

Grain growth beyond the Mullins model, capturing the complex physics behind universal grain size distributions

R. Backofen,¹ K. Barmak,² K.R. Elder,³ and A. Voigt¹

¹*Institut für Wissenschaftliches Rechnen, Technische Universität Dresden, 01062 Dresden, Germany*

²*Department of Applied Physics and Applied Mathematics,
Columbia University, New York, NY 10027, US*

³*Department of Physics, Oakland University, Rochester, MI 48309-4487, US*

(Dated: April 30, 2022)

Grain growth experiments on thin metallic films have shown the geometric and topological characteristics of the grain structure to be universal and independent of many experimental conditions. The universal size distribution, however, is found to differ both qualitatively and quantitatively from the standard Mullins curvature driven model of grain growth; with the experiments exhibiting an excess of small grains (termed an "ear") and an excess of very large grains (termed a "tail") compared with the model. While a plethora of extensions of the Mullins model have been proposed to explain these characteristics, none have been successful. In this work, large scale simulations of a model that resolves the atomic scale on diffusive time scales, the phase field crystal model, is used to examine the complex phenomena of grain growth. The results are in remarkable agreement with the experimental results, recovering the characteristic "ear" and "tail" features of the experimental grain size distribution. The simulations also indicate that while the geometric and topological characteristics are universal, the dynamic growth exponent is not.

Most metals, ceramics and minerals are polycrystalline materials containing grains of different crystal orientation. The size, shapes and arrangements of these grains strongly affect macroscale material properties, such as fracture, yield stress, coercivity and conductivity. In magnetic systems, for example, the coercivity (or magnetic 'hardness') can change by four or five orders of magnitude with a change in grain size [1]. Thus, understanding and controlling polycrystalline structures is of great importance in the production of many engineering materials and has motivated numerous experimental and theoretical studies of grain growth.

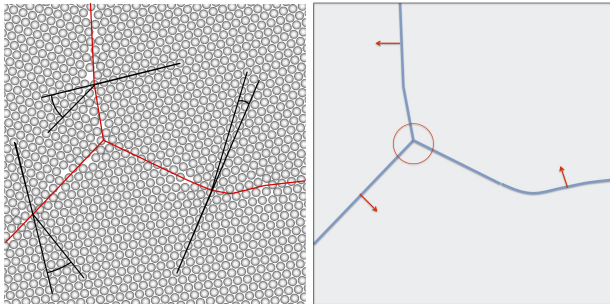


FIG. 1: Schematic comparison between atomistic description of polycrystalline material and coarse grained picture of a smooth grain boundary network. Shown is a low angle grain boundary with aligned dislocations and two high angle grain boundaries in an otherwise hexagonal lattice.

Grain growth in thin metallic films is one example where extensive research has been conducted. One very interesting experimental finding in such systems is that the grain size distributions and topological characteristics appear to be independent of many experimental conditions [2]. More specifically, it has been found that for a

large collection of Al and Cu thin films a universal grain size distribution emerges that is independent of the substrate, annealing temperature, purity, thickness and annealing time. Unfortunately the universal distribution is qualitatively and quantitatively different from the results of extensive computational studies on grain growth [3, 4], which are based on the Mullins model [5]. In this model the problem is reduced to the evolution of a grain boundary network by relating the normal velocity v_n to the curvature κ of the grain boundary, $v_n = \mu\gamma\kappa$, with mobility μ and surface tension γ , and specifying the Herring condition [6] at triple junctions. Various attempts have been made to extend the Mullins model and to include more realistic effects, such as interactions of the film with the substrate, anisotropy in the grain boundary energy and mobility, grain boundary grooving, and solute and triple junction drag. However, no single cause is able to explain the experimental grain growth behavior [2, 7].

In addition to the grain size distribution, the rate of growth of the average grain size has also been examined in detail. The Mullins model and its extensions all seem to predict that the average grain size, represented by its radius $r(t)$ has a power law behavior of the form $\sim t^{1/2}$, which follows immediately from the linear relationship between grain boundary velocity and curvature. Experimentally a much slower coarsening or even stagnation of grain growth in thin films is observed. This may be due to the fact that the Mullins model ignores the crystalline structure of the grains, the dissipation due to lattice deformations and the Peierls barriers for dislocation motion. It is difficult to reconcile Mullins type models with the atomistic features of grain boundaries, which (for low angles) can be seen as an alignment of dislocations where

