Effects of Triple Grain Junctions on Equilibrium Boundary Angles and Grain Growth Kinetics

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Abstract. Triple grain junctions in polycrystals become important at the nanoscale, as the fraction of atoms in them reaches a considerable value. They have an associated line tension, as grain boundaries have a boundary tension. We discuss the definition of line tension and its effects on: a) the equilibrium angles at which three-dimensional (3D) grain boundaries meet; b) the kinetics of 3D grain growth, particularly the kinetic exponent in the power relation between average grain diameter and time, and the possible existence of a scaling regime in grain growth. We conclude that the triple junctions tend to slow down grain growth and predict “anomalous” effects when the line tension is negative.

Triple Lines and Triple Line Tension in Polycrystals

The grain boundaries (GB) in a polycrystal are high energy regions, in the sense that the energy of a (large) number of atoms at the boundary is larger by $\Delta E_1$ relative to the energy of $N$ atoms in the bulk of the grains. The GB tension $\gamma$ (or specific free energy or, simply, energy) is defined by $\gamma = \Delta E_1 / S$, where $S$ is the area of boundary occupied by the $N$ atoms. Of course, the boundary has a non-zero thickness that depends on the criterion used to define a “grain boundary atom”; and the boundary area is the area of the mid boundary surface.

In a polycrystal the GB’s meet three by three at triple junctions (TJ) or triple lines, as schematically represented in Fig. 1, where the TJ is shown as a triangular region. Also shown in Fig. 1 is one of the GB prolongations or the TJ. $N$’ atoms at the TJ have energy larger by $\Delta E_2$ relative to the same number of atoms at the GB’s. The line tension $\tau$ is defined as $\tau = \Delta E_2 / L$, where $L$ is the length of TJ occupied by the $N$’ atoms. This excess energy $\tau$ can be positive or negative, depending on the misorientation of the grains and inclination of the GB’s and TJ. The total excess energy $\Delta E$ of the polycrystal, relative to a perfect crystal with the same number of atoms is

Fig. 1-Section of a symmetrical triple line, showing the grain boundaries (GB) and the triple junction (TJ). The prolongation of one of the boundaries into the TJ is shown dashed.

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\[ \Delta E = S \gamma + L\tau \]  \hspace{1cm} (1)

where \( S \) and \( L \) are the total area of GB’s and total length of TJ’s, respectively. Note that \( \tau/\gamma \) has the dimension of a length and it is in the nanometer range. We ignore the contribution of quadruple junctions.

**Equilibrium with Triple Junctions**

At (stable) equilibrium for uniform \( \gamma \) and zero line tension \( (\tau = 0) \), the GB’s have constant mean curvature and meet at TJ’s at 120° to each other. These are the Plateau rules [1, 2], which were first enunciated for liquid foams. They imply a local minimum of energy. When \( \tau \neq 0 \), the TJ’s have a contractile tendency if \( \tau > 0 \) or an expanding tendency if \( \tau < 0 \). The corresponding force per unit length is \( \tau/\rho \), where \( \rho \) is the local radius of curvature of the TJ [3]; it is directed to the centre of curvature of the TJ if \( \tau > 0 \), and vice-versa. The equilibrium condition at a TJ is now

\[ \sum_{i=1}^{3} \hat{n}_i + \frac{\tau}{\rho} \vec{n} = 0 \]  \hspace{1cm} (2)

where \( \hat{n}_i \) is a vector of modulus \( \gamma \) tangent to grain boundary \( i \) and normal to the triple line and \( \vec{n} \) is the principal normal to the triple line, directed to its centre. The equilibrium angles between boundaries are no longer 120°; but, of course, their mean value is 120°. In Fig. 2a we show a simple tricrystal, with a lens shaped grain sitting at a planar boundary. The curved grain boundaries are spherical and meet at a circular triple line of radius \( \rho \); the angle \( \theta \) between them is given by the equilibrium condition (2), which in this case simplifies to

\[ \gamma (1 - 2 \cos \frac{\theta}{2}) = \frac{\tau}{\rho} \]  \hspace{1cm} (3)

In Fig. 2b we plot the deviation of \( \theta \) from 120° as a function of \( \tau/\gamma \rho \); the deviation increases as \( \rho \) decreases (nanocrystals) and is positive \((\theta > 120°)\) for \( \tau > 0 \).

![Diagram](a) (a) A lens shaped grain at a planar boundary. The triple line is circular, of radius \( \rho \). The angle \( \theta \) deviates from 120° when the triple line tension \( \tau \neq 0 \), as shown in b).

**Grain Growth Driven by Grain Boundary and Triple Junction Energy**

In recent years, several papers [4-6] dealt with the effect of TJ’s on grain growth. However, these studies did not provide a definitive answer as to whether TJ’s accelerate [4] or retard [5] grain growth. In the present paper we address this problem, based on the kinetic equation recently proposed by Deus et al. [7] for the rate of change of the diameter \( a \) of a grain with an (excess)
energy density \( E \) (energy per unit volume). The grain diameter \( a \) is defined such that \( V = a^3 \), where \( V \) is the volume of the grain. The kinetic equation for grain growth driven by differences in the energy density \( E \) among the grains is

\[
\frac{da}{dt} = -k (E - E^*)
\]  

(4)

where \( k \) is a kinetic constant, proportional to the grain boundary mobility. The quantity \( E^* \) in eq. (4) can be regarded as a threshold energy; grains with \( E < E^* \) grow, and vice-versa. Imposing the constancy of the total volume, \( V_n = \sum a^3 \), we obtain [7]

\[
E^* = \frac{<a^2 E>}{<a^2>}
\]

(5)

Thus \( E^* \) is the average of \( E \) weighed by \( a^2 \), which is proportional to the GB area.

