Morphological instability at the solid-liquid interface by the maximum entropy production rate principle

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Morphological instability at the solid-liquid interface by the maximum entropy production rate principle

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Abstract

We examine the morphological instability from planar to non-planar cellular morphology with the maximum entropy production rate (MEPR) principle. An expression that quantifies the maximum entropy production rate density at the solid-liquid interface (SLI) during direction solidification is presented which lead to an instability criterion for dilute binary alloys. The instability criterion also affords to theoretically calculate the instability solidification growth velocity. The model considers steady state solidification at close-to and far-from equilibrium conditions.

Keywords: Maximum entropy production rate (MEPR) principle, planar morphology, cellular morphology, morphological transition, solid-liquid interface

1. Introduction

When an alloy melt is directionally solidified, a planar morphology is first noted at the solid-liquid interface (SLI), usually at a very low velocity of transformation. As the velocity is increased (e.g. either by increasing the cooling rate or the solidification growth rate), the planar interface becomes unstable to other shapes and transforms to a macroscopically jagged/wavy cellular shaped morphology with several variations in topography [1]. When a planar to non-planar topographical transition occurs during solidification it is expected to be a consequence of a thermodynamic driving force and the new shape formed provides stability compared to other shapes [2]. This morphological instability was first studied for a sharp interface condition by Tiller,
Rutter, Jackson, and Chalmers [3] under the constitutional undercooling theory (CUT) and later by Mullins and Sekerka [4] under the linear stability theory (LST). A sharp interface is when there is no density change at the interface between the fully liquid and the fully solid, i.e., the free energy change with respect to density is zero. At instability, the CUT and LST are described by equations (1) and (2) respectively.

\[
\left( \frac{V}{G_L} \right)_C = \frac{D_L}{\Delta T_O}
\]

\[
\left( \frac{V}{G_L} \right)_C = \frac{D_L}{\Delta T_O} \frac{2K_L}{(K_S+K_L)S}
\]

where \( V \) (ms\(^{-1}\)) is the solidification growth velocity, \( G_L \) (K m\(^{-1}\)) is the temperature gradient in the liquid, \( D_L \) (m\(^2\)s\(^{-1}\)) is the solute diffusion coefficient in the liquid and \( \Delta T_O \) (K) is the equilibrium solidification range \((T_l - T_S)\) for a liquid at composition \( C_O \) (mole m\(^{-3}\)). Also, \( T_l \) (K) and \( T_S \) (K) are the equilibrium liquidus and solidus temperatures that are measured from the phase diagram. Also, S (no units) is Mullins and Sekerka stability constant [4] which is approximately equal to one for low velocities and, \( K_L \) and \( K_S \) (J m\(^{-1}\)K\(^{-1}\)s\(^{-1}\)) are the thermal conductivities for the rigorous solid and liquid respectively. The subscript \((C)\) refers to the critical condition for instability.

The CUT and LST models converge for the limit where \( K_L \) approaches \( K_S \).

On the hand, the same problem has been studied for a diffuse interface condition by Cahn [5, 6] using a near equilibrium thermodynamic approach and by Sekhar [2] using the maximum entropy production rate (MEPR) principle. A diffuse interface (DI) is considered when there is a defined gap between the fully liquid and the fully formed solid. It considers a free energy change with respect to density to be greater than zero. Generally, the MEPR is an extremum thermodynamic principle which was first proposed by Ziman [7] and later by echoed by Jaynes [8] with its rigorous theoretical
foundation laid by Ziegler [9, 10]. The principle has also seen major theoretical
exposition and expansion by Dewar [11], and by Martyushev and Seleznev [12].
Generally, modelling of complex systems and formulation of dynamical equations in
sufficient detail are difficult and often could be problematic [13] but with MEPR it has
been of considerable utility [14, 15, 16, 17]. The role of MEPR is to take the place of
the dynamics in such formulations [13] with applications to linear and nonlinear
thermodynamics [9, 10]. According to MEPR, a non-equilibrium system subject to
perturbations of sufficiently large amplitude selects a state characterized by maximum
entropy production rate [12, 2]. The MEPR principle has been further considered for
self-organizing behavior in chemical reactions [18], Belousov–Zhabotinsky type
reactions [2, 19], complex biochemical reactions [20, 21] and climatology [22].
In the field of solidification and crystal growth, MEPR has been used to study the
morphological instability and curvature in non-equilibrium systems [23, 2, 24, 25]. In
his seminal paper, Sekhar [2] showed that the MEPR principle considers that entropy
generation occurs in all irreversible processes and become maximized as a way of
determining its pathway. He used well known concepts to find a connection between
entropy and key material properties relevant to directional solidification of the
Bridgman type. He showed that for a control volume i.e. the solid-liquid interface (SLI)
in diffuse form, the entropy generation rate density \( \dot{S}_E \) (J m\(^{-3}\)K\(^{-1}\)) which describes the
new entropy generated due to exchange of matter at the SLI is given as:

