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## THEORY OF PHASE TRANSITIONS AT INTERNAL INTERFACES

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**Abstract** — A variety of phase transitions are possible at internal interfaces. I will systematically describe from a pedagogical point of view the various classes of phase transitions which are possible. Experiments which have been performed will be mentioned at the appropriate places. Theories which predict these phase transitions and which explain the behavior associated with the transitions are emphasized. Possibilities for phase diagrams are suggested. Wetting and melting of internal interfaces will also be discussed.

### 1. Background.

A decade ago the possibility of phase transitions occurring at internal interfaces would have been discounted by many researchers. For those who would have agreed with this possibility, many would not have been convinced that the evidence was strong enough to give conclusive evidence for such transitions. Today, the evidence is conclusive. Theorists and experimentalists alike are predicting and exploring a variety of transitions in grain boundaries. (The evidence for other solid-solid interfaces, such as interphase interfaces, antiphase boundaries, and stacking faults, is not yet as convincing.) People are beginning to consider how to take advantage of phase transitions which occur in internal interfaces by the appropriate processing of materials to produce the desired microstructural properties.

In this article the many types of phase transitions which are possible in internal (i.e., solid—solid) interfaces are described. I hope to provide some general principles on how to decide what is or is not a phase transition and on what the possible phase diagrams might be. A classification of most (if not all) of the work done on these transitions is provided. I intend to provide a fairly complete bibliography which will reference articles which have modeled such phase transitions and also observed them in both computer and “real” experiments. The thermodynamics of such phase transitions, which has been addressed in the past [1,2], will be discussed here where clarification is helpful. I am neglecting from consideration interface phase transitions associated with magnetism or other similar effects. For up-to-date collections of recent work in grain boundaries and other internal interfaces, I recommend one book [3], one review article [4], and two conference proceedings [5,6]. Other recent review articles which discuss grain-boundary phase transitions may also be found [7].

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## 2. General considerations.

What qualifies as a phase transition in an internal interface? For the purposes of this article, I will denote an interface phase transition (or transformation) as the physical phenomena associated with a distinct region (called a phase boundary), characterized by thermodynamic<sup>(1)</sup> variables, where an interface free energy  $\gamma$  has a qualitatively different behavior, depending on how a point of the phase boundary is approached as a thermodynamic variable is varied (i.e., depending on which phase you are in). For example, if we fix all of the thermodynamic parameters (allowed by the Gibbs phase rule) except for temperature  $T$ , then we find a first-order (i.e., discontinuous) "structural" phase transition occurring at a temperature  $T_o$  if the slope of  $\gamma$ , namely,  $\partial\gamma/\partial T$ , has a different value depending on whether  $T_o$  is approached from below ( $T < T_o$ ) or above ( $T > T_o$ ). If the slope is continuous but a nonanalyticity is still present, the structural phase transition becomes second order (i.e., continuous). My use of the word "distinct" disqualifies from my definition fuzzy ranges where the system varies from one type of behavior to another, without a sharp change, which are sometimes called transitions [8,9]. A phase diagram then constitutes a plot of such phase boundaries in the space of the thermodynamic variables (for which an interface may exist at equilibrium) of interest. As a practical matter, phase diagrams are generally drawn with certain thermodynamic variables held constant (such as fixing pressure at atmospheric pressure). A simple mathematical definition of the phase diagram is the locus of nonanalyticities in  $\gamma$ . Coexistence of interfacial phases is only possible for first-order phase transitions.

Which thermodynamic variables shall we use to determine interfacial phase transitions and phase diagrams? I will take a rather practical point of view here in light of the transitions seen in computer and "real" experiments.<sup>(2)</sup> The variables of interest may be grouped into two classes. The first class is made up of *bulk variables* which are well defined even when an interface is absent. For these I choose  $T$ , pressure  $P$ , and compositions  $c_i$ ,  $i = 1, \dots, N$ . These variables characterize the system far away from all surfaces or interfaces. The second class is made up of *interface variables* which characterize the geometrical aspects of the interface. For these I choose the *average* orientation of the boundary plane  $\hat{n}$  which separates the two grains/phases and the axis  $u$  and angle  $\theta$  which characterize the misorientation between the two grains/phases. These angular variables clearly depend on the reference state with respect to which the axes are defined and the angles are measured. This list is by no means exhaustive. The two phases may have different crystal structures. There is also a translational degree of freedom related to the displacement of the bulk grains/phases from each other.

