THERMAL SMOOTHING OF ROUGH SURFACES IN VACUO

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Derivation of equations governing the smoothing of rough surfaces, based on Mullins' (1957, 1960, 1963) theories of thermal grooving and of capillarity-governed solid surface morphology. As an example, the smoothing of a one-dimensional sine-shaped surface is discussed.

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Rough metal surfaces are not stable at high temperatures: their structure alters over time. Lengthy baking generally results in a smoothing of the original roughness. The fact that grooving at grain boundaries may occasionally result in new irregularities is not discussed here (we refer to the bibliography [1]). The mechanism of surface alteration is presently understood by the concepts of W. W. Mullins [1-3]. In this paper, the equations for the smoothing are derived and the most important constants are given.

1. The Behavior of Surfaces in Thermodynamic Equilibrium

Before describing the time behavior of unstable surfaces, we shall briefly go into the thermodynamics of a surface. The most important thermodynamic quantity is the surface tension [4]:

$$\gamma = \frac{\partial F}{\partial A}$$  \hspace{1cm} (1)

Here, $\partial F$ indicates the work that must be done to increase the area $A$ by $\partial A$ at constant pressure, constant temperature and constant volume.

*Numbers in the margin indicate pagination in the original text.*
The surface tension of solids is between 1000 and 3000 erg cm\(^{-2}\), i.e., greater than that of liquids by a factor of 10. It is only poorly understood that this is very sensitive to impurities and also depends on the temperature and the orientation. Figure 1 shows the orientation function of tungsten for the [011]-zone [5]. This is very slight, and shall therefore be disregarded hereafter.

![Diagram of surface tension of W for the [011]-zone](image)

Fig. 1. Surface tension of W for the [011]-zone [5]: \( \gamma_{110} \) - surface tension in the direction 110, used as the abscissa (other directions 100, 111, 112 and 332 are shown as radii); \( \gamma \) - surface tension in any given direction. Key: a - adjusted surface tension \( \gamma/\gamma_{110} \).

The equilibrium form of a solid at constant volume is given by the condition [1]:

\[
\delta \gamma \, dA = 0
\]  

(2)

If equation (2) does not apply, the surface is not in equilibrium: it changes over time.
2. Characteristic Roughness Functions

There are several possibilities of mathematical description of roughness:

1. The roughness function \( z = f(x,y) \) gives the position of the surface (in terms of the height \( z \) above the reference plane) at any given point of the surface (with coordinates \( x \) and \( y \)), relative to a fixed reference plane. This function is very suitable for a graphic description.

2. The roughness can also be characterized by the vapor pressure, which depends on the surface curvature. We have [1]:

\[
RT \ln \left( \frac{p}{p_0} \right) = \gamma V_M K
\]  

(3)

with \( R \) as the general gas constant, \( T \) as the Kelvin temperature, \( V_M \) as the molar volume of metal, or the volume specific to the quantity of matter, \( p_0 \) as the vapor pressure of the regular surface and \( p \) as the vapor pressure above the curved surface. The factor \( K \) gives the average curvature multiplied by \(-2\) [6], which for slight inclinations can be expressed by the Laplace operator, applied to the roughness function \( f \):

\[
K = -\Delta f
\]  

(4)

Thus, equation (3) is simplified:

\[
RT \ln \left( \frac{p}{p_0} \right) = -\gamma V_M \Delta f
\]  

(5)

3. Instead of the curvature-dependent vapor pressure, we can use the chemical potential \( \mu \) corresponding to the particular vapor pressure:

\[
\mu = \mu_0 + RT \ln \left( \frac{p}{p_0} \right)
\]  

(6)
where $\mu_0$ is the chemical potential of the equilibrium vapor pressure $p_0$ above a regular surface. Between $\mu$ as per equation (6) and $\Delta f$, according to equations (3) and (4), the relation obtains:

$$\mu = \mu_0 - \gamma V_M \Delta f$$  \hspace{1cm} (7)

3. The Smoothing Equations

Three mechanisms are responsible for alteration of surface structures: 1) the mechanism of evaporation, 2) volume diffusion, 3) surface diffusion. In order to derive the smoothing equation for the evaporation mechanism, we proceed from equation (3) and calculate the curvature-dependent evaporation current density $i$:

$$i = \frac{1}{\sqrt{2\pi MRT}} \frac{p_0}{V_M} R \kappa RT$$  \hspace{1cm} (8)

where $M$ is the molar mass (assuming an evaporation coefficient $\alpha = 1$). The evaporation current density $i$ produces an eventual change in the roughness function $f$:

$$i = -\frac{1}{V_M} \frac{\partial f}{\partial t}$$  \hspace{1cm} (9)

where $t$ is the time.