\[
\dot{S}_E = \frac{V}{A_{SLI}} \frac{\Delta h_{sl} (\Delta T_{SLI})}{T_{si} T_{li}} \quad (3a)
\]

where \( \Delta h_{sl} \) (J m\(^{-3}\)) is the heat of fusion, \( T_{li} \) (K) and \( T_{si} \) (K) are liquidus and solidus
temperatures at the SLI boundaries respectively, \( G_{SLI} \) (Km\(^{-1}\)) is the linear temperature
gradient across the SLI and \( \Delta T_{SLI} \) (K) is the difference between \( T_{li} \) and \( T_{si} \). Sekhar
showed that the heat of fusion of the solid with defects, \( \Delta h_m \) (J m\(^{-3}\)) and the heat of
fusion, \( \Delta h_{sl} \) are related by, \( \Delta h_{sl} = \Delta h_m + \omega_D \), where \( \omega_D \) (J m\(^{-3}\)) is the energy of defects
(such as grain boundaries or dislocations) per unit volume. He assumed that \( \omega_D \) is
relatively small term compared to $\Delta h_m$ and therefore could be simplified as, $\Delta h_{sl} = \Delta h_m$. Also, $T_{li}$ and $T_{si}$ are not readily known but for dilute binary materials they can be approximated to be equal to the melting temperature, $T_M$ (K). From this, then equation (3a) can be simplified as:

$$\hat{S}_E = \frac{V \Delta h_{sl} g_{SLI}}{T_M^2}$$  (3b)

Sekhar further showed that within the liquid melt the entropy rate density which describes the force-flux entropy generated by the existence and maintenance of solute gradient is [2]:

$$\hat{S}_{LG} = \frac{\Delta T_O}{D_L} \frac{V^2 R g \ln(1/k)}{4 m_L}$$  (4)

where $R$ (J mole$^{-1}$ K$^{-1}$) is the molar gas constant, $k$ (no units) is the partition coefficient that can be obtained from the binary phase diagram and $m_L$ (Km$^3$ mole$^{-1}$) is the slope of the liquidus line at the solid-liquid boundary for a binary material. It should be noted that equation (4) is slightly modified and simplified from the original terse derivation by Sekhar. An expanded derivation of equation (4) is given in the appendix.

In spite of the advances made by Sekhar, he inaccurately assumed equation (3) to be equivalent to the maximum entropy generation rate density for binary alloys, which lead to morphological instability criterion, as given in equation (5). Using equation (5) as basis, he linked equations (3) and (4) to obtain an approximated instability solidification growth velocity as given in equation (6).

$$V \delta_C \cong 2 D_L$$  (5)

$$\left( \frac{V}{g_{SLI}} \right)_C = 4 \left[ \frac{\Delta S_{sl}}{R} \right] \left[ \frac{1}{(1-k)} \right] \frac{D_L}{\Delta T_O}$$  (6)

where $\delta_C$ (m) is the solute boundary layer, $R$ (Jm$^{-3}$K$^{-1}$) is the volumetric gas constant, $\Delta S_{sl}$ (Jm$^{-3}$K$^{-1}$) is the entropy change during solidification per unit volume.
Despite the advances made by Sekhar, it is worth noting that, equation (5) which is the instability criterion has a weak dependence on MEPR. Furthermore, the consideration of equation (3b) as a measure of MEPR is not entirely correct for the case of binary alloys. In this article, we take a step further beyond Sekhar’s MEPR theory and develop an expression for the maximum entropy generation rate density ($\dot{\phi}_{max}$) as a measure of MEPR at the SLI in the case of directional solidification for binary alloys. Through an entropy balance approach we establish a connection between the maximum entropy generation rate density and the other forms of entropy developed by Sekhar in equations (3) and (4). From the entropy balance expression we arrive at an instability criterion and a new expression for calculating solidification growth velocity at the critical condition for binary metal and non-metal alloys. The results are compared with that of CUT and LST.

