Available online at www.sciencedirect.com

SCIENCE DIRECT®

Scripta Materialia 51 (2004) 611–616

Scripta MATERIALIA

www.actamat-journals.com

On the validity of the von Neumann–Mullins relation

G. Gottstein [a,*], A.D. Rollett [b], L.S. Shvindlerman [a,c]

[a] *Institut für Metallkunde und Metallphysik, RWTH Aachen University, Kopernikusstr. 14, D-52056 Aachen, Germany*
[b] *Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213-3890, USA*
[c] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow 142432, Russia*

Received 4 March 2004; accepted 12 May 2004

Abstract

We present a new analysis of the relative rate of growth or shrinkage of grains in a two-dimensional network, based on the classical von Neumann–Mullins (VN–M) analysis. We find that an analysis of the stability of the grain shape during shrinkage or growth shows that any change in the regular 2D grain leads to changes in the shape. We also re-examine a recent analysis that claims to have invalidated the VN–M relationship, but find that it is still valid, and that the cited analysis, in fact, confused a second order correction with a first order problem, partly because their derivation was in error. The erroneous magnitude of the discrepancy led them to use unphysical issues to explain the discrepancy. The way in which the curvature is distributed along the perimeter of a grain only gives rise only to second order corrections to the rate of change of area as a function of grain topology (number of sides).

Keywords: Grain growth; von Neumann–Mullins relation

1. Introduction

The von Neumann–Mullins (VN–M) relation [1,2] constitutes a basis for practically all theoretical and experimental investigations as well as computer simulations of microstructural evolution in 2D polycrystals in the course of grain growth [3–5].

For grain growth in a 2D system, Mullins [2] derived a fundamental relation, which was originally formulated by von Neumann for 2D soap froth [1] based on differential pressures between adjacent cells in the froth. von Neumann's analysis makes certain very fundamental assumptions, namely:

(1) All grain boundaries possess equal mobilities and surface tensions, irrespective of their misorientation and the crystallographic orientations of the boundaries;
(2) The mobility of a grain boundary is independent of its velocity;
(3) The triple junctions do not affect grain boundary motion; therefore, the contact angles at triple junctions are always in equilibrium and, due to the first assumption, are equal to 120°.

Consider a 2D grain with area S (Fig. 1) [1,2].

In the time interval $\mathrm{d}t$, all points on the grain boundaries of the grain will be displaced normal to the grain boundaries by the amount $V\mathrm{d}t$, where V is the grain boundary migration rate. Accordingly, the rate of change of the grain area S can be expressed by

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\oint V\,\mathrm{d}\ell \tag{1}$$

* Corresponding author. Tel.: +49-2418026860; fax: +49-2418022608.
E-mail address: gottstein@imm.rwth-aachen.de (G. Gottstein).

1359-6462/$ - see front matter © 2004 Published by Elsevier Ltd. on behalf of Acta Materialia Inc.
doi:10.1016/j.scriptamat.2004.05.023

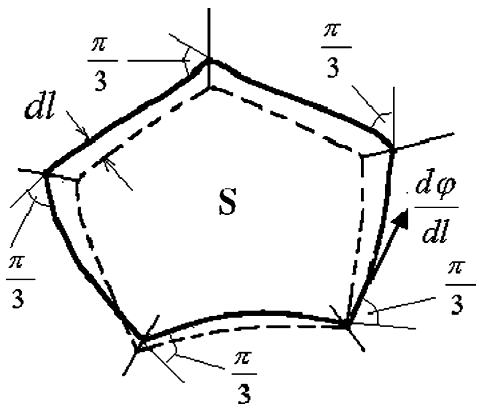

Fig. 1. Definition of parameters for the effect of triple junctions for a calculation of change of area of a grain.

where $d\ell$ is an element of the grain perimeter. For grain growth

$$V = \gamma_b m_b K \equiv A_b K \tag{2}$$

where m_b is the grain boundary mobility, γ_b is the grain boundary surface tension, κ is the local curvature of the grain boundary:

$$\kappa = \frac{d\varphi}{d\ell} \tag{3}$$

where φ is the tangential angle at any given point of the grain boundary.

