

# VARIOUS APPROACHES TO THERMODYNAMICS

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## ABSTRACT

The paper surveys classical and recent approaches to thermodynamic analysis. Each approach is characterized by the type of questions asked and the types of results obtained. We conclude with a number of current challenges and open problems for thermodynamic analyses.

## THE CLASSICAL THERMODYNAMIC PARADIGMS

The word thermodynamics conjures up a very definite subject in the minds of most scientists and engineers. Interestingly, the subjects it conjures up for a physicist, a chemist, a biologist, a mechanical engineer, and a chemical engineer have remarkably little overlap. Of course, all versions of the subject share the three laws and the associated constructs such as free energy, entropy, etc.. The basic cause of divergence is their focus on different systems of interest.

The differences in thermodynamics as viewed by the different types of thermodynamicists become apparent by comparing the paradigm texts in standard use. The physics version of the subject is embodied in Callen's well-known text [1]. For the chemists, Lewis and Randall's classic text revised by Pitzer and Brewer [2] is the definitive treatment. We should also mention that both physics and chemistry curricula are steadily evolving toward more statistical mechanics based approaches which are displacing these classical paradigms. It is harder to point to a definitive text for biologists. Typically they begin with some training in the chemists' version of thermodynamics at the level of an undergraduate physical chemistry course, but then refine this to a currency driven picture of cellular processes which generate or consume ATP and other similar molecules that serve as the free energy currency for cellular processes. This picture was nicely developed in Lehninger's Bioenergetics [3] whose essential themes survive in modern biochemistry texts such as the one by Lehninger, Nelson, and Cox [4]. The paradigm among the mechanical engineering community is probably best exemplified in Joseph Keenan's classic work [5]; modern texts elaborate further on the points that Keenan selected out as defining the mechanical engineers' topics of interest. Availability (exergy) is one such topic whose importance has grown considerably since Keenan resurrected

it from Gibbs' original treatise [6]. Chemical engineers typically cut their thermodynamic teeth on the analyses presented in texts such as Smith [7].

Built upon these different paradigms comes a slew of contenders for new types of thermodynamics. This paper attempts to give an admittedly biased overview of a sample of these different approaches in response to a request from our chairman, Professor Ishida. We conclude with a list of modern challenges for thermodynamic analyses.

## NEWER CONTENDERS

The most mature among these contenders is irreversible thermodynamics which dates back to the 1930's and the work of Onsager. In fact one might question listing this as a "new" contender since Callen's text devotes several chapters to the subject. We chose to list it explicitly here, since it represents an active and developing field of endeavor. The power of this formalism, based on a linear flux-flow relationship, is limited to the near-equilibrium regime. In this regime, irreversible thermodynamics gives accurate expressions for the rate of entropy production. It also gives rise to Prigogine's theorem characterizing near equilibrium steady states as ones which minimize the entropy production rate, and leads further to the idea of dissipative structures. The approach has made some tantalizing, albeit less than quantitative, inroads to our understanding of far from equilibrium phenomena including some systems of biological interest.

Extended irreversible thermodynamics (EIT), as the name implies, is an outgrowth of irreversible thermodynamics. It extends the fundamental equation often referred to as the first law expressing the differential of energy in terms of the differentials of the traditional thermodynamic variables by adding terms involving the differentials of the fluxes. The statistical mechanical formulations of the theory have been worked out and confirm the macroscopic ansatz postulating such an expansion. Attempts to justify EIT at a more fundamental level based on the Boltzmann equation lead to difficulties and leave this approach ultimately deriving its justification from a maximum entropy hypothesis. Such hypotheses belong to the information theoretic approach to thermodynamics.

The information theoretic formulation of thermodynamics became a definitive paradigm in the now classic papers by Jaynes [8]. This formulation has had many successes outside traditional thermodynamics as attested by the annual MaxEnt conferences, the nineteenth of which, Maxent99, will be held this August in Boise, Idaho [9]. The information theoretic approach has also led to important work within the traditional domain of thermodynamics problems, notably in chemical physics where it has led to the notions of different temperatures for different degrees of freedom (vibrational, rotational, translational, spin) and has been an important tool for analyzing nascent product distributions in chemical dynamics.

One important lesson from both EIT and the information theoretic approach concerns the idea of separability of time scales in a process. Basically, this idea assures us that when different processes in a system occur on widely different time scales, then a thermodynamic description which treats some degrees of freedom as completely equilibrated (fast) and others as completely frozen (slow) can give an accurate description of the process on intermediate time scales. This is how we arrive at, say vibrational temperature for processes in which the vibrational energy is separately conserved. In fact, the idea of time scales is crucial in any thermodynamic description, since we always ignore certain degrees of freedom as being too slow to be of interest, e.g. nuclear transitions at room temperature in most materials. As pointed out in Tolman's classic monograph [10], without this assumption, all equilibrium systems would be composed mostly of Fe56. Recent progress in singular perturbation theory has shown how to improve on the thermodynamic description when the time scales are only weakly separable [11].