The bulk phase diagram provides important information concerning the restricted range of the bulk thermodynamic variables over which the interface is well defined. For example, grain boundaries are not well defined above the melting temperature (liquidus)  $T_m$ . Similarly, antiphase boundaries are permitted only in the ordered-phase region of the bulk phase diagram. Interphase interfaces differ from grain and antiphase boundaries in that, for interphase phases, an additional restriction is present which guarantees equilibrium of the two bulk phases [11]. One can imagine drawing an interphase phase diagram by first starting with the bulk phase diagram and then marking the location of the interface transitions on the two-phase coexistence regions of the bulk phase diagrams. Interface variables then provide additional axes. The majority of this paper focuses on grain-boundary phase transitions since stacking-fault and interphase- and antiphase-boundary transitions have only been studied in a few cases (see section 7).

<sup>(1)</sup>Theorists working with microscopic models will use a more general definition in which any variable which appears in their model is an appropriate variable to characterize a phase diagram even though this variable is not a thermodynamic variable.

<sup>(2)</sup>A more general discussion may be found in [10].

Dissociation “transitions” occur when one phase or grain replaces a single interface, thus producing two interfaces. A particularly common example is grain-boundary melting, when a film of melt separating two grains becomes macroscopic. When the replacement phase is a distinct bulk phase (different from those the interface separates without replacement), the dissociation occurs in the limit as the bulk variable being varied approaches a bulk first-order phase transition, where a new coexistence of phases is possible. In a trivial sense, whenever a bulk phase transition occurs an interfacial one does as well, since the interface must change its nature if one or both of the bulk phases which it separates undergoes a transition. Thus, in this same trivial sense, grain-boundary melting is an interface phase transition, but so is the case in which the boundary does not melt as  $T_m$  is approached. In this article I will reserve the word “transition” to those nontrivial cases in which the nature of the dissociation experiences a distinct change as one moves along coexistence. In the physics literature these transitions, which are usually called “wetting transitions,” have been studied extensively for solid-vapor interfaces [12]. These surface systems often show a thin-film to thick-film transition (called prewetting) away from coexistence as well as transitions associated with the buildup of each layer. Certain transitions (called grain-boundary wetting in the literature) may, in fact, be analogous to prewetting transitions (see section 6). A single transition associated with an increase of solute at a grain-boundary has been predicted (see section 3.2), but the analog to multilayer formation has not yet been found.

### 3. Structural transitions at grain boundaries.

A structural transition is a transition which occurs as a bulk variable changes while all of the interfacial variables are held fixed.

The theory behind *first-order* structural transitions may be explained as the crossing of the (possibly metastable) grain-boundary (GB) free energies  $\gamma_1$  and  $\gamma_2$  of competing structures due to changes in either  $T$  or  $c_i$ . Such phase transitions may, in fact, be quite common since metastable structures, with energies slightly larger than the ground-state energy, are often observed (e.g., [13]) at  $T=0$  K in pure materials. If  $T$  is the variable of interest, then the high- $T$  structure will have a larger GB energy  $E_{gb}$  and entropy  $S_{gb}$  than the low- $T$  structure, so that the  $\gamma = E_{gb} - (k_B T) S_{gb}$  of the two GB phases are equal at the transition temperature  $T_o$ . Similarly, a structure metastable at zero solute concentration  $c$  may become stable at a critical  $c_o$  if a more rapid decrease of  $\gamma$  with  $c$  occurs for the structure metastable at  $c=0$  as compared to the structure stable at  $c=0$  [14]. Clearly, for nonzero  $c$  and  $T$  the two transitions may be interrelated, just as bulk melting may occur with a variation in either  $T$  or  $c_i$ .