From Eqs. (1)–(3), it follows that

$$\frac{dS}{dt} = -A_b \oint d\varphi \tag{4}$$

If the grain were bordered by a smooth line, the integral in Eq. (4) would equal 2π. However, because of the discontinuous angular change at every triple junction, the angular interval $\Delta\varphi = \pi/3$ is subtracted from the total value 2π for each triple junction. Consequently

$$\frac{dS}{dt} = -A_b\left(2\pi - \frac{n\pi}{3}\right) = \frac{A_b\pi}{3}(n-6) \tag{5}$$

where n is the number of triple junctions for each respective grain, i.e. the topological class of the grain. Thus the rate of area change is independent of the shape of the boundaries and determined by the topological class n only. Grains with $n > 6$ will grow and those with $n < 6$ will disappear [2].

We would like to emphasize especially *the generality* of the approach considered and its consequences. Since the result expressed in Eq. (5) does not depend on the shape of the moving boundaries, the rate of grain area change is determined only by the number of the adjacent (neighboring) grains, i.e. by the topological class of the grain represented by the number of triple junctions of the grain. That is why an attempt to revise the VN–M relation attracts considerable attention from materials scientists. The case in point is the paper of Gusak and Tu [6], on, as they wrote, *the invalidity* of von Neumann–Mullins (VN–M) theorem. Therefore we analyse the problem, given in [6], in more detail.

The authors of [6] limit their analysis of the validity of the VN–M relation to a consideration of a 3-sided grain whose boundaries are circular arcs. Of course, the relation is still valid for this specific, restricted case. Thus, the authors consider the growth or rather shrinkage behaviour of a "*regular* convex triangle" under *three* assumptions, which comply with the derivation of the VN–M relation.

Their derivation yields that the rate of grain area change is given by

$$\frac{dS}{dt} = \sum_{i=1}^{n} l_i V_i = -m_b\gamma_b \sum_{i=1}^{n} \frac{l_i}{R_i} = \frac{\pi m_b \gamma_b}{3}\cdot(n-6)$$
$$= C\cdot(n-6) \tag{6}$$

where the constant C does neither depend on time and size, nor on the "number of neighbors".

"We will demonstrate below",—the authors write,—"that the above mentioned assumptions are not self-consistent and the VN–M-theorem is invalid. To prove the 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 a 3-sided (based on a right triangle) grain shrinking *symmetrically* [6]. For this purpose the authors considered the shrinkage of a regular convex triangle, using the VN–M theorem and a "direct derivation" by computing the area change of a regular convex triangle.

The VN–M approach gives, naturally:

$$\frac{dS}{dt} = -\pi m_b \gamma_b \tag{7}$$

whereas the "direct derivation" of grain area change in the case, when the regular convex triangle is shrinking, they give as

$$\frac{d\left(\frac{1}{2}a^2\frac{\sqrt{3}}{2} + 3\left(\frac{1}{2}R^2\frac{\pi}{3} - \frac{1}{2}a^2\frac{\sqrt{3}}{2}\right)\right)}{dt} = \frac{d}{dt}\left(\frac{\pi-\sqrt{3}}{2}a^2\right)$$
$$= -2(\pi-\sqrt{3})m_b\gamma_b \tag{8}$$

The authors attempt to explain the discrepancy by considering in greater detail the motion of different parts of a moving grain boundary. The VN–M theory indeed deviates from the exact solution, which, however, is a correction of second order.

2. Second order corrections

Gusak and Tu (GT) [6] examined a 3-sided grain with uniformly curved sides and attempted to relate the area rate of change to its area for which a simple analytical formula gives the area. With 120° dihedral angles, the equivalent radius of the circular arcs comprising its sides is equal to the chord connecting each pair of vertices. According to the VN–M theorem, the area rate of change is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\pi m_{\mathrm{b}}\gamma_{\mathrm{b}}(3-6)}{3} = -\pi A_{\mathrm{b}} \tag{9}$$

This formula clearly assumes that each arc moves uniformly towards its center of curvature. One can think of the geometry as three 60° sectors of a circle where each sector is contracting at the same rate. Note that, for uniformly curved sides, there is a small additional loss of area at each vertex because of the overlap between each pair of arcs (Fig. 2). The correction is of order $\mathrm{d}R^2$ where $\mathrm{d}R$ is the decrement in the radius.

