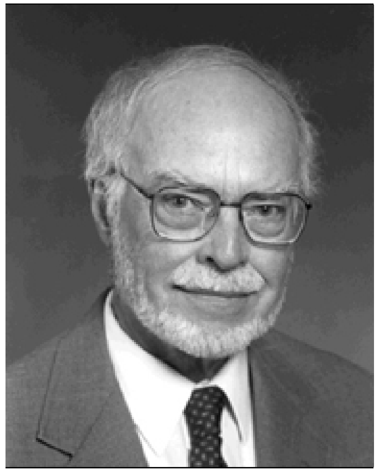
NATIONAL ACADEMY OF SCIENCES

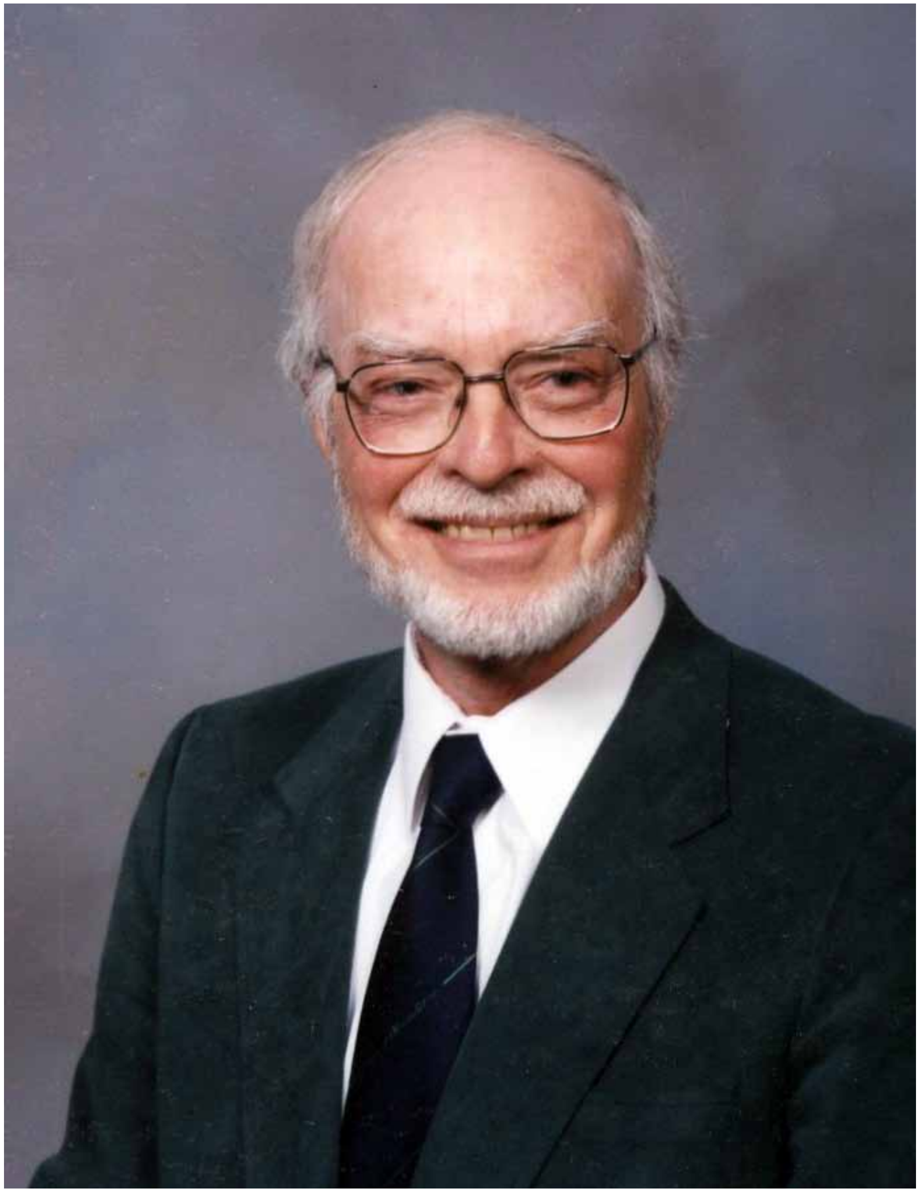


WILLIAM W. MULLINS

1927-2001

A Biographical Memoir by

ROBERT F. SEKERKA



W. W. Mullins

WILLIAM WILSON MULLINS

March 5, 1927–April 22, 2001

BY ROBERT F. SEKERKA

WILLIAM ("BILL") MULLINS was born in Boonville, Indiana, to parents of Scottish and English descent; several ancestors were early settlers of Jamestown in the 1600s. His father, Thomas Clinton Mullins, was an industrialist in coal and oil and served as mayor of Boonville for several years before Bill was born. Bill's mother was Ruth Wilson, the daughter of the owner of a large dry goods store situated on Boonville's main square. The family moved to Chicago in 1930.

Bill grew up in Chicago, where he was enrolled in the Lab School of the University of Chicago, a program that began in kindergarten and lasted seamlessly through high school, college, and graduate school. He was a precocious student; an upper classman in the same program remembered him as a scholar-athlete—a "golden boy." Bill received three degrees in physics from the University of Chicago: a Ph.B. in 1949, an M.S. in 1951, and a Ph.D. in 1955. At the Lab School in the seventh grade, he met his future wife, June Bonner, whom he married on June 26, 1948, about the time that Bill was finishing his undergraduate degree after two years in the Navy. They eventually had four sons, William Wilson, Jr., and Oliver Clinton, born in Chicago, and Timothy Bonner and Garrick Russell, born after the family moved to Pittsburgh.

During his distinguished career, Bill became well known for his seminal research in physics, primarily on theoretical problems in materials science, as well as for his work in academic administration. The principal impact of his research was to bring to materials science the power of mathematical modeling, which enabled the quantification of complex phenomena.

Bill's doctoral work involved the measurement of grain boundary energies in bismuth and boundary motion induced by application of a magnetic field, which led to his first publication in 1956. His father Clint, a businessman, was skeptical about Bill's pursuit of a higher degree but seemed to satisfy himself by remarking, "Well, bismuth, now bismuth is a useful metal." Perhaps Bill hadn't strayed too far since his uncle, George Mullins, was a professor of mathematics at Columbia University. Bill's doctoral work was directed by Cyril Stanley Smith, a principal in the founding of Chicago's Institute for the Study of Metals.