Two different types of *second-order* structural phase transitions have been investigated. The first occurs when one GB structure has a structural unit (the repeating unit cell in the GB plane) which is larger than that required by geometry, as determined by the atoms far from the GB plane. Increasing  $T$  or changing  $c_i$  may result in an order-disorder transformation where the structural unit reduces in size to the minimum-allowed size. The second type, associated with the vanishing of cusps in the interfacial variables (for fixed values of the interfacial variables), will be discussed in section 4.

**3.1 TEMPERATURE EFFECTS.** — A first-order structural transition has been observed at a  $T_o$  well below the melting temperature in a molecular-dynamics simulation of a  $\Sigma=5$  GB using a Lennard-Jones potential [15]. A second-order transition has been suggested from an ordered checkerboard structure of two alternating units at  $T=0$  K to a configurationally disordered structure [13].

**3.2 COMPOSITION EFFECTS.** — First-order structural transitions due to changes in composition  $c_i$  have been found in both models and experiments. Computer calculations show drastic changes in GB structure at  $T=0$  K upon adding P to Fe [16] and Bi to Cu [17]. A regular-solution model of a GB treated as a uniform slab predicts a  $T_c$  below which a phase coexistence of two different GB phases of different GB compositions is found [18]. A  $c_i$ -induced phase transition has been suggested in experiments with Fe-Te and Fe-Se [2,19]. Perhaps the most convincing evidence of a GB structural phase transition is recent observations of low-angle (small- $\theta$ ) GB's in Fe-Au [20]. The GB was found to be composed of two different coexisting dislocation structures above a critical composition  $c_{Au}^{crit}$  of the solute Au. A  $c_i$ - $\theta$  phase diagram was drawn based on measurement of  $c_{Au}^{crit}(\theta)$ . Finally, a  $c_i$ -induced change in GB structure may be one of the ingredients in explaining the complex observations on the influence of Fe solute of low-angle GB's in MgO [21].

It is appropriate here to comment on the coexistence of two GB phases, one solute-rich and one solute-poor. In principle, if the grains which the GB divide are sufficiently large, then these grains will act as a sink or source of solute without a significant change in the bulk solute  $c_i$ . We then expect such coexistence to occur only at a single critical  $c_i$  of the bulk solute, not a range of compositions. The net adsorbed solute at the GB is, after all, determined by the Gibbs adsorption equation and is not a parameter independent of the bulk  $c_i$ . If, on the other hand, the diffusion out of the GB into the grains is sufficiently slow compared to the local equilibration of the GB structures (which is related to lateral diffusion along the GB), it may then be appropriate to treat the "GB composition" as an independent variable. Possibly the behavior of such a two-phase system, in "partial" equilibrium, is the same as if "full" equilibrium were present, with the bulk  $c_i$  equal to its critical value.

#### 4. Orientational transitions at grain boundaries.

As mentioned earlier, the GB free energy  $\gamma$  depends not only on bulk variables but also on interface variables which are geometric in nature. Typically cusps are found [3-6] in plots of  $\gamma$  versus grain-grain misorientation  $\theta$  or GB orientation  $\hat{n}$ . The bottoms of the cusps correspond to low- $\Sigma$  GB's which have a relatively small unit cell (the repeating structural unit) in the GB plane. The presence of a cusp indicates the existence of an orientational phase transition as an interfacial variable changes. Another possible GB phase transition occurs when the cusp disappears (i.e., smooth out) as a bulk variable changes. Since the interfacial variables are fixed in this case, the transition is technically a structural transition (as defined in section 3). However, this transition will be discussed in this section because of the close relationship with interfacial variables.

