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Acta Materialia 51 (2003) 3895–3904

Acta MATERIALIA

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Theory of normal grain growth in normalized size space

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Received 24 November 2002; received in revised form 1 April 2003; accepted 12 April 2003

Abstract

Simple mean-field deterministic theory of normal grain growth in both 3-dimension and 2-dimension cases is presented, predicting the Rayleigh size distribution. The main idea is an application of standard thermodynamics to normalized size space with unit length proportional to average size. In the normalized space, the change of normalized free energy caused by the size change of an arbitrary grain is independent of the reservoir, which consists of all the other grains. Such "decoupling" enables us to use the original Burke-Turnbull approach to relate driving force to velocity of grain growth in the normalized space.
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Keywords: Grain growth; Size distribution; Surface energy; Normalized size space; Mean-field analysis

1. Introduction

Grain growth (GG) has been studied for more than 50 years [1–10]. It is one of the fundamental subjects in materials science and processing. The physical properties of a polycrystalline solid depend strongly on its microstructure, which is affected by grain growth, as texture influences magnetic properties. Grain growth is intriguing that it tends to obey a parabolic growth law, but no long-range atomic diffusion is required. The process of grain growth seems simple, yet the 3-dimentional (3D) nature of the microstructure makes it a difficult subject to model or analyze.

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Experimental data of grain size distributions can usually be fitted by one of three distributions—Rayleigh, lognormal, and Weibull [8–10]. These distributions differ mainly in the range of small grains, and they all give a smoothly decreasing distribution function for large grains, if the abnormal grain growth is excluded. According to recent detailed investigations by Carpenter et al. [11] for a large ensemble of grains, the lognormal distribution, though not the ideal fit, is shown to be the best fit among the known distributions.

In general, there exist two basic theoretical approaches to the description of GG—deterministic and stochastic (and, of course, a whole range of combined, intermediate models). In deterministic approach (the well-known examples are Burke-Turnbull model [1], Hillert's theory [2], Fradkov-Marder topological model [12–14]), the behavior of each grain is unambiguously determ-

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doi:10.1016/S1359-6454(03)00214-3

ined by its state parameter(s): size (radius, cross-section area, or volume), number of neighboring grains and others (if any). In stochastic approach, first introduced by Louat [15–16], and then modified by many authors, grains are treated as "drunken sailors" randomly walking in a semi-infinite size space with boundary zero point serving only as a sink (without the possibility of nucleation of new grains). Since there is always nonzero probability for random walkers to reach zero point and, hence, to disappear, the number of walkers (grains) decreases, meaning increasing average size.

Deterministic approach seems physically more acceptable since it refers explicitly to the driving force of GG, which is due to the decrease of total GB energy. Nevertheless, this approach in standard form leads to wrong predictions of the grain size distributions. [2,10] To obtain reasonable size distributions, Fradkov et al. [12,13] and Marder [14] increased the number of state parameters (the additional parameter being the number of sides per grain), but this approach is so far, to our knowledge, applied only to 2D-systems.

Stochastic approach is much more successful in predicting reasonable size distributions—even in the very first paper [15] Rayleigh-type distribution was obtained. Later, Pande [17,18] added a drift term which is inversely proportional to the grain size and negative, meaning that the drift leads to shrinking of an arbitrary grain (which seems to be absolutely incorrect for usual size space—but reasonable for normalized space—see section 2). Pande demonstrated that the adding of the drift term into random walk equations has converted Rayleigh distribution into approximately lognormal distribution. Yet, the physical sense of stochastic approach remains unclear, the same as the meaning of "diffusivity" in the size space. Moreover, the role of driving force of GG in this case also remains unclear.

