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Introduction to "The Molecular Mechanism of Solidification", by J.W. Cahn, W.B. Hillig and G.W. Sears.

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By the mid 1950's, crystal-vapor interfaces were commonly believed to be atomically smooth and to advance by a stepwise growth mechanism: a monolayer nucleation barrier prevented continuous local motion of the interface normal to itself; growth was mediated by two-dimensional nucleation and lateral spreading of new monolayers or by growth spirals emerging from screw dislocations). Crystal-melt interfaces were commonly believed to be atomically rough and to advance by continuous local motion of the interface normal to itself without the need for these stepwise growth mechanisms.

In 1960 Cahn published "Theory of Crystal Growth and Interface Motion in Crystalline Materials" [Cahn 1960], in which he predicted that all interfaces would advance by a stepwise mechanism at sufficiently low driving force and by a continuous growth mechanism at sufficiently large driving force. These conclusions were the result of applying to interfaces involving crystalline materials the Cahn-Hilliard diffuse-interface theory [Cahn 1958], containing a gradient-squared energy cost associated with any spatially varying order parameter. The two phases were distinguished by a single order parameter. An equilibrium spatial profile of order parameter vs. distance normal to the interface was determined, and from it the interfacial tension, σ , was determined. If the profile is displaced by a fraction of a monolayer spacing, the resulting interfacial tension is higher: the interface has a stable equilibrium position. As the interface is moved normal to itself, σ varies approximately sinusoidally from its minimum value at stable equilibrium positions separated by the monolayer spacing, to a maximum value halfway between stable positions. The relative increase in σ from minimum to maximum value, characterized by the parameter $g = (\sigma_{\max} - \sigma_{\min})/\sigma_{\min}$, decreases very rapidly with increasing interface diffuseness.

For a nonzero driving force for solidification, the change in free energy as the interface moves normal to itself is obtained by adding this sinusoidally varying interface tension to a linear ramp. At sufficiently small driving forces local minima still exist, and the interface will advance not by moving uniformly across the barrier between minima but rather by one of the stepwise growth mechanisms mentioned above. For sufficiently large driving forces the barrier will give way to a monotonically decreasing free energy function of interface position, eliminating the need for lateral growth and permitting uniform normal growth. The transition from lateral growth to normal growth with increasing driving force occurs at a critical value of the driving force that depends so strongly on interface diffuseness that it is envisaged to be undetectably low for some interfaces and unattainably high for others, but detectable for interfaces of intermediate diffuseness.

The transition between lateral and normal growth regimes occurred via a transitional regime in driving force, which Cahn examined with the Cahn-Hilliard diffuse-interface theory for nucleation [Cahn 1959]. Previously, steps on a crystal surface or interface had been generally thought of as atomically sharp. Cahn pointed out that steps could be diffuse laterally, much as an interface could be diffuse in a direction normal to itself. He derived the analogous expression for the equilibrium diffuseness of a step and examined the implications of diffuse steps for the stepwise growth mechanisms. As the driving force increases, the radius of the critical nucleus for two-dimensional nucleation decreases. When the radius of the critical 2D nucleus approaches the step diffuseness,

the classical kinetic relationships for interface velocity vs. interface undercooling, which are based on sharp-interface models, begin to break down and the transitional regime is entered. As the transitional regime is traversed, the barrier to 2D nucleation should vanish, as it does for 3D nucleation [Cahn 1959]. If one insists on evaluating this reduced barrier using classical sharp-step concepts, one would infer for the step a vanishing effective σ_e , the tension associated with the "riser" of the step. A similar transitional regime was identified for screw dislocation-mediated spiral growth, as the spacing between adjacent arms of the spiral decreased with increasing driving force.

In 1964 Cahn, Hillig, and Sears applied Cahn's concepts specifically to solidification. They derived and refined kinetic rate laws for the dependence of interface velocity on interfacial undercooling for the limiting regimes of screw dislocation growth, 2D nucleation-limited growth, and continuous growth, and for the transition between them. They enumerated the various experimental criteria that could be used to distinguish between stepwise and continuous growth and interpreted the meaning of various experimental observables. They surveyed the existing experimental literature and found important evidence for stepwise growth at low undercoolings in a number of cases. And they pointed out the necessary critical experiments that were required for further progress to be made in the comparison of theory and experiment.