**4.1 FREE-ENERGY CUSPS IN  $\theta$ .** — A cusp in  $\theta$  centered at  $\theta_o$  is due to the presence of GB dislocations which have a density proportional to  $|\Delta\theta| = |\theta - \theta_o|$ . It is important to note that, for symmetric GB's at  $T=0$  K, a cusp is expected to be present for each allowed value of  $\Sigma$ , no matter how large, just by symmetry arguments.<sup>(3)</sup> The strength of the cusp should roughly decrease as  $\Sigma$  increases. The sometimes heated arguments which occur among those who perform computer simulations (at  $T=0$  K) on the existence of cusps for various GB's must be interpreted as a resolution effect, i.e., whether or not the strength of the cusp is large enough to be resolved for the techniques which are used to analyze such cusps. Such a symmetry argument can only be broken at nonzero  $T$ , where contributions to the internal entropy unique to the interface (different from those of the bulk) may wash out the cusp at a second-order transition (in fact, a structural transition, since only  $T$  changes) in a way somewhat analogous to the disappearance of cusps associated with crystal surfaces [22]. It is also worth noting that a cusp may be either a  $|\Delta\theta| \ln(1/|\Delta\theta|)$  cusp (this is

required at  $T=0$  K due to the long-range stress field of a GB dislocation [23,24]) or simply a  $|\Delta\theta|$  cusp. It is indeed possible, and not unreasonable, that, as  $T$  increases from  $T=0$  K, an interface (fixed  $\theta=\theta_o$ ) undergoes one second-order transition at  $T_1$  at which it goes from a  $|\Delta\theta| \ln(1/|\Delta\theta|)$  to a  $|\Delta\theta|$  cusp and another at  $T_2$  at which the  $|\Delta\theta|$  cusp disappears. Such a distinction is rarely addressed in the literature. However, a measurement of the rotation rate of a Cu sphere on a Cu substrate has suggested the presence of  $|\Delta\theta|$  cusps [25], suggesting that a phase transition must have occurred at a lower  $T$  corresponding to the disappearance of the  $|\Delta\theta| \ln(1/|\Delta\theta|)$  cusp. Also, recent theoretical work on low-angle GB's ( $\theta_o=0$ ), which calculates the decrease in the strength of the  $|\Delta\theta| \ln(1/|\Delta\theta|)$  cusp [26], may be useful in understanding this disappearance.

The existence of a cusp in  $\gamma(\theta)$  at  $\theta_o$  may result [27,28] in changes in the slopes of various properties as a function of  $\theta$ . Recent experiments on the GB diffusivity of Cu have been interpreted as due to the presence of such a cusp [27].

Several experiments have been interpreted in terms of the vanishing of the cusps in  $\gamma(\theta)$ . The changes in the orientations of Cu spheres sintered onto a copper substrate come about because of the disappearance of the weaker cusps at  $T$  increases [29]. Similar experiments have been performed for Ag in which the cusps disappeared with an increase in  $c_i$  of a solute [30] and hydrostatic pressure [31]. Also, a host of experimental results has recently been reviewed [32] in an attempt to determine the  $T$  at which a special GB becomes a nonspecial (general) GB, which may be interpreted as the  $T$  at which the cusp disappears. These authors have drawn a  $T-\theta$  diagram,<sup>(4)</sup> which characterizes not only the presence but also the strength of such cusps. Finally, a theoretical paper [33] has used a Debye model of lattice vibrations to calculate the free energy of two-dimensional lattices of atoms to suggest the  $T$  at which special GB's of a given  $\Sigma$  become general GB's.

**4.2 FREE-ENERGY CUSPS IN  $\hat{n}$ .** — The plot of  $\gamma$  as a function of  $\hat{n}$  is a Wulff plot which is used in deriving an equilibrium grain shape. Suppose we consider only one of the two angles which  $\hat{n}$  defines, say,  $\phi$ , such that the cusp is centered about  $\phi=0$ . Early arguments [24] suggested that, at  $T=0$  K, the cusps in  $\phi$  go as  $|\phi| \ln(1/|\phi|)$  for low-angle (small- $\theta$ ) GB's. However, recent work (D. P. DiVincenzo and C. Rottman, unpublished) concerning low-angle GB's, which may be generalized to high-angle GB's, argues for simple  $|\phi|$  cusps at  $T=0$  K. The disappearance of these cusps at a second-order phase transition has been predicted for low-angle GB's [34], yielding a  $T-\phi$  phase diagram. It appears that similar arguments may be used to predict when the analogous cusps for high-angle GB's will disappear. The strength of these  $|\phi|$  cusps gives the size of the corresponding facet in the grain shape, which is also a GB free energy [35]. The cusps in  $\gamma(\phi)$  and the borders of the facets correspond to the same second-order phase transition.

