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Stress relaxation during crystal growth

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Abstract – Recent experiments have shown that the theory used to descibe the Asaro-Tiller-Grinfeld instability is inadequate. The problem is identified and shown to arise from an ambiguity in the equilibrium condition formulated by Gibbs. Classical theories of solidification by Baker and Cahn (macroscopic) and by Frank and van der Merwe (microscopic) are extended to resolve the ambiguity. New experiments are presented that support the theoretical treatment.

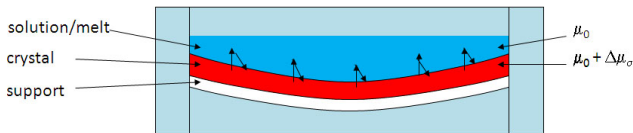**Introduction. –** **This is a sample of the working document 31/10/2011**

Fig. 1: Schematic of a simple experiment. A flat crystal placed on a support is in contact with a saturated solution. Then the support is bent and the crystal becomes compressively stressed. The change in chemical potential of the crystal will drive a mass flux to redistribute mass in the system.

ATG experiments and simulations. Consider the simple experiment illustrated in Figure 1. The crystal that is originally in equilibrium with the solution (they have the same chemical potential, μ_0 and there is no macroscopic change) is bent to generate compressive stress in the region adjacent to the fluid. The resulting change in the chemical potential of the crystal is

$$\Delta\mu = (1-\nu^2)\sigma^2/2E + \gamma\kappa, \tag{1}$$

where σ is the differential stress parallell to the interface, ν is Poissons ratio, E is Youngs modulus, γ is the interfacial tension and κ the local curvature of the interface. $\Delta\mu$ causes dissolution of the crystal. However, if the solution volume is finite this will raise the chemical potential of the solution above its equilibrium value μ_0 and this will tend to drive precipitation (growth). If possible, the excess dissolved material will precipitate (grow) on the existing crystal surface. What are the possible final outcomes of this experiment? The lowest free energy end state is clearly complete dissolution of the stressed crystal and growth of a new, unstressed crystal with the same volume and equilibrium crystal shape. What path will the system take and will it ever reach this low energy configuration?

The ATG instability

A solid under compressive stress with a rough solid-liquid interface will have higher stress in the grooves than at the peaks. This will generate a chemical potential gradient between stressed grooves and less stressed peaks and therefore there is a tendency to dissolve at the grooves and precipitate at the peaks (see Figure 2). This is the basic idea of the surface instability that was originally analysed by Asaro and Tiller [4] and Grinfeld [5]. The elastic energy tends to roughen the interface and the interfacial tension tends to smooth it. The critical lengthscale for which the two contributions balance (for a sinusoidal perturbation of the interface) is

$$\lambda_c = \frac{E\gamma\pi}{\sigma^2(1-\nu^2)}. \tag{2}$$

Linear stability analysis of the Asaro-Tiller-Grinfeld (ATG) instability indicates that there is a maximum unstable wavelength which is 3/2 to 2 times λ_c depending on the rate limiting process: diffusion or dissolution [1]. Kassner, Misbah et al. [2,3] showed that in the non-linear regime the ATG model predicts a coarsening and crack-like growth of the deepest valleys [6]. This cracking under compression reduces the strain energy of the compressed system in the same manner that fractures relieve the strain energy under tensile stress.
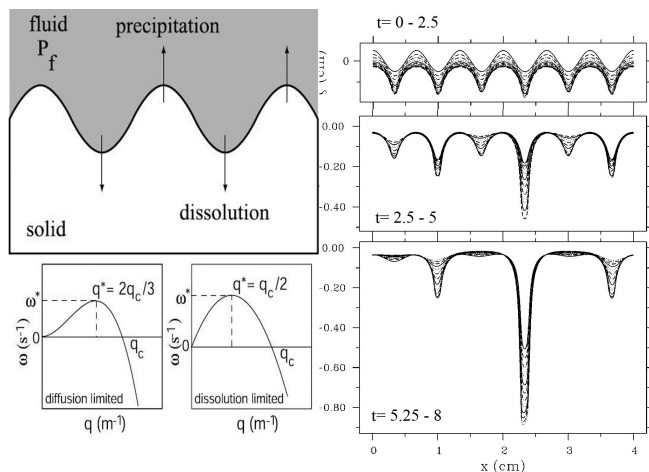
Fig. 2: Schematic of the Asaro Tiller Grinfeld (ATG) instability. **Left side**: In a solid under compressive stress in the horizontal direction a chemical potential gradient will exist between stressed valleys and less stressed ridge tops, and this gradient drives a mass flux from the valleys to the tops. A linear stability analysis of this situation yields a maximally unstable wave numbers depending on the rate limiting process: diffusion or dissolution [1]. **Right side**: Phase field modeling of the non-linear behaviour of the stress induced interface instability. Time evolution of an originally sinusoidal interface from top graph to bottom graph and between each dashed line in each graph [2,3].

