MATERIALS MICROSTRUCTURES: ENTROPY AND CURVATURE-DRIVEN COARSENING

KATAYUN BARMAK

Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027

EVA EGGELING

Fraunhofer Austria Research GmbH, Visual Computing, A-8010 Graz, Austria

MARIA EMELIANENKO

Department of Mathematical Sciences, George Mason University, Fairfax, VA 22030

YEKATERINA EPSHTEYN

Department of Mathematics, The University of Utah, Salt Lake City, UT, 84112

DAVID KINDERLEHRER

Department of Mathematical Sciences, Carnegie Mellon University, Pittsburgh, PA 15213

RICHARD SHARP

Microsoft Corporation One Microsoft Way Redmond, WA 98052

SHLOMO TA'ASAN

Department of Mathematical Sciences, Carnegie Mellon University, Pittsburgh, PA 15213

For Hiroshi Matano

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ABSTRACT. Cellular networks are ubiquitous in nature. Most engineered materials are polycrystalline microstructures composed of a myriad of small grains separated by grain boundaries, thus comprising cellular networks. The grain boundary character distribution (GBCD) is an empirical distribution of the relative length (in 2D) or area (in 3D) of interface with a given lattice misorientation and normal. Material microstructures evolve by curvature driven growth, seeking to decrease their interfacial energy. During the growth, or coarsening, process, an initially random grain boundary arrangement reaches a steady state that is strongly correlated to the interfacial energy density. In simulation, if the given energy density depends only on lattice misorientation, then the steady state GBCD and the energy are related by a Boltzmann distribution. This is among the simplest non-random distributions, corresponding to independent trials with respect to the energy.

Here we an describe an entropy based theory which suggests that the evolution of the GBCD satisfies a Fokker-Planck Equation, an equation whose stationary state is a Boltzmann distribution. The properties of the evolving network that characterize the GBCD must be identified and appropriately upscaled or 'coarse-grained'. This entails identifying the evolution of the statistic in terms of the recently discovered Monge-Kantorovich-Wasserstein implicit scheme. The undetermined diffusion coefficient or temperature parameter is found by means of a convex optimization problem reminiscent of large deviation theory.

CONTENTS

1. INTRODUCTION

Cellular networks are ubiquitous in nature. They exhibit behavior on many different length and time scales and are generally metastable. Most technologically useful materials are polycrystalline microstructures composed of a myriad of small monocrystalline grains separated by grain boundaries, and thus comprise cellular networks. Here we are concerned with the boundary network whose energetics and connectivity play a crucial role in the

properties of a material across a wide range of scales. A central problem of materials science is to develop technologies capable of producing an arrangement of grains that provides for a desired set of material properties. Traditionally the focus has been on distributions of geometric features, like cell size, and a preferred distribution of grain orientations, termed texture. Attaining these gives the configuration order in a statistical sense. More recent mesoscale experiment and simulation permit harvesting large amounts of information about both geometric features and crystallography, and subsequently the energetics, of the boundary network, [2],[1],[37],[53],[54]. This has led us to the notion of the Grain Boundary Character Distribution (GBCD).

The grain boundary character distribution (GBCD) is an empirical distribution of the relative length (in 2D) or area (in 3D) of interface with a given lattice misorientation and grain boundary normal.

We describe two discoveries about the GBCD. First is that during the growth process, an initially random grain boundary arrangement reaches a steady state that is strongly correlated to the interfacial energy density. In simulation, a stationary GBCD is always found. Moreover there is consistency between experimental GBCD's and simulated GBCD's. The boundary network of a cellular structure is naturally ordered. For a perspective on these issues, we recommend the article by R. V. Kohn [39].

A second discovery is that if the given interfacial energy density depends only on lattice misorientation, then the steady state GBCD and the density are related by a Boltzmann distribution. This is among the simplest non-random distributions, corresponding to independent trials with respect to the density. Such straightforward dependence between the character distribution and the interfacial energy offers evidence that the GBCD is a material property. It is a leading candidate to characterize texture of the boundary network [37].

Here we describe our recent work developing an entropy based theory that suggests that the evolving GBCD satisfies a Fokker-Planck Equation, [10],[15], cf. also [11], [9], [16], to which we refer for a more complete exposition. Coarsening in polycrystalline systems is a complicated process involving details of material structure, chemistry, arrangement of grains in the configuration, and environment. In this context, we consider just two competing global features, as articulated by C. S. Smith [55]:

- interface growth according to a local evolution law and
- space filling constraints, or, confining the configuration to a fixed region.

We shall impose the familiar curvature driven growth for the local evolution law, cf. Mullins [49]. Space filling requirements are managed by critical events, rearrangements of the network involving deletion of small contracting cells and facets. The properties of this system that characterize the GBCD must be identified and appropriately upscaled or 'coarse-grained'. A general platform for this investigation is large scale computation. Numerical simulations are well established as a major tool in the analysis of many physical systems, see for example [60],[42],[43],[26],[27],[21],[57],[56],[23],[24], [40],[51],[22],[44],[46]. However, the idea of large scale computation as the essential method for the modeling and comprehension of large complex systems is relatively new. Porous media and groundwater flow

is an important case of this, see for example [30],[5],[4],[7],[6]. For coarsening of cellular systems, it is a natural approach as well. The laboratory is the venue to assess the validity of the local evolution law. Once this law is adopted, we appeal to simulation, since we cannot control all the other elements present in the experimental system, many of which are unknown. On the other hand, *in silico* we may exercise, or at least we may attempt to exercise, precise control of the variables appropriate to the evolution law and the constraint.

There are many large scale metastable material systems, for example, magnetic hysteresis, [18], and second phase coarsening, [45],[62]. In these, the theory is based on mesoscopic or macroscopic variables simply abstracting the role of the smaller scale elements of the system. There is no general 'multiscale' framework for upscaling from the local behavior of individual cells to behavior of the network when they interact and change their character. This is the principal challenge of the theory for coarsening. We must attempt to tease the system level information from the many coupled elements of which it consists. This information will be available primarily from the dissipation relation (2.6) which is implied by the balance of forces at triple junctions (2.3), due to Herring, [31],[32]. Lax resolution of the Herring Condition gives rise to an unreliable GBCD.