<sup>(3)</sup>This argument assumes that the interatomic potential is not strictly short range. For strictly short-range potentials cusps would not be expected for GB's with  $\Sigma > \Sigma_o$ , where the size of the GB unit cell corresponding to  $\Sigma_o$  is comparable to the range of interaction.

<sup>(4)</sup>I prefer not to call these phase diagrams, since I do not feel that there are transitions associated with a cusp at  $\theta_o$  for  $\theta \neq \theta_o$ . Shrinking the areas to lines at the appropriate  $\theta_o$ 's does, in my opinion, constitute a phase diagram.

**4.3 FACETING TRANSITIONS.** — In discussing faceting it is important to be clear about the way in which this term is used. The term “faceting transition” has sometimes been used [35] to discuss the transition associated with the disappearance of the  $|\phi|$  cusp, as discussed in section 4.2. At other times “faceting” has been used to refer to the fact that the structure of the repeating unit of the GB structure is not strictly two dimensional but rather has approximately planar parts misoriented with respect to each other (see, for example, [36]). However, here “faceting” refers to a preference for an initially planar interface to restructure itself into a hill-and-valley structure [22] composed of at least two distinct orientations  $\hat{n}_1$  and  $\hat{n}_2$ . This is, in fact, the interfacial analog of phase separation, where  $\hat{n}_1$  and  $\hat{n}_2$  characterize the two different interfacial phases [10,37]. The coarsening phenomena corresponds to the elimination of the edges (“interfaces”) between the facets (GB phases), resulting in macroscopic facets. The phenomena of faceting will appear whenever the equilibrium shape has a “sharp” corner (with slope discontinuities). As one transverses the orientations in the equilibrium shape (which is an interfacial free energy [35]), one moves from one phase ( $\hat{n}_1$ ) to another ( $\hat{n}_2$ ) at a first-order transition.

Dislocation theory predicts faceting transitions in low-angle GB's [38]. Faceting transitions have been observed experimentally for low-angle GB's in Au [39,40] and many high-angle GB's, such as in Ag [41], Au [39,40,42], Cu [43], Nb [44], Zn [45], Cu-Bi [46], Fe-Si [47], Fe-Te [48], and  $\text{Al}_2\text{O}_3$  [49]. A faceting transition has been used [10,50] to explain discontinuities of dihedral angles at GB triple junctions which have been observed [51] in Pb as a function of  $T$ .

## 5. Dissociation transitions at grain boundaries.

**5.1 GRAIN-BOUNDARY MELTING.** — The gradual change in GB structure into a liquidlike film which continuously increases in thickness to a macroscopic liquid film as the solidus is approached has been observed<sup>(5)</sup> and explained in many circumstances. Recently molecular dynamics has been used to model this phenomenon in both two [54] and three [9,55,56] dimensions. A two-dimensional lattice model shows such a phenomenon [8] and the effect of a solute on GB melting has been studied theoretically [57]. Recently it has been argued that, for systems with van der Waals forces, such a melting transition cannot occur [58,59]. The possibility of a first-order prewetting transition (below the bulk melting transition) is deferred to section 6.

**5.2 GRAIN-BOUNDARY-MELTING TRANSITIONS.** — A transition may be found in the wetting behavior from the wetting of the GB by the melt (i.e., the GB melting of section 5.1) to the situation in which the melt does not wet the GB. In experiments second-order transitions have been seen as  $c_i$  [60] and  $T$  [61] have been varied. Also, a first-order melting transition has been observed as  $\theta$  is varied [62]. Note that the variation of  $c_i$  and  $T$  are interrelated since the variation must follow the liquid-solid coexistence region in the bulk phase diagram.

