plot of the energy versus entropy of the material subsystem. The bounding solid curve represents the set of equilibrium states and the two red points are possible non-equilibrium states. The SEAQT equation of motion provides a unique path from an initial state (red point on the right) to stable equilibrium along the dashed gray curve. Techniques like density functional theory and kinetic Monte Carlo methods minimize energy without regard to energy dissipation so there is no thermodynamic path between an initial state and final equilibrium. (Right) The entropy production that drives the subsystem from a non-equilibrium initial state to equilibrium along the kinetic path determined by the SEAQT equation of motion. Entropy of the composite system increases despite the fact that heat transferred out of the subsystem into the reservoir reduces the entropy of the material subsystem.
equilibrium states along the system’s kinetic path are shown in Figure 7.

In the precipitate coarsening simulation, the evolution of roughly circular precipitates is seen (Figure 6). The evolution of the precipitates is similar to the sintering results with respect to the stages of particle size evolution occurs. However, in the case of precipitate coarsening, the ending lag is not observed. This is likely a consequence of the limited size of the simulation domain.

As mentioned previously, the size distribution during precipitate coarsening is expected to be invariant in time and to form a normal distribution around the normalized grain size value. In the present model, approximately circular particles are appear throughout the lattice, and the square root of the calculated area for each precipitate is utilized to approximate precipitate size or diameter. The observed precipitate size distribution follows a log-normal distribution, which is consistent with the Lifshitz-Slyozov-Wagner theory often used to describe precipitate coarsening behavior. Furthermore, this theory states that the evolving precipitate size is proportional to the time, \( t \), such that \( R \propto t^{1/3} \). Note, however, that this type of distribution is often inconsistent with experimentally observed behavior in many alloy systems.

As seen in Figure 7, the general shape of the precipitate size distribution for the system is maintained for a majority of the simulation runtime. Near the end, as the energy of the system decreases, a bimodal distribution begins to appear, which eventually transforms into a normal distribution centered around a normalized average grain size value of 1.

This bimodal distribution develops mainly because of the thermodynamic driving force that favors denser and denser structures as the energy of the system decreases and its state approaches mutual stable equilibrium with the heat reservoir. In other words, as equilibrium is approached, the system prioritizes the growth of a singular large-precipitate structure with smaller degeneracies and, thus, bypasses any potential configurations in which two or more similarly-sized precipitates grow in parallel. As a result, only a few very small grains at distinct locations appear, leading to a significant bimodal gap for precipitate size distributions associated with lower subsystem energies.

Finally, when the images of the representative microstructures in Figure 7 are compared to those of physical systems, it is seen that the state-space evolution is able to capture the approximately circular growth of the \( \delta' \) precipitates (Figure 6b and c) as well as disappearance of the small ones (Figure 6d and e) and the eventual dominance of large ones (Figure 6f) during the coarsening process.

C. Grain Growth

The kinetics of grain growth predicted by the SEAQT framework from the aforementioned energy landscape (Section II A and Figure 1) can be simulated by starting with an initial state that represents a fully dense solid with a collection of up to 50 different grain orientations represented by different pixel colors. The representative microstructures predicted by the SEAQT equation of motion are shown for various annealing times in Figure 8.

The physical size of the initial grains represented by the pixel size was set at 1 nm on a side, which corresponds approximately to the initial grain size in a nanocrystalline Pd system [46]. The surface boundary energy used for this system is 1.47 J/m\(^2\) taken from a weighted average found in Tran [17]. The grain boundary energy utilized is 0.8 J/m\(^2\) [46]. This system is chosen for its similarities with the microstructural descriptors calculated previously.

The initial state begins with a near-maximum number of grain boundaries, i.e., adjacent pixels all have different colors and, thus, represent grains of different orientations. To consider only grain boundary changes independent of any changes in surface energy, the initial state is a single solid block of individual grains selected to have a minimum number of surface pixels. Because of periodic boundary conditions, this yields planar top and bottom surfaces in Figure 8. There are no internal voids for this simulation of pure grain growth. Figure 8b is a very different initial condition from that of sintering (Figure 2b) and precipitate coarsening (Figure 6b), but each of these simply represent different starting states that can be found on the general energy landscape of Figure 1.

The microstructural changes predicted by the SEAQT framework in Figure 8 follow the general expectations of grain growth: the average grain size increases in Figures 8a) through 8c) as small grains coalesce into larger grains and the larger grains continue to grow at the expense of the smaller grains. At stable equilibrium (Figure 8f), the system consists of a single grain with minimum surface area.