Our strategy is to introduce a simplified coarsening model that is driven by the boundary conditions and reflects the dissipation relation of the grain growth system. This will be more accessible to analysis. It resembles an ensemble of inertia-free spring-mass-dashpots. For this simpler network, we learn how entropic or diffusive behavior at the large scale emerges from a dissipation relation at the scale of local evolution. The cornerstone is a novel implementation of the iterative scheme for the Fokker-Planck Equation in terms of the system free energy and a Kantorovich-Rubinstein-Wasserstein metric [34], cf. also [33], which will be summarized later in the presentation.

The network level nonequilibrium nature of the scheme leaves undetermined the diffusion constant in the Fokker-Planck Equation, or equivalently the 'temperature parameter' of the Boltzmann Distribution we are seeking. We employ the Kullback-Leibler relative entropy, cf. (4.2), and find a convex duality problem for this parameter. It has a statistical interpretation, or information theory interpretation, in terms of an optimal prefix code, cf. eg. [52], and moreover has evident connections to large deviations. This suggests that had we simply asked to identify an optimal distribution via a known statistical method, we would have been led *full circle* to entropy methods.

In the Closing comments we address some general issues.

2. Reprise of Mesoscale theory

Our point of departure is the common denominator theory for the mesoscale description of microstructure evolution. This is growth by curvature, the Mullins Equation (2.2) below, for the evolution of curves or arcs individually or in a network, which we employ for our local law of evolution. Boundary conditions must be imposed where the arcs meet. This condition is the Herring Condition, (2.3), which is the natural boundary condition at equilibrium for the Mullins Equation. Since their introduction by Mullins, [49], and Herring, [31], [32], a large and distinguished body of work has grown about these equations.

Most relevant to here are [29], [19], [36], [50]. Curvature driven growth has old origins, dating at least to Burke and Turnbull [20]. Let α denote the misorientation between two grains separated by an arc Γ, as noted in Figure 1, with normal $n = (\cos\theta, \sin\theta)$, tangent direction b and curvature κ. Let $\psi = \psi(\theta, \alpha)$ denote the energy density on Γ. So

$$\Gamma : x = \xi(s,t), \quad 0 \leqq s \leqq L, \ t > 0, \tag{2.1}$$

with

$$b = \frac{\partial\xi}{\partial s} \ \text{(tangent) and} \ \ n = Rb \ \text{(normal)}$$

$$v = \frac{\partial\xi}{\partial t} \ \text{(velocity) and} \ v_n = v \cdot n \ \text{(normal velocity)}$$

where R is a positive rotation of $\pi/2$. The Mullins Equation of evolution is

$$v_n = (\psi_{\theta\theta} + \psi)\kappa \ \text{on} \ \Gamma. \tag{2.2}$$

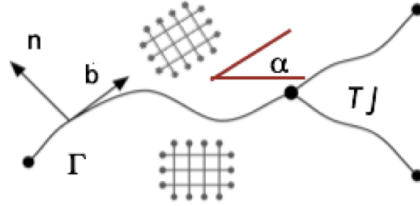We assume that only triple junctions are stable and that the Herring Condition holds at

FIGURE 1. An arc Γ with normal n, tangent b, and lattice misorientation α, illustrating lattice elements.

triple junctions. This means that whenever three curves, $\{\Gamma^{(1)}, \Gamma^{(2)}, \Gamma^{(3)}\}$, meet at a point p the force balance, (2.3) below, holds:

$$\sum_{i=1,..,3} (\psi_\theta n^{(i)} + \psi b^{(i)}) = 0. \tag{2.3}$$

It is easy to check that the instantaneous rate of change of energy of Γ is

$$\frac{d}{dt}\int_\Gamma \psi|b|ds = -\int_\Gamma v_n^2 ds + v \cdot (\psi_\theta n + \psi b)|_{\partial\Gamma} \tag{2.4}$$

Consider a network of grains bounded by $\{\Gamma_i\}$ subject to some condition at the border of the region they occupy, like fixed end points or periodicity, cf. Figure 2. The typical simulation consists in initializing a configuration of cells and their boundary arcs, usually by a modified Voronoi tessellation, and then solving the system (2.2), (2.3), eliminating facets when they have negligible length and cells when they have negligible area, [38],[35]. The total energy of the system is given by
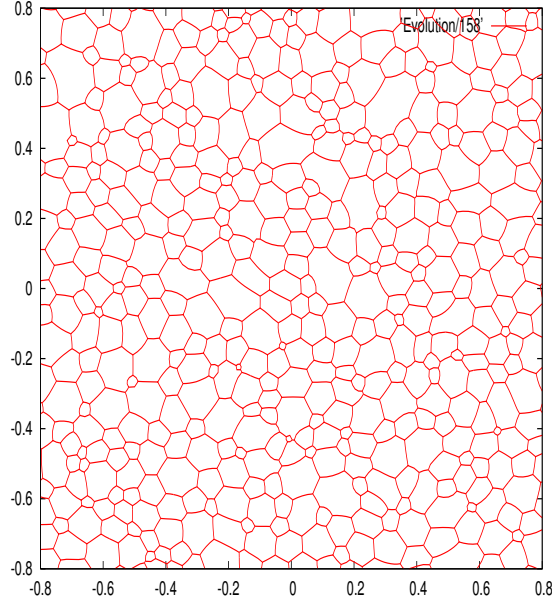
FIGURE 2. Example of an instant during the simulated evolution of a cellular network. This is from a small simulation with constant energy density and periodic conditions at the border of the configuration.

$$E(t) = \sum_{\{\Gamma_i\}} \int_{\Gamma_i} \psi |b| ds \qquad (2.5)$$

Owing exactly to the Herring Condition (2.3), the instantaneous rate of change of the energy

$$\begin{aligned} \frac{d}{dt} E(t) &= - \sum_{\{\Gamma_i\}} \int_{\Gamma_i} v_n^2 ds + \sum_{TJ} v \cdot \sum (\psi_\theta n + \psi b) \\ &= - \sum_{\{\Gamma_i\}} \int_{\Gamma_i} v_n^2 ds \\ &\leqq 0, \end{aligned} \qquad (2.6)$$

rendering the network dissipative for the energy in any instant absent of critical events. Indeed, in an interval $(t_0, t_0 + \tau)$ where there are no critical events, we may integrate (2.6) to obtain a local dissipation equation

$$\sum_{\{\Gamma_i\}} \int_{t_0}^{t_0 + \tau} \int_{\Gamma_i} v_n^2 ds dt + E(t_0 + \tau) = E(t_0) \qquad (2.7)$$

which bears a strong resemblance to the simple dissipation relation for an ensemble of inertia free springs with friction. In the simulation, the facet interchange and cell deletion are arranged so that (2.6) is maintained.