Bismuth is diamagnetic but magnetically anisotropic; so grains of different orientation will have different magnetic energies per unit volume in an applied magnetic field, which results in a driving force for grain boundary motion. I recall Bill remarking about his frustration in trying to get the grain boundaries in bismuth to move, but ultimately a large-enough magnetic field induced their motion. This experience was probably the motivation for Bill's subsequent intense interest in the topography of metal surfaces, because features such as scratches and grooves could impede the motion of grain boundaries that intersect a surface.

In 1955, Bill was hired by Clarence Zener of the Westinghouse Research Laboratories in Pittsburgh, where he worked until 1960 on various problems involving metal surfaces and grain boundary motion. A (second) 1956 paper of Bill's dealt with idealized two-dimensional grain boundaries that moved with velocities proportional to their local curvature. He was able to show that the time rate of increase of the area of a grain with arbitrarily curved boundaries and surrounded by a number n of other grains was proportional to $n - 6$, provided that all boundaries make angles of 120 degrees when they intersect the other grains at triple junctions. This was a generalization of the $n - 6$ rule of John von

Bill had a special talent for explaining scientific ideas in a simple way, even to those who lacked his facility with physics and mathematics.

Neumann, who treated an idealized soap froth with boundaries having uniform curvature. In that same paper, Mullins determined the shapes of curved boundaries that can be magnified without change of shape, translated with constant velocity, or rotated with constant angular velocity.

In 1957, Mullins also developed a quantitative theory of grain boundary grooving, according to which a grain boundary that intersects a surface gives rise to an ever-deepening groove. This happens because the need to balance surface tensions and grain boundary tension requires a local V-shaped triple junction, which in turn causes surface curvatures whose related chemical potentials provide a driving force for transport away from the junction. In a 1958 paper, Bill treated moving grain boundaries and showed how grain boundary grooves could impede their motion. In 1959, in collaboration with Paul Shewmon, the predicted kinetics of grain boundary grooving were verified by means of experiments involving copper bi-crystals, for which groove shapes after a period of annealing were measured by interferometry. Mullins and Shewmon also collaborated on experiments involving scratch decay and surface melting.