In this paper we demonstrate that there exists a simple improvement of original Burke-Turnbull mean-field deterministic approach and a reasonable size distribution function is obtained. We believe that the main reason of inadequacy of the existing deterministic grain growth theories is the lacking of proper account of cooperative movement of grain boundary (GB) network. Any boundary in a GB network cannot change its length (2D) or area (3D) without changing the length or area of other boundaries. To make this coupling idea obvious, we shall consider a system of N grains, consisting of an arbitrary grain of size r (we define it as the "central" grain) and the rest of N-1 grains with a mean size $\bar{r}$ as the "reservoir." The reservoir can be regarded as a "mean-field" for the central grain. Considering all grains as spheres for simplicity, we have the constraint of constant volume in the form:

$$V^{total} = \frac{4}{3}\pi(r^3 + (N-1)\bar{r}^3) = const, \tag{1a}$$

so that (if all grains in the reservoir change equally)

$$d\bar{r} = -dr\left(\frac{r}{\bar{r}}\right)^2 \frac{1}{N-1}. \tag{1b}$$

It means that a change of size of the "central" grain leads to a change of other grains due to the constraint of total volume. While this change is small for each grain in the reservoir, it gives a non-negligible effect on the total GB surface:

$$\begin{aligned} dS^{total} &= \frac{1}{2}4\pi\cdot d(r^2 + (N-1)\bar{r}^2) \\ &= 4\pi\left(\frac{1}{r}-\frac{1}{\bar{r}}\right)r^2 dr. \end{aligned} \tag{2}$$

Thus, the driving force of grain growth of the central grain is

$$-\frac{\partial F}{dr} = -\gamma\frac{\partial S^{total}}{\partial r} = 4\pi\gamma r^2\left(\frac{1}{\bar{r}}-\frac{1}{r}\right), \tag{3}$$

where $F = \gamma S^{total}$ is a free energy of the whole system, and γ is surface energy per unit area. The driving force contains comparable inputs from both the central grain and the reservoir. Such coupling at thermodynamic and kinetic levels may lead to cross-term effects between a grain and its surrounding, therefore the analysis is rather complicated and has obstructed progress of the theory of grain growth in the past. We demonstrate below that this basic difficulty can be circumvented, by using the normalized size space.

2. Grain growth in 3D case

Let $R(t)$ be some average characteristics of the grains, being proportional to all kinds of averages of the same dimension:

$$R \propto < r > \propto \sqrt{< r^2 >} \propto \sqrt{\frac{< r^3 >}{< r >}} \propto ...$$

The proper choice of R will be made below to satisfy the constraint of constant total volume. We introduce a non-dimensional space with R being a unit length, and furthermore we shall consider GG in this space.

In real space, the free energy, related to GBs, is given as $F = \frac{1}{2}\Sigma_{i=1}^{N}\gamma S_i$, where S_i is then surface area of i-th grain, $S_i = q_3 r_i^2, r_i \equiv \left(\frac{3V_i}{4\pi}\right)^{1/3}$, q_3 is a geometrical factor (equal to 4π for sphere), which is constant under the assumption of fixed shape, and V_i is volume of the i-th grain.

In real space, the dimension of free energy is kg·m^2/s^2. In the normalized space the free energy is represented by $\tilde{F} = \frac{F}{R^2}$, with a dimension of kg /s^2,

$$\tilde{F} = \frac{1}{2}\gamma q_3 \sum_{i=1}^{N} \tilde{r}_i^2, \tilde{r}_i = \frac{r_i}{R}. \tag{4}$$

In the framework of mean-field approach, we shall consider an arbitrary grain 1 as the "central" grain, and all the others as the reservoir:

$$\tilde{F} = \frac{1}{2}\gamma q_3\left(\tilde{r}^2 + \sum_{i=2}^{N}\tilde{r}_i^2\right) = \frac{1}{2}\gamma q_3(\tilde{r}^2 + (N-1) < \tilde{r}^2 >) \tag{5}$$

Since R is proportional to average size, the ratio $\frac{< r^2 >}{R^2} = <\tilde{r}^2>$ is constant. The number of grains N can be treated as constant when the change of size is infinitesimal. Thus, the second term in Eq. (5) is constant, and the change of normalized free energy of the central grain (defined in normalized size space) is independent on reservoir. The influence of reservoir will be present only after the transition back to real space: $dF = R^2 d\tilde{F} + \tilde{F}dR^2$.