Suppose, for simplicity, that the energy density is independent of the normal direction, so $\psi = \psi(\alpha)$. It is this situation that will concern us here. Then (2.2) and (2.3) may be expressed

$$
\begin{aligned}
v_n &= \psi\kappa \text{ on } \Gamma & (2.8) \\
\sum_{i=1,...,3} \psi b^{(i)} &= 0 \text{ at } p, & (2.9)
\end{aligned}
$$

where p denotes a triple junction. (2.9) is the same as the Young wetting law. When $\psi = $ const, then (2.9) means that the interior angles at triple junctions are $2\pi/3$. In this case, the celebrated Mullins-von Neumann rule holds,[48],[61]. This states that the area $A_n(t)$ of an $n-$faceted cell grows according to the formula

$$
A'_n(t) = c(n - 6), \tag{2.10}
$$

This is thought to hold approximately when anisotropy is small. It has recently been extended, in a dramatic and profound fashion, to arbitrary dimension by MacPherson and Srolovitz, [47].

For this situation we define the grain boundary character distribution, GBCD,

$$
\rho(\alpha, t) = \text{relative length of arc of misorientation } \alpha \text{ at time } t,
$$

normalized so that $\displaystyle\int_\Omega \rho d\alpha = 1.$ (2.11)

We may express the energy of the boundary network in terms of ρ as

$$
E_0(t) = \int_\Omega \psi\rho d\alpha, \tag{2.12}
$$

up to a scale factor involving the network total length. However we do not know how to interpret the velocity term in (2.7). This is one of the motivations for turning to the simplified problem below.

3. A Simplified coarsening model with entropy and dissipation

The coarsening process is irreversible because of its dissipative nature. Even in an interlude when there are no rearrangement events, (2.7) shows that a configuration cannot evolve to a former state from a later one. This could be viewed as a source of entropy for the system. In our investigation, we view the principal source of entropy to be configurational since we observe the evolution of an 'upscaled' ensemble represented by a single statistic, the misorientation α, neglecting the remaining information. This is also a source of irreversibility since we have forgotten information. We return to this shortly.

A significant difficulty in developing a theory for the GBCD, and understanding texture development in general, lies in the lack of understanding of consequences of rearrangement events or critical events, facet interchange and grain deletion, on network level properties.

For example, in Fig. 3, the average area of five-faceted grains during a growth experiment on an Al thin film and the average area of five-faceted cells in a typical simulation both increase with time. The von Neumann-Mullins Rule (2.10) mentioned above does not fail in the example, of course, but cells observed at later times had 6, 7, 8, ... facets at earlier times. Thus in the network setting, changes which rearrange the network play a major role.
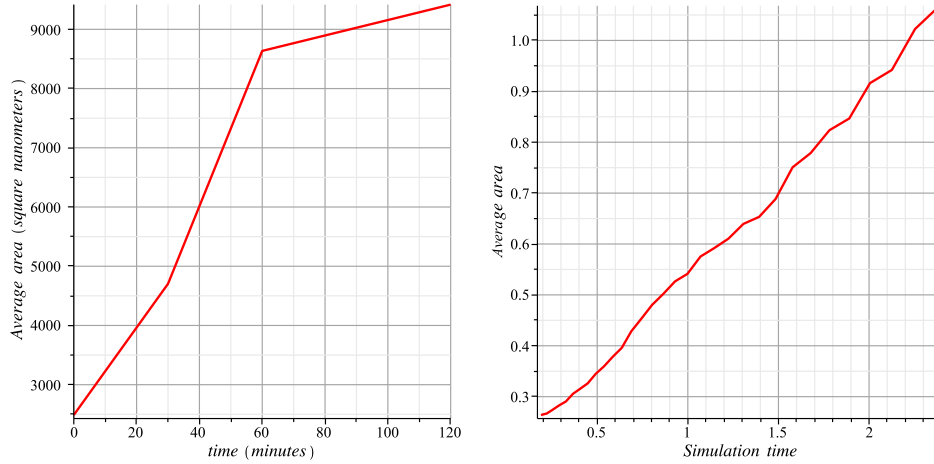

FIGURE 3. The average area of five-sided cell populations during coarsening in two different cellular systems showing that the von Neumann-Mullins $n - 6$-Rule (2.10) does not hold at the scale of the network. (left) In an experiment on Al thin film, [8], and (right) a typical simulation (arbitrary units).

To address these issues, we will introduce a much simpler 1 D model which retains kinetics and critical events but neglects curvature driven growth of the boundaries. In our view, there are two important features of the coarsening system:

- the evolution of the network by the dissipative mechanism of curvature driven growth and
- the irreversible rearrangement of the network at certain discrete times, which is necessary because the entire configuration is confined.

We have used this model to develop a statistical theory for critical events, [13],[14],[12]. It has been found to have its own GBCD as well, [9],[11],[10],[15], which we shall now review.

Our main idea in [9],[11],[10],[15] is that the GBCD statistic for the simplified model resembles the solution of a Fokker-Planck Equation via the mass transport implicit scheme, [34]. In studying the GBCD, we are not averaging some fine-level properties to arrive at a mesoscale property. Rather, it represents some number of fine-level possibilities. This change in the ensemble gives rise to an entropic contribution, which we take to be proportional to configurational entropy. In [9],[11],[10],[15] the simplified model is formulated

as a gradient flow which results in a dissipation inequality analogous to the one found for the coarsening grain network. Because of this simplicity, it will be possible to 'upscale' the network level system description to a higher level GBCD description. A more useful dissipation inequality is obtained by modifying the viscous term to be a mass transport term, which now brings us to the realm of the Kantorovich-Rubinstein-Wasserstein implicit scheme. This then suggests the Fokker-Planck paradigm.