When Bill was at Westinghouse, I had the good fortune to be hired right after graduation from high school as his technician. While I built laboratory apparatus, polished samples (including bismuth, which was

Mullins as a young man. ≡

easy to scratch), and did numerical calculations on a mechanical calculator, Bill patiently taught me about the science that was involved, and I was inspired to try to merge this knowledge with my own education that was going on simultaneously at night school; Bill had a special talent for explaining scientific ideas in a simple way, even to those who lacked his facility with physics and mathematics. This led to our friendship, a long period of scientific collaboration and mentoring, and ultimately to my own Ph.D. in physics.

Bill's love of and aptitude for teaching resulted in 1960 to his joining the Carnegie Institute of Technology (CIT) as an associate professor in the Department of Metallurgical Engineering. There, together with his graduate student Roy King and Westinghouse collaborators Malcomb Fraser and Robert Gold, he continued to develop quantitative descriptions of surface scratch decay (1962) and grain boundary motion. Scratch decay, like grain boundary grooving, is driven by transport from regions of large curvature, and therefore high chemical potential, to regions of smaller curvature. His analysis relied on the assumption of local equilibrium, which enabled chemical potential to be related to local curvature—differences in chemical potential would drive processes such as diffusion, which led to change of surface shape.

During the summers of my graduate education at Harvard University in the early 1960s, I returned to Pittsburgh to work with Bill at CIT. Our first paper together (1962) involved an extension of Herring's treatment of faceting on crystal surfaces.

We used the dual theorem of linear programming to show that facets of more than three orientations could not lower the free energy more than those of only three orientations, and the orientations that gave the greatest reduction of free energy by faceting were identified in terms of the distance to a contact plane of the equilibrium shape.

Perhaps stimulated by the instability of crystal surfaces to faceting, Bill conjectured that many of the idealized shape-preserving solutions of the Stefan problem for precipitation from solution and solidification (crystallization from the melt) were unstable. Such solutions had been developed by G. P. Ivantsov [1] and Frank Ham [2] for growing cylinders, spheres, and ellipsoids as well as for translating paraboloids. Bill suggested that I investigate this matter by assuming that the growth was quasi-static and governed by Laplace's equation, so that there was an analogy to electrostatic problems. We found an exact solution due to Maxwell for charged metal spheres that intersected one another at right angles. If one such sphere is very small compared to the other, it appears to be a perturbation in the shape of a small hemispherical "boss," and the potential gradient in the neighborhood of the boss was found to be much larger than the gradient near the rest of the sphere. Translated into the precipitation problem, this meant that a small perturbation on a growing sphere (the boss) would grow faster than the sphere itself, thus leading to an instability of shape—to a morphological instability. We wrote our findings up for publication but the paper was rejected by the reviewers, who felt that there was an unrealistic effect of the discontinuity of slope where the boss met the sphere. One reviewer demonstrated this by an expansion in Legendre polynomials.

Bill and I felt intuitively that the basis of the instability was correct and we proceeded to prove it. He decided to analyze the problem by using an expansion in spherical harmonics to represent the perturbed shape, possibly inspired by Fermi's liquid drop model of nuclear fission or Bill's previous work on the decay of sinusoidal perturbations of surfaces. This approach also enabled the treatment of the effect of interface curvature on chemical potential, and hence on concentration or temperature. The result was a robust linear theory of instability brought about by a variation of local gradients related to shape, but a theory that also accounted for the stabilizing effect of capillary forces related to the variation of local chemical potential. The interplay of destabilizing gradients and stabilizing capillarity led to the conclusion that some perturbations would grow while others would decay, thereby providing a size effect for such morphological instability, which is a precursor to dendritic growth. This finding was later published in our 1963 paper "Morphological stability of a particle growing by diffusion or heat flow."

In 1961, with the support of Guggenheim and Fulbright fellowships, Bill went on sabbatical leave to Paris for a year. He and June and their four boys, aged three to eleven, crossed the Atlantic on the French ocean liner *Liberté*, and the time in France was an exciting experience for every member of the family as well as one of the most productive years of Bill's scientific career. He collaborated with Jacques Friedel to study the effect of interface curvature on solute partitioning between interstitial solid solutions. Meanwhile, Bill and I continued to work on the morphological stability problem by snail mail (unfortunately, no email at that time) to finish our 1963 paper and especially to extend the analysis to the unidirectional solidification of a binary alloy.