With the area of the figure given by

$$S = \frac{(\pi-\sqrt{3})}{2}R^2 \tag{10}$$

$$\frac{\mathrm{d}S}{\mathrm{d}R} = (\pi-\sqrt{3})R \tag{11}$$

When one decreases the size of the 3-sided grain by $\mathrm{d}R$, this is not equal to the amount by which the each circular arc moves in towards its center of curvature. The change in R is the sum of two changes, i.e. the motion of the curved arc by $\mathrm{d}\varepsilon$ and the motion of the opposite vertex towards the center, $\mathrm{d}\rho$ The area rate of change given by the VN–M formula can be related to the motion of an equivalent circular arc of (arc) length $\pi\varepsilon$:

$$\frac{\mathrm{d}S}{\mathrm{d}R} = \pi\varepsilon \tag{12}$$

In order to relate the two approaches to estimating the area rate of change, all we need is the ratio of $\mathrm{d}\varepsilon$ to $\mathrm{d}\rho$ which by inspection of Fig. 2 is

$$\cos 30^{\circ}\mathrm{d}\rho = \mathrm{d}\varepsilon \Rightarrow \mathrm{d}R = \mathrm{d}\varepsilon + \mathrm{d}\rho = \left(1+\frac{2}{\sqrt{3}}\right)\mathrm{d}\varepsilon \tag{13}$$

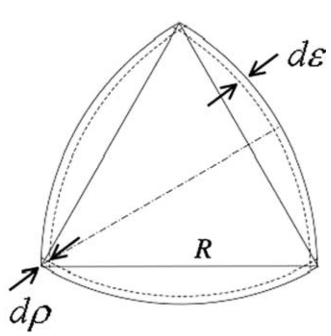

Fig. 2. Diagram of a 3-sided grain with an inscribed equilateral triangle with sides of length R. Each boundary of the grain is an arc of a circle and the internal dihedral angle at each corner is 120°, corresponding to local vertex equilibrium and isotropic grain boundary energy. If the grain shrinks in size by $\mathrm{d}R$ each vertex of the inscribed triangle moves in by $\mathrm{d}\rho$ and each boundary arc moves in by $\mathrm{d}\varepsilon$, where $\mathrm{d}R=\mathrm{d}\varepsilon+\mathrm{d}\rho$.

Considering the area of the particular geometrical figure thus yields a slightly different value for the area rate of change:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -(\pi-\sqrt{3})\left(1+\frac{2}{\sqrt{3}}\right)A_{\mathrm{b}} \tag{14}$$

The numerical difference between these two equations (9) and (10) is of order 3%. This is much smaller than the quantity claimed by the cited paper and no additional ad hoc assumptions are required in order to understand it. Note that this discrepancy depends on an assumption of a symmetrical figure with equal curvature at all points on the perimeter. Deviations of the perimeter shape that place the curvature away from the triple points will decrease the difference. There is an equivalent correction for all the regular grain shapes with equally curved perimeters. For the simplest case of an infinitely large grain, for which the VN–M formula predicts an area rate of change that is

$$\frac{1}{n}\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{n}\frac{\pi A_{\mathrm{b}}(n-6)}{3} \approx \frac{\pi A_{\mathrm{b}}}{3} \tag{15}$$

The geometry of each circular segment is simple and the distance between two triple points is R, where R is the radius of the segment. Therefore the area rate of change per segment is R. From this specific geometry, the area rate of change per circular segment is simply this:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -M\gamma \tag{16}$$

The difference between these two estimates is $\pi/3=1.0472$. Here again the discrepancy is very small and will also be affected by the actual path of the grain boundary between the two triple junctions because it is only motion of the grain boundary immediately adjacent to the triple junction that leads to an excess or deficit compared to the VN–M formula.

3. Constant curvature approach

The discrepancy between this result [6] and the VN–M relation of 2D-grain growth concerns the magnitude of the growth or shrinkage rate of a grain of topological class n. Both approaches yield a rate of area change in proportion to $(n-6)$. The two approaches, however, cannot yield the same numerical result, since both assume different boundary conditions. The VN–M approach only makes use of the correct physical behaviour that the growth rate of a grain boundary segment scales with the local curvature (Eq. (2)) and does not assume any particular shape of the boundary. Hence, every boundary element is displaced normal to itself according to its curvature.