Thus, in the normalized size space we can follow the original Burke-Turnbull approach [1] by considering only the energy change of the "central" grain, with the correct sign for interrelation among pressure, mobility and velocity:

$$\tilde{p} = -\frac{\partial \tilde{F}}{\partial \tilde{V}} = -\frac{\partial\left(\frac{\gamma q_3}{2}\tilde{r}^2\right)}{\partial\left(\frac{4\pi}{3}\tilde{r}^3\right)} = -\frac{\gamma q_3}{4\pi}\frac{1}{\tilde{r}}. \tag{6}$$

$$\frac{d\tilde{r}}{dt} = \tilde{M}\tilde{p} = -\tilde{M}\frac{\gamma q_3}{4\pi}\frac{1}{\tilde{r}} \tag{7}$$

Here $\tilde{M}$ is mobility in the normalized size space. The "minus" sign means that in the normalized size space it is thermodynamically favorable to decrease the size of any grain. In real space it translates to mean that even if some grain is growing, its growth rate is less than the rate of change of the mean size grain. (One can check that this characteristics is valid in the case of Lifshiz-Slezov-Wagner (LSW) ripening for all sizes [19,20], except the maximal, $r_{\max} = \frac{3}{2}r_{crit}$, for which $\frac{d\tilde{r}}{dt} = 0$).

Note that Eq. (7) is similar to Pande's drift term [18] in his combination of stochastic and deterministic approaches, but in our case Eq. (7) is for normalized space and it is physically clear.

A simple analysis of the dimension of ($[\tilde{M}] = \frac{[d\tilde{r}/dt]}{[-\partial\tilde{F}/\partial\tilde{V}]}$) leads to the conclusion,

$$\tilde{M} = \frac{M}{R^2}, \tag{8}$$

where M is mobility in real space. Following Burke-Turnbull's approach [1], we take M to be constant. Actually, this is a major assumption of most grain growth theories. Substituting Eq. (8) into Eq. (7), we obtain the rate equation for grain sizes in the normalized space:

$$\frac{d\tilde{r}^2}{dt} = -\frac{k_3}{R^2(t)}, \tag{9}$$

$$k_3 = M\frac{\gamma q_3}{2\pi}. \tag{10}$$

To relate R to average values, we use the constraint of constant total volume in real space:

$$\begin{aligned} 0 &= \sum r_i \frac{dr_i^2}{dt} = \sum R\tilde{r}_i \frac{d(R^2\tilde{r}_i^2)}{dt} = \\ &= R\sum \tilde{r}_i\left(R^2\cdot\left(-\frac{k_3}{R^2}\right) + \tilde{r}_i^2\frac{dR^2}{dt}\right) \\ &= RN\left(-k_3 < \tilde{r} > + \frac{dR^2}{dt} < \tilde{r}^3 > \right). \end{aligned} \tag{11}$$

Thus,

$$\frac{dR^2}{dt} = k_3\frac{< \tilde{r} >}{< \tilde{r}^3 >} = R^2\frac{< r >}{< r^3 >}, \tag{12}$$

so that

$$\frac{d\ln R^2}{dt} = k_3\frac{< r >}{< r^3 >}. \tag{13}$$

Substituting the condition of (12) or (13) into Eq. (9), we have the growth/shrinkage equation for grain sizes in real space:

$$\frac{dr^2}{dt} = k_3\left(\frac{r^2 < r >}{< r^3 >} - 1\right), \tag{14a}$$

or

$$\frac{dr}{dt} = \frac{1}{2}k_3\left(\frac{r < r >}{< r^3 >} - \frac{1}{r}\right). \tag{14b}$$

Substituting Eq. (14b) into the continuity equation in size space (or Eqs. (9) and (12) into the continuity equation in the normalized size space), we obtain

$$\frac{\partial f}{\partial t} = -\frac{k_3}{2}\frac{\partial}{\partial r}\left(f\left(\frac{r < r >}{< r^3 >} - \frac{1}{r}\right)\right), \tag{15}$$

where $f(t,r)$ is a size distribution. By using a standard mathematical procedure of separation of variables, for example, see [21], the following asymptotical size distribution is obtained, which practically coincides with Rayleigh distribution, and in general it fits experimental observations well;

$$f(t,r) = \frac{const}{\left(\frac{2}{3}k_3t\right)^2}\frac{r}{\left(\frac{2}{3}k_3t\right)^{1/2}}\exp\left(-\frac{r^2}{\frac{2}{3}k_3t}\right), \tag{15a}$$