The average grain size and grain size distribution are the descriptors used to characterize grain growth evolution with time. The evolution of the average grain area, a descriptor calculated from averaged configurations of the states represented by the probability distributions, is shown in Figure 9. The predicted average grain size curve has an overall “S-shape” that matches the growth kinetics of nanocrystalline Pd [46] quite well at short times. At longer times (beyond annealing times of 20 hours) the experimental data deviates from the predicted kinetics, but there are a couple of possible explanations for this deviation. Grain growth in thin, transmission electron microscopy samples is expected to slow as the grain size approaches the sample thickness (on the order of 100\(\mu m\)) and thermal grooving begins to pin grain boundary migration. Ames et al. [45] also note that Pd grain growth begins with an initial slow grain growth followed by a period of rapid abnormal grain growth, and ends with a potential reoccurrence of the initial steady grain growth. The abnormal grain growth violates the statistical self-similarity postulate for a sintering system, which states...
FIG. 6. Sequence of representative microstructures during coarsening of Li-rich δ′ precipitates (yellow) in an aluminum matrix (purple). Each image represents a weighted average of the expected states obtained from the SEAQT equation of motion and a descriptor that links the energy levels to the microstructure.
that evolving systems in time should retain the statistical similarity of their geometric features. Nonetheless, the abnormal behavior is generic in nano-grained systems and may be caused by the release of microstrain as grain size increases [46].

D. Discussion

The compatibility of the SEAQT framework predictions of microstructural evolutions with those of traditional kinetic models is complicated by a few issues. As stated previously, a representative lattice for a given energy level determined from the Replica Exchange Wang-Landau algorithm, will appear visually distinct from that determined along a given kinetic path of a KMC modeled system. One specific example is the presence of individual pixel grains that remain in the conformational space of the simulation. The presence of these peculiar grains is due to the nature of the Replica Exchange, Wang-Landau process, which estimates the density of states independent of a modeled kinetic path. Often to reach these energy levels, physically unexpected but intuitively easier transitions occur. Transitioning to higher energy levels by placing a grain currently in contact with a larger coarsening mass into a vacant void site is often easier than complex conformations of the existing structure. Multiple similar transitions can lead to individual grains located significantly far apart from the majority of the coarsening mass. Thus, small grains, in proportion to the larger coarsening mass, are partially ignored in the present descriptor calculations such as those for the relative density and precipitate size distribution calculations since their variable locations can nonphysically bias the values output. Future work to counteract this behavior could bias transitions to reduce the probability of particle and vacant site exchanges or restrict translational movement during grain transitions.

Another method to potentially further distinguish between these variable microstructural formations would be the addition of other energetic terms. One example is the addition of 2nd nearest neighbor energetic considerations. This addition would allow grain agglomeration to be more easily differentiated energetically because of the higher number of grain sites considered in the energy interaction of a single grain. It would also distinguish lattices with a large number of grains surrounded by vacant sites attributable to the higher energy associated with the transition. This and other additional energetic considerations would result in an increased computational cost from the higher number of energy levels and could potentially limit the size of the simulated system.

The data presented for the precipitate coarsening and grain growth case should be regarded as demonstrating qualitative trends. Although the data aligns closely to expected results, it is intended here to only demonstrate the applicability and flexibility of the SEAQT framework rather than a particular quantitative result. Such a result could be had with a more precise energy landscape. For example, with regard to modeling the precipitate coarsening kinetics, the volume fraction of the precipitate \(\delta'\) in the simulated or experimental systems is significantly lower than in the system shown in these articles [41, 44, 45, 48–52]. Commonly simulated values for the volume fraction do not exceed \(>30\%\) [44]. In experimental work the volume fraction trends towards \(<12\%\). The constraints on this fraction are either physical and due to solubility limits on the amount of precipitate phase formed or conform to kinetic theory, which relies on a lower density to match experimental results more closely. Thus, the main inadequacy of using the current eigenstructure or landscape with the SEAQT equation of motion to predict precipitate coarsening kinetics is the higher volume fraction of the precipitate phase, which increases the potential for interactions between individual coalesced particles. The resultant formations can impede the formation of spherical particles and skew the expected precipitate size distribution. Improving the calculation of precipitate coarsening kinetics will require calculating a new, more accurate eigenstructure that accounts for particle interactions or has a smaller solute concentration. In that case, a new eigenstructure could also be constructed to remove grain boundary interactions as a free parameter. Removing this degree of freedom in the model and thus, reducing the number of occupied grain sites would also allow for the possibility of simulations of larger systems with higher spatial resolution. Additionally, this would make a more efficient estimation of the density of states possible due to the reduction in the number of available energy levels.

