

Viewpoint Paper

Four questions about triple lines

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Abstract—The identification of triple lines as one of a hierarchy of defects is presented. There are several distinct cases of triple junctions, and these are sorted into classes. Viewpoints about open questions and directions for future research are offered, including: (1) the effect of induced order on the structure and energy of a triple line; (2) considerations of interfacial (complexion) transitions; (3) suggestions of methods for the direct measurement of triple line energy; (4) observations of the possibility of triple line anisotropy. © 2010 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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1. Introduction

It is customary for materials scientists to catalog defects as point, line, interface or bulk defects. In this schema triple junctions are one of many species in the family of linear defects. However, the categorization does not expose the hierarchical nature of triple junctions, in that they are necessarily and geometrically linked to interfaces. Bulk materials must have at least one external interface, and may have internal interfaces, and thus triple lines exist if these interfaces intersect.

Interfaces continue to be a central research focus in materials science, especially when the microstructural length scale is reduced. There are many objectives of fundamental research on interfaces, as they play a significant role in the properties of materials [1] and the microstructural evolution of materials [2,3] and present fascinating problems regarding the thermodynamics and atomistic structure at the planar intersection between bulk phases.

Less focus has been placed on triple lines. Nevertheless, the behavior of triple lines plays a role in the behavior of interfaces: they govern the geometry and motion of interfaces and they provide sources and sinks for interface diffusion. In this opinion we summarize four questions about triple lines that we consider unresolved and worthy of further research.

2. Taxonomy

The term ‘triple line’ identifies the intersection of three interfaces and, therefore, occurs in the proximity of three separable volumes. However, there are many varieties of triple lines (Fig. 1). These are differentiated by the presence of a grain boundary, while it is important for this argument to consider that a grain boundary is not a phase boundary.

Three phase triple lines.

- Three internal interfaces. These require three phase equilibria and thus their equilibrium properties can only be described for ternary and higher order component systems.
- One internal and two surficial interfaces (there are two cases with respect to the degrees of freedom in the system).
 - If the vapor phase consists of only those components that are soluble in the bulk phases then the total pressure is fixed by the sum of the component partial pressures. These may be in continuous equilibrium for two and higher component systems (e.g. a liquid aluminum drop on a sapphire surface with $P_{\text{total}} = P_{\text{O}_2} + P_{\text{Al}}$ [4]) (see Fig. 1a).
 - The vapor phase contains insoluble components and the applied pressure exceeds the sum of the partial pressure. These may be in continuous equilibrium for single and higher component systems (e.g. a liquid water drop on pure ice) (see Fig. 1b).

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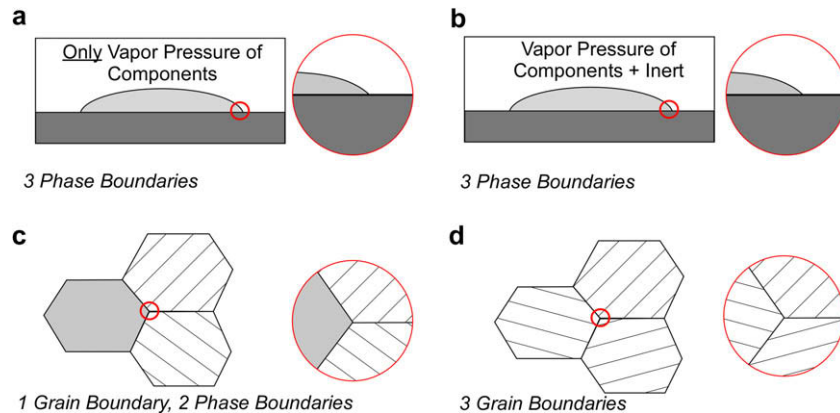


Figure 1. A schematic of the four examples of triple junctions. (a) When the vapor phase consists of only those components that are soluble in the bulk phases then the total pressure is fixed by the sum of the component partial pressures for the three phases. (b) When the vapor phase contains insoluble components the applied pressure has an additional thermodynamic degree of freedom. (c) A grain boundary in contact with the other phase (two phase triple line). (d) Where three grain boundaries intersect to form a single phase triple line.