$$\begin{aligned} &< r > = \frac{\sqrt{\pi}}{2}\left(\frac{2}{3}k_3t\right)^{1/2}, < r^2 > = \frac{2}{3}k_3t, \\ &< r^3 > = \frac{3\sqrt{\pi}}{4}\left(\frac{2}{3}k_3t\right)^{3/2}, \\ &\frac{< r^3 >}{< r >} = k_3t. \ \frac{d\ln R^2}{d\ln t} = 1. \end{aligned} \tag{16}$$

3. Grain growth in 2D case

Since the basic idea remains the same, we will streamline the consideration and derivations of this case, indicating only the key equations. The total free energy of GBs for the system, consisting of a "central" grain and a "reservoir" of all the other grains, is:

$$F = \frac{1}{2}\gamma\left(l + \sum_{i=2}^{N} l_i\right) = \frac{1}{2}\gamma q_2\left(r + \sum_{i=2}^{N} r_i\right), \tag{17}$$

where γ is a GB free energy per unit length of grain-boundaries in an ordinary 2D-space, l_i is the perimeter length of i-th grain, $l_i = q_2 r_i$, $r_i \equiv \sqrt{S_i/\pi}$, S_i is the grain's area, and q_2 is a geometrical factor, equal to 2π for circular grains.

The free energy in the normalized space is

$$\tilde{F} = \frac{1}{2}\gamma q_2\tilde{r} + const. \tag{18}$$

The pressure has the same dimension as in the 3D-case and is equal to

$$\tilde{p} = -\frac{\partial\tilde{F}}{\partial\tilde{S}} = -\frac{\partial\left(\frac{1}{2}\gamma q_2\tilde{r}\right)}{\partial(\pi\tilde{r}^2)} = -\frac{\gamma q_2}{4\pi}\frac{1}{\tilde{r}}. \tag{19}$$

The grain velocity in the normalized size space is

$$\frac{d\tilde{r}}{dt} = \tilde{M}\tilde{p} = -\tilde{M}\frac{\gamma q_2}{4\pi}\frac{1}{\tilde{r}} \tag{20}$$

Since velocity and pressure in the normalized 2D-case have the same dimensions as in the normalized 3D-case, we have for mobility, $\tilde{M} = \frac{M}{R^2}$, and

$$\frac{d\tilde{r}^2}{dt} = -\frac{k_2}{R^2}, \tag{21}$$

with

$$k_2 = M\frac{\gamma q_2}{2\pi}. \tag{22}$$

The constraint of conservation of total area, $\Sigma r_i \frac{dr_i}{dt} = 0$, leads to the condition for R:

$$\frac{d\ln R^2}{dt} = \frac{k_2}{< r^2 >}, \text{ or } \frac{dR^2}{dt} = \frac{k_2}{< \tilde{r}^2 >}, \tag{23}$$

so that the growth/shrinkage law in the ordinary 2D-case is

$$\frac{dr^2}{dt} = k_2\left(\frac{r^2}{< r^2 >} - 1\right), \tag{24a}$$

or

$$\frac{dr}{dt} = \frac{1}{2}k_2\left(\frac{r}{< r^2 >} - \frac{1}{r}\right). \tag{24b}$$

The corresponding size distribution coincides well with Rayleigh distribution and fits most part of experimental observations [8]:

$$f(t,r) = \frac{const}{(k_2 t)^{3/2}} \frac{r}{(k_2 t)^{1/2}} \exp\left(-\frac{r^2}{k_2 t}\right), \tag{25}$$

$$< r^2 > = k_2 t. \tag{26}$$

Thus, we obtained very reasonable size distributions and parabolic time dependence for normal grain growth in both 3D and 2D cases in the frame of deterministic approach. The main idea of our analysis is based on the decoupling of a “central” grain from a “reservoir” consisting of all the other grains (a mean-field approach), by means of transition to a normalized size space.

