

# This Week's Citation Classic

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An attempt to calculate the exact concentration profile of a coherent interface in an alloy in a miscibility gap resulted in the discovery of mathematical solutions representing modulated structures, ordering domains, and critical nuclei. A diffusion equation, taking concentration gradients into account, could then be constructed. It can describe the development of any fluctuation in composition. [The SC<sup>®</sup> indicates that this paper has been cited over 155 times since 1961.]

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"As a student in Stockholm, I met Gudmund Borelius, who taught that there should be no nucleation barrier for alloys inside the spinodal. He also argued that nucleation outside the spinodal should occur by a gradually growing composition difference, contrary to the popular belief in a gradual growth in size. Attempts to combine the two approaches had failed.

"In 1953, I went to MIT to study with Morris Cohen and was intrigued by his teaching of the nucleation theory by Becker, who estimated the surface energy from the difference in composition between nucleus and matrix by counting the bonds crossing the interface. His surface energy came out proportional to the square of the composition difference.

"A roommate of mine, Erwin Underwood, studied the decomposition of Au-Ni alloys and observed discontinuous precipitation inside the spinodal, contrary to Borelius's prediction that the matrix should be unstable. I wondered how the concentration profile should look at the reaction front and started with Becker's model. It struck me that the surface energy could decrease to half if the sharp discontinuity in composi-

tion splits up into two steps and even further by a wider spread. The most favourable composition could be found by minimizing the free energy. I thus obtained a difference equation involving a unit of four atomic planes. After choosing the compositions of three planes, the next one could thus be calculated, etc., through the whole system. Different starting values gave different concentration profiles and it was fascinating to discover their relation to various well-known phenomena. Some oscillated periodically like the modulated structure sometimes observed inside the spinodal. One profile showed a gradual change between the two stable compositions of the miscibility gap and described an equilibrium interface. Negative interaction energies gave an ordered structure with domains. Finally, alloys outside the spinodal gave a profile showing a critical nucleus. It seemed that I had accidentally hit upon that combination between the two different approaches to nucleation that people had been looking for. The work was completed by modifying the equation of diffusion.

"The work was presented in my doctoral thesis in 1956 and finally published in 1961. My theory was rapidly accepted largely due to the fact that another of my roommates, John Hilliard, brought a copy of my thesis with him to General Electric in Schenectady where he met John Cahn. Together they put the theory in a more general mathematical form which made possible further developments, e.g., the generalization to three dimensions which was particularly valuable for the application to nucleation. An important factor was also Cahn's inclusion of coherency stresses which explained Underwood's results.<sup>1</sup> Finally, my work inspired Cahn's important contributions on diffuse interfaces.<sup>2</sup>

"I believe my paper is often cited because it led to the acceptance of a special class of reaction, the spinodal decomposition. My simple mathematics may still have the advantage that it can describe all stages of a reaction. A more recent review appears in *Phase Transformations*.<sup>3</sup>

1. Underwood E E. *Precipitation in gold-nickel alloys*. PhD thesis. Cambridge, MA: Massachusetts Institute of Technology, 1954.
2. Cahn J W. Theory of crystal growth and interface motion in crystalline materials. *Acta Metallurgica* 8:554-62, 1960.
3. Hillard J E. Spinodal decomposition. *Phase transformations*. Metals Park, OH: American Society for Metals, 1970. p. 497-560.