In contrast, GT impose an additional boundary condition that the boundaries have a constant curvature such that the contact angles at the triple junctions are in equilibrium. For each displacement of a boundary, for instance of a triangular grain, the curvature has to be readjusted to account for equilibrium at the junctions. In fact, the curvature will increase with progressing grain growth owing to the fact that the grain shrinks. Therefore an additional adjustment of the grain boundary geometry has to occur in order to maintain the proper curvature. In the VN–M approach, such an adjustment is not enforced, since the boundary shape can be arbitrary. Equilibrium at the junctions is established locally, and the curvature driven grain boundary motion maintains or reduces the curvature in contrast to the GT approach. Therefore, the GT and VN–M approach cannot yield the same result, since both consider a different motion of the boundaries. In the GT approach two steps of motion are involved, curvature driven growth and subsequent readjustment of the curvature to reestablish constant curvature and junction equilibrium. The VN–M approach considers only curvature driven growth and disregards curvature adjustment at junctions as an effect of second order. There is actually no physical principle that would require constant curvature and the GT approximation is a very special case determined entirely by geometry which however is not realised in nature.

Therefore, we contend that the VN–M relation is valid, and that GT have considered a special case and arrived at incorrect conclusions. We will show in the following in terms of specific geometries that both approximations cannot be reconciled.

4. Stability of polygonal shapes

A restatement of the fourth, additional tacit assumption is that the regular convex triangle can vanish, *while still remaining a regular convex triangle*, Fig. 3. In other words the angle θ (Fig. 3) is required to remain equal to 30° during grain growth, or, equivalently, the derivative

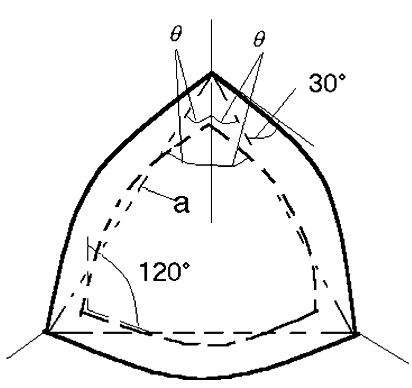

Fig. 3. Shrinking of triangle grain [6].

$d\theta/dt$ should be equal to zero in the course of grain growth (or grain shrinkage):

$$\left[\frac{d\theta}{dt}\right]_{\theta=\pi/6} = 0$$

as shown in more detail in the Appendix A.

$$\left.\frac{d\theta}{dt}\right|_{\theta=\pi/6} = -\frac{4m_b\gamma_b\pi}{a^2}\cdot\left.\frac{1}{B_1(\theta)}\right|_{\theta=\pi/6} \approx \frac{1.78\pi m_b\gamma_b}{a^2} \tag{17}$$

Clearly the value $d\theta/dt$ for $\theta=\pi/6$ is not equal to zero, which points to the fact that the evolution of "regular convex triangle" during grain growth does not follow the scenario given in [6], namely the shrinking as a self-similar regular triangle. If the regular convex triangle is left to its own devices, it becomes an isosceles triangle and collapses as a triangle of irregular shape. Its state as a regular triangle is only one possibility among infinite others. The correctness of the VN–M relation cannot be judged from the behaviour of a grain of a particular shape.

In other words, the alleged invalidity of the VN–M theorem, derived from the example of shrinkage of a regular convex triangle, was based on an incorrect assumption. That is why the conclusions, made by the authors of [6], are contrary to fact.

It is interesting to consider in this context the more general problem, namely, the behaviour of a general n-sided 2D grain in the course of 2D grain growth. Specifically, an n-sided convex grain is considered, however, it is easy to see, the same result would be obtained for a concave grain. All curved boundaries are assumed to be circular arcs. We examine a regular n-sided polygon, assuming that one angle of the polygon is changed to the nonequilibrium angle θ, which naturally, causes the two adjacent angles to change from $\gamma = \pi/n(n-2)$ to

$$\gamma_1 = \frac{3\gamma - 2\theta}{2} \tag{18}$$

After a lengthy calculation we arrive at

$$\frac{d\theta}{dt} = \frac{8m_b\gamma_b}{a^2B(\theta)}\left[(n-2)\left(\frac{\pi}{n}-\frac{\pi}{6}\right)+2\left(\frac{\pi}{3}-\theta\right)\right] \tag{19}$$

The expression in square brackets is equal to zero if

$$(n-2)\left(\frac{1}{n}-\frac{1}{6}\right)+2\left(\frac{1}{3}-\frac{\theta}{\pi}\right) = 0 \tag{20}$$

or

$$n = 6\left(1-\frac{\theta}{\pi}\right) \pm \sqrt{36\left(1-\frac{\theta}{\pi}\right)^2 - 12} \tag{21}$$

The expression $(1-\theta/\pi)$ can only assume values in the range $1 > 1-\theta/\pi > 1/\sqrt{3}$. Moreover, n must be an integer. Only, $\theta=\pi/3$ complies with all conditions and $n^* = 4 \pm 2$; $n_1^* = 6$; $n_2^* = 2$.