4. Discussion

So far, the case of 2D grain growth has been analyzed much more thoroughly than the 3D-case. Therefore, it is necessary to compare our approach with known results on 2D-grain growth. To our knowledge, von Neumann-Mullins (NM) theorem [3,4,10] is generally regarded as the most rigorous result for 2D-grain growth. According to NM-theorem, the rate of grain area change is proportional to the difference $n-6$ (n = number of sides) with a coefficient which does not depend on time, size, nor on number of sides. In our mean-field approach we have not used the number of sides. Yet, we can use the semi-empirical law, [22]

$$n \cong 3\cdot\left(1 + \frac{r}{R}\right), \tag{27}$$

where we will take the average size as $R = \sqrt{< r^2 >}$. Substituting Eq. (27) into Eq. (24a), we obtain

$$\frac{dA}{dt} = \frac{\pi k_2}{9} n\cdot(n-6). \tag{28}$$

This equation conserves the special role of $n - 6$, but differs from NM-law by the additional proportionality to number of sides. This discrepancy with NM-theorem has led us to analyze NM-theorem more thoroughly. In Appendix A we demonstrate that NW-theorem is invalid. Therefore, the recent development of deterministic theory for 2D grain growth [23] on the basis of this theorem also becomes invalid.

Our model predicts the Rayleigh distribution rather than the log-normal distribution. Authors of the experimental paper [11] have processed a much larger number of grains than usual cases and also have made a more detailed statistical analysis of size distribution. They claimed that the log-normal distribution is the best fit with their experimental curves. No doubt, this is a challenge for our model, so we propose the following arguments to defend our model.

1. Among deterministic approaches, our mean-field approach in normalized space gives the best fit, since Rayleigh distribution deviates

from Carpenter's (et al) [11] data only for small grains.
2. Any two-parametric distribution (as log-normal one) can always be fitted better than the one-parametric distribution (as Rayleigh one).
3. Inclusion of a stochastic term into our equations for distribution in the normalized space can lead to two-parametric distribution, which will fit much better (see discussion below and Appendix B).

We note that the present approach keeps all the shortcomings of mean-field theories. Naturally, different grains of the same size but with different shape and different local environment will actually demonstrate some spread of velocities in size space (Langevine term in expression for velocity and "diffusion" term in the corresponding Fokker-Planck equation for size distribution function). A new approach to this problem of stochastic environment and short-range order (SRO) has recently been developed by Di Nunzio [24]. If one neglects the SRO effect, an account for "noise effect" can be made by reformulation of Pande' formalism [18] by combining drift and random walk in the normalized space. The corresponding mathematics is presented in Appendix B. The main finding is that the inclusion of the drift term can lead to linear dependence of area distribution or, in other words, cube dependence of radii distribution, for small sizes. This gives a much better agreement to experimental data than the one-parametric Rayleigh distribution.

Less evidently, the deterministic mean-field grain growth might be formulated directly in real space by taking into account the cooperative movement of the GB network. In this case the mobility ceases to be constant. For example, the widely known Hillert's model [2] can lead to a reasonable size distribution, provided that

1. average size $R(t)$ is the mean-squared radius $\sqrt{<r^2>}$ in 2D-case, and $\sqrt{\dfrac{<r^3>}{<r>}}$ in 3D-case
2. the mobility is modified from a constant M (in Hillert's theory) to $M' = M \cdot \left(1 + \dfrac{r}{R}\right)$, so that

$$\frac{dr}{dt} = M' \cdot \left(\frac{1}{R} - \frac{1}{r}\right) \tag{29a}$$

It is interesting to note that in 2D-case, taking empirical relation (27) into account, we can write down Eq. (29a) using the derivative of the average side length:

$$\frac{d(2\pi r/n)}{dt} = \left(\frac{2\pi}{3}\right) M \cdot \left(\frac{1}{R} - \frac{1}{r}\right). \tag{29b}$$

In this case a modified equation for evolution,

$$\frac{\partial f}{\partial t} = -M \frac{\partial}{\partial r}\left(f\left(\frac{r}{R^2} - \frac{1}{r}\right)\right) \tag{30}$$

will lead to Rayleigh-type size distributions, $f(t,r) = C\dfrac{r}{t^2}\exp\left(-\dfrac{r^2}{2Mt}\right)$ for 2D-case (constant total area $\propto \int r^2 f dr$), $f(t,r) = C\dfrac{r}{t^{5/2}}\exp\left(-\dfrac{r^2}{\frac{4}{3}Mt}\right)$ for 3D-case (constant total volume $\propto \int r^3 f dr$), without a sharp drop at some maximal size, characteristic for LSW-type models.