The extension involved simultaneous treatment of two coupled fields—a thermal field with a long-length scale and a solute field with a considerably shorter-length scale—plus capillary effects. The problem was vexing because the difference in scale lengths gave rise to a difference in time scales for heat flow and diffusion, so both could not simultaneously be described by quasi-static fields. This complication was eventually alleviated by analyzing a steady state in a moving frame of reference. The resulting instability, as published in our 1964 paper, was explained by solving the dynamical equations for heat flow and diffusion for a perturbed interface; this supplanted the constitutional-supercooling concept advanced by Tiller, Rutter, Jackson, and Chalmers [3] to rationalize the cellular and dendritic instabilities that are so prevalent in experimental studies of solidification of alloys. Although nearly 60 years have passed, that 1964 paper ("The stability of a planar interface during solidification of a binary alloy") is still on the most-cited list of the *Journal of Applied Physics*.

The methodology of the morphological stability work was subsequently applied to many related problems in materials science. See [4] for a more detailed account of its early development. In 1980 it was brought into the mainstream of the physics community by means of Jim Langer's article [5] in *Reviews of Modern Physics*. In a follow-up article [6] Langer wrote:

> The Mullins-Sekerka analysis can be viewed as doing for solidification theory approximately what Rayleigh and Chandrasekhar [7] did in identifying the onset of Bénard convection patterns; both analyses compute the way in which the quiescent state of a system becomes linearly unstable against infinitesimally weak pattern-forming deformations.

Subsequent to Langer's review, there was a flurry of related activity in the physics community—which extended the analysis to more complicated phase transformations (eutectic solidification, for example) and into the nonlinear regime—to understand pattern formation during crystal growth and dendritic solidification from the melt.

Shortly after returning from leave in Paris, Bill took on responsibilities of academic administration, first as head of the Department of Metallurgy (1963–1966) and then as dean of the Carnegie Institute of Technology (1966–1970), a college that combined science and engineering departments. Among other innovations, he established a promotions policy that stressed documentation of excellence in scholarship and started the Department of Biological Sciences. Perhaps Bill's greatest accomplishment as dean was playing a key role in the formation of Carnegie Mellon University from the merger of the Mellon Institute with Carnegie Institute of Technology. He essentially split CIT into two colleges: an engineering college that retained the original CIT name; and a science college, the Mellon College of Science, that included the new Department of Biological Sciences as well as the budding Department of Computer Science. Amazingly, during those administrative years, he continued to conduct first-rate scientific research.

The methodologies that Bill pioneered to quantify surface morphological changes led to a series of related studies with his graduate students. He and his student Fred Nichols developed a theory of changes of a surface of revolution driven by capillarity-induced surface diffusion (1965), and this theory was used to understand the blunting of field emitter tips of electron microscopes. Bill and Eugene Gruber developed an extended analysis of surface scratch smoothing as well as a theory of the anisotropy of surface free energy in 1967. Much later (1993), with his student François Génin and in

Mullins studies a bubble raft model of a two-dimensional crystal, circa 1956. Evident are grains, grain boundaries, vacancies and surface structure. Photo courtesy William Mullins Jr.

collaboration with Paul Wynblatt, Bill returned to theories of surface morphology change, including thermal pitting at grain boundaries and the effect of stress on grain boundary grooving.

Another area of interest was phase transformations and associated processes. Examples are microscopic kinetics of step motion and growth processes with John Hirth in 1963; growth of austenite into ferrite with David Grozier and Harry Paxton in 1965; growth of nitrogen austenite into alloyed ferrite with John Pavlik and Paxton in 1966; and hydrogen embrittlement and periodic precipitation in silver with Ronald Klueh.

Bill's curiosity about common physical phenomena often triggered diverse ventures in stochastic modeling. For example, he was intrigued with the fact that the time for an hourglass to empty was so reproducible, even though it involved the stochastic flow of many particles. This led to a theory of particle flow under gravity (1972) and later to experimental studies. Two unusual applications outside the realm of materials science were Bill's estimation of the size distribution of overlapping impact craters in 1976; and his observations of the flickering patterns of light at the bottom of a swimming pool, which led to his studies of thresholds of random optical patterns (1978). Other of Bill's studies of stochastic modeling included treatment of diffusion with stochastic jump times and as a Markoff process.