2. Method

2.1. Model and entropy generation at the solid-liquid interface

Consider the changeover region between a solidifying liquid to solid in directional solidification (DS) system that has a finite dimension over which a temperature gradient and other gradients are established. This changeover zone is called a solid-liquid interface (SLI) region with a thickness $\zeta$ (m). The SLI is considered diffuse (or a diffuse interface) since it contains a mixed of rigorous liquid and solid (crystals). The entropy rate balance for the control volume is given by [2]:

$$\frac{dscv}{dt} = \dot{s}_{in} - \dot{s}_{out} + \dot{s}_{gen}$$

(7)

where $\frac{dscv}{dt}$ (Jm$^{-3}$K$^{-1}$s$^{-1}$) is the total steady state entropy rate change in the control volume, $\dot{s}_{in}$ (Jm$^{-3}$K$^{-1}$s$^{-1}$) and $\dot{s}_{out}$ (Jm$^{-3}$K$^{-1}$s$^{-1}$) are the rate of entropy entering and
leaving the control volume respectively, and \( \dot{s}_{\text{gen}} \) \( (\text{J m}^{-3}\text{K}^{-1}\text{s}^{-1}) \) is the irreversible entropy generation rate in the SLI region. The rates of entropy entering \((\dot{s}_{\text{in}})\) and leaving \((\dot{s}_{\text{out}})\) the control volume is respectively given by:

\[
\dot{s}_{\text{in}} = \frac{V}{\zeta} \left( \frac{\Delta h_{\text{li}}}{T_{\text{li}}} + s_{\text{LG}} + s_{\text{SG}} \right) \tag{8}
\]

\[
\dot{s}_{\text{out}} = \frac{V}{\zeta} \left( \frac{\Delta h_{\text{si}}}{T_{\text{si}}} + s_{\text{SG}} \right) \tag{9}
\]

where the subscripts \((\text{LG})\) and \((\text{SG})\) refer to solute gradients in the liquid and solid respectively, \( s_{\text{LG}} \) \( (\text{J m}^{-3}\text{K}^{-1}) \) is the entropy generation density due to solute gradient in the liquid, \( s_{\text{SG}} \) \( (\text{J m}^{-3}\text{K}^{-1}) \) is the entropy generation density due to solute gradient in the solid. By combining equations (8) and (9) into equation (7) yields the control volume expression at steady state as:

\[
\frac{dS_{\text{cv}}}{dt} = \dot{s}_{\text{E}} + \dot{s}_{\text{LG}} + \dot{s}_{\text{gen}} \tag{10}
\]

where \( \dot{s}_{\text{LG}} \) \( (\text{J m}^{-3}\text{K}^{-1}) \) is the entropy generation rate density by the solute gradient in the liquid. Applying the steady state condition \( \left( \frac{dS_{\text{cv}}}{dt} = 0 \right) \) to equation (10), then the total entropy generation rate density at the interface (i.e., the SLI region) becomes:

\[
\dot{s}_{\text{gen}} = \dot{s}_{\text{E}} - \dot{s}_{\text{LG}} \tag{11a}
\]

If we consider that the morphological transition from a plane front to a cellular shape occurs when \( \dot{s}_{\text{gen}} \) reaches a maximum then, \( \dot{s}_{\text{gen}} \approx \dot{\varphi}_{\text{max}} \), and equation (11a) becomes:

\[
\dot{\varphi}_{\text{max}} = \dot{s}_{\text{E}} - \dot{s}_{\text{LG}} \tag{11b}
\]

The key hypothesis in this article is that, MEPR is operative with maximum entropy generation rate density, \( \dot{\varphi}_{\text{max}} \) \( (\text{J m}^{-3}\text{K}^{-1}\text{s}^{-1}) \) within the SLI, which has the capability of
predicting the most stable morphology. In the section below we derive an expression for the maximum entropy generation rate density \( \dot{\varphi}_{\text{max}} \).

### 2.2. Entropy generation and the conversion of kinetic energy

By the definition of the SLI established, we consider the motion of the SLI during directional solidification as a single unit of mass and not as individual mass of atomic particles or crystalline particles with velocity equal to the solidification growth velocity. The overall transformation from liquid to solid includes a density change given by:

\[
|\Delta \rho_k| = \left| \frac{\rho_l \Delta \rho}{\rho_s} \right| \tag{12}
\]

where \( |\Delta \rho_k| \) (kg m\(^{-3}\)) is the overall density shrinkage, \( \Delta \rho \) (kg m\(^{-3}\)) is the density change from liquid to solid (\( \rho_s - \rho_l \)); \( \rho_s \) (kg m\(^{-3}\)) and \( \rho_l \) (kg m\(^{-3}\)) are the densities of rigorous solid and liquid respectively. For the rest of this derivation the modulus sign for the density shrinkage is omitted. The volume shrinkage \( \Delta \Omega_s \) (m\(^3\)) associated with the liquid to solid transformation is given as:

\[
\Delta \Omega_s = A_{\text{SLI}} \zeta \Delta \rho_k \tag{13}
\]

where \( A_{\text{SLI}} \) (m\(^2\)) is the area of the SLI. The associated change in kinetic energy of the moving liquid transforming into the solid is expressed as:

\[
\Delta KE = \frac{1}{2} \rho_l \Delta \Omega_s V^2 \tag{14}
\]