However, we do not know that the statistic solves the Fokker-Planck PDE but we can ask if it shares important aspects of Fokker-Planck behavior. We give evidence for this by asking for the unique 'temperature-like' parameter, the factor noted above, such that the Kullback-Leibler relative entropy achieves a minimum over long time. The empirical stationary distribution and Boltzmann distribution with the special value of 'temperature' are in excellent agreement. This gives an explanation for the stationary distribution and the kinetics of evolution. At this point of our investigations, we do not know that the two dimensional network has the detailed dissipative structure of the simplified model, but we are able to produce evidence that the same argument employing the relative entropy does suggest the correct kinetics and stationary distribution.

3.1. **Formulation.** The simplified coarsening model, driven by the boundary conditions, reflects the dissipation relation of the grain growth system. It resembles an ensemble of inertia-free spring-mass-dashpots. It is an abstraction of the role of triple junctions in the presence of the rearrangement events.

Let $I \subset \mathbf{R}$ be an interval of length L partitioned by points $x_i, i = 1, \ldots, n$, where $x_i < x_{i+1}, i = 1, \ldots, n-1$ and x_{n+1} identified with x_1. For each interval $[x_i, x_{i+1}], i = 1, \ldots, n$ select a random misorientation number $\alpha_i \in (-\pi/4, \pi/4]$. The intervals $[x_i, x_{i+1}]$ correspond to grain boundaries (but not the 1D "grain") with misorientations α_i and the points x_i represent the triple junctions. Choose an energy density $\psi(\alpha) \geqq 0$ and introduce the energy

$$E = \sum_{i=1,\ldots,n} \psi(\alpha_i)(x_{i+1} - x_i). \tag{3.1}$$

To have consistency with the evolution of the 2D cellular network, we impose gradient flow kinetics with respect to (3.1), which is just the system of ordinary differential equations

$$\frac{dx_i}{dt} = -\frac{\partial E}{\partial x_i}, i = 1, ..., n, \text{ that is}$$
$$\frac{dx_i}{dt} = \psi(\alpha_i) - \psi(\alpha_{i-1}), i = 2...n, \text{ and } \frac{dx_1}{dt} = \psi(\alpha_1) - \psi(\alpha_n). \tag{3.2}$$

The velocity v_i of the ith boundary is

$$v_i = \frac{dx_{i+1}}{dt} - \frac{dx_i}{dt} = \psi(\alpha_{i-1}) - 2\psi(\alpha_i) + \psi(\alpha_{i+1}). \tag{3.3}$$

The grain boundary velocities are constant until one of the boundaries collapses. That segment is removed from the list of current grain boundaries and the velocities of its two neighbors are changed due to the emergence of a new junction. Each such deletion event rearranges the network and, therefore, affects its subsequent evolution just as in the

two dimensional cellular network. Actually, since the interval velocities are constant, this gradient flow is just a sorting problem. At any time, the next deletion event occurs at smallest positive value of

$$\frac{x_i - x_{i+1}}{v_i}.$$

The length $l_i(t)$ of the ith interval is linear in t until it reaches 0 or until a collision event, when it becomes linear with a different slope. In any event, it is continuous, so $E(t), t > 0$, the sum of such functions multiplied by factors, is continuous.

At any time t between deletion events,

$$\frac{dE}{dt} = \quad = -\sum \frac{dx_i}{dt}^2 \leqq 0. \tag{3.4}$$

Consider for the 1D system (3.2), a time interval $(t_0, t_0+\tau)$ with no critical events. Then we obtain a grain growth analog of the spring-mass-dashpot-like local dissipation inequality.

$$\sum_{i=1...n} \int_0^\tau \frac{dx_i}{dt}^2 dt + E(t_0 + \tau) = E(t_0) \tag{3.5}$$

With an appropriate interpretation of the sum, (3.5) holds for all t_0 and almost every τ sufficiently small. The dissipation equality (3.5) can also be rewritten in terms of grain boundary velocities as:

$$\frac{1}{4} \sum_{i=1...n} \int_0^\tau v_i^2 dt + E(t_0 + \tau) \leqq E(t_0) \tag{3.6}$$

The energy of the system at time $t_0 + \tau$ is determined by its state at time t_0.

As explained in [11],[10],[15], we can introduce the GBCD for the simplified 1D model. Let us consider a new ensemble based on the misorientation parameter α where we take $\Omega : -\frac{\pi}{4} \leqq \alpha \leqq \frac{\pi}{4}$, for later ease of comparison with the two dimensional network for which we are imposing "cubic" symmetry, i.e., "square" symmetry in the plane. The $GBCD$ or character distribution $\rho(\alpha, t)$ in this context is, as expected, the histogram of lengths of intervals sorted by misorientation α scaled to be a probability distribution on Ω. One may express (3.6) in terms of the character distribution ρ which amounts to

$$\mu_0 \int_{t_0}^{t_0+\tau} \int_\Omega |\frac{\partial \rho}{\partial t}(\alpha, t)|^2 d\alpha dt + \int_\Omega \psi(\alpha)\rho(\alpha, t_0 + \tau)d\alpha \leqq \int_\Omega \psi(\alpha)\rho(\alpha, t_0)d\alpha, \tag{3.7}$$

where $\mu_0 > 0$ is some constant.

The expression (3.7) is in terms of the new misorientation level ensemble, upscaled from the local level of the original system. We now introduce, as discussed earlier, the modeling assumption, consistent with the lack of reversibility when rearrangement/or critical events occur, consisting of an entropic contribution to (3.7). We consider a standard configurational entropy,

$$+ \int_\Omega \rho \log \rho d\alpha, \tag{3.8}$$

although this is not the only choice. Minimizing (3.8) favors the uniform state, which would be the situation were $\psi(\alpha) = $ constant. A tantalizing clue to the development of texture will be whether or not this entropy strays from its minimum during the simulation.

