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On equilibrium conditions at junctions of anisotropic interfaces

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The issue of mechanical equilibrium conditions at junctions of sharp anisotropic interfaces is addressed. The well known Herring conditions are valid for a given junction direction. It is shown that if a system of interface segments joint along a line is allowed to change line direction, some additional relations are applicable. They are derived using the Hoffman–Cahn formalism of capillarity vector. As an example proving significance of the additional relations, criteria for wetting of anisotropic boundaries are considered. If the direction of the triple line is fixed, the criteria are shown to be different from those known for isotropic interfaces.

1. Introduction

Triple junction equilibrium equations are of importance for various branches of interface science. Our interest in the subject stems from the experimental attempt to determine the relative grain boundary energy from the geometry of junctions [1]. The geometry is affected by the dependence of the boundary energy on the boundary orientation. This anisotropy is taken into account in the classical relations known as the Herring conditions for mechanical equilibrium of sharp interface junctions [2].

This paper puts emphasis on the overlooked fact that the junction equilibrium conditions are limited to the Herring conditions only if the direction of the junction line is fixed in space. In physically meaningful situations, this constraint cannot be justified and leads to awkward conclusions. As an example, we show that in the case of perfect wetting of boundaries, the Herring relations for the fixed junction direction lead to equations which are in contradiction with the energetic (Gibbs-Smith) principle. If the junction of interfaces is allowed to change orientation, the state of equilibrium is associated with additional requirements; we derive the necessary conditions at which such an unconstrained junction is stationary. Going back to the example of wetting, it is shown that the application of these new conditions in conjunction with the Herring relations leads to Gibbs-Smith principle. Finally, in concluding remarks, we consider a number of complex physical situations which potentially can be better understood if the presented more complete description of interactions at junctions of anisotropic interfaces is applied.

This communication points out the importance of global approach and indicates that analysis restricted to specific cases must be used with care. The example of wetting shows that the conclusions drawn from an analysis limited to two dimensional sections of junctions may differ from those reached when a larger three dimensional system is considered. Generally, clarification of the equilibrium conditions at boundary junctions is essential for understanding properties of polycrystalline aggregates with anisotropic interfaces since it strengthens the foundation on which more complete analyses (involving kinetic factors) are based.

2. Classical conditions

In the isotropic case, the mechanical equilibrium conditions for sharp interfaces coincident at a junction are known as Young's law [3]

$$\sum_k \gamma_k \boldsymbol{t}_k = \boldsymbol{0}, \tag{1}$$

where γ_k is the free energy density of the k-interface, and $\boldsymbol{t}_k$ is a unit vector perpendicular to the junction and tangent to the k-interface at the junction; the sense of $\boldsymbol{t}_k$ is chosen as in Fig. 1a.

For crystalline materials, the interface free energy may depend on the interface inclination with respect to the crystal lattice. The Herring relationship, which is applicable in this case, can be best expressed by the use of the so-called capillarity vector [4]. Let $\boldsymbol{s}$ be the 'area vector' with magnitude $|\boldsymbol{s}|$ equal to the interface area and direction normal to the interface. The capillarity vector $\boldsymbol{\xi}$ of the interface with the free energy density $\gamma = \gamma(\boldsymbol{s})$ can be seen as the 'generalized force' for the configuration determined by the parameters $\boldsymbol{s}$

$$d(\gamma|\boldsymbol{s}|) = \boldsymbol{\xi} \cdot d\boldsymbol{s}.$$

If the interface energy depends only on the unit vector $\boldsymbol{n}$ normal to the interface (i.e., if $\gamma(\alpha \boldsymbol{s}) = \gamma(\boldsymbol{s})$ for $\alpha \neq 0$),

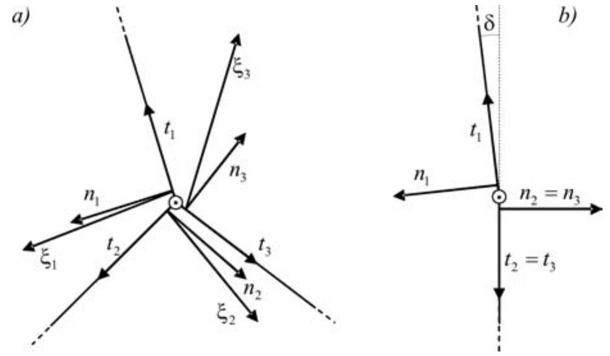

Figure 1 Schematic illustration of: (a) vectors involved in the analysis of a general triple junction, (b) geometry of wetting.

one can derive the relationship $\gamma = \boldsymbol{\xi} \cdot \boldsymbol{n}$ allowing γ to be calculated from $\boldsymbol{\xi}$ [4].[1]

Now, let $\boldsymbol{\xi}_k$ be the capillarity vectors of interfaces forming a junction parallel to a unit vector $\boldsymbol{l}$, and let the sense of $\boldsymbol{\xi}_k$ be such that $(\boldsymbol{l} \times \boldsymbol{t}_k) \cdot \boldsymbol{\xi}_k > 0$ for all k. The Herring condition simply expresses the fact that the net force in the plane perpendicular to $\boldsymbol{l}$ is zero [4–6]

$$\boldsymbol{l} \times \sum_k \boldsymbol{\xi}_k = \boldsymbol{0}; \tag{2}$$

the force component along the junction is immaterial for the in-plane equilibrium.