5. Summary

We presented a simple mean-field deterministic theory of grain growth for both 3D and 2D cases in a normalized size space, and we have predicted the Rayleigh size distribution of grains. It can be modified to approach the log-normal distribution by including a stochastic term. In the normalized space, the change of normalized free energy caused by the size change of an arbitrary grain is independent of all the other grains. Such "decoupling" enables us to use the original Burke-Turnbull approach to relate the driving force to velocity of grain growth in the normalized space. We believe that the idea of analyzing thermodynamics and kinetics in normalized space and also in normalized time might be useful for other applications in microstructure evolution.

Acknowledgements

The authors would like to acknowledge the supported by NSF (Contract #DMR-9987484), INTAS (grant #783) and Ministry of Education and Science of Ukraine. One of the authors (AMG) is grateful to Department of Materials Science and Engineering at UCLA for hospitality.

Appendix A. Invalidity of Neumann-Mullins theorem

Theorem of Neumann-Mullins (NM-theorem) is based on the following simple assumptions:

1. Each of three angles at each vertex is $2\pi/3$ (in the case of equal tension γ of each boundary) at each time moment (mechanical equilibrium is provided).
2. Each grain boundary (of length l_i) is an arc of a circle with some radius R_i and angle $\varphi_i = l_i/R_i$. Then a simple derivation shows that $\Sigma_{i=1}^{n}\varphi_i = \frac{\pi}{3}\cdot(6-n)$, where n is number of grain boundaries (number of neighbors) of an arbitrary grain.
3. Each point of i-th grain boundary moves along the local radius of curvature with velocity proportional to curvature: $V_i = -k\frac{\gamma}{R_i}$.

Then the rate of grain area change is given by

$$\frac{dA}{dt} = \sum_{i=1}^{n} l_i V_i = -k\gamma\sum_{i=1}^{n}\frac{l_i}{R_i} = \frac{\pi k\gamma}{3}\cdot(n-6) = C\cdot(n-6), \tag{A1}$$

where the constant C does not depend on time, size, nor on the number of neighbors.

We will demonstrate below that the abovementioned assumptions are not self-consistent and the NM-theorem is invalid. To prove invalidity of any theorem, it is enough to have just one example showing that it is wrong. We will consider a simple, symmetric case of 3-sided (based on a right triangle) grain shrinking symmetrically (Fig. 1).

To satisfy the equilibrium condition at each vertex, the grain boundaries should be convex forming angles $\pi/6$ with corresponding sides of triangle at the vertexes (then the total angle between two boundaries at the vertex will be $\pi/6 + \pi/3 + \pi/6 = 2\pi/3$ as it should be). One can easily check that in this case each vertex is a curvature center of the opposite arc (grain boundary) so that for each boundary $R = a$, where a is the linear side length of triangle at fixed time moment.

Now we present 2 different derivations of the rate of area change leading to contradicting results and then we present the reason of disagreement.

NM-theorem gives (for $n = 3$)

$$\left.\frac{dA}{dt}\right|_{\mathrm{I}} = -\pi k\gamma. \tag{A2}$$

Direct derivation: The area of a "convex triangle" can be given as $A = \frac{1}{2}a^2\frac{\sqrt{3}}{2} + 3\cdot\left(\frac{1}{2}R^2\frac{\pi}{3} - \frac{1}{2}a^2\frac{\sqrt{3}}{2}\right) = \frac{\pi-\sqrt{3}}{2}a^2$. Therefore