Given that (3.7) holds, we assume now that there is some $\lambda > 0$ such that for any t_0 and τ sufficiently small that

$$\mu_0 \int_{t_0}^{t_0+\tau} \int_\Omega (\frac{\partial \rho}{\partial t})^2 d\alpha dt + \int_\Omega (\psi\rho + \lambda\rho \log \rho)d\alpha|_{t_0+\tau} \leqq \int_\Omega (\psi\rho + \lambda\rho \log \rho)d\alpha|_{t_0} \qquad (3.9)$$

$E(t)$ was analogous to an internal energy or the energy of a microcanonical ensemble and now

$$F(\rho) = F_\lambda(\rho) = E(t) + \lambda \int_\Omega \rho \log \rho d\alpha \qquad (3.10)$$

is a free energy. The value of the parameter λ is unknown and will be determined in the Validation Section 4

3.2. The mass transport paradigm.
The kinetics of the simplified problem will be understood by interpreting the dissipation principle for the GBCD in terms of a mass transport implicit scheme. In fact, (3.9) fails as a proper dissipation principle because the first term

$$\mu_0 \int_{t_0}^{t_0+\tau} \int_\Omega (\frac{\partial \rho}{\partial t})^2 d\alpha dt \qquad (3.11)$$

does not represent lost energy due to frictional or viscous forces. For a deformation path $f(\alpha, t), 0 \leqq t \leqq \tau$, of probability densities, this quantity is

$$\int_0^\tau \int_\Omega v^2 f d\alpha dt \qquad (3.12)$$

where f, v are related by the continuity equation and initial and terminal conditions

$$\begin{aligned} f_t + (vf)_\alpha = 0 \text{ in } \Omega \times (0, \tau), \text{and} \\ f(\alpha, 0) = \rho(\alpha, 0), \ f(\alpha, \tau) = \rho(\alpha, \tau), \end{aligned} \qquad (3.13)$$

by analogy with fluids [41], p.53 et seq., and elementary mechanics. (We have set $t_0 = 0$ for convenience.)

On the other hand, by a result of Benamou and Brenier [17], given two probability densities f^*, f on Ω, the Wasserstein distance $d(f, f^*)$ between them is given by

$$\begin{aligned} &\frac{1}{\tau}d(f, f^*)^2 = \inf \int_0^\tau \int_\Omega v^2 f d\xi dt \\ &\text{over deformation paths } f(\xi, t) \text{ subject to} \\ &f_t + (vf)_\xi = 0, \text{ (continuity equation)} \\ &f(\xi, 0) = f^*(\xi), f(\xi, \tau) = f(\xi) \text{ (initial and terminal conditions)} \end{aligned} \qquad (3.14)$$

Let us briefly review the notion of Kantorovich-Rubinstein-Wasserstein metric, or simply Wasserstein metric. The reader can consult [59], [3] for more detailed exposition of the subject and [15] for additional discussion of its application in this context.

Let $D \subset \mathbf{R}$ be an interval, perhaps infinite, and f^*, f a pair of probability densities on D (with finite variance). The quadratic Wasserstein metric or 2-Wasserstein metric is defined to be

$$d(f, f^*)^2 = \inf_P \int_{D \times D} |x - y|^2 dp(x, y)$$

$$P = \text{joint distributions for } f, f^* \text{ on } \bar{D} \times \bar{D},$$

(3.15)

i.e., the marginals of any $p \in P$ are f, f^*. The metric induces the weak-$*$ topology on $C(\bar{D})'$. If f, f^* are strictly positive, there is a transfer map which realizes p, essentially the solution of the Monge-Kantorovich mass transfer problem for this situation. This means that there is a strictly increasing

$$\phi : D \to D \text{ such that}$$

$$\int_D \zeta(y) f(y) dy = \int_D \zeta(\phi(x)) f^*(x) dx, \ \zeta \in C(\bar{D}), \text{ and}$$

$$d(f, f^*)^2 = \int_D |x - \phi(x)|^2 f^* dx$$

(3.16)

In this one dimensional situation, as was known to Frechét, [25],

$$\phi(x) = F^{*-1}(F(x)), \ x \in D, \text{where}$$

$$F^*(x) = \int_{-\infty}^x f^*(x') dx' \text{ and } F(x) = \int_{-\infty}^x f(x') dx'$$

(3.17)

are the distribution functions of f^*, f. In one dimension there is only one transfer map. The conditions (3.14) are in 'Eulerian' form. Therefore, our goal is to replace (3.11) with (3.12). Since the associated metrics induce different topologies, an estimate must involve additional terms. Assume that our statistic $\rho(\alpha, t)$ satisfies

$$\rho(\alpha, t) \geqq \delta > 0 \text{ in } \Omega, t > 0.$$

(3.18)

This is a necessary assumption for our estimates below. In fact, to proceed with the implicit scheme introduced later, it is sufficient to require (3.18) just for the initial data $\rho_0(\alpha)$ since this property is inherited by the iterates. We now use the representation (3.14) and the deformation path given by ρ itself, that is $f = \rho$ and v determined so that

$$\rho_t + (v\rho)_x = 0.$$

Then calculate that for some $c_\Omega > 0$,

$$\frac{1}{\tau} d(\rho, \rho^*)^2 \leqq \int_0^\tau \int_\Omega v^2 \rho dx dt \leqq \frac{c_\Omega}{\min_\Omega \rho} \int_0^\tau \int_\Omega \frac{\partial \rho}{\partial t}(x, t)^2 dx dt,$$

$$\rho^*(x) = \rho(x, 0) \text{ and } \rho(x) = \rho(x, \tau),$$

(3.19)

where 0 represents an arbitrary starting time and τ a relaxation time.