Anisotropy and criterion for non-reactive wetting

Let us assume that the boundary 1 is to be wetted by a phase contained between faces 2 and 3. It is well known that in the isotropic case, wetting may occur if the energy of the appearing new interface segments does not exceed the energy of the vanishing boundary segment, i.e., the criterion for (perfect) wetting is $\gamma_2 + \gamma_3 \leq \gamma_1$. After [7], we will refer to this rule as Gibbs-Smith principle. The bounding condition of the rule can be written as

$$(\gamma_2 + \gamma_3)/\gamma_1 = 1. \tag{3}$$

The question is whether the Gibbs-Smith principle follows from the equilibrium conditions of Herring when some of the involved interfaces are anisotropic.

In order to verify this, the capillarity vector is expressed as $\boldsymbol{\xi}_k = \gamma_k \boldsymbol{n}_k + \boldsymbol{\tau}_k$, where $\boldsymbol{n}_k = \boldsymbol{l} \times \boldsymbol{t}_k$, and $\boldsymbol{\tau}_k$ is the torque term satisfying $\boldsymbol{\tau}_k \cdot \boldsymbol{n}_k = 0$. The Herring relations (2) take the form

$$\sum_k \gamma_k \boldsymbol{t}_k = \boldsymbol{l} \times \sum_k \boldsymbol{\tau}_k. \tag{4}$$

[1] The definition of the $\boldsymbol{\xi}$ vector given above is limited to boundary inclinations at which $\gamma|\boldsymbol{s}|$ is differentiable. In particular, that does not occur for inclinations corresponding to energy cusps. However, as already noted by Hoffman and Cahn [4], a given real interface has a unique $\boldsymbol{\xi}$ even if its inclination is 'special'. Accordingly, $\boldsymbol{\xi}$ vectors at edges of interfaces are uniquely determined and there is no ambiguity about forces acting at junctions.

The boundaries approach the wetting conditions when the angle between vectors $\boldsymbol{t}_2$ and $\boldsymbol{t}_3$ goes to zero (Fig. 1b). For $\boldsymbol{t}_2 = \boldsymbol{t}_3$, Equations 4 lead to

$$\begin{aligned} -\gamma_1 + (\gamma_2 + \gamma_3)\cos\delta &= \boldsymbol{n}_1 \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3) \text{ and} \\ \gamma_1 \cos\delta - (\gamma_2 + \gamma_3) &= \boldsymbol{n}_2 \cdot \boldsymbol{\tau}_1, \end{aligned} \tag{5}$$

where $\cos\delta = -\boldsymbol{t}_1 \cdot \boldsymbol{t}_2$, and only the cases with the angle δ close to 0 are considered. These relations link the geometrical elements $\boldsymbol{n}_1$, $\boldsymbol{n}_2$ and δ to the physical properties of the interfaces. For non-zero torque terms, the angle δ can be non-zero.

The meaning of (5) becomes clearer by considering simple particular cases. Let us assume that the two interfaces of low energy are isotropic ($\boldsymbol{\tau}_2 = 0 = \boldsymbol{\tau}_3$) and $\boldsymbol{\tau}_1$ is allowed to be non–zero. In this case, the bounding condition (3) is replaced by

$$(\gamma_2 + \gamma_3)/\gamma_1 = 1/\cos\delta \ \ (\geq 1). \tag{6}$$

On the other hand, if the high energy boundary is isotropic ($\boldsymbol{\tau}_1 = 0$), and there are no constraints on $\boldsymbol{\tau}_2$ and $\boldsymbol{\tau}_3$, one obtains

$$(\gamma_2 + \gamma_3)/\gamma_1 = \cos\delta \ \ (\leq 1). \tag{7}$$

By comparing (6) and (7) based solely on the Herring relations with the Gibbs-Smith principle, one gets an idea of the influence of anisotropy on wetting in the case of fixed junction direction. Roughly, wetting may occur for a lower energy ratio $(\gamma_2 + \gamma_3)/\gamma_1$ if the wetting medium has anisotropic interfaces, and a higher energy ratio is required if the boundary to be wetted is anisotropic.

