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LANDAU THEORY OF FLATTENING PHASE TRANSITION IN GRAIN BOUNDARIES

A. Brokman[1] and V.I. Marchenko[2]

[1]Division of Applied Physics, Graduate School of Applied Science and Technology, Hebrew University, Jerusalem 91904, Israel.
[2]Groupe de Dynamique des Phase Condensee, Universite Montpellier II, Science et Techniques du Languedoc, Place Eugene Bataillon, 34095 Montpellier CEDEX 5, France*

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In 1989, Hsieh and Balluffi observed, for the first time, the de-faceting transition of a grain boundary in aluminum and gold [1]. In this experiment, a sharply faceted boundary consisting of two symmetric boundary phases that coexisted along edges changed reversibly upon heating to a curved and asymmetric flat boundary. The (in)stability of the faceted boundary had long been anticipated, observed, and discussed by Cahn [2]. According to this theory, faceted to a flat structural change is possible by means of a first order phase transition originated at the orientation dependence of α, the boundary excess free energy. It is difficult to explain the new experimental results in view of this theory in terms of two aspects: a. Hsieh and Balluffi questioned the stability of the observed many-edge faceted phase as each edge increases the system energy. They concluded that the faceted state was not fully equilibrated, and farther coarsening may occur; b. The experiment demonstrated that the transition to a flat boundary occurs by a continuous amplitude reduction. In view of this result, flattening may be interpreted as a second order phase transition.

A decade ago, it was shown that the elastic strain field stabilizes the multi-edge faceted state of interfaces [3]. In fact, the observation of a multi-edge structure manifests the important role played by elastic deformation in this system. In the present work, we employ the Landau theory and show that the elastic strain effect leads to flattening of a rough curved-modulated phase via a second order transition. In this transition, the amplitude of the modulated boundary decreases continuously and vanishes with a fixed periodicity at the critical temperature. In absence of experimental data at the critical point, we regard the amplitude decrease with small variation of wavelength below the transition as an evidence for boundary curving towards flattening. Indeed, the micrographs presented in Ref. [1] demonstrate that the facet corner is curved and a modulated structure is built below transition. Therefore, we suggest that the faceted phase undergoes two consequent transitions[1] to a flat phase, namely (Figure 1): a. a facet to a modulated phase through a roughening transition. As a result of this transition, sharp edges are curved and extend at the expense of facets; and, b. a modulated to flat phase transition at a critical temperature higher than the roughening temperature.

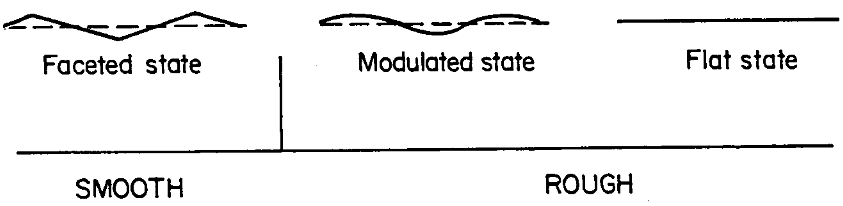

FIG. 1 The different states of grain boundary considered in this work. The "smooth" state consists of two-phase symmetric boundary facets coexisting at edges. As in the case of the smooth surface, perturbations in this state are localized to steps and grain boundary dislocations. Above roughening transition, we consider a "modulated" boundary phase which contains curved segments. This state is flattened through a second order phase transition which is the subject of the present discussion.

Consider a bi-crystal with asymmetric tilt grain boundary in the xy plane where y is the tilt axis, along which the bicrystal contains a reflection symmetry ($y \to -y$). The excess free energy of a boundary with a shape z(x,y) is

$$F^{gb} = \int \alpha(z'_x, z'_y)\sqrt{1+z'^{2}_x+z'^{2}_y}\,dxdy. \qquad (1)$$

To lowest order expansion in z', F^{gb} is given by $\frac{1}{2}(\tilde{\alpha}_{xx}z'^{2}_x+\tilde{\alpha}_{yy}z'^{2}_y)$ where the stiffness coefficients are $\tilde{\alpha}_{ij}=(\alpha\sqrt{1+z'^{2}_x+z'^{2}_y})''_{ij}$. ($\tilde{\alpha}_{xy}=\tilde{\alpha}_{yx}=0$ due to symmetry). Instability is evident when a stiffness coefficient is negative [4], in case of the above experiment: $\tilde{\alpha}_{xx}<0$. We Fourier expand the grain boundary free energy in its unstable modes (wavevectors parallel to the $\vec{q}_x$), i.e.:

$$F^{gb} \approx \frac{1}{2}\sum_{\vec{q}\,\|\,\vec{q}_x}\tilde{\alpha}_{xx}q^2|z_q|^2 \quad , \qquad (2)$$

and the instability combines growth of both the Fourier component of the boundary amplitude and its wavelength. However, higher order terms may (de)stabilize the boundary when $\tilde{\alpha}_{xx}$ is (positive) small. These terms are originated at possible curvature dependence of the boundary energy and the wavelength dependence of the strain field energy. We discuss each one of these terms separately.