Since it can be shown that $B(\theta)^{-1}|_{\theta=\pi/3}=0$ for 6- and 2-sided polygons at $\theta=\pi/3$ the rate of change of the angle $\theta(\mathrm{d}\theta/\mathrm{d}t)\to 0$.

Next we examine whether such "regular" curved configurations are stable, in other words whether it will return to the regular state after being displaced from this state. The sign of the derivative $\frac{\mathrm{d}}{\mathrm{d}\theta}(\frac{\mathrm{d}\theta}{\mathrm{d}t})|_{\theta=\pi/3}$ is an index of the stability of the studied shape. A shape will be stable only if the function $\mathrm{d}/\mathrm{d}\theta(\mathrm{d}\theta/\mathrm{d}t)$, is negative at the point $\theta=\pi/3$.

The derivative discussed can be represented as

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\frac{\mathrm{d}\theta}{\mathrm{d}t}\right)\bigg|_{\theta=\pi/3} = \eta(\theta,n)|_{\theta=\pi/3} \tag{22}$$

A lengthy trigonometrical calculation shows that at $\theta=\pi/3$ the expression $\eta(\theta,3)=0$. In other words, the derivative $\frac{\mathrm{d}}{\mathrm{d}\theta}(\frac{\mathrm{d}\theta}{\mathrm{d}t})|_{\theta=\pi/3}$ for the "basic" regular polygonal configurations considered at $\theta=\pi$ is insensitive to the angle changes $\mathrm{d}\theta$ which is to say that these configurations are *unstable*, despite the fact that the equality $\left(\frac{\mathrm{d}\theta}{\mathrm{d}t}\right)\big|_{\theta=\pi/3} = 0$ is fulfilled.

As for the "regular" curved triangle, which is analysed in [6], for this configuration even the time derivative of the characteristic angle θ is not equal to zero at $\theta = \pi(\frac{\mathrm{d}\theta}{\mathrm{d}t}|_{\theta=\pi/3} \neq 0)$.

This consideration can be extended to any n-sided polygon ($n\neq 6$) to yield that a regular polygon shape behaves unstable during grain growth even in case that $\mathrm{d}\theta/\mathrm{d}t=0$ for $\theta=\pi/3$.

5. Conclusions

A rexamination of the evolution of the shape of grains revealed that the VN–M relation, in the framework of physically and mathematically reasonable assumptions, is valid for all configurations of curvature of the perimeter.

The distribution of curvature along the perimeter of a grain can result in a second order correction to the rate of change of area, compared to the VN–M result.

Many of the "regular" grain shapes that can occur during grain growth are shown to be unstable and are therefore likely to disappear during grain growth.

A network of grains that is undergoing coarsening according to the VN–M relation is highly unlikely to adopt a configuration in which the plane is tessellated by a mosaic of regular shapes.

Acknowledgments

The authors gratefully acknowledge the support of their research by the Deutsche Forschungsgemeinschaft (Grant no. 436 RUS 113/714/0-1(R)). One of the authors (LSS) wishes to thank the Japan Society for the Promotion of Science and the Russian Foundation for Fundamental Research (Grant RFFI-DFG 03 02 04000) for financial support. ADR acknowledges support by the MRSEC program of the National Science Foundation under Award Number DMR-0079996 and the support of the Institut für Metallkunde und Metallphysik, RWTH-Aachen, during a sabbatical period in Germany.

Appendix A

We examine the evolution of a 2D "regular" curved triangular grain during grain growth under VN–M conditions. The main goal is to ascertain whether or not this statement—the equality $[\frac{\mathrm{d}\theta}{\mathrm{d}t}]_{\theta=\pi/6} = 0$—is justified in the course of grain growth process.