3. Additional conditions

The Herring condition expresses the mechanical equilibrium of forces in the plane perpendicular to a junction with a given direction. However, the spatial orientation of the junction is also a function of the interface properties. Each interface contributes some torque acting towards the change of the junction direction. To take that into account, one must consider the object comprising not only the junction line but also the adjacent interface segments. The simplest case is a junction of planar interfaces with equal areas.

Let $\boldsymbol{s}_k$ be the area vector of the k-th interface at the junction. With the interfaces limited by a cylinder of unit radius centered at the junction, the vectors $\boldsymbol{s}_k$ are given by $\boldsymbol{s}_k = \boldsymbol{l} \times \boldsymbol{t}_k$ $(= \boldsymbol{n}_k)$. Let the vector $d\boldsymbol{\omega}$ determine an infinitesimal rotation: the rotation axis (through the junction) is parallel to $d\boldsymbol{\omega}$, and the rotation angle equals $|d\boldsymbol{\omega}|$. The rotation changes the vector $\boldsymbol{s}_k$ by $d\boldsymbol{s}_k = d\boldsymbol{\omega} \times \boldsymbol{s}_k$. Hence, the change of the energy accumulated in the system is given by

$$\sum_k \boldsymbol{\xi}_k \cdot d\boldsymbol{s}_k = \sum_k ((\boldsymbol{l} \cdot \boldsymbol{\xi}_k)\boldsymbol{t}_k - (\boldsymbol{t}_k \cdot \boldsymbol{\xi}_k)\boldsymbol{l}) \cdot d\boldsymbol{\omega}.$$

For a stationary configuration, there occurs $\sum_k ((\boldsymbol{l} \cdot \boldsymbol{\xi}_k)\boldsymbol{t}_k - (\boldsymbol{t}_k \cdot \boldsymbol{\xi}_k)\boldsymbol{l}) = \boldsymbol{0}$. Since $\boldsymbol{t}_k$ are perpendicular to $\boldsymbol{l}$, we get

$$\sum_k \boldsymbol{t}_k \cdot \boldsymbol{\xi}_k = 0 \quad \text{and} \quad \sum_k (\boldsymbol{l} \cdot \boldsymbol{\xi}_k)\boldsymbol{t}_k = 0. \tag{8}$$

In conjunction with Herring relations, these are the conditions necessary for the stability of equal-area planar interfaces joined along a line.

With the capillarity vector expressed as $\boldsymbol{\xi}_k = \gamma_k \boldsymbol{n}_k + \boldsymbol{\tau}_k$, the relations (8) take the form

$$\sum_k \boldsymbol{t}_k \cdot \boldsymbol{\tau}_k = 0 \quad \text{and} \quad \sum_k (\boldsymbol{l} \cdot \boldsymbol{\tau}_k)\boldsymbol{t}_k = \boldsymbol{0}, \tag{9}$$

respectively. The Herring Equations 4 relate both the energies and the torques to the geometry of an equilibrated junction, whereas the additional conditions (9) involve only the torque components. In the isotropic case ($\boldsymbol{\tau}_k = \boldsymbol{0}$), the Herring conditions are reduced to the Young's law (1), whereas the additional conditions become trivial identities.

Wetting criterion revisited

It must be stressed again that the relations (5–7) are applicable only if the equilibrium conditions are based solely on Herring relations with the direction of the junction fixed. A different picture appears if also Equations 9 are taken into account. For the configuration corresponding to wetting ($\boldsymbol{t}_2 = \boldsymbol{t}_3$), the relations (9) take the forms

$$\boldsymbol{t}_1 \cdot \boldsymbol{\tau}_1 + \boldsymbol{t}_2 \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3) = 0, \tag{10}$$

$$(\boldsymbol{l} \cdot \boldsymbol{\tau}_1)\boldsymbol{n}_1 + (\boldsymbol{l} \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3))\boldsymbol{n}_2 = \boldsymbol{0}. \tag{11}$$

From (11) one obtains

$$\begin{aligned} &\boldsymbol{l} \cdot \boldsymbol{\tau}_1 = 0 = \boldsymbol{l} \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3) \quad && \text{if } \delta \neq 0 \quad \text{and} \\ &\boldsymbol{l} \cdot \boldsymbol{\tau}_1 = \boldsymbol{l} \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3) && \text{if } \delta = 0, \end{aligned}$$