Two phase triple lines. These include a grain boundary which lies in one or the other phase (Fig. 1c). These may exist with restricted equilibrium (i.e. one degree of thermodynamic freedom) for single component systems. These may exist with a continuous equilibrium in two component systems.

Single phase triple lines. These are composed of three grain boundaries and have a continuous equilibrium for single and higher component systems (Fig. 1d) [5,6].

3. Four questions

3.1. The influence of order and its proximity constraint

For solid–liquid (single or multiple component) interfaces it has been demonstrated that in the proximity of an interface a diffuse layer of ‘material’ exists which is partially ordered [7–10]. The structure of this layer does not exist in isolated bulk equilibrium, i.e. its presence and equilibrium structure is linked to the adjacent interface. For specified values of pressure and temperature and set of independent chemical potentials the equilibrium composition in the partially ordered layer will differ from those in the equilibrium bulk phases. Whether this composition should or should not be included in the interfacial adsorption Γ_i is arbitrary, but the sum of the contributions is fixed by the thermodynamic degrees of freedom (e.g. P, T and μ_i), and it is the sum that is governed by generalizations of the Clapeyron relation (e.g. the Gibbs adsorption isotherm).

The nature of this induced order is similar to composition profiles in the Cahn–Hilliard diffuse interface model [11,12]. Complete models of interfacial regions would include the combined effects of composition, order, geometrical configuration, strain, etc. However, induced order is fundamentally different from the other effects. Order is a so-called ‘hidden’ variable, in that the order field cannot be independently changed by experiment but appears as a result of equilibrium – it does not provide an additional degree of freedom.

The induced order is spatially correlated in planes parallel to the local interface, but the degree of correla-

tion decays with increasing distance from the interface [10]. However, for triple junctions there is a pseudo-abrupt change at the interface and the interfacial correlation fields must interact. Correlations probably occur in space and time. The in-plane correlations for any two interfaces will differ, as will their rate of decay in the normal direction. What is the nature of these interactions and what is their effect? Could they be observed directly via microscopy, simulated with atomistic techniques or modeled with statistical or classical thermodynamic methods? Since the recent advance of aberration corrected microscopes experimental evidence of the intersections is only a matter of time and, for the latter two techniques, it should be possible to provide structural observation and estimates of triple line energy. An experimental example [13] of such a possible intersection is presented in Figure 2, where induced order at two different solid–liquid interfaces is expected to meet at the triple junction.

3.2. Coupling to interfacial transitions in composition and structure

Interfaces can undergo first order transitions where one or more of their equilibrium adsorptions (Γ_i) have a discontinuous change in their value. It has been suggested that interfaces and grain boundaries can also undergo discontinuous changes in their structure (and any associated width of their structure). This is certainly the case for surface reconstruction [14] and equilibrium surficial films on ice [15] and oxides [16,17], and there is evidence of such geometric transitions for internal interfaces [2]. The identifier ‘complexion’ has been utilized to identify any of the possible combined equilibrium interfacial states [12,18]. Complexions are analogous to bulk phases, but differ because complexions cannot exist in the absence of abutting bulk phases. Furthermore, the appellation ‘complexion’ provides an unequivocal distinction between ‘phase transition’ and ‘complexion transition’ which, although similar and not completely independent, are different phenomena, and complexions do not add an additional degree of freedom to the Gibbs phase rule [3]. A complexion must