Another limitation of the present energy landscape or eigenstructure is its limited spatial resolution. The mass conservation constraint used in the model in Section 2.HC [17] forces the modeling of grain growth behavior to occur along a path of minimum surface boundaries. This is intended to mimic grain growth in a system with a defined number of vacant sites. However, because of the lack of spatial resolution for this particular landscape, the dimensional configurations are effectively limited to a single spatial direction. This can prevent the formation of spherical grains and bias the particle size distribution.

A more robust method of calculating grain growth would require a new eigenstructure where grain boundary energy is the only energetic parameter. Removing the degree of freedom of surface boundaries, as is done in the precipitate coarsening case, allows for the calculation of a larger number of available sites. Additionally, other types of kinetics, like recrystallization, could be modeled by including additional energy terms for stored plastic deformation in the energy eigenstructure.

Finally, it is important to note that most of the computational resources required by the SEAQT framework are needed to generate the energy landscape (Figure 1) via the Replica Exchange, Wang-Landau algorithm. This algorithm calculates the energy levels and their associated degeneracies via a non-Markovian Monte Carlo walk.
FIG. 7. Sequence of precipitate size distribution during coarsening of Li-rich $\delta'$ precipitates in an aluminum matrix. Each image represents the normalized frequency of grain size distribution averaged over multiple representative lattices for the given energy levels.
through the system’s energy spectrum. The computational time to do this depends upon the number of energy levels and the degrees of freedom of the problem of interest. However, a great benefit of the framework is that the landscape only needs to be calculated once. The kinetics are subsequently obtained from the SEAQT equation of motion, which is a system of first-order ordinary differential equations, applied to the energy landscape for a specific initial condition. This is a relatively modest problem and can easily be repeated for any number of different initial conditions. Furthermore, since the SEAQT equation of motion produces a single kinetic curve for each initial condition and expresses properties and descriptors as expected values, there is no need to repeatedly simulate any particular kinetic path over and over again and average the results, as must be done with traditional KMC approaches. Thus, the SEAQT framework is effectively computationally comparable to a couple of Monte Carlo simulations.

IV. CONCLUSIONS

The principle of steepest entropy ascent is applied to a simple energy landscape to describe the kinetics of three related physical processes (sintering, precipitate coarsening, and grain growth) under one framework without assuming the system is in local- or near-equilibrium and without ad hoc assumptions about the rate controlling mechanisms of the processes. The computationally efficient Replica Exchange, Wang-Landau algorithm is used to generate an energy landscape and the degeneracies associated with the energy levels, while a method is proposed for linking microstructural descriptors to state space. Once an accurate energy landscape and descriptors are constructed, the SEAQT framework is used to find a unique kinetic path via an equation of motion in the form of a system of first-order, ordinary differential equations. With respect to the comparisons of theory with experiment:

1. The SEAQT-predicted kinetics qualitatively agree with the available experimental kinetics for ZrO$_2$ sintering, Al$_3$Li precipitate coarsening, and grain growth in nanocrystalline Pd.

2. The predicted kinetics can be brought into quantitative agreement by simply adjusting the SEAQT relaxation parameter, $\tau$.

3. The kinetic path through state space predicted by the SEAQT framework can be linked directly to the microstructure through one or more descriptors averaged over the occupied energy levels.

4. The computational burden associated with applying the SEAQT framework to the three physical processes is limited primarily to constructing the energy landscape; solving the SEAQT equation of motion is straightforward and requires limited computational resources.

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FIG. 8. Sequence of representative microstructures during coarsening of Pd nano precipitates. Each image represents a weighted average of the expected states obtained from the SEAQT equation of motion and a descriptor that links the energy levels to the microstructure. The descriptor in this case is the average grain size. Panel a) shows the microstructure of the initial state of many small grains, panels b) through e) provide the microstructures for increasing annealing times, and panel f) is the microstructure of a single crystal at stable equilibrium.
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FIG. 9. The growth in average grain size (a microstructural descriptor linked to the energy levels) predicted by the SEAQT equation of motion. The red curve denotes the curve fitted to the experimental data. The black curve conversely is the prediction of the grain size evolution beyond the experimental data [46].