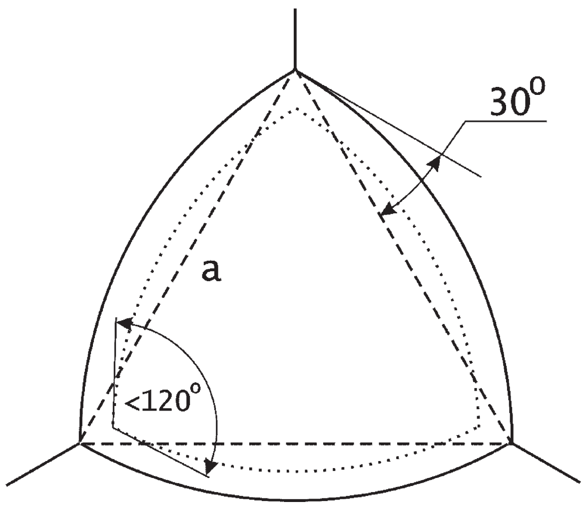

Fig. 1. Shrinking of triangle grain.

$$\left.\frac{dA}{dt}\right|_{\mathrm{II}} = \frac{\pi-\sqrt{3}}{2}\cdot 2a\frac{da}{dt} \tag{A3}$$

Since each linear side $a = R$ is simultaneously a curvature radius for the two arcs with centers in the other two vertexes, they become closer with time with velocity

$$\frac{da}{dt} = 2\cdot V = -2\cdot\frac{k\gamma}{a} \tag{A4}$$

Eqs (A3) and (A4) give:

$$\left.\frac{dA}{dt}\right|_{\mathrm{II}} = -2\cdot\left(\pi-\sqrt{3}\right)k\gamma. \tag{A5}$$

Thus, the above two derivations lead to contradicting results in (A2) and (A5) for the rate of area change.

We suggest the following reason for this discrepancy. When the arc moves along the curvature radii in each point, covering some distance Vdt, after this it has new curvature radius of $a-Vdt$ (but still the same curvature center), and intersects other arc in a new point—new vertex position (Fig. 2). In this new position the shifted boundaries (arcs) meet each other at angles different from the necessary value of $2\pi/3$. To satisfy the equilibrium condition for new vertex position, each boundary should become more convex, corresponding to new position of curvature center and new curvature radius $a-2\cdot Vdt$. The area change of a 3-sided convex grain is

$$dA|_{\mathrm{III}} = 3\cdot\left\{\left[\frac{1}{2}(a-Vdt)^2\cdot\left(\frac{\pi}{3}-2\cdot d\varphi\right)-\frac{1}{2}(a-Vdt)^2\sin\left(\frac{\pi}{3}-2\cdot d\varphi\right)\right]-\left[\frac{1}{2}(a-2\cdot Vdt)^2\cdot\left(\frac{\pi}{3}\right)-\frac{1}{2}(a-2\cdot Vdt)^2\sin\left(\frac{\pi}{3}\right)\right]\right\}$$

where $d\varphi \cong \frac{Vdt\cdot tg(\pi/6)}{R} = \frac{Vdt}{\sqrt{3}a}$. Simple algebra (neglecting the second order terms $\left(\frac{Vdt}{a}\right)^2$) gives

$$dA|_{\mathrm{III}} = \left(\pi-2\sqrt{3}\right)aVdt = -k\gamma\left(2\sqrt{3}-\pi\right)dt, \tag{A6}$$

which coincides with the difference between the expressions in (A2) and (A5). (This difference appears to be almost 10%).

We have demonstrated in the above that the assumptions of mechanical equilibrium and uniform motion of all points of the same boundary are inconsistent. To satisfy the equilibrium criteria, the different points of the same boundary with the same curvature should move with different velocities (or, after each uniform motion step, each point must adjust its position to a new vertex position, leading to a change of the grain area).

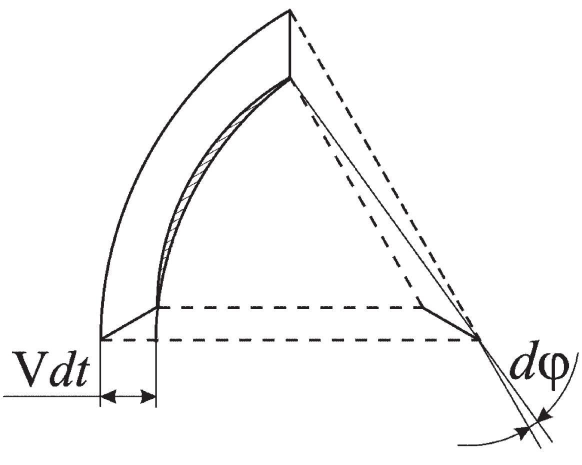

Fig. 2. Relaxation of GB to new vertex position.