For slight curvatures, $K$ can be expressed by equation (4) and equation (8) can be developed to the second term, which gives:

$$-\frac{1}{V_M} \frac{\partial f}{\partial t} = \frac{p_0}{\sqrt{2\pi MRT}} \left(1 - \frac{V_M \gamma}{RT} \Delta f\right)$$  \hspace{1cm} (10)

The first term on the right of (10) is equal to the evaporation current density over a regular surface and produces only a parallel displacement of the surface, but no smoothing. The smoothing proper is achieved only by the second term. If we ignore the parallel displacement, which has no significance to the smoothing,
we may describe the smoothing by the equation:

$$\frac{\partial f}{\partial t} = \frac{p_0}{\sqrt{2\pi MR}} \frac{V_M^2 \gamma}{RT} \Delta f$$

(11)

which was first derived by W. W. Mullins [2].

For a one-dimensional, sinusoidal roughness, described by:

$$z = z_0 \sin(kx)$$

(12)

where $z_0$ is the amplitude of $z$ and $k$ is a reciprocal length, the time function of the smoothness is given by:

$$z = z_0 e^{-\beta_{\text{verd}} t \sin(kx)}$$

(13)

with the evaporation parameter:

$$\beta_{\text{verd}} = \frac{p_0}{\sqrt{2\pi MR}} \frac{V_M^2 \gamma}{RT} k^2$$

(14)

The smoothness equations for the volume diffusion mechanism have also been derived by W. W. Mullins [1,3]. He proceeded on the assumption that the concentration of voids $C_L$ at the metal surface is dependent on the curvature and given by:

$$C_L = C_0 - C_0 V_M \frac{\gamma}{RT} K$$

(15)

$C_L$ can be either larger or smaller than the concentration of voids $C_0$ on a regular surface. This produces a diffusion stream of voids between the surface and the interior and a corresponding mass transport, resulting in smoothing. For a one-dimensional roughness,

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1For a further derivation of the integrodifferential equation describing the smoothing, cf. the bibliography [1,3].
given by equation (12), the time function can be calculated by:

\[ z = z_0 e^{-q_{vol} \sin(kx)} \]  

(16)

with the volume diffusion parameter:

\[ \beta_{vol} = \frac{D_{vol} \gamma V_M}{RT} k^2 \]  

(17)

in which \( D_{vol} \) is the self-diffusion coefficient for volume diffusion.

To derive the smoothness equations by the surface diffusion mechanism, following Mullins [1] we start with equations (6) and (7) and write the surface diffusion flow \( i_s \) by the Nernst-Einstein equation:

\[ i_s = -\frac{n_{s} D_{s}}{RT} \text{grad } \mu \]  

(18)

In (18), \( n_s \) is the surface concentration of diffusing particles and \( D_s \) is an empirical diffusion constant. Equation (18) can also be used for volume diffusion in a three-dimensional expansion [7].

Both empirical quantities \( n_s \) and \( D_s \) are combined by writing:

\[ i_s = -\frac{N_0 D_s}{RT} \text{grad } \mu \]  

(19)

with \( D_s = (n_s/N_0)D_d \). The quantity \( D_s \) is known as the surface diffusion constant; \( N_0 \) is the concentration of lattice particles at the surface. This concentration can be estimated from \( V_M \) and the Loschmidt number \( N_L \):

\[ N_0 = \frac{1}{\sqrt{N_L V_M}} \]  

(20)

Using the continuity equation:
and taking account of equations (19) and (7), we obtain the smoothing equation:

\[ \frac{1}{V_i} \frac{\partial f}{\partial t} + \text{div} \mathbf{u} = 0 \]  

(21)

and taking account of equations (19) and (7), we obtain the smoothing equation:

\[ \frac{\partial f}{\partial t} + V_i^2 \gamma \frac{N_0 D_s}{RT} \Delta \Delta f = 0 \]  

(22)

The symbol \( \Delta \Delta \) designates the double Laplace operator.