Placing equations (12) and (13) into equation (14) gives the overall gain or loss in kinetic energy \( \Delta KE \) (J) of the transforming liquid entering into the SLI as:

\[
\Delta KE = \frac{A_{\text{SLI}} \zeta \Delta \rho_k V^2}{2} \tag{15}
\]
The moving interface dissipates free energy equal to the lost work, $W_L (J)$ as given in equation (16) [9]. We consider that, the lost work is equivalent to the loss in kinetic energy given in equation (17), which is obtained by combining equations (15) and (16).

$$W_L = T_{av}(S_{gen})_{max}$$ (16)

$$(S_{gen})_{max} = \frac{A_{SLI} \xi \Delta \rho_k v^2}{2T_{av}}$$ (17)

where $(S_{gen})_{max} (J K^{-1})$ is the maximum entropy generation due to the lost work and $T_{av} (K)$ is the average temperature between $T_{li}$ and $T_{si}$ across the SLI.

Following the work term introduced in equation (16), the main assumption in this article is that the loss in kinetic energy is converted to heat which is further converted to some work subject now to the limitation of the second law of thermodynamics. The heat generation $Q (J)$ from the conversion of the loss in kinetic energy is given as:

$$Q = A_{SLI} \xi C_p \Delta T_{SLI}$$ (18)

where $C_p (J m^{-3}K^{-1})$ is the average heat capacity across the SLI. Equation (18) is the equivalence of the lost work potential from the heat generation. With equation (16), the equivalent entropy generation through heat dissipation, $(S_{gen})_{HD} (J K^{-1})$ may be approximated as:

$$(S_{gen})_{HD} = A_{SLI} \xi C_p \frac{\Delta T_{SLI}}{T_{av}}$$ (19)

where the subscript $(HD)$ indicates the heat dissipation. The temperature gradient at the SLI ($G_{SLI}$) maybe approximated as:

$$G_{SLI} = \frac{(G_S + G_L)}{2}$$ (20)
where \( G_S \) (K m\(^{-1}\)) is the temperature gradients in the solid. The maximum entropy generation due to the lost work is equal to the equivalent entropy generation through heat dissipation.

It is also assumed that the thermal gradient (similar to assumptions made in the Linear Stability model [4]) across the solid-liquid interface is linear and expressed as:

\[
\Delta T_{SLI} = T_i - T_{sl} = \zeta G_{SLI}
\] (21)

Combining equations (17) and (19) and substituting in equations (21) and (20) gives the heat capacity:

\[
C_p = \frac{\Delta \rho_k V^2}{2 \zeta G_{SLI}}
\] (22)

The maximum entropy generation rate density (MEPR), \( \phi_{max} \) (J m\(^{-3}\)K\(^{-1}\)s\(^{-1}\)) (equation 24), is now obtained by multiplying equation (22) by the change in the fraction of the liquid solidified per second (equation 23).

\[
\frac{df_s}{dt} = \frac{V}{\zeta}
\] (23)

\[
(C_p \frac{df_s}{dt})_{max} = \frac{d\phi_{max}}{dt} = \phi_{max}
\] (24a)

\[
\phi_{max} = \frac{\Delta \rho_k V^3}{2 \zeta^2 G_{SLI}}
\] (24b)

where \( f_s \) (dimensionless) is the fraction solidified and \( t \) (s) is time. Thus \( \phi_{max} \) becomes a function of \( \zeta, V \) and \( G_{SLI} \). When partitioning is feasible, the maximum entropy generated rate density can be expressed by combining with equations (3b), (4) and (24b) into equation (11b) as:

\[
\phi_{max} = \frac{V \Delta h_{SLI} G_{SLI}}{T_l \cdot T_{sl}} \left( \frac{\Delta T_D}{D_L} \right) \frac{V^2 R_g \ln(1/k)}{4 m_L}
\] (25)
The maximization of the entropy generation rate equation (25) is the pathway for the selection that the interface will prefer.

2.3. Morphological instability for a non-planar interface

We hypothesized that the onset of instability occurs only at the peak of the parabolic expression in equation (25) when \( \phi_{\text{max}} \) is graphed against the velocity. That is, the MEPR instability criterion is mathematically expressed as:

\[
\left( \frac{\partial \phi_{\text{max}}}{\partial V} \right)_{\zeta, C_O} = 0
\] (26)

Equation (26) is valid at the peak of \( \phi_{\text{max}} \) against velocity. By taking the partial derivative of the maximum entropy generation rate density with respect to the velocity while holding \( \zeta \) and \( C_O \) constant gives:

\[
\left( \frac{\partial \phi_{\text{max}}}{\partial V} \right)_{\zeta, C_O} = \frac{\Delta h_{\text{SI}} G_{\text{SLI}}}{T_{\text{ii}} \cdot T_{\text{si}}} - \frac{\Delta T_O V R_g \ln(1/k)}{D_L} \frac{2}{m_L}
\] (27)