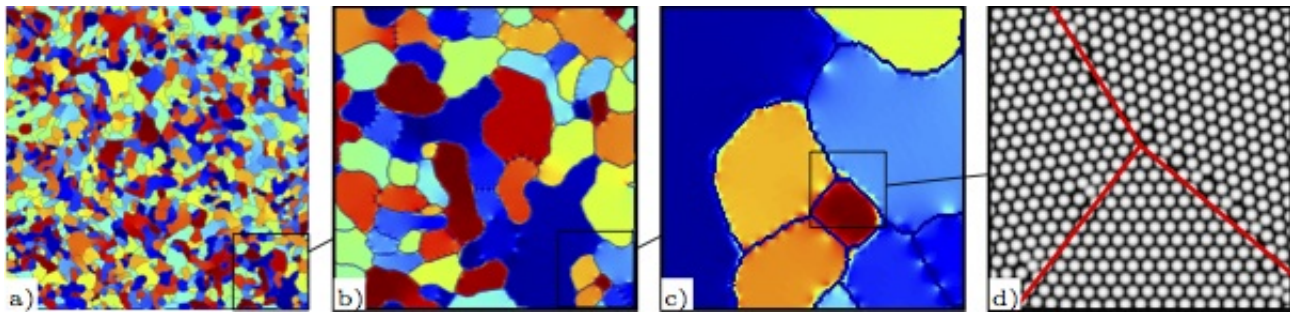


FIG. 2: a) - c) Grain structure obtained from postprocessing a PFC simulation at an intermediate time. The color coding indicates the averaged local lattice orientation for each of the maxima in the density field. An enlargement by a factor of four is used for each figure. The grain boundaries are visualized. d) Visualization of the density field, where each maximum is associated with a dot. The red lines indicate the grain boundaries.

the driving force for grain growth is the stress associated with dislocation motion. The differences of the description are shown schematically in Fig. 1.

Atomistic descriptions can incorporate the important physical features missing in the Mullins model and have led to some important observations. It has been shown that the complex dislocation structure along curved grain boundaries gives rise to a misorientation-dependent mobility [8]. Further studies indicate that grain boundaries undergo thermal roughening associated with an abrupt mobility change, leading to smooth (fast) and rough (slow) boundaries [9], which can eventually lead to stagnation of the growth process. The defect structure at triple junctions can lead to a sufficiently small mobility limiting the rate of grain boundary migration [10, 11]. Also tangential motion of the lattices are possible. For low-angle grain boundaries, normal and tangential motion are strongly coupled as a result of the geometric constraint that the lattices of two crystals change continuously across the interface while the grain boundary moves [12]. As a consequence of this coupling, grains rotate as they shrink which leads to an increase in the grain boundary energy per unit length, although the overall energy decreases since the size of the boundary decreases [13–15]. Each of these phenomena can be simulated using molecular dynamics (MD), see [16] for a review. However, to study the effect of these phenomena on scaling laws, grain size distributions or stagnation of growth requires a method which operates on diffusive time scales.

In this work, we employ the phase field crystal (PFC) method [17]. The model has been shown to successfully model grain boundary energies as a function of misorientation [18] and non-classical grain rotation during grain shrinkage and drag of triple junctions [19]. In addition lower coarsening exponents were already observed for hexagonal lattices [20–22]. The aim of this Letter is to use the PFC model on large scales to obtain statistical data for scaling laws and grain size distributions and to compare them with simulation results of the Mullins model and experimental data for thin metallic

films. Since the experimental results in [2] seem to be universal, we do not fit the PFC parameters to a specific material but consider an artificial setting within the simplest PFC model introduced in [17]. In dimensionless form the equation reads $\partial_t \psi = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \psi}$, where the order parameter ψ , is related to the time-averaged atomic density, t is time, Γ is the mobility and free energy is $\mathcal{F} = \int \psi(-\epsilon + (\nabla^2 + 1)^2 \psi / 2 + \psi^4 / 4) dr$, see [18, 23–25] for details on the relationship to classical dynamic density functional theory (DDFT) and material specific parameterization.

