

# Advanced Engineering Thermodynamics

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# **Advanced Engineering Thermodynamics**

*To my Cristina and Teresa*



# Preface

I have assembled in this book the notes prepared for my advanced class in engineering thermodynamics, which is open to students who have had previous contact with the subject. I decided to present this course in book form for the same reasons that I organized my own notes for use in the classroom. Among them is my impression that the teaching of engineering thermodynamics is dominated by an abundance of good introductory treatments differing only in writing style and quality of graphics. For generation after generation, engineering thermodynamics has flowed from one textbook into the next, essentially unchanged. Today the textbooks describe a seemingly “classical” engineering discipline, that is, a subject void of controversy and references, one in which the step-by-step innovations in substance and teaching method have been long forgotten.

Traveling back in time to rediscover the history of the discipline and looking into the future for new frontiers and challenges are activities abandoned by all but a curious few. This situation presents a tremendous pedagogical opportunity at the graduate level, where the student’s determination to enter the research world comes in conflict with the undergraduate view that thermodynamics is boring and dead as a research arena. The few textbooks that qualify for use at the graduate level have done little to alleviate this conflict. On the theoretical side, the approach preferred by these textbooks has been to emphasize the abstract reformulation of classical thermodynamics into a sequence of axioms and corollaries. The pedagogical drawback of overemphasizing the axiomatic approach in engineering is that engineers do not live by axioms alone, and that the axiomatic reformulation seems to change from one revisionist author to the next. Of course, there is merit in the simplified phrasing and rephrasing of any theory: this is why a comparative presentation of various axiomatic formulations is a component of the present treatment. However, I see additional merit in proceeding to show how the theory can guide us through the everexpanding maze of contemporary problems. Instead of emphasizing the discussion of equilibrium states and relations among their properties, I

see more value in highlighting irreversible processes, especially the kind found in practical engineering systems.

With regard to the presentation of engineering thermodynamics at the graduate level, I note a certain tendency to emphasize physics research developments and to deemphasize engineering applications. I am sure that the engineering student—his<sup>†</sup> sense of self esteem—has not been well served by the implication that the important and interesting applications are to be found only outside the domain chosen by him for graduate study. If he, like Lazare and Sadi Carnot two centuries earlier, sought to improve his understanding of what limits the “efficiency” of machines, then he finished the course shaking his head wondering about the mechanical engineering relevance of, say, negative absolute temperatures.

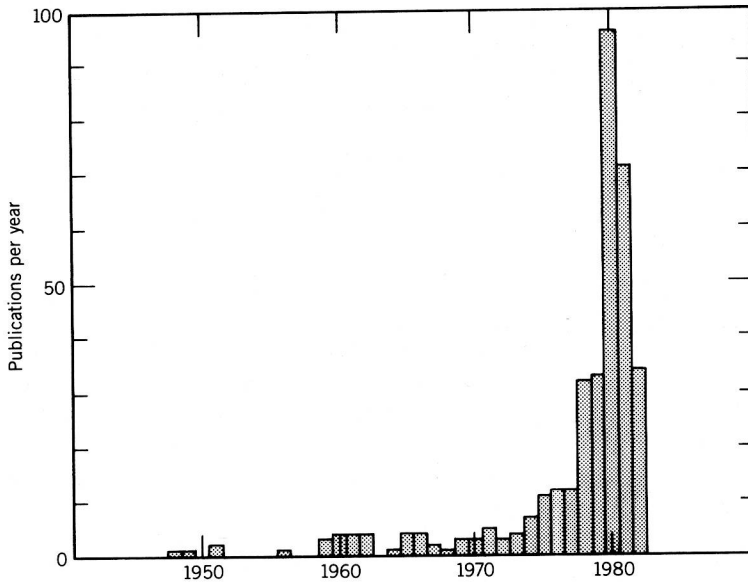
These observations served to define my objective in designing the present treatment. My main objective is to demonstrate that engineering thermodynamics is an active and often controversial field of research, and to encourage the student to invest his creativity in the future growth of the field. That there is opportunity for research in engineering thermodynamics is amply documented by Liu and Wepfer’s recent survey of publications in just one portion of the field, namely, in the area of second-law analysis [1]<sup>‡</sup>. The explosion of interest in this area is illustrated in Fig. P.1, which is reproduced from Ref. 2; it is further accentuated by the publication of no less than seven monographs and textbooks in the three years preceding Liu and Wepfer’s survey [3–9].