The energy density \( E \) can be due to external fields (e.g. electric, magnetic,…) or simply associated with the GB and TJ contributions to energy. These are, for a grain of diameter \( a \), proportional to \( 1/a \) and \( 1/a^2 \), respectively. We then write

\[
E_n = \frac{A_n}{a^n}
\]

(6)

where \( n = 1 \) applies to GB driven growth and \( n = 2 \) to TJ driven growth. \( \lambda_t \) is proportional to \( \gamma \) while \( \lambda_f \) is proportional to \( \tau \). The corresponding \( E_n^* \) are

\[
E_n^* = \lambda_n \frac{<a^{2-n}>}{<a^2>}
\]

(7)

In ref. [7] it was found that a scaling regime, in which the distribution of \( a / <a> \) becomes time invariant, is reached at sufficiently long times in pure GB driven growth. This scaling regime is characterized by a power law kinetics \( <a> \propto t^\alpha \), with the kinetic exponent \( \alpha = 1/2 \) (parabolic growth). For pure TJ driven growth (with \( \tau > 0 \)) we expect an exponent \( \alpha = 1/3 \), i.e., cubic growth. This is confirmed in the simulations (see below).

When the two effects (GB and TJ driven growth) superimpose, the growth equation (4) is replaced by

\[
\frac{da}{dt} = -k [ (E_i - E_i^*) + \lambda(E_f - E_f^*) ]
\]

(8)

with \( E_n \) and \( E_n^* \) given by eqs. (6) and (7). The constant \( \lambda \) measures the relative importance of the two driving forces; note that \( \lambda < 0 \) if the line tension \( \tau < 0 \).

When the two effects are superimposed and growth is governed by (8) it is unlikely that a scaling regime is reached. The kinetics at long times is not expected to follow a power law. The kinetic exponent \( \alpha \) is probably between 1/2 and 1/3 but is not expected to remain constant, even at long times. The simulations confirm these predictions.

**Numerical Simulation of Grain Growth**

All simulations were carried out for an initial Hillert distribution of grain diameters [8]. The distribution, shown in Fig. 3, was truncated at \( a / <a> = 1.8 \); the initial number of grains was 10000 and the initial average diameter was \( <a> = 1 \). The evolution of the individual grains was calculated by eq. (8) for various values of \( \lambda \), including negative values, and also for pure GB growth (\( \lambda = 0 \)) and for pure TJ growth (\( 1/\lambda = 0 \)). In each case, we also calculated \( <a> \) and the standard deviation \( s^2 = (<a> - <a>^2)^2 > <a>^2 \) as a function of time. The distribution of \( a / <a> \)
changed with time, but at large times it seemed to remain nearly invariant (Fig. 3) with $\langle a \rangle$ approaching a power law with exponent 1/2 for pure GB growth and with exponent 1/3 for pure TJ growth. For $\bar{\lambda} > 0$, a scaling regime was not detected (i.e. $s^*$ did not reach a constant value) and the kinetic exponent $\alpha$ in eq. (8) was between 1/3 and 1/2, at long times. In conclusion, for $\tau > 0$, the triple junctions retard grain growth, at least at long times. At short times, the kinetics is quite different, and triple junctions may accelerate or retard growth, depending on $\bar{\lambda}$. This is shown in the curves of Fig. 4, based on the simulations. At short times, pure TJ growth is the fastest and pure GB growth the slowest. This behaviour is likely to depend also on the initial distribution of $a$, but we did not investigate this.

Fig. 3. Top diagrams: the initial distribution of grain diameters (Hillert’s distribution) used in the calculations (smooth curves) and the distribution at long times (serrated curves) for a) pure GB curvature growth; b) pure TJ growth; c) combined effect with $\bar{\lambda} = 1$. Bottom diagrams: the time evolution of the average diameter $\langle a \rangle$ and of the standard deviation $s^*$. 
Fig. 4. The kinetics of grain growth at short and long times for $\tau > 0$ with crossover of the $<\alpha>(t)$ curves (schematic).

When $\tau < 0$ ($\lambda < 0$), grains are not eliminated because the $1/a^2$ term dominates for small $a$, which originates growth. We also found that $<\alpha>$ can either increase or decrease with time, depending on $\lambda$, as shown in the examples of Fig. 5 for $\lambda = -0.1$ and $\lambda = -1$. When $<\alpha>$ increases with time, the grain diameters tend to uniformization ($s^2 = 0$) while in the other case the distribution broadens ($s^2$ increases with time). These “anomalous” effects for negative line tension are likely to depend on the initial distribution, in addition to the dependence on $\lambda$.

Fig. 5. Effect of a negative line tension ($\tau < 0$) on grain growth. For $\lambda = -1$ (left) $<\alpha>$ increases and all grains evolve to the same diameter, with $<s^2>$ approaching zero. For $\lambda = -0.1$ (right) the average diameter $<\alpha>$ decreases and the distribution of $a$ broadens ($s^2$ increases).
References


