

Roughening Transition of Crystals – Classical Thermodynamic Approach

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Abstract

In this contribution, we attempted a theoretical analysis on the validity of the widely-accepted idea that rough and singular surfaces can coexist in a crystal at equilibrium. By manipulating the Cahn and Hoffman capillarity vector, the conclusion that a crystal at equilibrium should be composed either of singular surfaces or of rough ones was reached.

Keywords : equilibrium crystal shape, roughening transition, interface structure, wulff theorem, capillarity vector

1. Introduction

It is well-known that the surfaces of crystals are either atomically ordered or disordered in accordance with the thermodynamic conditions imposed. The surface of an ordered structure, normally called singular surface, is enthalpy-dominant. On the other hand, the disordered surface, which is usually called rough surface, is entropy-dominant. When all the thermodynamic conditions except temperature are fixed, surfaces of a crystal tend to be singular at a relatively low temperature and rough at a higher temperature. This means that each state of the crystal surfaces is reversibly interchangeable, and the transition is called the roughening transition.

The importance of the presence of the roughening transition lies in the fact that the growth mode of crystals is critically dependent on the nature of the surface structure, i.e. whether the surface of interest is singular or rough. When the surface is rough, the surface advances continuously, because there is little energy barrier for the atomic attachment. In the other case, however, a driving force, which is large enough to trigger the formation of 2-dimensional nucleation, is needed for the surface to advance, because the atomic attachment onto a singular surface is energetically unfavorable.

It is commonly believed that the roughening transition of surfaces of a different crystallographic orientation takes places separately, because the enthalpy contribution to the crystal surfaces is greatly dependent upon the crystallographic orientation but the entropy contribution is practically orientation independent.[1-4] This indicates that under certain circumstances rough and singular surfaces should coexist in a crystal at equilibrium. There have been few objections to the idea in that external morphologies consisting of macroscopically faceted and curved surfaces

are frequently observed in a number of systems.[5]

Recently, there was a report on the coarsening kinetics of edge-rounded NbC crystals dispersed in a liquid-phase Co during a liquid-phase sintering.[6] Contrary to the common belief, it was found that the alleged rough surfaces, which are represented by a macroscopically observable curvature, in the crystal survived during the course of an active growth situation. Note that rough surfaces coexisting with singular surfaces should disappear as a result of an active growth because the growth rate of rough surface is far greater than that of singular surface.

To mediate the conflict between the theory and the experimental fact, the possibility that rough and singular surfaces can coexist in a crystal was reevaluated from the classical thermodynamic point of view. The result indicated that the coexistence of rough and singular surfaces is implausible.

2. Theory

A surface of a crystalline substance can be considered as a phase from the thermodynamic point of view, because the surfaces constituting a crystal shape is the Legendre transformation of the projected surface free energy of each surface. It means that any topic related to the equilibrium of crystals can be studied in terms of the well-established theory of phase equilibria.[1,7] Besides, in the phase equilibria among crystal surfaces, the atomic bonding direction and the crystallographic orientation correspond each to the component and the phase, respectively.

When a hypothetical crystal, which undergoes a morphological change by the application of thermal energy, is considered, the system belongs to a multi-phase reacting system. Note that the areal fraction of each surface tends to be

identical as the temperature increases. Therefore, an appropriate description for the Helmholtz free energy of a crystal under isometric and isothermal conditions can be written as

$$dF = \sum_{i,j} \bar{\gamma}_i^j dA^j \quad (1)$$

, where A refers to the area of each surface, and the superscript j and subscript i refer to phase and component, respectively. Notice that in Eq. (1) the partial molar property of the surface energy $\bar{\gamma}_i$ is used instead of the usual surface free energy γ_i , since the system of interest is the multi-phase reacting system. This partial molar property $\bar{\gamma}_i$ is deliberately contrived by Cahn and Hoffman and is called the capillarity vector.[8,9]

The application of the capillarity vector in the study of equilibrium crystal shape can be made easy by employing its graphical representation. From the definition of the capillarity vector, it is easy to see that the capillarity vector of a specific orientation corresponds to the diameter of a sphere tangent to the gamma plot at the orientation and passing through the origin as shown in Fig. 1.

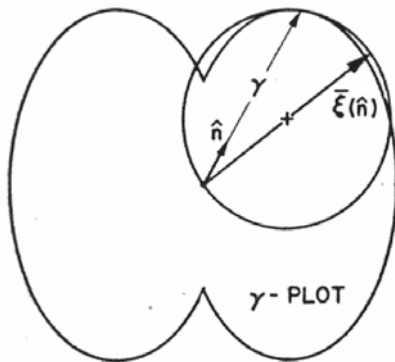


Fig. 1. A graphical representation of the capillarity vector. Adopted from Ref. 9.

Consider a hypothetical cube-shaped crystal, which is composed of singular $\{100\}$ surfaces with curved edges. Suppose that the constituting atoms are cube-shaped with 6 bonds, and the number of components and phases can be determined to be 2 and 3, respectively for a $[010]$ projected portion of the crystal as is shown in Fig. 2. Then, it is quite straight-forward from Fig. 2 (a) and (b), that the curved surface of a diagonal direction should be stepped and it can not be rough in definition.

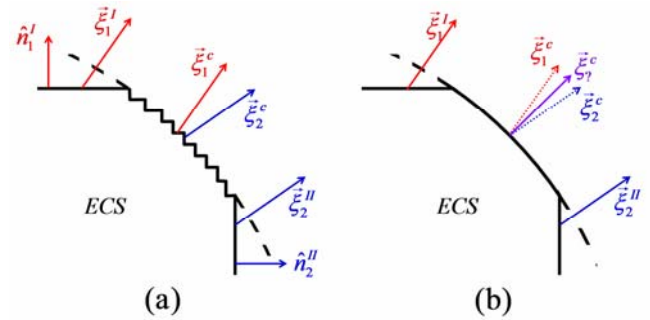


Fig. 2. Thermodynamic consideration on a hypothetical crystal consisting both of flat singular surfaces and of curved ones. Only when the curved surface is considered as a stepped one as shown in (a), the condition for the equilibrium is satisfied. For the curved surface to be atomically rough, an additional component should be newly introduced, which is logically implausible.

3. Summary

From the classical thermodynamic point of view, rough surfaces cannot be in equilibrium with singular ones, and the macroscopically observed curved surfaces are stepped singular surfaces.

4. References

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