The other considerations that have contributed to defining the objective of the present treatment are hinted at by the title *Advanced Engineering Thermodynamics*. The focus is being placed on “engineering” thermodynamics, that is, on that segment of classical thermodynamics that addresses the production of mechanical power and refrigeration in the field of engineering practice. I use the word “thermodynamics” in spite of the campaign fought on behalf of “thermostatics” as the better name for the theory whose subjects are either in equilibrium or, at least, in local equilibrium (more on this later, pp. 69–72). I must confess that I feel quite comfortable using the word “thermodynamics” in the broad sense intended by its creator, William Thomson (Lord Kelvin): this particular combination of the Greek words *therme* (heat) and *dynamis* (power) is a most appropriate name<sup>§</sup> for the field that united the “heat” and “work” lines of activity that preceded it (Table 1.2, pp. 31–33).

<sup>†</sup>Masculine pronouns are used throughout this treatment only for succinctness. They are intended to refer to both males and females.

<sup>‡</sup>Numbers in square brackets indicate references listed at the end of each chapter.

<sup>§</sup>The appetite for the “thermostatics” nomenclature is stimulated by comparisons with the dynamics/statics differentiation that is practiced in the field of mechanics: I believe that the contemporary mechanics meaning of “dynamics” is being mistakenly viewed as the *origin* of “-dynamics” in “thermodynamics.”



**Figure P.1** Research publication activity in the area of second-law analysis [2].

Finally, I view this as an “advanced” course in engineering thermodynamics because it is the natural outcome of my own interaction with the research arena and with students who were previously acquainted with the subject of classical thermodynamics. There are at least two ways in which every subject can be advanced by a second course such as this. One is a “horizontal” expansion into the more remote fields intersected by the subject; the other is a “vertical” expansion, that is, a deepening of our understanding of the most basic concepts that define the subject. In the present treatment, I have followed the second approach because I see it as a more effective means of conveying a bird’s-eye-view of engineering thermodynamics. An exhaustive coverage of the horizontal type already exists in the “handbooks”; and justice to each peripheral domain can be done only in specialized courses such as compressible fluid dynamics, combustion, turbomachinery, refrigeration and air conditioning, cryogenics, etc.

I have followed the vertical approach in order to make a statement of what I consider effective as a pedagogical tool. Although it has become fashionable to associate completeness and volume with “goodness,” in this course I have made a conscious effort to focus on the structure of the field. I invite the research student to make his own contributions to this structure. For this last reason, the more applied segments of the present treatment are dominated by the topics that have attracted my own interest as a researcher.

To summarize, the combined research and pedagogical mission of this effort is to take a second look at the field, to make this view accessible in a one-semester course taken by individuals whose initial understanding of the



subject is by no means homogeneous. Depth is provided through a comparative discussion of the various ways in which the fundamentals have been stated over the years, and by reestablishing the connection between fundamentals and contemporary research trends such as the “exergy” methodology.

\* \* \*

The preceding words are the true preface because I wrote them in 1984, as I was starting the research for this book. I was then in the middle of a sabbatical leave at the University of Western Australia, which happened to be my first official assignment as a professor at Duke. Upon my arrival at Duke, I decided to use my enhanced freedom for the purpose of bettering my research and my life in general. Thinking in depth about engineering thermodynamics was one result of that decision. The fact that large numbers of thermal engineers continued to regard the field as mature is precisely why I picked engineering thermodynamics as a treatise topic: I not only saw merit in questioning the established point of view, but I also knew that a true research frontier is, quite often, the territory overlooked by the crowd.

As I look back at the past 3 to 4 years, I see a most gratifying project, a constant source of intellectual pleasure and new ideas. This project forced me to think on my own about those areas—the gaps—of which I knew the least. It challenged me to be creative and produce my own version of what fits best in any particular blank area. Overall, this book helped me diversify and enrich my research, which is why during this period I was able personally to take steps in new directions, such as the axiomatic formulation of classical thermodynamics (chapter 2), the graphic condensation of the relations between thermodynamic properties (chapters 4 and 6), the design of power plants for maximum power (chapter 8), the theory of the ideal conversion of solar radiation (chapter 9), and the design of refrigeration plants for maximum refrigeration effect per unit time (chapter 10). And, relative to engineering thermodynamics as a whole, this book gave me the opportunity to assemble in the same place many of the modern as well as the long-forgotten references. I also used every opportunity to do what I like best—produce original graphics.

Working on this book has been recreational. I did most of my thinking while walking through the Duke Forest between my West Campus office and our house in the Forest Hills section of Durham. I spent many hours consulting the truly exceptional collection of books of the libraries of Duke University. Ours is one university that from its early days in the 1800s invested in the important things. I made also many trips to the Library of Congress in Washington, DC, where, while reading the original writings, I had a chance to use the French, German, Latin, and Russian I learned in school.