Appendix B. Inclusion of a Stochastic Term in the NGG Approach

To calculate the effect of stochastic term, it will be useful to reformulate the derivation of our deterministic theory. We will write down the equations for the 2D case, but for the 3D case it is very similar. According to our deterministic mean-field approach, the velocity of squared grain size in the normalized size space is $\frac{d\tilde{r}^2}{dt} = -\frac{k_2}{R^2}$. So, for reduced area $\tilde{A} = \pi\tilde{r}^2$ we have

$$\frac{d\tilde{A}}{dt} = -\frac{\pi k_2}{R^2} \tag{B1}$$

Together with continuity equation in normalized space for distribution of normalized (reduced) grain areas it gives:

$$\frac{\partial f(t,\tilde{A})}{\partial t} = -\frac{\partial}{\partial \tilde{A}}\left(f\frac{d\tilde{A}}{dt}\right) = \frac{\pi k_2}{R^2}\frac{\partial f}{\partial \tilde{A}}. \tag{B2}$$

Solution of this equation can be found by separation of variables and is

$$f(t,\tilde{A}) = \frac{const}{t}\exp\left(-\frac{\tilde{A}}{<\tilde{A}>}\right),$$

where

$$<\tilde{A}> = \pi <\tilde{r}^2> = \pi. \tag{B3}$$

Of course, it is the same Rayleigh distribution, but over areas instead of radii:

$$f(t,\tilde{r}) = f(t,\tilde{A})\frac{d\tilde{A}}{dr} = 2\pi r * f(t, \tilde{A} = \pi\tilde{r}^2) \tag{B4}$$

To include stochastic term, we add "diffusion flux" into continuity equation in the normalized space:

$$\frac{\partial f(t,\tilde{A})}{\partial t} = -\frac{\partial}{\partial \tilde{A}}\left(f\frac{d\tilde{A}}{dt} - \tilde{D}_A\frac{\partial f}{\partial \tilde{A}}\right). \tag{B5}$$

Analytical solution of Eq. (B5) exists if we take

$$\tilde{D}_A = \frac{const}{R^2} = \pi\frac{k_2 d}{R^2}, d = const. \tag{B6}$$

so that the equation for distribution function becomes:

$$\frac{R^2}{\pi k_2}\frac{\partial f(t,\tilde{A})}{\partial t} = \frac{\partial}{\partial \tilde{A}}\left(f + d\frac{\partial f}{\partial \tilde{A}}\right). \tag{B7}$$

The additional parameter (d) gives us more freedom to choose the boundary condition. We propose a boundary condition, close to experimental data: $f(t,\tilde{A} = 0) = 0$. Then by taking the usual procedure of separation of variables, we obtain the next solution: $f(t,\tilde{A}) = \frac{const}{t}(\exp(-z_1\tilde{A}) - \exp(-z_2\tilde{A}))$,

$$\tilde{A} = \pi r^2/R^2, R^2 = k_2 t \tag{B8}$$

with

$$z_1 = \frac{1-\sqrt{1-4\frac{d}{\pi}}}{2d}, z_2 = \frac{1+\sqrt{1-4\frac{d}{\pi}}}{2d}. \tag{B9}$$

Large noise, $d > \pi/4$, would lead to oscillatory (unreasonable) solutions. If noise is small, $d \ll \pi/4$, then distribution can be approximated as $f(t,\tilde{A}) = \frac{const}{t}(\exp(-\tilde{A}/\pi) - \exp(-\tilde{A}/d))$.

For small sizes (after expansion of exponents) this distribution $f(A)$ will be proportional to A^1 and the distribution of radii $f(\tilde{r}) = 2\pi\tilde{r}f(\tilde{A} = \pi\tilde{r}^2)$ will be proportional to r^3. Thus, the main outcome by the inclusion of stochastic term is a change mainly about the distribution of small sizes; it becomes more close to a log-normal distribution.

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