We consider grain growth (or, more correctly, grain shrinkage) of a convex triangle, where two sides are equal and different from the third one of the isosceles convex triangle shown in Fig. 4. The radii R_1 and R_2 are equal to $R_1 = \frac{a}{2\sin(\frac{\pi}{3}-\theta)}$ and $R_2 = \frac{a\cdot\sin\theta}{\sin(2\theta-\frac{\pi}{6})} = \frac{a\cdot\sin\theta}{\cos(\frac{2}{3}\pi-2\theta)}$, respectively. The area of this convex triangle can be represented as

$$S = 2\frac{\pi R_1^2}{2\pi}\left(\frac{2}{3}\pi - 2\theta\right) - 2\frac{R_1^2}{2}\sin\left(\frac{2}{3}\pi - 2\theta\right) + \frac{\pi R_2^2}{2\pi}\left(4\theta - \frac{\pi}{3}\right) - \frac{R_2^2}{2}\sin\left(4\theta - \frac{\pi}{3}\right) + \frac{1}{2}a^2\sin 2\theta \tag{A.1}$$

A small change of S can be expressed as

$$\mathrm{d}S = \frac{a^2}{4}\cdot B_1(\theta) \tag{A.2}$$

where $B_1(\theta)$ is some trigonometrical function of the angle θ. On the other hand, the same change of S can

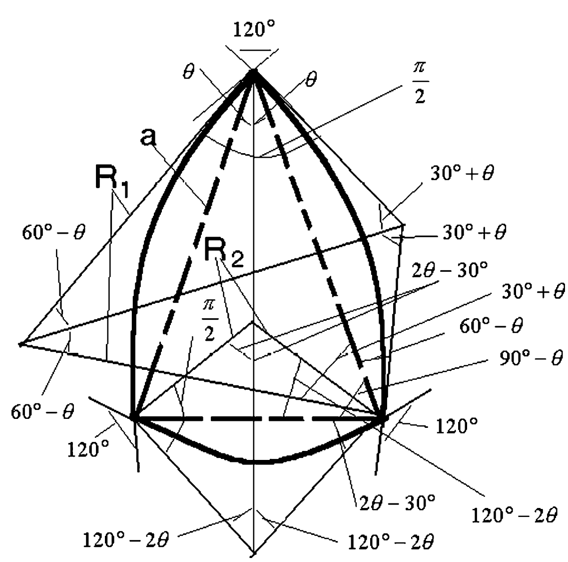

Fig. 4. A grain whose shape is a "convex isosceles triangle".

be found by considering the displacement of the perimeter Π of a grain, which is the VN–M approach:

$$\mathrm{d}S = -V\,\mathrm{d}t \cdot \Pi = -2\frac{m_\mathrm{b}\gamma_\mathrm{b}}{R_1} \cdot \frac{2\pi R_1}{2\pi}\left(\frac{\pi}{3} - 2\theta\right)\mathrm{d}t - \frac{m_\mathrm{b}\gamma_\mathrm{b}}{R_2} \cdot \frac{2\pi R_2}{2\pi}\left(4\theta - \frac{\pi}{6}\right) = -m_\mathrm{b}\gamma_\mathrm{b}\pi\,\mathrm{d}t \quad (\mathrm{A}.3)$$

This is the expected result.

From (A.2) and (A.3) we arrive at

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = -\frac{4m_\mathrm{b}\gamma_\mathrm{b}\pi}{a^2} \cdot \frac{1}{\{B_1(\theta)\}} \quad (\mathrm{A}.4)$$

A simple calculation shows that the value of $\mathrm{d}\theta/\mathrm{d}t$ in the vicinity of θ=30°.

$$\left[\frac{\mathrm{d}\theta}{\mathrm{d}t}\right]_{\theta=\pi/6} \approx \frac{1.78\pi m_\mathrm{b}\gamma_\mathrm{b}}{a^2} \quad (\mathrm{A}.5)$$

References

[1] von Neumann J. Metal interfaces. Cleveland: American Society for Testing Materials; 1952 p. 108.
[2] Mullins WW. J Appl Phys 1956;27:900.
[3] Lücke K, Heckelmann I, Abbruzzese G. Acta Metall Mater 1992;40:533.
[4] Anderson MP, Srolovitz DJ, Grest GS, Sahni P. Acta Metall 1984;32:783.
[5] Fradkov VE, Shvindlerman LS, Udler DG. Scripta Metall 1985;19:1285.
[6] Gusak AM, Tu KN. Acta Mater 2003;51:3895–904.