The work of Cahn and coworkers stimulated substantial debate about the nature of the crystal/melt interface and the mechanism of solidification. An alternative point of view [Jackson 1967] was that the crystal/melt interface is always atomically sharp but it can be atomically rough or atomically smooth; the roughness of the interface and the growth mechanism are independent of driving force and depend solely on the equilibrium entropy change of the transformation and on the fraction of the nearest neighbors that are in the plane of the interface -- high entropy-of-fusion materials having atomically smooth interfaces and requiring stepwise growth.

In hindsight, my own interpretation of this debate is that for solidification, the theory of Cahn and coworkers is strictly applicable only if all order parameters distinguishing the crystal and melt have the same behavior as the single order parameter used in the model. This "criticism" does not imply that the crystal/melt interface cannot be diffuse, as envisaged by their model, and move as such. However, we should not be surprised should we find qualitative, rather than quantitative, agreement with experimental results for solidification. Related models with multiple order parameters were developed much later [Oxtoby 1982, Curtin 1989, Khanna 1997].

As were several of Cahn's early models, this is a mean field model, permitting much of the essential physics to be illuminated at the lowest possible level of complexity. As such, it ignores certain types of fluctuations - in this case, equilibrium fluctuations in the position of the interface (and the step) with lateral position. Because this model preceded the application of renormalization group theory to interface fluctuations [Weeks 1979, Nozieres 1987], the implications of fluctuations were not yet fully appreciated. At the time, it was not recognized that fluctuations were very important in determining the qualitative behavior of an interface at and above the thermodynamic roughening transition. At the roughening transition the corrugation in the free energy vs. mean interface position curve vanishes. Hence as the equilibrium properties of the interface are varied so as to create greater roughness and approach the thermodynamic roughening transition, one should expect the driving force range encompassing stepwise growth to shrink to zero, rather than merely to be restricted to unobservably small driving forces as predicted by mean field.

The difficulty of performing reliable quantitative experiments that are demonstrably free of possible artifacts has permitted the questions, "How sharp is the crystal/melt interface?" and "What determines the growth mechanism?" to remain open for almost three decades. The difficulty of direct experimental probes of the structure of a crystal/melt interface, and the difficulty of knowing the interfacial undercooling, have been important contributors to the lingering uncertainties.

However, by the mid 1980's several molecular dynamics simulations with realistic interatomic potentials were producing interfaces of finite diffuseness, and, with one exception, by the early 1990's the key qualitative predictions of experimental behavior from the model of Cahn and coworkers were confirmed, namely:

- (1) Stepwise growth should be observed at small enough undercoolings regardless of entropy of fusion or interface orientation;
- (2) As the undercooling is increased in the stepwise growth regime, eventually a positive deviation should be observed from the velocity as a function of undercooling predicted by the classical sharp-interface models of 2D nucleation-limited growth or spiral growth and extrapolated from the data from lower undercoolings;
- (3) Continuous growth should be observed at large enough undercoolings regardless of entropy of fusion or interface orientation;
- (4) The presence of dislocations should affect the growth rate only below the transition to continuous growth.

Stepwise growth has been observed at small driving forces for many materials (but not for all materials for reasons discussed above), partially confirming prediction (1). Strong microstructural and kinetic evidence now exists for a transition from stepwise to continuous growth at sufficiently large undercoolings, even for materials with huge entropies of fusion such as germanium ($\Delta S_f = 3.6 \text{ k}$) [Evans 1990, Li 1995], confirming prediction (3). Most significantly, a thorough investigation of the solidification kinetics of liquid gallium by Peteves and Abbaschian [Peteves 1991a, Peteves 1991b] has confirmed all four predictions for this system. They observed all three mechanisms operating for both (001) and (111) interface orientations. Most notably, in confirmation of prediction (2), their interpretation of the measured 2D nucleation-limited growth kinetics using a sharp interface and sharp steps resulted in a fitted value of σ_e that was constant for a range of undercooling, and then dropped precipitously with further increases in undercooling.

The work of Cahn and coworkers was the first to predict the now commonly-accepted notion of "kinetic roughening" [Gilmer 1984, Weeks 1979], i.e., at sufficiently large driving forces the growth mode changes from lateral to normal. As such, it anticipated by more than two decades the ideas of kinetic roughening of the crystal-vapor interface during growth, which is currently an area of intense research activity [Krug 1997]. The model of Cahn, Hillig, and Sears has been further developed at the fundamental end by density-functional theories of the crystal-melt interface [Oxtoby 1982, Curtin 1989, Khanna 1997] and fluctuation theory [Nozieres 1987], and at the practical end by phase-field models of solidification [Boettinger 1996, Fried 1997]. As the seminal work in the structure and mobility of the crystal/melt interface, it will continue to serve as the starting point for our understanding of these issues.

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