Fig. 2 shows a snapshot of a typical simulation. All simulations are performed in a periodic domain of square size $L = 8,192$ starting from a randomly perturbed constant value of the particle density ψ . After an initiation phase in which the white noise is damped rapidly, grains nucleate, grow and impinge on one another. Thereafter the number of maxima in the particle density ψ remains mainly constant and coarsening starts. Statistical results are collected after grains have reached a minimal size of 100 atoms. Fig. 3 shows the obtained scaling results for the average domain area as a power law in times, i.e., t^q , where q is $1/2$ in the Mullins curvature driven model. In our simulations it is not clear that this relationship is valid as the value of q can be seen to change in time and be dependent on the parameters of the simulation and initial conditions. For case "A", we either obtain an initial value of $q = 1/3$, which turns into $q = 1/5$, or a constant value of $q = 1/5$, depending on the initial grain size. The constant scaling exponent is observed for larger initial grains. For case "B", corresponding to a softer material, the growth exponent increases to a value of $q = 2/5$, whereas for case "C", a harder material it decreases to $q = 1/20$. For all three cases, the growth exponent is significantly lower than the expected value $q = 1/2$ for the Mullins model. Similar low coarsening exponents have been found for hexagonal lattices in [20, 21] and in experiments for thin films of CoPt and FePt [26]. Extensive computational studies in [21, 22] further show a strong dependency of the scaling expo-

ment on additional noise, which enhances the coarsening process. It has also been noted [22] that the addition of higher order time derivatives can change the growth exponent, which may be appropriate for three dimensional samples. In two-dimensional thin films (i.e., films with columnar grain structures), however, it is expected that the substrate/film coupling provides an effective friction for rotation or translation that eliminates the need for such corrections. In either case, it is likely that the growth exponents are transient, because for very large grain sizes the Peierls-Nabarro barriers are likely to inhibit further coarsening. This effect already occur at early times for quenches to lower temperatures, as confirmed for points in the phase diagram in the solid region at $(\psi_0, \epsilon) = (-0.31, -0.25)$ and $(\psi_0, \epsilon) = (-0.29, -0.18)$ which show a frozen configuration.

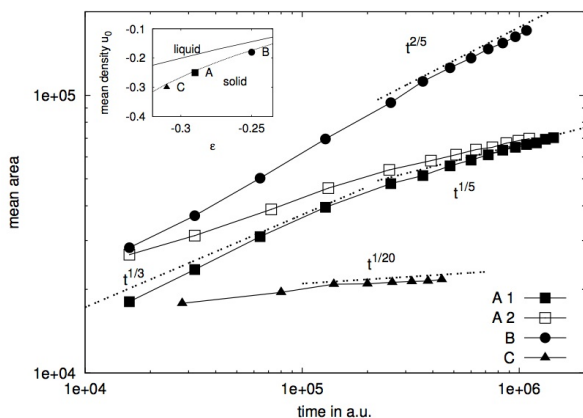


FIG. 3: Mean area as a function of time together with the fitted scaling exponents for various points in the phase diagram depicted in the inset. "A1" and "A2" have different initial grain sizes ($A1 < A2$), the parameters are "A": $(\psi_0, \epsilon) = (-0.29, -0.25)$; "B": $(\psi_0, \epsilon) = (-0.25, -0.18)$; "C": $(\psi_0, \epsilon) = (-0.31, -0.30)$.

While it is not entirely clear if there is a single, well-established dynamical exponent, the grain size distribution functions appear to be much more robust. Fig. 4 shows the grain size distributions of the PFC simulations for the considered points in the phase diagram together with the experimental results of [2] and the results of the Mullins model taken from [3].

A considerable discrepancy between the experimental results and the Mullins model is already discussed in [2, 7]. They differ in two important respects. First, the experimental grain structures have a larger number of small grains as evidenced by the peak of the experimental reduced area probability density residing to the left of that for the simulations based on the Mullins model, a feature that has been termed the "ear". Second, the experimental grain structures have "tails" that extend to significantly larger sizes than those seen in simulations based on the Mullins model. While only very few grains

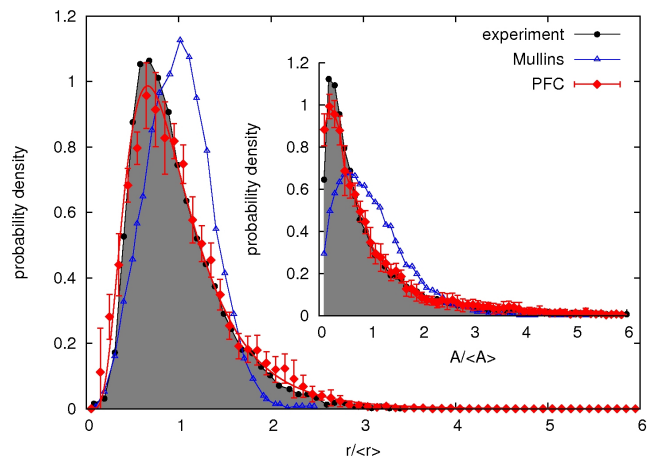


FIG. 4: Grain size distribution with reference to radius (area in inlet). Shown is the mean distribution, obtained as the average of the last time steps in the considered cases in Fig. 3. The curve are fitted to a lognormal distribution with parameters $(\mu, \sigma) = (-0.13, 0.53)$. The experimental data and the results of the Mullins model are taken from [2]