Note that, \( \left( \frac{\partial^2 \phi_{\text{max}}}{\partial V^2} \right)_{\zeta, C_O} \), is negative for a maximization condition. From equations (26) and (27), the ratio of velocity to that of the temperature gradient is given by:

\[
\left( \frac{V}{G_{\text{SLI}}} \right)_C = \frac{D_L}{\Delta T_O T_{\text{ii}}^2 R_g \ln(1/k)} \frac{2 m_L \Delta h_{\text{SI}}}{m_L}
\] (28)

The expression given in equation (28) enables the prediction of the \( V/G_{\text{SLI}} \) ratio when the partition coefficient measured from the phase diagram is used.
3. Results and Discussions

We have derived an expression to quantify the MEPR for a binary alloy system, which is the maximum entropy generation rate density \( \dot{\phi}_{\text{max}} \), as given in equation (24). If the solidification growth velocity and the interface thickness are known, then it means \( \dot{\phi}_{\text{max}} \) will contain all information needed to select a pathway that leads to a maximization of entropy generated and as such will lead to a morphological instability.

The value for \( \dot{\phi}_{\text{max}} \) cannot be less than zero since it is subject to the limitations of the second law of thermodynamics as shown in equation (16). This implies that regardless of the sign of \( G_{\text{SLI}} \), the critical \( \dot{\phi}_{\text{max}} \) can only have minimum value of zero even for a planar interface and at a zero solidification growth velocity. Thus a non-planar shape can always overtake a plane front morphology for a negative temperature gradient or in other words \( G_{\text{SLI}} < 0 \) will always imply a breakdown into cells or other patterns. Additionally, because cellular shapes are seemingly restricted by the bounds of entropy, any other shape which offers an additional configurational entropy production rate increase because of complex features (e.g. dendrites) which will always emerge unless a wide diffuse interface are formed.

When solute partitioning is possible, the entropy rate generation rate density term indicates a maximum, when plotted as a function of velocity (equation 25). As long as no other interface configuration is feasible (ones that display a higher entropy rate generation e.g. a jagged interface), the interface will remain planar during growth. The instability criterion given in equation (26) enables the prediction of the \( V/G_{\text{SLI}} \) ratio derived under equation (26). The \( V/G_{\text{SLI}} \) ratio calculated from the MEPR criterion is compared with experimental data for a number of binary alloy materials as shown in table-2. The computed \( V/G_{\text{SLI}} \) ratio from the current MEPR criterion generally shows a much better agreement and close match with the experimental data as compared to the CUT, LST and the Sekhar's MEPR criterion. It is important to note that the predictive capability of the CUT is much reliable than the LST at instability. The deviation of the current MEPR results from that of experiment is mainly due to the near equilibrium
assumption used in the derivation of equation (4) particularly, the use of the equilibrium partition coefficient as an approximation of the effectively partition coefficient for the case of a non-equilibrium system like a steady state directional solidification process. Also the much wider deviation of the Sekhar’s theory are mainly due to the over approximation of equation (6).

The model prediction in figure-1 shows the relationship between the calculated maximum entropy generation rate density and $V/G_{SLI}$, for different classes of binary materials which displays a typical symmetric parabolic profile. The maximum entropy generation rate density reaches a peak value and falls because the solute gradient in the liquid region begins to create new entropy compared to the amount being created by the exchange of matter across the SLI. In figure-2 shows the symmetric parabolic profile for Al-Cu at varying copper concentration. At very dilute copper concentration (Al-0.00001 wt% Cu) an indefinitely increasing entropy generation with a linear relationship to $V/G_{SLI}$ is observed. This implies that the Al-Cu alloy is approaching that of a pure material.

4. Summary and Conclusions

The key MEPR condition for SLI topographical change and breakdown is primarily as a result of the maximization entropy rate density at the SLI. It is thus related to the solidification growth velocity and the temperature gradient encountered in the solid-liquid zone, the composition and partition coefficient when a solute gradient in the liquid is established. The MEPR model postulates that that entropy generation is maximized when an interface transition occurs to a different configuration of a topographical variant. The model for binary materials is able to quantitatively predict the critical solidification growth velocity from plane front to cellular morphology. A comparison of the critical solidification growth velocity from the MEPR criterion with that of experimentally measured data for a number of binary materials shows a good match. Furthermore, a comparison of the results obtained show that the current MEPR
approach to studying instability of solid-liquid interface is reliable than the traditionally known CUT and LST approaches.