Thus from (3.9) there is a $\mu > 0$ such that for any relaxation time $\tau > 0$,

$$\frac{\mu}{2} \int_0^\tau \int_\Omega v^2 \rho d\alpha dt + F_\lambda(\rho) \leqq F_\lambda(\rho^*)$$

(3.20)

We next replace (3.20) by a minimum principle, arguing that the path given by $\rho(\alpha, t)$ is the one most likely to occur and the minimizing path has the highest probability. For this step, let $\rho^* = \rho(\cdot, t_0)$ and $\rho = \rho(\cdot, t + \tau)$. We then have that, from (3.14), a minimum principle in the form

$$\frac{\mu}{2\tau}d(\rho, \rho^*)^2 + F_\lambda(\rho) = \inf_{\{\eta\}}\{\frac{\mu}{2\tau}d(\eta, \rho^*)^2 + F_\lambda(\eta)\} \tag{3.21}$$

For each relaxation time $\tau > 0$ we determine iteratively the sequence $\{\rho^{(k)}\}$ by choosing $\rho^* = \rho^{(k-1)}$ and $\rho^{(k)} = \rho$ in (3.21) and set

$$\rho^{(\tau)}(\alpha, t) = \rho^{(k)}(\alpha) \text{ in } \Omega \text{ for } k\tau \leqq t < (k+1)\tau. \tag{3.22}$$

We then anticipate recovering the GBCD ρ as

$$\rho(\alpha, t) = \lim_{\tau \to 0} \rho^{(\tau)}(\alpha, t), \tag{3.23}$$

with the limit taken in a suitable sense. It is known that ρ obtained from (3.23) is the solution of the Fokker-Planck Equation, [34],

$$\mu\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial \alpha}(\lambda\frac{\partial \rho}{\partial \alpha} + \psi'\rho) \text{ in } \Omega, 0 < t < \infty. \tag{3.24}$$

We might point out here, as well, that a solution of (3.24) with periodic boundary conditions and nonnegative initial data is positive for $t > 0$.

4. Validation of the scheme

We now begin the validation step of our model. The procedure which leads to the implicit scheme, based on the dissipation inequality (3.6), holds for the entire system but does not identify individual intermediate 'spring-mass-dashpots'. The consequence is that we cannot set the temperature-like parameter σ, but in some way must decide if one exists. Introduce the notation for the Boltzmann distribution with parameter λ

$$\rho_\lambda(\alpha) = \frac{1}{Z_\lambda}e^{-\frac{1}{\lambda}\psi(\alpha)}, \alpha \in \Omega, \text{ with } Z_\lambda = \int_\Omega e^{-\frac{1}{\lambda}\psi(\alpha)}d\alpha. \tag{4.1}$$

With validation we would gain qualitative properties of solutions of (3.24):

- $\rho(\alpha, t) \to \rho_\sigma(\alpha)$ as $t \to \infty$, and
- this convergence is exponentially fast.

The Kullback-Leibler relative entropy for (3.24) is given by

$$\Phi_\lambda(\eta) = \Phi(\eta\|\rho_\lambda) = \int_\Omega \eta \log \frac{\eta}{\rho_\lambda}d\alpha \text{ where}$$
$$\eta \geqq 0 \text{ in } \Omega, \int_\Omega \eta d\alpha = 1, \tag{4.2}$$

with ρ_λ from (4.1). By Jensen's Inequality it is always nonnegative. In terms of the free energy (3.10) and (4.1), (4.2) is given by

$$\Phi_\lambda(\eta) = \frac{1}{\lambda}F_\lambda(\eta) + \log Z_\lambda. \tag{4.3}$$

(Note: In our earlier work [10, 15], we defined relative entropy to be λ times (4.2).) A solution ρ of (3.24) has the property that

$$\Phi_\lambda(\rho) \to 0 \text{ as } t \to \infty. \tag{4.4}$$

Therefore, we seek to identify the particular $\lambda = \sigma$ for which Φ_σ defined by the GBCD statistic ρ tends monotonically to the minimum of all the $\{\Phi_\lambda\}$ as t becomes large. We then ask if the terminal, or equilibrium, empirical distribution ρ is equal to ρ_σ. Note that since

$$f(x,y) = x \log x - x \log y, \ x, y > 0,$$

is convex, $\Phi(\eta\|\rho_\lambda)$ is a convex function of (η, ρ_λ). We assign a time $t = T_\infty$ and seek to minimize (4.2) at T_∞. With

$$\psi_\lambda = \frac{\psi}{\lambda} + \log Z_\lambda, \tag{4.5}$$

this minimization is a convex duality type of optimization problem, namely, to find the σ or ψ_σ for which

$$\int_\Omega \{\psi_\sigma \rho + \rho \log \rho\} d\alpha = \inf_{\{\psi_\lambda\}} \int_\Omega \{\psi_\lambda \rho + \rho \log \rho\} d\alpha \tag{4.6}$$

Note that

$$\int_\Omega e^{-\psi_\lambda} d\alpha = 1$$

which gives the minimization in (4.6) the form of finding an optimal prefix code, eg. [52]. Here the potential ψ_λ, the code, is minimized in a family rather than the unknown density ρ itself, which corresponds to the given alphabet. For practical purposes, note that

$$\Phi(\rho\|\rho_\lambda) = \int_\Omega \rho \log \rho \, d\alpha + \frac{1}{\lambda} \int_\Omega \psi \rho \, d\alpha + \log Z_\lambda \tag{4.7}$$

is a strictly convex non-negative function of the 'inverse temperature' $\beta = \frac{1}{\lambda}, \beta > 0$, and thus admits a unique minimum.

The information theory interpretation is that we are minimizing the information loss among trial encodings of the alphabet represented by the statistic ρ. In this sense we see that asking for an optimal distribution ρ_σ to represent our statistic ρ, necessarily introduces (relative) entropy in our considerations, returning us, as it were, full circle.

In addition, the method is known in statistics as an M estimator or a Z estimator, [58].

From a given simulation, we harvest the GBCD statistic. It is a trial. The convexity of $\Phi(\rho\|\rho_\lambda)$ suggests that we can average trials. For trials $\{\rho_1, \ldots \rho_N\}$,

$$\Phi(\frac{1}{N} \sum_{i=1\ldots N} \rho_i \| \rho_\lambda) \leqq \frac{1}{N} \sum_{i=1\ldots N} \Phi(\rho_i \| \rho_\lambda). \tag{4.8}$$

So we can seek the optimal $\lambda = \sigma$ by optimizing with the averaged trial. We shall illustrate this for the validation process for the two dimensional simulation.