The main contributor to the rewarding atmosphere of this project was Mary. I have benefited from her wisdom, sense of strategy and intellectual honesty during all my projects, big and small. This time, however, her participation transcended a number of much more important projects: the birth of child, the move from Colorado to North Carolina (via Western Australia!), and the triumphant completion of her PhD in business administration at the University of California, Berkeley. What I owe her is best condensed in the dedication that opens my *Convection Heat Transfer*.

I also benefited from my year-long association with Dr. Peter Jany of the Technical University of Munich, who generously contributed a most up-to-date section on critical-point phenomena in chapter 6. I will always remember the many conversations in which we compared notes on American engineering versus the German version, which had so much influence in Central Europe and Russia.

I recognize also the contribution made by Linda Hayes, who not only typed the manuscript, but also volunteered her rare talent of organization and sense of symmetry to the raw material that I have produced. Her work can be viewed directly in the *Solutions Manual*, which is available as a separate book. This manual can be obtained by writing to Wiley-Interscience (605 Third Avenue, New York, NY 10158) or directly to me.

At various stages, I was helped by old friends, colleagues in academia, and new students. Ren Anderson, Shigeo Kimura, Dimos Poulikakos, and Osvald V. Trevisan kept me in touch with their respective corners of the frontier and the literature. I am very grateful to my thermodynamics colleagues at Duke, Prof. C. M. Harman, Prof. E. Elsevier, and Prof. J. B. Chaddock, for commenting critically on early versions of the manuscript. While using those early drafts in the classroom, I collected many useful suggestions from the students, among whom I must mention: J. Gottwald, J. L. Lage, P. A. Litsek, A. Mahajan, D. P. Mendivil, M. Wang, Z. Xia, and Z. Zhang. Looking ahead, I will appreciate it very much if users of this book will write to call my attention to the imperfections that may have slipped into the final version.

ADRIAN BEJAN

Durham, North Carolina  
October 1987

## REFERENCES

1. Y. A. Liu and W. J. Wepfer, Theory and applications of second law analysis: A bibliography, in R. Gaggioli, ed., *Thermodynamics: Second Law Analysis*, Vol. II, American Chemical Society Symposium Series, ACS, Washington, DC, 1983, Chapter 18.
2. A. Bejan, Second law analysis: The method for maximizing thermodynamic

efficiency in thermal systems, invited position paper presented at the ASME-NSF Workshop on Research Goals and Priorities in Thermal Systems, Ft. Lauderdale, FL, April 25-27, 1984; published in W. O. Winer, A. E. Bergles, C. J. Cremers, R. H. Sabersky, W. A. Sirignano and J. W. Westwater, *Research Needs in Thermal Systems*, ASME, New York, 1986.

3. J. E. Ahern, *The Exergy Method of Energy System Analysis*, Wiley, New York, 1980.
4. M. V. Sussman, *Availability (Exergy) Analysis*, Mulliken House, Lexington, MA, 1981.
5. R. N. S. Rathore and W. F. Kenney, *Thermodynamic Analysis for Improved Energy Efficiency*, AIChE Today Series, AIChE, New York, 1980.
6. A. Bejan, Second law analysis in heat transfer and thermal design, in *Advances in Heat Transfer*, Vol. 15, pp. 1-58, 1982, Chapter 1.
7. M. J. Moran, *Availability Analysis: A Guide to Efficient Energy Use*, Prentice-Hall, Englewood Cliffs, NJ, 1982.
8. A. Bejan, *Entropy Generation through Heat and Fluid Flow*, Wiley, New York, 1982.
9. J. D. Seader, *Thermodynamic Efficiency of Chemical Processes*, Manual 1 in E. P. Gyftopoulos, ed., *Industrial Energy-Conservation*, MIT Press, Cambridge, MA, 1982.



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A.B.



## About the Author

Adrian Bejan received his B.S. (1972, Honors Course), M.S. (1972, Honors Course), and Ph.D. (1975) degrees in mechanical engineering, all from the Massachusetts Institute of Technology. He taught at M.I.T. until 1976 as a Lecturer and Research Associate. From 1976 until 1978 he was a Fellow of the Miller Institute for Basic Research in Science, at the University of California, Berkeley.

Adrian Bejan joined the faculty of the University of Colorado as an assistant professor in 1978 and was promoted to associate professor in 1981. Three years later he was appointed full professor with tenure at Duke University.

Professor Bejan is the author of 130 technical articles on a diversity of topics in natural convection, combined heat and mass transfer, convection through porous media, transition to turbulence, second law analysis and design, solar energy conversion, cryogenics, applied superconductivity, and energy policy. He is the author of two earlier graduate-level textbooks, *Entropy Generation through Heat and Fluid Flow* (Wiley, 1982) and *Convection Heat Transfer* (Wiley, 1984).



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