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Reference


List of symbols

A_{SLI} (m^2): area of the SLI

C_p (J m^{-2} K^{-1}): average heat capacity across the SLI

C_O (mol m^{-3}): solute concentration in the binary alloy material

V (ms^{-1}): solidification growth velocity

\Delta h_f (J m^{-3}): heat of fusion

T_{li} (K): liquidus temperature at the SLI boundary

T_{si} (K): solidus temperature at the SLI boundary

T_{av} (K): average temperature between \( T_{li} \) and \( T_{si} \) across the SLI

G_{SLI} (Km^{-1}): linear temperature gradient across the SLI

\Delta h_{in} (J m^{-3}): heat of fusion of the solid with defects

\omega (J m^{-3}): energy of defects

f_s (dimensionless) is the fraction solidified

t (s) is time

T_M (K): melting temperature

R_g (J mole^{-1} K^{-1}): molar gas constant

k (no units): partition coefficient

m_L (Km^{-3} mole^{-1}): slope of the liquidus line at the solid-liquid boundary for a binary material

D_L (m^2/s): diffusion coefficient of solute in a solvent

\Delta T_O (K): solidification temperature range

\delta_C (m): solute boundary layer

R (Jm^{-3}K^{-1}): volumetric gas constant

\Delta S_{sl} (J m^{-3} K^{-1}): entropy change during solidification per unit volume

\frac{dS_{sc}}{dt} (J m^{-3} K^{-1}s^{-1}): total steady state entropy rate change in the control volume

\dot{s}_{in} (J m^{-3} K^{-1}s^{-1}): rate of entropy entering the control volume

\dot{s}_{out} (J m^{-3} K^{-1}s^{-1}): rate of entropy leaving the control volume

\dot{s}_{gen} (J m^{-3} K^{-1}s^{-1}) is the irreversible entropy generation rate in the SLI region

s_{LG} (J m^{-3} K^{-1}): entropy generation density due to solute gradient in the liquid

s_{SG} (J m^{-3} K^{-1}): entropy generation density due to solute gradient in the solid

\dot{s}_{LG} (J m^{-3} K^{-1}): entropy generation rate density by the solute gradient in the liquid

\dot{s}_E (J m^{-3} K^{-1}): entropy generation rate density which describes the new entropy generated due to exchange of matter at the SLI

\phi_{max} (J m^{-3} K^{-1}s^{-1}): maximum entropy generation rate density which is a measure of MEPR at the SLI

\Delta \rho_s (kg m^{-3}): overall density shrinkage

\Delta \rho (kg m^{-3}): density change from liquid to solid

\rho_s (kg m^{-3}): density of the rigorous solid

\rho_l (kg m^{-3}): density of the rigorous liquid

\Delta \Omega_s (m^3): volume shrinkage associated with the liquid to solid transformation

W_L (J): lost work

(S_{gen})_{max} (J K^{-1}): maximum entropy generation due to the lost work
Q (J): lost work potential from heat generation

$(S_{\text{gen}})_{\text{HD}}$ (J K$^{-1}$): equivalent entropy generation through heat dissipation

$G_S$ (K m$^{-1}$): temperature gradient in the solid

$G_L$ (K m$^{-1}$): temperature gradient in the liquid
Table-1. Data and physical constant used. Experimental data is individually referenced in [1]. Note that $G_{SLI}$ was assumed to be equal to $G_L$ for equation (26).