4.1. **An example of the simplified problem.** For the simplified coarsening model, we consider

$$\psi(\alpha) = 1 + 2\alpha^2 \text{ in } \Omega = (-\frac{\pi}{4}, \frac{\pi}{4}), \tag{4.9}$$

and shall identify a unique such parameter, which we label σ, by seeking the minimum of the relative entropy (4.2), namely by inspection of plots of (4.6) and (4.7), and then comparing ρ with the found ρ_σ. This ψ the development to second order of $\psi(\alpha) = 1 + 0.5 \sin^2 2\alpha$ used in the 2D simulation. Moreover, since the potential is quadratic, it represents a version of the Ornstein-Uhlenbeck process. We agree that $T_\infty = T(80\%) = 6.73$ represents time equals infinity. This is the time at which 80% of the segments have been deleted and corresponds to the stationary configuration in the two-dimensional simulation. For the simplified critical event model we are considering, it is clear that by computing for a sufficiently long time, all cells will be gone. This time may be quite long. For comparison, $T(90\%) = 30$ and $T(95\%) = 103$. There may be additional criteria for choosing a T in the neighborhood of $T(80\%)$ and we may wish to discuss this later. The results are reported in Fig. 4.
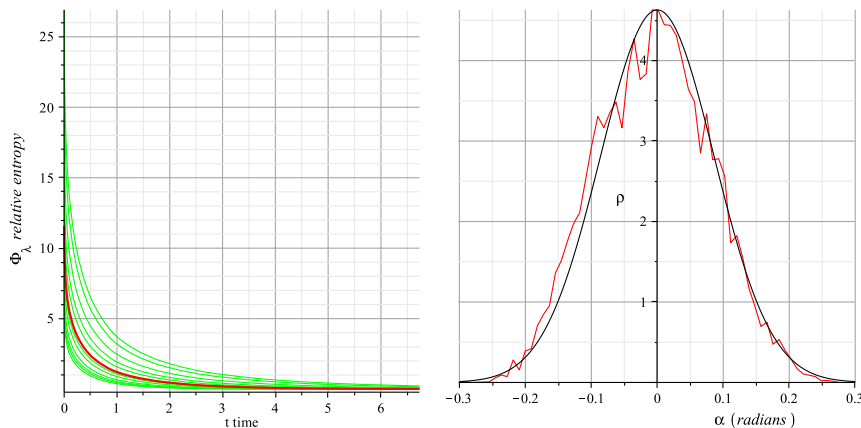

FIGURE 4. Graphical results for the simplified coarsening model. (left) Relative entropy plots for selected values of λ with Φ_σ noted in red. The value of $\sigma = 0.0296915$. (right) Empirical distribution at time $T = T_\infty$ in red compared with ρ_σ in black.

5. THE ENTROPY METHOD FOR THE GBCD

5.1. **Quadratic interfacial energy density.** We shall apply the method of Section 4 to the GBCD harvested from the 2D simulation. For reasons of limited space, we consider a single typical simulation with the energy density

$$\psi(\alpha) = 1 + \epsilon(\sin 2\alpha)^2, \ -\frac{\pi}{4} \leqq \alpha \leqq \frac{\pi}{4}, \ \epsilon = 1/2, \tag{5.1}$$

Figure 5, initialized with 10^4 cells and normally distributed misorientation angles and terminated when 2000 cells remain. At this stage, the simulation is essentially stagnant.

Five trials were executed and we consider the average of ρ of the empirical GBCD's. Possible 'temperature' parameters λ and ρ_λ in (4.1) for the density (5.1) are constructed. This ρ_λ then defines a trial relative entropy via (4.2). We now identify the parameter σ, which turns out to be $\sigma \approx 0.1$, and the value of the relative entropy $\Phi_\sigma(T_\infty) \approx 0.01$, which is about 10% of its initial value, Figure 6. From Figure 7 (left), we see that this relative entropy Φ_σ has exponential decay until it reaches time about $t = 1.5$, after which it remains constant. The averaged empirical GBCD is compared with the Boltzmann distribution in Figure 7 (right). The solution itself then tends exponentially in L^1 to its limit ρ_σ by the Kullback-Csiszar Inequality.
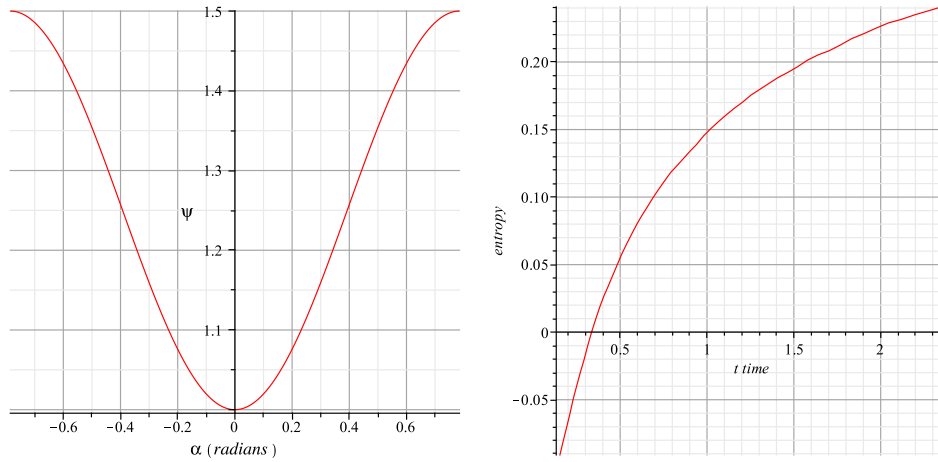

FIGURE 5. (left) The energy density $\psi(\alpha) = 1 + \epsilon \sin^2 2\alpha$, $|\alpha| < \pi/4$, $\epsilon = \frac{1}{2}$. (right) The entropy of $\rho(\alpha, t)$ as a function of time t is increasing, suggesting the development of order in the configuration.