seen in simulations exceed 4 times (and only rarely do they exceed 5 times) the mean area, the experimental grain structures exhibit maximum grain areas that are between 8 and 42 times the mean, with a sizable fraction of grains whose areas exceed 4 times the mean grain area ($\sim 3\%$ by number, representing $\sim 18\%$ of the total area).

Various closed form distributions have been proposed to fit the results of the Mullins model, e.g. the Louat, Hillert, Rios and Weibull distribution (see [3] and the references therein). They all not only differ in the "ear" and "tail" region, but they also peak at $r/\langle r \rangle > 1$, again in disagreement with the experimental results. The PFC simulations not only recover the qualitative behaviour of the experimental results, they almost perfectly fit the distribution, and can be very well described by a lognormal distribution. The grain size distribution appears to be self-similar which is analysed in detail for case "A1" in Fig. 5. All results are obtained without additional noise. However, simulations that included noise (not shown) produced grain distributions consistent with the zero noise case. Further analysis indicates that, also in agreement with the experimental data, small grains are primarily 3 and 4-sided, whereas large grains have primarily more than 6 sides.

The importance and prevalence of the formation and properties of polycrystalline materials has lead to an enormous amount of theoretical and experimental research. Unfortunately theoretical progress has been hindered by the lack of computational methods that can capture the essential physics on the time and lengths that are appropriate for such phenomena. While MD simulations are currently unable to reach time scales required

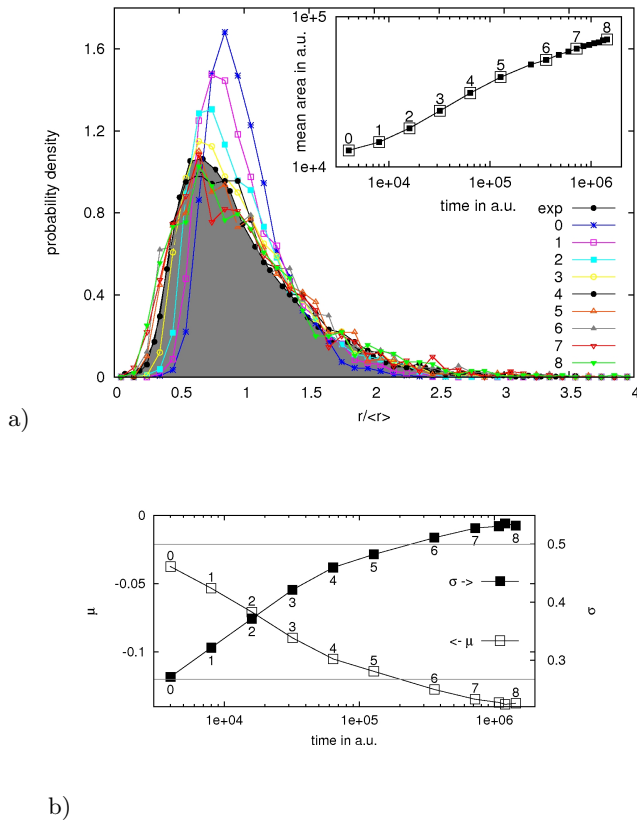


FIG. 5: a) Grain size distribution with reference to radius at the labeled times in the inlet, corresponding to case "A1" in Fig. 3, in comparison with the experimental results from [2]. The initially narrow distribution broadens rapidly and its peak shifts towards smaller grains. For large times the grain size distribution appears to be self-similar which is further illustrated in b) showing the time evolution of the parameters σ and μ of a log-normal distribution fitted to the considered snapshots, again in comparison with the experimental results from [2] shown as the horizontal solid lines.

to observe self-similar growth regimes, coarse grained descriptions based on the Mullins model seem to lack the essential atomistic features allowing for bulk dissipation during grain growth. In this work large scale numerical simulations of the PFC model were used to examine the phenomenon of grain growth in two dimensional systems. The results of these simulations are in remarkable agreement with universal aspects of the geometric and topological characteristics of the grain structures in thin metallic films. Among other features they capture both the "ear" and "tail" characteristics of grain distributions that have proven difficult to obtain with previous models and methods. Thus the PFC model provides a key resource for future research in which realistic grain structures are required. Although not examined in this work, the model also incorporates mechanical properties of the system and thus can be used to study, for exam-

ple, the relationship between growth conditions and the structural stability of polycrystalline materials.