The best documented experimental observation of the ATG instability was reported by Balibar et al [7,8] in helium crystals at 1 K under stress. They reported quantitative agreement between the maximally unstable length-scale predicted by the ATG linear stability analysis and the observed corrugations of about 7 mm. They also reported a relaxation of the corrugated pattern, but details were not given and they have never been explained.

Brittle salt in brine

Sodium chlorate ($NaClO_3$) is a brittle, ionic crystal which is very soluble in water. We have performed a series of different experiments on sodium chlorate under compressive stress in contact with its aqueous solution with an initial $NaClO_3$ concentration that is in equilibrium with the unstressed solid. Figure 3 shows images from one experiment [9] and the schematic interpretation of the whole set of experiments [9–11]. Initially, the originally smooth crystal-solution interface becomes rough with grooves perpendicular to the main stress direction and with a wavelength close to the maximally unstable wavelength predicted by the ATG model. Then the pattern coarsens and the length scale increases while the amplitude does not increase. Finally the surface becomes smooth again. Why does the interface topography go through the smooth - rough - smooth sequence while no external parameter is changed? The only possible interpretation is that the initial smooth crystal surface under compressive stress has a higher chemical potential than the solution while the final
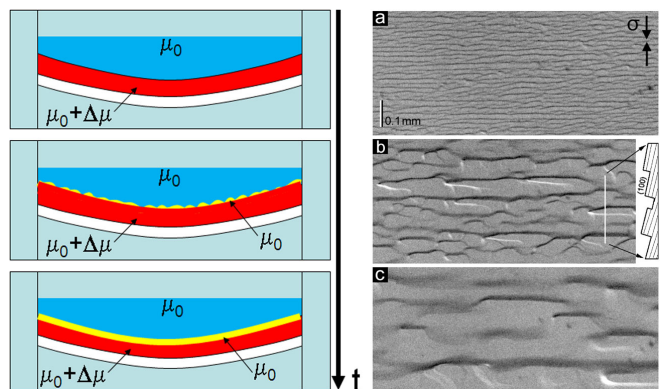

Fig. 3: Time evolution (top to bottom) of a compressively stressed crystal in contact with its solution. **Left side**: Schematic cross section of the experiment and the interpretation: an unstressed film is formed on the surface of the stressed crystal. **Right side**: Microscopy images of the crystal surface during one experiment showing the formation of grooves with the spacing predicted by the ATG theory and the subsequent coarsening of the pattern towards a smooth final state.

smooth crystal surface has the same chemical potential as the solution. In some of the experiments we could exclude the possibility that the chemical potential of the solution was raised to $\mu_0 + \Delta\mu$. The conclusion is therefore that the chemical potential of the crystal at the interface is close to μ_0. This indicates that there is a gradient in stress in the solid crystal from $\mu_0 + \Delta\mu$ in the bulk to μ_0 at the solid-liquid interface. The next section will show that this interpretation complies well with both experimental observations and microscopic theories from the field of epitaxial growth in vacuum.

Ambiguity in Gibbs' equilibrium of non-hydrostatically stressed solids. Dissolution is relatively simple to understand because the intitial and final states of the system are well specified. Precipitation on the other hand is more challenging because the final state of a volume of solute precipitated on a stressed solid is not necessarily obvious The implicit assumption in continuum models of dissolution and precipitation is that the precipitate inherits the stress state of the existing solid. The underlying microscopic picture is that precipitation proceeds by epitaxial growth, which implies that that atoms or molecules are added in perfect crystalline order to the existing crystalline lattice. Even in the ATG theory that is developed for perfectly isotropic solids (that is, for amorphous solids) the assumption that the precipitate "inherits" the stress state of the existing solid is maintained. Given this assumption it is not possible for the ATG theory to reach the final state of the experiment: a stress gradient inside the solid with a smooth surface. In fact there is no compelling reason why the assumption of a stressed precipitate should hold.