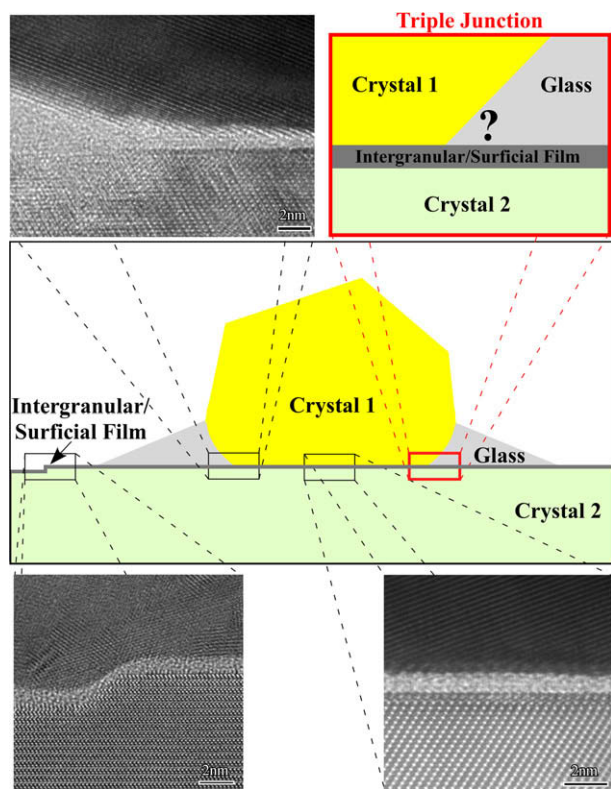


Figure 2. The center schematic represents an example of an experiment in which a crystal lies within a glass droplet on another crystal. As a result, an intergranular film is formed at the interface, as well as a surface film on the surface of one crystal. Aberration corrected HRTEM micrographs from such experiments on Au–anorthite–sapphire are presented (the experimental configuration has been described elsewhere [13]). Order is found in the films adjacent to one crystal and is expected to exist at the interface with the other crystal. The question is ‘what happens when the two order-induced interfaces intersect at the triple junction’.

be identified by a discontinuity in its characteristics: for example, states for which $\Gamma_i(\mu_j, P, T)$ have continuous values would be considered the same complexion; otherwise, the adsorptions would need further identification $\Gamma_i^\alpha(\mu_j, P, T)$ and $\Gamma_i^\beta(\mu_j, P, T)$, as would any other identifier, such as radial distribution functions or Fourier spectra. The angles from Young’s equation would have a discontinuity in their derivatives or values at complexion transitions, which have been used as empirical evidence for such transitions [17].

Complexion transitions of one or more interfaces adjoining a triple line must affect the local characteristics of the triple line. How are complexions and their transitions coupled to triple lines? There is certainly a hierarchy: a bulk phase transition must force a complexion transition, but not vice versa; a complexion transition must force a transition at a triple line, but not vice versa. It seems probable that triple lines could undergo coupled transitions in their local composition and structure in the absence of complexion or bulk transitions. Any description of such transitions must include identifiers such as a linear adsorption density and linear energy density (i.e. line tension). Grain boundary pre-melting is an example [19].

3.3. Rational independent measurement of triple line energies

Surface tensions have been directly measured via force/extension balance (e.g. zero creep experiments [20–22]). Relative surface tensions have been directly measured by observing equilibrium angles and then inferring ratios via Young’s equation (or its anisotropic analog) [23].

In the case of force/extension balance measurements, any change in triple line geometry with extension must participate in the total force if the triple line has an associated linear energy density; a line energy [24]. Since geometric models for the interface morphology as a function of extension [25] are generally difficult to calculate, so are relations for triple line length. The absence of a good model makes such experiments difficult to interpret and the experiments are generally difficult to perform under perfectly controlled conditions. The ratio of the two force contributions will scale with system size and thus can be used as a rough inference of triple line energy; but experimental difficulties still exist.

Measurement of angles is less equivocal and suggests another mechanism for triple line energy determination, but for the following observation: force balances that dictate the equilibrium angles are resolved in a plane that is normal to the triple line. Forces from the triple line, if they exist, should therefore have no direct effect on the angle. Therefore, angle measurements alone would not determine surface tension. A triple line energy would affect the shape of a sessile drop and this is calculatable by minimizing simple geometries. A negative line tension should induce rumples in the triple line of a sessile drop; resolution of such rumples and their stability with a constant mean curvature surface would be an interesting exercise. In principle, these calculations would be a subclass of those we suggest in the next section.