5.2. **Remarks on a Theory for the Diffusion Coefficient σ or the Temperature-Like Parameter.** The network level nonequlibrium nature of the iterative scheme introduced in our theory Sections 3 - 4, leaves free a temperature-like parameter σ. However, as we showed in Section 4, we can uniquely identify σ. But can we a priori determine or control this temperature-like parameter? There are different approaches to this question, none of which have been especially successful at this point. One possible approach is to consider a different theory that is developed for the simplified model based on the kinetic equations description in [14]. However, this particular description [14] would have to be improved, since it does not produce a very good result for σ at this point. However, this method would still have only an empirical flavor: the value of σ will be obtained once the solution of kinetic equations is computed. Another direction to consider here is based
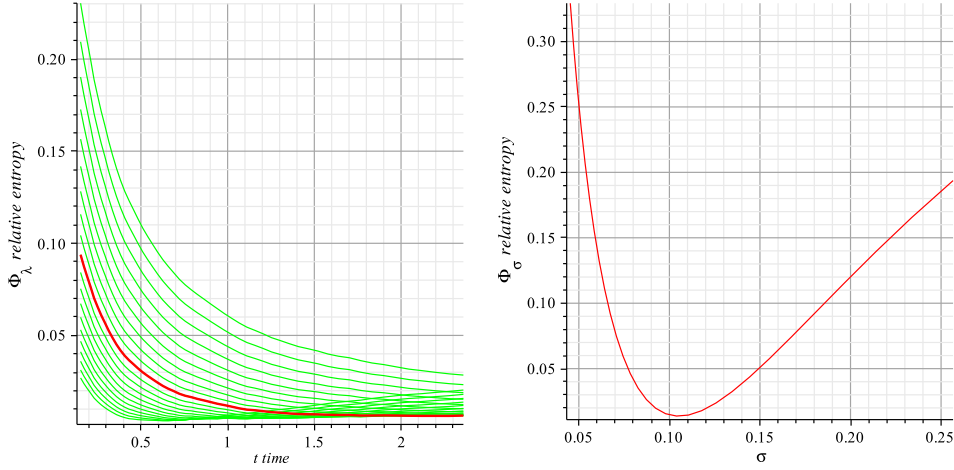
FIGURE 6.   In these plots, the GBCD ρ is averaged over 5 trials. (left) The relative entropy of the grain growth simulation with energy density (5.1) for a sequence of Φ_λ vs. t with the optimal choice $\sigma \approx 0.1$ noted in red. (right) Relative entropy for an indicated range of values of temperature parameter λ at the terminal time t = 2.3. The minimum value of the relative entropy is ≈ 0.01.
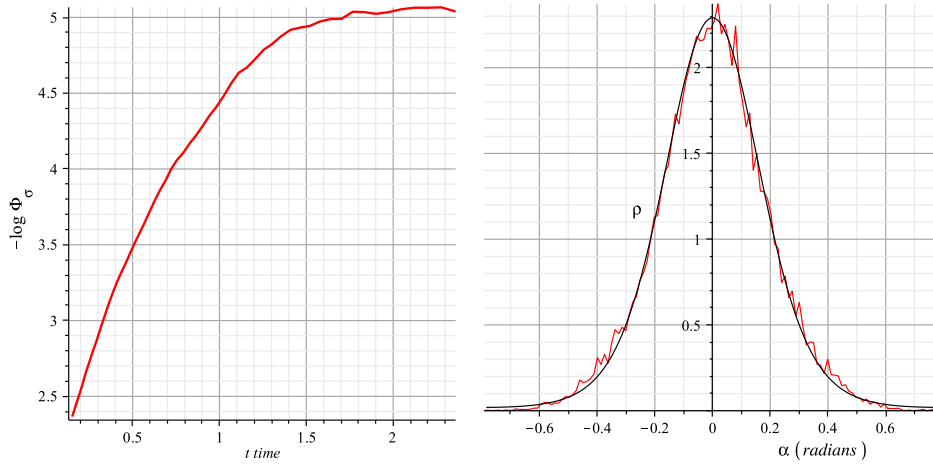

FIGURE 7.   In these plots, the GBCD is averaged over 5 trials. (left) Plot of $-\log\Phi_\sigma$ vs. t with energy density (5.1). It is approximately linear until it becomes constant showing that Φ_σ decays exponentially.(right) GBCD ρ (red) and Boltzmann distribution ρ_σ (black) for the potential ψ of (5.1) with parameter $\sigma \approx 0.1$ as predicted by our theory.

on the statistical analysis of the data obtained from many trials and to understand the possible connection to branching processes.

6. Closing comments

Engineering the microstructure of a material is a central task of materials science and its study gives rise to a broad range of basic science issues, as has been long recognized.

Central to these issues is the coarsening of the cellular structure. Here we have outlined an entropy based theory of the GBCD which is an upscaling of cell growth according to the two most basic properties of a coarsening network: a local evolution law and space filling constraints. The theory accomodates the irreversibility conferred by the critical events or topological rearrangements which arise during coarsening. It adds to the body of evidence that the evolution of the boundary network is the primary origin of texture development. It accounts both for the GBCD and its kinetics.

Finally we remark about the scope of the theory. The dissipation relation, (2.6) and (2.7), shows that only interfacial energy and functions of it, like the Herring Condition, are responsible for coarsening. This gives rise to the GBCD. Other statistics, like cell size and orientations, although they may be easily measured and well behaved, are secondary. The evolution should have a Markov character. The initial conditions at a given state determine subsequent evolution. Perhaps this is not the case precisely as correlations tend to develop over time and simple coarsening is impeded by configurational hinderance, but let us suppose so for the moment. Then the GBCD is a solution of the forward Kolmogorov equation of the process, which is linear.

Now consider momentarily an upscaled dissipation relation. It would have a form, using the mass transport paradigm we have been discussing derived from the gradient flow

$$\frac{\mu}{2\tau}d(\rho, \rho^*)^2 + \int_\Omega \Phi(\rho, x)dx = \min \tag{6.1}$$

The stationary equation corresponding to this is

$$A\rho = \frac{d^2}{dx^2}(-\rho\Phi_\rho + \Phi) - \frac{d}{dx}\Phi_x \tag{6.2}$$

As a function of ρ it must be linear. To check this in a simple way, compute the adjoint pairing, which is the backward Kolmogorov equation. This reveals that

$$\Phi(\rho, x) = a\rho \log \rho + b(x)\rho, \text{ with } a \text{ constant.} \tag{6.3}$$

which yields the Fokker-Planck equation already found with, notably, constant diffusion. In sum, a dissipation relation gives rise to essentially only one Markov process, the one we have discovered. We do not know the implications of this.

Acknowledgements

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E-mail address: kb2612@columbia.edu

E-mail address: eva.eggeling@fraunhofer.at

E-mail address: memelian@gmu.edu

E-mail address: epshteyn@math.utah.edu

E-mail address: davidk@cmu.edu

E-mail address: rsharp@gmail.com

E-mail address: shlomo@andrew.cmu.edu