**5.3 OTHER GRAIN-BOUNDARY DISSOCIATION TRANSITIONS.** — In GB melting the GB is wet (replaced) by its melt. Another interesting possibility is the replacement of the GB by another grain. For example, from a particular dependence of  $\gamma(\theta)$ , we can determine by a simple construction (J. W. Cahn, private communication) whether or not a GB of misorientation  $\theta_0$  prefers to be replaced by a grain of intermediate misorientation  $\theta_1$ , producing two GB's of misorientation  $\theta_1$

<sup>(5)</sup>For some rather old reviews of experiments, see [52]. Recent experiments may be found in [53].

and  $\theta_2 = \theta_0 - \theta_1$ . The mathematical property of a function  $\gamma(\theta)$  such that

$$\gamma(\theta_1) + \gamma(\theta_2) \geq \gamma(\theta_1 + \theta_2),$$

called subadditivity in the mathematics literature [63], has not been studied extensively for functions such as  $\gamma$  defined on the unit circle or the unit sphere.

Theoretical aspects of such GB dissociation transitions have been studied in [10]. A microscopic model which predicts such transitions has been proposed recently [59]. Experimentally GB dissociations have been seen in Au [39] and in Fe-doped MgO [21].

## 6. Other claims of grain-boundary transitions.

Indirect evidence sometimes suggests the possibility that a GB phase transition has occurred. A discontinuity in the dihedral-angle measurements of a Bi GB-melt trijunction has been interpreted in terms of a phase transition of the Bi GB [62]. However, a careful thermodynamic analysis [50] of this experiment reveals that such discontinuities indicate the existence of a (faceting) transition in the solid-melt interface, not the GB.

Computer simulations of GB's provide evidence for two transitions at  $T$  distinctly below  $T_m$ . In two dimensions [54] a reorientation transition is found, in which  $\theta$  changes its value. In both two and three dimensions [54,56,64] a change in behavior is found associated with the sudden appearance of a liquid-like layer. This later transition may be analogous to the prewetting transition, as discussed in section 2.

Several measurements of kinetic properties of GB's have also resulted in claims of phase transitions. Discontinuities have been observed in the activation energies for GB mobility [65] and sliding [66]. A phase transition due to segregation has been proposed to explain the embrittlement properties of certain steels [67]. At present, it is not known for certain which of the various types of phase transitions (as described in sections 3-5) correspond to such effects.

## 7. Phase transitions in other internal interfaces.

The theoretical study of phase transitions in internal interfaces other than grain boundaries has been limited almost exclusively to systems in which a single lattice structure describes the positions of the atoms on each side of the interface. Neither a change in lattice parameter nor a rotation is allowed across the interface in these models. Interfaces in such lattice models have been studied extensively, although the applications have often been to situations in which a fluid (liquid or vapor) is involved [68]. Here I will only discuss those lattice models which have been explicitly used to study phase transitions in internal interfaces.

A second-order structural transition has been predicted in antiphase boundaries in  $\text{Cu}_3\text{Au}$  [69], corresponding to a change in the way in which the sublattice layers are ordered as the boundary is transversed. Both theory [69] and experiment [70] have shown antiphase boundaries to be wet by the disordered phase. A second-order wetting transition (as defined in section 2) of an antiphase boundary by the disordered phase has been found [71,72] in experiments on Fe-Al. In stacking faults in dilute Co alloys the experimental evidence for fluctuations in the segregation of Co to the stacking fault has been explained by a second-order order-disorder transition [73]. Vanishing of cusps in the boundary-plane orientation  $\hat{n}$  have been found [74] in the coherent-interface-boundary free energy  $\gamma(\hat{n})$ . Sharp corners in equilibrium shapes of second-phase particles (e.g., precipitates), which correspond to faceting transitions, are commonly observed in experiments [71,75]. Such a sharp corner also follows directly (C. Rottman, unpublished) from the  $\hat{n}$  dependence of  $\gamma$  in the dislocation description of misfit boundaries [76].



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