Bill also studied the related topics of size distributions in precipitation, coarsening of microstructures, and grain growth. Examples were the statistical self-similarity hypothesis in grain growth and coarsening (1986); and, with Jorge Viñals, self-similarity in processes driven by surface free-energy reduction, which led in 1998 to a theory of self-similarity and coarsening of

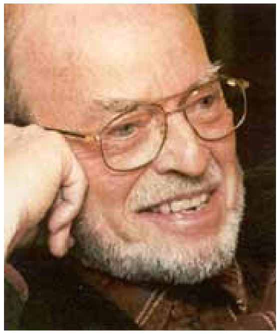
It was during those periods that I learned more about Bill's deep physical intuition. He had the incredible ability to guess the form of the final answer, which often took me many hours to verify by detailed calculation.

three-dimensional particles. Coarsening of a particle population occurs because the smaller particles have greater surface curvature, and hence higher chemical potential, than the larger particles, resulting in a flux of material from smaller to larger particles and in eventual disappearance of small particles from the population. If there is self-similarity, the particle-size distribution function takes on a fixed shape if all particle sizes are scaled with the size of the particle that, at that moment, is neither growing nor decaying. Bill extended these scaling ideas to a variety of transformations, including grain growth.

Throughout his career, Bill made important contributions to fundamental aspects of thermodynamics and kinetics as they relate to materials. These findings included a proof that the two-dimensional shape of minimum surface free energy is convex; development of variational principles and bounds for the conductance of a heterogeneous, locally anisotropic body (1979); and determination of conditions for thermodynamic equilibrium of a crystalline sphere in a fluid (1984). In this same category of research, I had the great pleasure of collaborating with Bill on deducing conditions for which the transport matrix for diffusion and heat flow in fluid systems is symmetric (1980) and on unifying the thermodynamics of crystalline solids (1985). We worked together on the 1980 paper and the 1985 paper for about five years each in an attempt to make them as general as possible without sacrificing accuracy.

It was during those periods that I learned more about Bill's deep physical intuition. He had the incredible ability to guess the form of the final answer, which often took me many hours to verify by detailed calculation. The focus of the 1980 paper was the identification of a measurable set of forces, frames, and fluxes for which the Onsager symmetries would be valid, as opposed to relying on abstract forces and fluxes for which these symmetries can sometimes be violated.

For the 1985 paper, Bill supplied the key idea of expressing thermodynamic quantities per unit cell (suitably coarse-grained), rather than in terms of per unit volume or mass, and without specifying the details of the cell and by allowing all chemical components of the cell to vary independently by virtue of unspecified point defects. This approach allowed for a unified treatment of chemical potentials that could later be specialized to more specific models of crystals—such as a Gibbs crystal consisting of one immobile supercomponent (Gibbs' substance of the solid [8]); or a Larché-Cahn crystal [9] for which substitutional atoms could move only by exchange with vacancies or each other (leading to diffusion potentials); or to crystals having self-interstitial defects and sublattices. We were also able to make contact with Herring's two alternative chemical potentials [10], one based on holding lattice sites constant and



Bill Mullins, late 1990's.

the other based on holding "holes" (vacancies minus interstitials) constant.

Throughout his career, Bill received many awards, including the Mathewson Gold Medal of the American Institute of Mining, Metallurgical, and Petroleum Engineers in 1963, election to the National Academy of Sciences in 1984, the Robert Franklin Mehl Award of the Minerals, Metals & Materials Society in 1994, the von Hippel Award—the highest accolade of the Materials Research Society—in 1995, and the Cyril Stanley Smith Award of the International Conference on Grain Growth in 1998. Many of these awards had associated prestigious lectures [11], and Bill was known to be a marvelous lecturer, organized, complete, and precise but always able to capture and convey the essence of esoteric ideas in a simple way. Those same characteristics permeated his teaching as well as his discussions with colleagues. Bill loved to teach science, formally or informally, to family and friends. I quote his oldest son, William:

> Science lessons from Dad were a constant in our house. He had that propensity so common to physicists and mathematicians to mull over his current research problems during most of his waking hours, and he frequently did so out loud, carefully explaining the problems along the way. Dad tried to teach me the concept of logarithms starting at about age nine, fruitlessly. I don't know how many times he drew the hyperbola and talked about the area underneath, and I could not understand what possible interest or utility that held. When I was 10, he explained the four-color problem to me, and for a couple of years I brought him dozens of possible solutions—which he would patiently recolor using just four colors. My mother said that Dad believed he could teach calculus to anyone until he tried to teach it to her—and realized there are people who are incapable of learning calculus, even under his tutelage!