It may be preferable to decouple the interfacial force balance from the triple line force balance. We suggest that sharp features – whether geometrical, such as an edge, or chemical, such as the border between a hydrophilic and hydrophobic patch – may provide such a decoupling. Such a measurement is suggested in Figure 3, which is a variation of a wetting balance experiment calculated using Surface Evolver [26]. At sharp features a continuous range of angles satisfy the force balance, but the triple line energy should remain constant along the feature. Independent geometrical measurements of the contact angle away from such features, combined with measurements of the triple line length, should supply a method to distinguish the two effects. When coupled with a force/extension apparatus (e.g. a wetting balance; Fig. 3) the values of surface tensions and line energies should be directly obtainable.

3.4. Anisotropy of triple lines

Consider the case of a liquid sessile drop on a crystal-line surface and suppose (for the moment) that the crystal-liquid and the crystal-vapor interfacial tensions are isotropic. It is plausible that it may be energetically favored for the triple line to lie parallel to particular crystallographic directions (Fig. 4). Furthermore, the discussions on induced order at the beginning of this

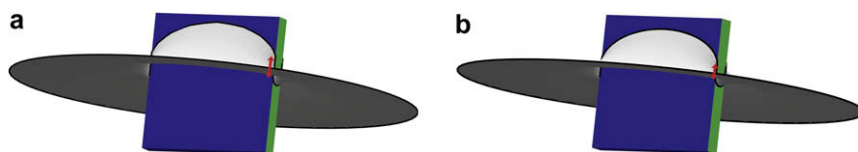


Figure 3. Surface Evolver [26] computation of a rectangular prism. On the narrow faces the liquid is in contact with a ‘hydro’phobic surface and on the wide face the contact is with a ‘hydro’philic surface. (a and b) Numerical solution of the minimal energy configuration (a) with triple line tension not taken into consideration and (b) with all line tensions considered. The triple line length is marked by a red line. The dependence of this line length on line tension should provide, in combination with contact angle determination, the dimensions of the prism and forces, a method for line tension measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

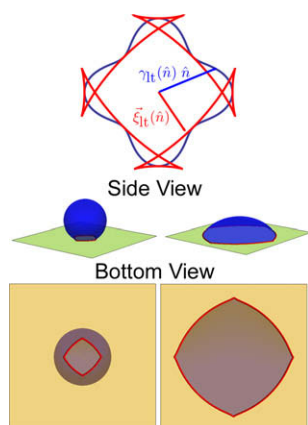


Figure 4. Surface Evolver [26] computations of the shape of a sessile drop with isotropic surficial tension and with anisotropic triple line tension. On the left the ratio of isotropic surface tensions is such that the contact angle would be 135° if not for the line tension, and on the right the contact angle would be 45°. The drop volumes are the same in each. For 135° the ratio of interface energy to line tension energy is 0.85, for 135° it is 0.98. The line tension anisotropy is given by the top in blue, while the ‘line-energy Wulff’ shape is the area underneath the line energy ξ vector, plotted in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

paper imply that some anisotropy should develop in the vicinity of the triple line. What would be the effect of anisotropy of a triple line? The force balance of line tension would include torque terms and, therefore, line tension would have components that interact with the interfacial force balance. The shape of the triple line would not be determined by a two-dimensional Wulff construction on the orientation-dependent line tension for at least two reasons: a line tension Wulff construction would not account for an increased area of the adjoining interfaces and there is no constraint that fixes the ‘covered’ area. If either the vapor–crystal or liquid–crystal interfaces are also anisotropic [27] calculations of droplet morphology must couple these to triple line energies.

Anisometric sessile drops have been observed on solid substrates and their presence has been associated with rough textures or chemically patterned patches [28]. Any measurement of triple line energy anisotropy should probably eliminate these macroscopic effects, or at least account for them.

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