RB and AV acknowledge support from the DFG under Grant No. Vo899/7. KE acknowledges support from the NSF under Grant No. DMR-0906676. We acknowledge computing resources at the JSC provided under grant HDR06. Part of the work has been done while AV was guest of HIM at Universität Bonn and KB, KE and AV were guests of IPAM at UCLA.

- [1] G. Herzer, *Acta Mater.* **61**, 718 (2013).
- [2] K. Barmak, E. Eggeling, D. Kinderlehrer, R. Sharp, S. Ta'asan, A. Rollett, and K. Coffey, *Prog. Mat. Sci.* (<http://dx.doi.org/10.1016/j.pmatsci.2013.03.004>).
- [3] M. Eusey, S. Esedoglu, and P. Smereka, *Proc. Roy. Soc. A* **467**, 381 (2011).
- [4] D. Kinderlehrer, I. Livshits, and S. Ta'Asan, *SIAM J. Sci. Comput.* **28**, 1694 (2006).
- [5] W. Mullins, *J. Appl. Phys.* **27**, 900 (1956).
- [6] C. Herring, in *The Physics of Powder Metallurgy*, edited by W. Kingston (1951), p. 143.
- [7] K. Barmak, J. Kim, C. Kim, W. Archibald, G. Rohrer, A. Rollett, D. Kinderlehrer, S. Ta'Asan, H. Zhang, and D. Srolovitz, *Scripta Mater.* **54**, 1059 (2006).
- [8] M. Winning, G. Gottstein, and L. Shvindlerman, *Acta Mater.* **49**, 211 (2001).
- [9] E. Holm and S. Foiles, *Science* **328**, 1138 (2010).
- [10] S. Srinivasan, J. Cahn, H. Jonsson, and G. Kalonji, *Acta Mater.* **47**, 2821 (1999).
- [11] M. Upmanyu, D. Srolovitz, L. Shvindlerman, and G. Gottstein, *Acta Mater.* **50**, 1405 (2002).
- [12] J. Cahn and J. Taylor, *Acta Mater.* **52**, 4887 (2004).
- [13] Z. Shan, E. Stach, J. Wieszorek, J. Knapp, D. Follstaadt, and S. Mao, *Science* **305**, 654 (2004).
- [14] M. Upmanyu, D. Srolovitz, A. Lobkovsky, J. Warren, and W. Carter, *Acta Mater.* **54**, 1707 (2006).
- [15] Z. Trautt and Y. Mishin, *Acta Mater.* **60**, 2407 (2012).
- [16] Y. Mishin, M. Asta, and J. Li, *Acta Mater.* **58**, 1117 (2010).
- [17] K. Elder, M. Katakowski, M. Haataja, and M. Grant, *Phys. Rev. Lett.* **88**, 245701 (2002).
- [18] A. Jaatinen, C. Achim, K. Elder, and T. Ala-Nissila, *Phys. Rev. E* **80**, 031602 (2009).
- [19] K.-A. Wu and P. Voorhees, *Acta Mater.* **60**, 407 (2012).
- [20] D. Boyer and J. Vinals, *Phys. Rev. Lett.* **89**, 055501 (2002).
- [21] H. Ohnogi and Y. Shiwa, *Phys. Rev. E* **84**, 051603 (2011).
- [22] A. Adland, Y. Xu, and A. Karma, arXiv p. 1303.0577 (2013).
- [23] K. Elder, N. Provatas, J. Berry, P. Stefanovic, and M. Grant, *Phys. Rev. E* **75**, 064107 (2007).
- [24] K.-A. Wu and A. Karma, *Phys. Rev. B* **76**, 184107 (2007).
- [25] S. van Teeffelen, R. Backofen, A. Voigt, and H. Loewen, *Phys. Rev. E* **79**, 051404 (2009).
- [26] R. Ristau, K. Barmak, K. Coffey, and J. Howard, *J. Mater. Res.* **14**, 3263 (1999).