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<tr>
<th>Binary material</th>
<th>$G_L$ (K/m)</th>
<th>$D_L$ ($\times 10^{-9}$ m$^2$/s) at $T_S$</th>
<th>$T_i$ (K)</th>
<th>$T_j$ (K)</th>
<th>$k$ (no units)</th>
<th>$\Delta h_{sl}$ (J/m$^3$)</th>
<th>$K_S$ (J/mKs)</th>
<th>$K_L$ (J/mKs)</th>
<th>$T_M$ (K)</th>
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<td>1.33</td>
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<td>247</td>
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<td>934.27</td>
<td>934.49</td>
<td>0.094</td>
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<td>247</td>
<td>94.05</td>
<td>933.60</td>
</tr>
<tr>
<td>Al-0.025 wt%Cu</td>
<td>920</td>
<td>7.452</td>
<td>932.93</td>
<td>933.54</td>
<td>0.41</td>
<td>9.25$\times 10^8$</td>
<td>247</td>
<td>94.05</td>
<td>933.60</td>
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<td>7.147</td>
<td>920.86</td>
<td>932.41</td>
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<td>9.25$\times 10^8$</td>
<td>247</td>
<td>94.05</td>
<td>933.60</td>
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<tr>
<td>Al-0.20 wt%Cu</td>
<td>2500</td>
<td>7.332</td>
<td>921.19</td>
<td>933.09</td>
<td>0.41</td>
<td>9.25$\times 10^8$</td>
<td>247</td>
<td>94.05</td>
<td>933.60</td>
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<tr>
<td>Al-0.083 wt%Zn</td>
<td>970</td>
<td>4.442</td>
<td>933.31</td>
<td>933.48</td>
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<td>933.60</td>
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<td>Al-0.096 wt%Zn</td>
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<td>4.439</td>
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<td>247</td>
<td>94.05</td>
<td>933.60</td>
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<td>Al-0.375 wt%Zn</td>
<td>1310</td>
<td>4.398</td>
<td>932.26</td>
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<td>9.25$\times 10^8$</td>
<td>247</td>
<td>94.05</td>
<td>933.60</td>
</tr>
<tr>
<td>Pb-0.01 wt%Sn</td>
<td>540</td>
<td>1.656</td>
<td>600.60</td>
<td>600.62</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
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<tr>
<td>Pb-0.03 wt%Sn</td>
<td>820</td>
<td>1.655</td>
<td>600.51</td>
<td>600.56</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
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<td>Pb-0.05 wt%Sn</td>
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<td>1.654</td>
<td>600.41</td>
<td>600.49</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
<tr>
<td>Pb-0.06 wt%Sn</td>
<td>1220</td>
<td>1.653</td>
<td>600.36</td>
<td>600.47</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
<tr>
<td>Pb-0.1 wt%Sn</td>
<td>1200</td>
<td>1.652</td>
<td>600.17</td>
<td>600.35</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
<tr>
<td>Pb-0.15 wt%Sn</td>
<td>1300</td>
<td>1.649</td>
<td>599.93</td>
<td>600.19</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
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<tr>
<td>SCN-0.7 wt%Sal</td>
<td>3800</td>
<td>0.685</td>
<td>328.57</td>
<td>330.76</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
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<tr>
<td>SCN-0.5 wt%Sal</td>
<td>10000</td>
<td>0.904</td>
<td>329.34</td>
<td>330.90</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
<tr>
<td>SCN-0.5 wt%Ace</td>
<td>2400</td>
<td>9.681</td>
<td>314.24</td>
<td>329.53</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
<tr>
<td>SCN-0.1 wt%Ace</td>
<td>6500</td>
<td>1.455</td>
<td>327.84</td>
<td>330.91</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
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<tr>
<td>SCN-0.165 wt%Ace</td>
<td>1700</td>
<td>3.039</td>
<td>330.68</td>
<td>325.63</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
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<td>600.65</td>
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<td>3800</td>
<td>1.102</td>
<td>327.64</td>
<td>330.89</td>
<td>0.18</td>
<td>2.48$\times 10^8$</td>
<td>33.6</td>
<td>15.4</td>
<td>600.65</td>
</tr>
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</table>
Table 2. A summary of results for $V/G_L$ at instability conditions for experimental breakdown compared with the current MEPR criterion and other instability theories. The deviation from experimental results is given for each theory.

<table>
<thead>
<tr>
<th>Binary material</th>
<th>$(V/G_L)_{EC}$ at breakdown ($\times 10^9 m^2/Ks$)</th>
<th>Percent deviation from expt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt</td>
<td>Current MEPR</td>
</tr>
<tr>
<td>Al-0.102 wt%Cr</td>
<td>24.596</td>
<td>9.269</td>
</tr>
<tr>
<td>Al-0.201 wt%Cr</td>
<td>11.565</td>
<td>4.717</td>
</tr>
<tr>
<td>Al-0.328 wt%Cr</td>
<td>7.541</td>
<td>2.901</td>
</tr>
<tr>
<td>Al-0.025 wt%Cu</td>
<td>23.913</td>
<td>7.839</td>
</tr>
<tr>
<td>Al-0.47 wt%Cu</td>
<td>12.069</td>
<td>0.399</td>
</tr>
<tr>
<td>Al-0.20 wt%Cu</td>
<td>4.8</td>
<td>0.963</td>
</tr>
<tr>
<td>Al-0.73 wt%Cu</td>
<td>1.1</td>
<td>0.250</td>
</tr>
<tr>
<td>Al-0.083 wt%Zn</td>
<td>37.835</td>
<td>25.862</td>
</tr>
<tr>
<td>Al-0.096 wt%Zn</td>
<td>24.868</td>
<td>22.349</td>
</tr>
<tr>
<td>Al-0.375 wt%Zn</td>
<td>6.526</td>
<td>5.654</td>
</tr>
<tr>
<td>Pb-0.01 wt%Sn</td>
<td>309.259</td>
<td>110.861</td>
</tr>
<tr>
<td>Pb-0.03 wt%Sn</td>
<td>89.634</td>
<td>36.951</td>
</tr>
<tr>
<td>Pb-0.05 wt%Sn</td>
<td>53.261</td>
<td>22.169</td>
</tr>
<tr>
<td>Pb-0.06 wt%Sn</td>
<td>61.475</td>
<td>18.474</td>
</tr>
<tr>
<td>Pb-0.1 wt%Sn</td>
<td>47.250</td>
<td>11.083</td>
</tr>
<tr>
<td>Pb-0.15 wt%Sn</td>
<td>25.615</td>
<td>7.387</td>
</tr>
<tr>
<td>SCN-0.7 wt%Sal</td>
<td>0.589</td>
<td>0.267</td>
</tr>
<tr>
<td>SCN-0.5 wt%Sal</td>
<td>1.087</td>
<td>0.494</td>
</tr>
<tr>
<td>SCN-0.5 wt%Ace</td>
<td>0.833</td>
<td>0.396</td>
</tr>
<tr>
<td>SCN-0.1 wt%Ace</td>
<td>0.600</td>
<td>0.297</td>
</tr>
<tr>
<td>SCN-0.165 wt%Ace</td>
<td>0.765</td>
<td>0.376</td>
</tr>
<tr>
<td>SCN-0.106 wt%Ace</td>
<td>0.429</td>
<td>0.212</td>
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</table>
Figure 1. A graph showing model prediction of calculated maximum entropy generation rate density $\dot{\Phi}_{\text{max}} \,(J/m^3Ks)$ against $(V/G_{SI})$ as per equation (25) for a number of binary materials. At the peak of the curve is the instability criterion described by equation (26).
Figure 2. A graph showing the model prediction of calculated \( \phi_{\text{max}} \) (\( J/m^3Ks \)) against the \( (V/G_{\text{SLI}}) \) as per equation (25) for Al-Cu at different solute concentrations. The \( \phi_{\text{max}} \) increases with decreasing solute concentration. At very low solute concentration the binary material behaves like a pure material and \( \phi_{\text{max}} \) increases indefinitely with \( V/G_{\text{SLI}} \) ratio as a result of the partition coefficient approaching one.
Appendix