Bill and his wife June were world travelers, interested in learning about history and other cultures but also about natural phenomena. I recall his excitement after traveling far to see a total solar eclipse. He was fascinated by natural optical phenomena, such as the aurora borealis and the "green flash" that could be seen at sunset just as the last rays were disappearing. Of course, a science lesson followed every time he mentioned such a phenomenon. While at Westinghouse, I recall Bill's obtaining a special pass from the lab director, Zener, so that we could go to the roof of the building and watch Mercury rise. One of the security officers wondered aloud why we needed to be on the roof to "see the mercury rise," which he associated with a thermometer, but he was not about to challenge Zener's authorization. We had a good chuckle all the way to the roof.

Bill and June Mullins, 1996.

Bill and June were strong supporters of social causes, such as improvement of the environment, conservation, gender equality, and world peace. Bill once had aspirations, and certainly the aptitude and stature, to be a college president, but his love of science outweighed the hassles of higher academic administration and his own ambition. So he left administration in 1970 to become professor of applied science at CIT and was later elevated to the special rank of University Professor, the highest academic honor of Carnegie Mellon University. Meanwhile, June taught at a school for disabled children and completed graduate work in special education at the University of Pittsburgh, earning her Ph.D. in 1968. Subsequently she served on the Pitt faculty for 30 years.

During the Vietnam War days, there was much student unrest and Bill marched with the students both in Pittsburgh and Washington, DC. During the latter march, he became very upset upon witnessing the harsh treatment of marchers by security forces, so much so that he returned home and wrote a substantial check to the campaign of George McGovern. Shortly afterward, Bill's name appeared on Richard Nixon's political "Enemies List," a status of pride to Bill and June alike.

The couple celebrated their 50th wedding anniversary in 1998 at a gala party at the Pittsburgh Athletic Association, attended by over 100 friends and family and featuring a classical music recital by an excellent Pittsburgh trio. Sadly, this love of life and things intellectual would come to a premature close because a year later each of them was embroiled in a battle with cancer. June died on March 16, 2000, and Bill followed on April 22 of the following year. Even as Bill was fighting his losing battle with illness, he continued his scientific research nearly every day. He remarked that "Science is my temple," a place where he could mentally dwell and be at peace, even as his physical condition deteriorated. Fittingly, some of Bill's work—including energy barriers to shape changes of faceted crystals, with Gregory Rohrer and Cathy. Rohrer (2001); and on a linear bubble model of abnormal grain growth, with Viñals (2002)—was published posthumously because Bill continued to work and collaborate with colleagues even in his final days.

NOTES

1. Ivantsov, G. P. 1947. Temperature field around spherical, cylindrical, and needle-shaped crystals which grow in supercooled melt. *Dokladi Akademii Nauk SSSR* 58:567–569. English translation by G. Horvay. 1959. General Electric Research Report 60-RL-(2511M). Schenectady, NY: GE Research Information Section.

2. Ham, F. S. 1959. Shape-preserving solutions of the time-dependent diffusion equation. *Quart. J. Appl. Math* 17:137–145.

3. Tiller, W. A., K. A. Jackson, J. W. Rutter, and B. Chalmers 1953. The redistribution of solute atoms during the solidification of metals. *Acta. Met.* 1:428–437.

4. Sekerka, R. F. 2004, The theory of morphological stability. In R. S. Feigelson (ed.). 50 years progress in crystal growth. Amsterdam: Elsevier, 81–86; originally published 1986 in *AACG Newsletter* 16:1–3.