For a one-dimensional sinusoidal roughness, the eventual subsidence, according to equation (22) can be described by:

\[ z = z_0 e^{-\beta_{ob} t \sin(kx)} \]  

(23)

with \( \beta_{ob} \) as the surface diffusion parameter:

\[ \beta_{ob} = \frac{V_i^2 \gamma N_0 D_s}{RT} k^4 \]  

(24)

4. Comparison of the Smoothing Mechanisms

Figure 2 shows, using the example of smoothing of a one-dimensional sinusoidal roughness on a tungsten surface, the temperature/wavelength regions in which the individual mechanisms prevail. The lines bordering the regions are given by:

\[ \beta_{\text{real}}/\beta_{\text{vol}} = 1 \]  

(25a)

and

\[ \beta_{\text{vol}}/\beta_{ob} = 1 \]  

(25b)

The constants \( D_{\text{vol}} \) and \( D_s \) required for the calculation (Fig. 3,4), as well as the vapor pressures, have been taken from [8]. Figure 2 reveals that, for low temperatures and small wavelength of roughness, the surface diffusion mechanism prevails.
Fig. 2. Regions in which surface diffusion, volume diffusion and evaporation are the prevailing smoothing mechanisms on a tungsten surface: A-C, region of surface diffusion, volume diffusion and evaporation; a and b, boundary curves as per equations (25a) and (25b); $\lambda$, wavelength of the roughness, $T$, Kelvin temperature; $T_s$, melting point. Key: 1 - adjusted reciprocal temperature.

Fig. 3. Surface diffusion constants $D_s$ for cubic body centered metals: $T_s$, Kelvin temperature; $T_s$, melting point; $a$, curve of equation (26); other values of $D_s$ taken from a table in [9] and from [10]; specifically: b for W after B. C. Allen (1966), c for Mo after B. C. Allen (1969), d for Mo with 0.003% C after B. C. Allen (1966), e for W after J. P. Barbour (1960), f for Mo after R. W. Strayer (1965), g for W after P. Bettler (1965). Key: 1 - adjusted reciprocal temperature.
Fig. 4. Volume diffusion constants $D_{\text{Vol}}$ for cubic body centered metals: $T$ and $T_S$ as in Fig. 3; the values for $D_{\text{Vol}}$ for the metals indicated on the curves taken from [11] (a is the curve of equation (27)). The numbers on the lines for Li, Mo and Nb designate the $\frac{1}{T/T_S}$ regions for which measurements are available for these lines according to [11]. For better clarity, these lines are not fully shown. Since the trend of the lines for Li and Na is very similar, only the Li line is shown and Na is indicated in parentheses at the Li line. Key: 1 - adjusted reciprocal temperature; 2 - $1.1.35$.

Fig. 5. Surface diffusion constants $D_S$ for cubic face centered metals: $T$ and $T_S$ as in Fig. 3; a, curve of equation (28); the values for $D_S$ taken from a table in [9], specifically: b for Cu after N. A. Gjostein (1961), c for Ag after G. Rhead (1965), d for Cu after F. J. Bradshaw (1964), e for Ni (two measurement series) after P. S. Maija (1967). Key: 1 - adjusted reciprocal temperature.
5. Empirical Relations for Surface and Volume Diffusion

A simple empirical rule obtains for both surface and volume diffusion, which can be used to determine the diffusion coefficients of many metals. In Fig. 3 through 6, the measured values of the surface diffusion coefficients and the volume diffusion coefficients are plotted against the reciprocal temperature $T$, adjusted to the melting point $T_S$. It can be seen that the diffusion constants may be approximately calculated by the simple empirical relations. For cubic body centered metals we have:

$$\frac{D_s}{\text{cm}^2 \text{s}^{-1}} = 3.5 \times 10^{-11} \frac{T}{e}$$  \hspace{1cm} (26)

$$\frac{D_{\text{vol}}}{\text{cm}^2 \text{s}^{-1}} = 1.0 \times 10^{-17} \frac{T}{e}$$  \hspace{1cm} (27)

and for cubic face centered metals:

$$\frac{D_s}{\text{cm}^2 \text{s}^{-1}} = 20 \times 10^{-12} \frac{T}{e}$$  \hspace{1cm} (28)
\[
\frac{D_{\text{vol}}}{\text{cm}^3\text{s}^{-1}} = 0.45 e^{-18 \frac{T}{T}}
\]

(29)

It was N. A. Gjostein [9] who first selected such representation of the surface diffusion constants.

Bibliography


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