Derivation of the entropy generation from the solute gradient in the liquid

For steady state conditions, the solute flux \( J_s \) (mole s\(^{-1}\)) in the liquid entering the interface for a given flux area \( A_f \) (m\(^2\)) is related to the Fick’s first law of diffusion [26] as:

\[
J_s = -A_f D_L \left( \frac{dC_{LG}}{dz} \right)
\]

(29)

where \( \left( \frac{dC_{LG}}{dz} \right) \) (mole m\(^{-1}\)) is the change in solute gradient in the liquid, \( dz \) (m) is the change in the position length of the solute, and \( dC_{LG} \) (mole m\(^{-3}\)) is the change in concentration at a distance, \( z \) from the interface. The solute gradient in the liquid can be replaced with \((-\Delta C_0/\delta c)\) [26] where \( \delta_c \) (m) is the diffusion boundary layer and the negative sign represents the depletion of solute along the distance, \( z \). Entropy is also generated when the solute in the liquid travels across the interface to form a solid through an established solute gradient. The driving force \( \Delta \mu_c \) (J mole\(^{-1}\)) associated with the solute gradient is given as:

\[
\Delta \mu_c = R_g T_m \ln(1/k)
\]

(30)

Although \( k \) is non-dimensional the numerical value depends on the concentration units chosen. However, for the entropy generation calculations this is multiplied by the composition difference. It is also recognized that when comparing interface configurations for stability the value of \( k \) for a diffuse interface based configuration will be different than that when the interface has a atomistically smooth topography. Multiplying equation (29) by equation (30) and diving by the melting temperature \( T_m \) (K) of the material gives the flux entropy rate \( S_f \) (J K\(^{-1}\)s\(^{-1}\)) as:

\[
S_f = A_f D_L R_g \left( \frac{\Delta C_0}{\delta_c} \right) \ln(1/k)
\]

(31)

The change in solute gradient in the liquid \( \Delta C_0 \) (mole m\(^{-3}\)), the flux volume \( \Omega_f \) (m\(^3\)) and the diffusion boundary layer \( \delta_C \) (m) are respectively given as:

\[
\Delta C_0 = \frac{\Delta \mu_o}{m_L}
\]

(32)
\[ \Omega_f = A_f \delta_c \]  

(33)

where \( m_L (\text{Km}^3 \text{ mole}^{-3}) \) is the slope of the equilibrium liquidus line at the solid-liquid boundary for a binary material obtained from the phase diagram. Now rearranging equations (30) and (5) into equation (31) and dividing by equation (33) gives the entropy rate density which describes the force-flux entropy generated by the existence (support) of maintaining the solute gradient as:

\[ \dot{S}_{LG} = \frac{\Delta T_L V^2 R_g \ln(1/k)}{4 m_L} \]  

(4)

For the entropy generation inside the boundaries of the solid liquid zone this gradient entropy reduces the total amount of the irreversible entropy generated as may be noted from equation (7).