5. Langer, J. S. 1980. Instabilities and pattern formation in crystal growth. *Rev. Mod. Phys.* 52:1–28.

6. Langer, J. S. 1984. Dynamics of dendritic pattern formation. *Materials Science and Engineering* 65:37–44.

7. Chandrasekhar, S. 1961. *Hydrodynamic and hydromagnetic stability*. London: Oxford University Press.

8. Gibbs, J. W. 1961. *The scientific papers of J. Willard Gibbs, Volume 1: Thermodynamics*. New York: Dover Publications. Originally published in 1906 by Longmans, Green, and Company.

9. Larché, F., and J. W. Cahn. 1978. Nonlinear theory of the thermochemical equilibrium of solids under stress. *Acta Met.* 26:53–60.

10. Herring, C. 1953. The use of classical macroscopic concepts in surface energy problems. In *Structure and properties of solid surfaces*, R. Gomer and C. S. Smith (eds.). Chicago: University of Chicago Press.

11. Mullins, W. W. 1996. Remarks on the evolution of materials science (von Hippel Award address). *Mat. Res. Soc. Bulletin* 21:20–27.

SELECTED BIBLIOGRAPHY

1956

Magnetically induced grain boundary motion in bismuth. *Acta Met.* 4:421–432.

Two-dimensional motion of idealized grain boundaries. *J. Appl. Phys.* 27:900–904.

1957

Theory of thermal grooving. *J. Appl. Phys.* 28:333–339.

1958

The effect of thermal grooving on grain boundary motion. *Acta. Met.* 6:414–427.

1959

With P. G. Shewmon. The kinetics of grain boundary diffusion in copper. *Acta Met.* 7:163–170.

1962

With R. T. King. Theory of the decay of a surface scratch to flatness. *Acta. Met.* 10:601–606.

With R. F. Sekerka. Application of linear programming theory to crystal faceting. *J. Phys. Solids* 23:801–803.

1963

With R. F. Sekerka. Morphological stability of a particle growing by diffusion or heat flow. *J. Appl. Phys.* 34:323–329.

With J. P. Hirth. The microscopic kinetics of step motion in growth processes. *J. Phys. Chem. Solids* 24:1391–1404.

1964

With R. F. Sekerka. The stability of a planar interface during solidification of a binary alloy. *J. Appl. Phys.* 35:444–451.

SELECTED BIBLIOGRAPHY

1965

With J. D. Grozier and H. W. Paxton. The growth of austenite into ferrite in the iron-nitrogen system. *Trans. AIME* 233:130–142.

With F. A. Nichols. Morphological changes of a surface of revolution due to capillarity-induced surface diffusion. *J. Appl. Phys.* 36:1826–1835.

1967

With E. E. Gruber. On the theory of anisotropy of crystalline surface tension. *J. Phys. Chem. Solids* 28:875–887.

1972

Stochastic theory of particle flow under gravity. *J. Appl. Phys.* 43:665–678.

1976

An estimator of the underlying size distribution of impact craters. *Icarus* 29:113–123.

1978

With R. F. Quick and R. N. Lucas. Contrast thresholds of random patterns. *Photographic science and engineering* 22:72–75.

1979

Variational principles and bounds for the conductance of a homogeneous, locally anisotropic body. *J. Appl. Phys.* 50:6754–6760.

1980

With R. F. Sekerka. Proof of the symmetry of the transport matrix for diffusion and heat flow in fluid systems. *J. Chem. Phys.* 73:1413–1421.

1984

Thermodynamic equilibrium of a crystalline sphere in a fluid. *J. Chem Phys.* 81:1436–1442.

1985

With R. F. Sekerka. On the thermodynamics of crystalline solids. *J. Chem. Phys.* 82:5192–5202.

SELECTED BIBLIOGRAPHY

1986

The statistical self-similarity hypothesis of grain growth and coarsening. *J. Appl. Phys.* 59:1341–1349.

1993

With F. Y. Génin and P. Wynblatt. The effect of stress on grain boundary grooving. *Acta Met. et Mater.* 41:3541–3547.

1998

With J. Viñals. Self-similarity and coarsening of three-dimensional particles on a one- or two-dimensional matrix. *J. Appl. Phys.* 83:621–628.

2001

With G. S. Rohrer and C. L. Rohrer. Nucleation energy barriers for volume-conserving shape changes in crystals with nonequilibrium morphologies. *J. Am. Ceram. Soc.* 84:2099–2104.

2002

With J. Viñals. Linear bubble model of abnormal grain growth. *Acta Mat.* 50:2945–2954.