When α depends on the boundary curvature (hence, on z''_{xx}), the linear term in z''_{xx}, i.e. $\int z''_{xx}z'_x\,dxdy$ is possible by symmetry, nevertheless, it vanishes since the integrand represents a total derivative. Therefore,

where γ is constant, assigned positive to maintain stability.
The elastic contribution to the bi-crystal energy is similar (to a multiple constant) to the one found for the case of curved surface by Andreev [5]. According to this result, the elastic contribution is proportional to $-|q||h(q)|^2$ where h(q) is the Fourier transform of the boundary slope z_x ($|h(q)|^2 = q^2|z_q|^2$):

$$F^{el} = -\beta \sum_q |q|^3 |z_q|^2 \quad , \tag{4}$$

where β is some positive number combines Lame constants and the components of the surface stress tensor [6]. Noteworthy is the minus sign in Eq.(4) which reflects a decrease of the system's free energy due to elastic relaxation.
In order to recover the second order term of the free energy expansion in the order parameter z_q, we add the different contributions of Eq.(2) through (4):

$$F_2 = \sum_{\vec{q} \| \vec{q}_x} (\frac{1}{2}\tilde{\alpha}_{xx} q^2 - \beta|q|^3 + \gamma q^4)|z_q|^2 \ . \tag{5}$$

It is seen that striction enhances the phase transition when $\tilde{\alpha}_{xx}$ is positive (yet small). Figure 2 plots the function in the bracket of Eq.(5) , g(q), at the critical temperature, T_C, for which g vanishes and obtains a local minimum at a finite wavelength, $q = q_0$.

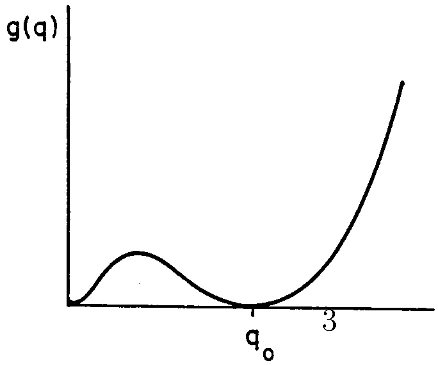

FIG. 2 A plot of the function $g(q) = \frac{1}{2}\tilde{\alpha}_{xx} q^2 - \beta|q|^3 + \gamma q^4$ at the critical temperature.

We now expand the free energy near q_0 when approaching T_C:

$$F_2 = \frac{1}{2} \sum [a(T - T_C) + b(|q| - q_0)^2]|z_q|^2 \tag{6}$$

$$F = \frac{1}{2}a(T - T_C)\left|z_{q_0}\right|^2 + C(q_0)\left|z_{q_0}\right|^4 \quad , \qquad (7)$$

where the third order term vanishes by translation symmetry of the flat phase (A three-vector star can not be formed with aid of the two vectors $\vec{q} = \pm q_0\hat{x}$), and expansion of Eq.(1) in z'_x yields $C \prec q_0^4$. Eq. (7) indicates a modulated-flat state second order phase transition. On approaching the critical temperature, the order parameter vanishes as $|T - T_C|^{1/2}$. At the critical temperature, the transition occurs at a fixed wavelength q_0.

In conclusion, an unwieldy problem combining the dependence of the bi-crystal free energy on grain boundary orientation, curvature and elastic strain field, reduced to a simple problem in the Landau representation. To its well recognized limitations (e.g. Ginzburg-Levanyuk criteria for validity), this representation makes the prediction of the flattening transition possible. This transition may qualitatively explain some of the experimental observations mentioned above, including the possible dependence of this transition on additional thermodynamic variables, such as the grain boundary solute atom concentration [7,8]. Farther application of the present theory requires refined experimental data, most importantly, the investigation of the boundary state at a temperature close to T_C. The application to the rough surface is obvious, and may open a door for future study.

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