The approaches above have come primarily from physics and chemistry. The biological version of the subject has evolved steadily but this evolution has merely supplied the detail required for an accurate quantitative understanding of energetics in biological systems. While a comparison of Lehninger's 1970 biochemistry book [12] with his 1994 book [4] reveals tremendous progress, new syntheses are lacking. Such new syntheses are likely to come soon, however, as foreshadowed by the recent success of the quantum mechanical description of photosynthesis in purple bacteria. In addition, our ability to experimentally manipulate these systems has improved greatly and this offers another omen of great strides to come.

Before proceeding to new approaches related to engineering thermodynamics, we pause to mention a school of thermodynamics that has emerged primarily from mathematics departments. The approach is known as rational thermodynamics [13] and has as its primary concern the problem of finding a rigorous axiomatic framework that can accommodate complex thermodynamic systems such as milk and concrete. While these formulations have added some insight into the mathematical structure of the thermodynamic formalism, better progress has been made in our understanding of the thermodynamics of complex systems from the work of the chaos / nonlinear dynamics community using the tools of statistical mechanics.

Progress in engineering thermodynamics has come primarily from the approach known as exergy analysis. This approach has been successful at forging reliable tools to quantify detailed analyses of exergy degradation in a plant. Such analyses can pinpoint potential savings and how such savings can be achieved. A similar, though much less demanding approach to energy integration in plant

operations is known as pinch analysis. The basic problem considered in this approach is how to combine heating and cooling demands in a way that minimizes the use of additional sources and sinks.

In this context, we mention also the approaches of thermoeconomics [14] and exergoeconomics [15]. These schools of thought carry out analyses which blend the economic and the thermodynamic variables to understand problems such as global economic policy and chemical plant design respectively.

Finally we come to a group of approaches which we will call control thermodynamics. Included in this group is finite-time thermodynamics [14] and entropy generation minimization [16]. These approaches were left for last in part because the blending of control ideas and thermodynamics is the author's candidate for major progress in the near future. The basic question concerns the characterization of what is achievable during the control of a thermodynamic process. Note that this is a natural extension of that portion of traditional thermodynamics which deals with reversible processes: the ultimate bounds to what can be achieved. Note further that systems in which some agent exercises control of the process include biological systems, computing systems, and engineering systems. Reversible control is usually excluded by the demand that the process take place at a finite rate using finite resources.

The name control thermodynamics originated with Anatoly Tsirlin's work [17] exploring the optimal control of the thermodynamic processes. Criticisms voiced at ECOS'98 for the name finite-time thermodynamics were convincing. Michel Feidt suggested that something closer to finite resource thermodynamics might be more a propos. While Adrian Bejan's name of entropy generation minimization is another possible candidate, this name misses a large part of the potential control space admissible for many interesting problems. For example, it misses the difference between minimum entropy production operation and maximum power operation for a process. In summary, we advocate adopting Tsirlin's name of control thermodynamics for this family of approaches.

Note an important difference between control thermodynamics and the other approaches described above. In control thermodynamics, the aim is not to describe what happens but what might possibly happen. The immediate next question is: how much does it cost to make a thermodynamic process proceed at a certain finite rate? We conclude by mentioning a debate in this community concerning the extent to which various irreversibilities must be counted. The engineering members would insist that all irreversibilities be counted [18], while the science members (the present author among them) would argue that to understand each mode of exergy degradation, it is best to shut off all but one or at most a few modes and see what can be achieved.

## **SOME CURRENT CHALLENGES**

We conclude this survey of approaches to thermodynamics by listing some current challenges to thermodynamic analysis. The problem of finding thermodynamic characterizations of living systems has been with us for a few generations but it is only now that sufficiently detailed information is pouring in. In fact, the accelerating rate of progress in most fields of science and engineering poses numerous challenges to thermodynamic understanding. For example, the achievement of ultra low (nanokelvin)

temperatures using atom stopping techniques poses a challenge to heat engine theory to provide a thermodynamic analysis of such cooling and to predict limits to the efficiency with which such cooling can be carried out. In the field of chemical thermodynamics, the big challenges are posed by combinatorial reactions, biosequence analysis, and protein folding. Computing poses its own set of thermodynamic questions. For quantum computing: How fast is coherence lost during a quantum computation and how much work does it cost to counteract such loss? What about fundamental bounds to how well conventional computer algorithms can perform? What are the limits of information mining algorithms such as simulated annealing for global optimization? And finally: What can one achieve with a coding channel given finite resources? Ever improving encryption algorithms pose challenges for information theoretic analyses which would give control thermodynamic versions of Shannon's "reversible" bound.

We conclude with our admitted bias: control thermodynamics. One central open problem here is of an engineering nature: How can one design an economically practical heat engine which can carry out a heat shuffle between many sources and sinks more efficiently than pinch analysis would dictate. An efficient and adaptable engine of this type would revolutionize energy integration.

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