Gibbs understood the necessity of growth of a solid that was only hydrostatically stressed in order to reach equi-
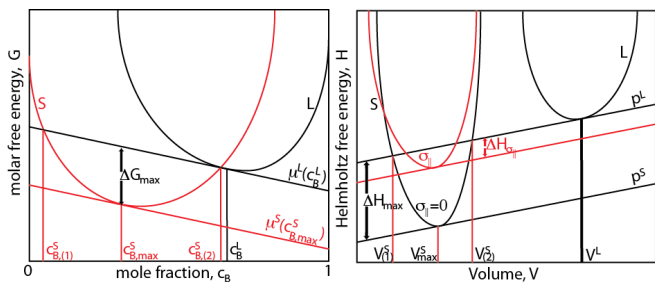
Fig. 4: Thermodynamic tangent diagrams to predict solidifying phase. **Left:** Gibbs energy diagram for solidifying composition after Baker and Cahn [13]. **Right:** Helmholtz energy diagram for solidifying volume and stress.

librium (In the section *The conditions of Internal and External Equilibrium for Solids in contact with Fluids with regard to all possible States of Strain of the Solid*, pp. 184-218 of [12]):

> ... yet the presence of the solid which is subject to the distorting stresses, will doubtless facilitate the commencement of the formation of a solid of hydrostatic stress upon its surface, to the same extent, perhaps, in the case of an amorphous body, as if it were itself subject only to hydrostatic stress.
>
> But in the case of a solid of continuous crystalline structure, subjected to distorting stresses and in contact with solutions satisfying the conditions deduced above, although crystals of hydrostatic stress would doubtless commence to form upon its surface (if the distorting stresses and consequent superaturation of the fluid should be carried too far), before they would commence to be formed within the fluid or on the surface of most other bodies, yet within certain limits the relations expressed by equations (393)-(395) must admit of realization, especially when the solutions are such as can be easily supersaturated.

For an amorphous, non-hydrostatically stressed solid the case was clear to Gibbs, whereas for a crystalline solid the equilibrium conditions he had formulated must be met *unless hydrostatically stressed crystals are precipitated*. This conditional statement of equilibrium is highly unsatisfactory in the otherwise pure equilibrium thermodynamics of Gibbs, and it has been the root of endless scientific debates.

Macroscopic theory of solidification. –

Microscopic theory of stress relaxation during growth. – In the treatment of phase change of one solid to another the grain boundary between the two phases (1 and 2) is considered to be coherent if the lattice parameters, a_i, match perfectly: $a_1 = a_2$. If there is only a small degree of mismatch, $\epsilon = (a_1 - a_2)/a_1$, an array

of dislocations at the grain boundary will be found. The coherent (or epitaxial) growth of one crystal on another crystal is technologically very important and the mechanism of dislocation incorporation has been studied in great detail since the seminal work of Frank and van der Merwe [14–16]. The energy cost of including a dislocation array with spacing p is

$$E_d = \frac{\mu b^2}{2\pi(1 - \nu)p}(1 + \ln h/r_0), \qquad (3)$$

where μ is the shear modulus, ν the Poisson ratio, b the Burgers vector and r_0 the core diameter of the dislocation and h is the thickness of the strained layer. The elastic energy gained by including the dislocation array is

$$E_e = \frac{2\mu(1 + \nu)\epsilon^2 h}{1 - \nu}. \qquad (4)$$

It follows that there is a critical thickness $h_c \propto 1/\epsilon$ for which the energy cost, E_d, and gain, E_e, are equal. This thickness is typically of the order of a nanometer for $\epsilon = 0.01$. The theory of critical thickness and the dynamics of inclusion of dislocations agrees well with experiments and atomistic scale simulations [16,17].

If we now consider growth on a crystal that is subject to elastic stress parallel to the growing surface, the lattice parameter of the stressed crystal is a_1 and that of the equilibrium crystal is a_2. The surface normal stress is equal to the pressure of the fluid from which the crystal grows. It follows from the treatment above that if the size of the stressed crystal (normal to the growing interface) is more than h_c the stressed crystal will gain more energy by forming misfit dislocations during growth than it costs to include these dislocations. Recent experiments on uniaxially stressed crystals in contact with its aqueous solution showed growth of an unstressed crystal on the stressed "substrate" [9].

Perspective. It follows from the simple result above that growth from a fluid phase on a non-hydrostatically stressed crystal can not be considered to be coherent except (perhaps) in the special case of excess surface normal stress (so-called force of crystallizon [18]). In the case of surface parallel stress the original stressed crystal and the unstressed growing phase are best considered two separate phases separated by a grain boundary.

Conclusions. – Recent experiments have shown that the theory used to descibe the Asaro-Tiller-Grinfeld instability is inadequate. The problem is identified and shown to arise from an ambiguity in the equilibrium condition formulated by Gibbs. Classical theories of solidification by Baker and Cahn (macroscopic) and by Frank and van der Merwe (microscopic) are extended to resolve the ambiguity. New experiments are presented that support the theoretical treatment.

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