i.e. the torque components parallel to $\boldsymbol{l}$ can be non-zero only if $\delta = 0$. Moreover, the torque $\boldsymbol{\tau}_1$ can be expressed as $\boldsymbol{\tau}_1 = (\boldsymbol{\tau}_1 \cdot \boldsymbol{t}_1)\boldsymbol{t}_1 + (\boldsymbol{\tau}_1 \cdot \boldsymbol{l})\boldsymbol{l}$ and, similarly, $\boldsymbol{\tau}_2+\boldsymbol{\tau}_3 = ((\boldsymbol{\tau}_2+\boldsymbol{\tau}_3)\cdot\boldsymbol{t}_2)\boldsymbol{t}_2+((\boldsymbol{\tau}_2+\boldsymbol{\tau}_3)\cdot\boldsymbol{l})\boldsymbol{l}$. Hence, one has $\boldsymbol{n}_2 \cdot \boldsymbol{\tau}_1 = (\boldsymbol{n}_2 \cdot \boldsymbol{t}_1)(\boldsymbol{\tau}_1 \cdot \boldsymbol{t}_1)$ and $\boldsymbol{n}_1 \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3) = (\boldsymbol{n}_1 \cdot \boldsymbol{t}_2)((\boldsymbol{\tau}_2+\boldsymbol{\tau}_3)\cdot \boldsymbol{t}_2)$. Because of (10) and $\boldsymbol{n}_1 \cdot \boldsymbol{t}_2 = -\boldsymbol{n}_2 \cdot \boldsymbol{t}_1$, there occurs $\boldsymbol{n}_2 \cdot \boldsymbol{\tau}_1 = \boldsymbol{n}_1 \cdot (\boldsymbol{\tau}_2 + \boldsymbol{\tau}_3)$, i.e. the right-hand sides of Equations 5 are equal. Consequently, equality of their left-hand sides leads to

$$(\gamma_2 + \gamma_3)/\gamma_1 = 1.$$

Thus, if the junction is allowed to change its orientation, wetting of anisotropic interfaces is determined by the basic Gibbs-Smith rule.

4. Concluding remarks

The considered example of wetting shows that in the presence of anisotropy, the Gibbs-Smith principle is not consistent with the fixed direction of the triple line. The principle is applicable if equilibrium of a larger object involving planar interface segments is considered. This observation is particularly important for the investigation of melt distribution in equilibrated partially molten geological systems (cf. [8]). The example sheds light on the complexity of interactions at interface junctions. More generally, understanding the influence of anisotropy on equilibrated junctions may be helpful in clarifying certain instabilities in anisotropic systems.

For instance, the described impact on wetting may explain some aspects of the penetration of liquid along grain boundaries in systems with unstable boundary grooves [9, 10]. In such cases, the occurrence of regular grooves appears to be random, penetration channel profiles are poorly reproducible, and faceting in solid/liquid interfaces is observed. The boundary anisotropy is recognized as a factor contributing to these intricate wetting geometries [11]; therefore, also anisotropy related complex interactions at grooves' roots (junctions) must play a role in 'destabilizing' the grooves.

Similar destabilizing effects are likely in polycrystals with solid/solid boundaries. Since rotations lead to large displacements at finite distances from rotation axes, in real materials, the torque component can be satisfied only locally by corrugation. With all boundaries of a junction contributing some torque, boundaries near the junction can be expected to be more corrugated than at a distance from it. (In fact, increased density of fine facets in the vicinity of junctions was observed in annealed tungsten [12].) Ultimately, one may expect corrugated triple lines but such events would be difficult to detect.

The conditions near boundary perimeter are known to influence evolution of the microstructure. In simple terms, a displacement of a given interface at a junction requires movement or extension of the other interfaces meeting there and, as a result, junctions are considered to be a cause of pinning. The issue has a more subtle aspect related to the conditions considered above. One can easily see that there is one degree of freedom when only Herring relations are enforced: for a fixed $\boldsymbol{l}$, one can arbitrarily select $\boldsymbol{t}_1$ perpendicular to $\boldsymbol{l}$ and then, vectors $\boldsymbol{t}_2$ and $\boldsymbol{t}_3$ are determined by the Herring equilibrium conditions. There is no such freedom if all (2) and (8) are effective because the number of conditions is equal to the number of independent variables; this means that junctions which reached the equilibrium state will have a pinning effect on adjacent boundaries. If the actual junctions behave similarly to the model with planar interfaces, they must have an impact on the evolution of the boundary network and must contribute to considerable differences between microstructures of annealed materials with anisotropic boundaries and those with isotropic boundaries and triple junctions restricted only by the Young's law. In the isotropic model of grain growth, the grain boundary network evolves smoothly towards a global minimum of the energy stored in the boundaries. In materials with highly anisotropic boundaries, with inevitable pinning events, the process must be more 'jerky' as it involves states with parts of the boundary network trapped at local energy minima.

There is a trend to depict junctions as autonomous entities having structured 'cores' (e.g. [13]), and characterized by distinct mobilities (e.g., [14]) and energies (e.g., [15], see also [16–18]). However, because of complicated interactions, it is difficult to extricate the inherent characteristics of junctions from properties of other elements of the boundary network. The above extension of the Herring conditions demonstrates that the interactions are even more complex than once thought, and it puts emphasis on seeing a junction through the prism of attributes of adjacent boundaries.

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