MICROANALYTIX

# The Classical Thermodynamics and Statistical Mechanics of Interacting Systems

**A Prospectus for Classical Theory,**
**Volume 2 of The Theory of Interacting Systems**

**by**
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**"Something there is that doesn't love a wall . . ."**

The paradox of thermodynamics is the need to reconcile the irreversible behavior of macroscopic bodies with the reversible mechanics of the microscopic particles that compose them. This paradox is compounded by the fact that current thermodynamics is not dynamic, so we are forced to encompass a changing world within a timeless formalism.

An adequate account of macroscopic bodies requires a thermodynamics in space and time that is based in the particle mechanics and keeps account of the transfer of conserved quantities between them. Central to this effort is understanding the significance of boundaries between these bodies. Robert Frost's lines speak of the costs associated with the division of the world into parts. Niels Bohr examined its implications for what we can know and what we can say. These ideas are the starting point for framing a thermodynamics in space and time constructed out of the mechanics of the microscopic particles.

Portions of the text of this Prospectus are excerpted from the Preface, Table of Contents, Chapter 1, and the Back Cover of *The Theory of Interacting Systems, Volume 2, Classical Theory* published by MicroAnalytix. It is referred to as CIS in this document. Similarly, The Theory of Interacting Systems is referred to as TIS.

## 1. Problems with Current Thermodynamics

The work in this series stemmed from a statement made by Niels Bohr in his 1930 lecture to the Faraday Society in England. He felt that new classical ideas, similar to the concept of complementarity in quantum mechanics, would play a role in the proper understanding of the relation of thermodynamics to statistical mechanics. When I turned to the literature for an explanation of how thermodynamics is related to the interacting particles described by statistical mechanics, I found that no general theory of the connection between the quantities defined in thermodynamics and the underlying particles existed. The existing theory of this relationship at equilibrium cannot deal with change and no generalization into non-equilibrium thermodynamics had been widely considered as successful. The work of Maxwell and then Boltzmann came the closest to providing a nonequilibrium theory, but their work was marred by persistent paradoxes associated with the conflict between the irreversibility of thermodynamics and the reversibility and recurrence properties of the equations of particle motion. Examining these issues, I found that the standard resolutions offered for the paradoxes surrounding irreversibility, recurrence, the second law of thermodynamics and entropy, were neither satisfying physically nor mathematically cogent.

Because Bohr's analysis of the epistemological issues in physics was the impetus for this investigation, his understanding of the fundamental issues has played an important role. For this reason, the first volume in the series was concerned with the Bohr's analysis of the connections between knowledge, theory, and experiment, in light of the changes in physics brought by quantum mechanics.

In the face of interpretational problems associated with the uncertainty relations and the wave-particle duality, Bohr was concerned with finding and expressing conditions sufficient for obtaining unambiguous answers in experiments. Bohr addressed two important issues in his analysis of this problem that have significant implications for thermodynamics and statistical mechanics. The first is the requirement that the variables associated with distinct interacting macroscopic systems of particles are independent. This is in accord with the standard practice in physics of singling out a particle system for study and representing the forces exerted on it by its environment using arbitrary potentials and boundary conditions. In quantum theory, the requirement of independent variables itself turned out to be important in determining the representation of the particle system in the quantum formalism and the interpretation of experiments. This independence requirement also plays a central role in the Theory of Interacting Systems as a condition on the mathematical representation of interacting systems.

The second issue that Bohr addressed with significance to thermodynamics is concerned with the need to distinguish the proper domains of application for our concepts. Pursuing this in the TIS investigation of thermodynamics

led to a distinction between concepts that are macroscopic in origin, such as the volume occupied by a system of particles, and those that are microscopic, such as the particle momentum. This distinction plays an important role in conjunction with the independence requirement in understanding the entropy and the resolution of the paradoxes of thermodynamics.

In a review of the literature, undertaken as part of the examination of the foundations of thermodynamics in TIS, other issues came readily to hand. As I looked more deeply into the formulas of standard equilibrium thermodynamics, for example, I could not see clearly how they emerged from the underlying particle dynamics. As one example of this problem of interpretation, I recall that I was often confronted in the literature by formulas of the form

$$\mathrm{P} = -\int d\Gamma\, F(\Gamma, t) \frac{\partial \mathcal{H}(\Gamma, t)}{\partial V}.$$

This formula expresses the pressure P of a system of particles as minus the average over the particle probability distribution density $F$ of the volume derivative of the system Hamiltonian energy $\mathcal{H}$. For a system with $\mathcal{N}$ particles, the quantity $d\Gamma$ represents a differential for the particle variables taking values in a $6\mathcal{N}$-dimensional particle phase space. The quantity $F(\Gamma, t)$ represents the system probability distribution density as a function of these phase space variables and the time. $\mathcal{H}(\Gamma, t)$ is the system Hamiltonian and $\partial\mathcal{H}/\partial V$ is the derivative of this Hamiltonian with respect to the volume.

There is a major problem with this formula and others like it because the particle system Hamiltonian is not a function of the volume. The volume we attribute to a collection of particles is based on a macroscopic choice of where to place the boundaries of the macroscopic object to which they belong. There is no intrinsic connection between this choice and the properties of the underlying microscopic mechanics. In other words, the volume of a collection of particles is not part of the Hamiltonian mechanics of the particle system. There were attempts to get around this problem by Clausius, Boltzmann, and Gibbs, by including a set of "constraint parameters" in the system Hamiltonian that in most cases used a large potential at the boundary to confine the particles. As discussed in detail in the book, this solution is not acceptable in TIS because it introduces macroscopic parameters into the microscopic quantities that determine the particle motion. In short, I could attach no physical meaning to the symbol $\partial H/\partial V$ in the standard theory.

A number of concerns eventually came to play a role in shaping the emerging theory. While these can be expressed in a logical order, the actual evolution of the ideas underlying the theory did not follow a logical progression. In response to the problem illustrated above concerning formulas used in thermodynamics that had no meaning, it became a requirement that every physical quantity in thermodynamics must have a microscopic analog that is a function of the particle phase space coordinates. Using a general time-dependent particle distribution density, a thermodynamic quantity was

defined as the time-dependent phase average of its analog over the distribution. The next step was to compute the evolution of these thermodynamic quantities in time as a consequence of the evolution of the underlying particle distribution. This led to an analysis of the boundaries of systems, their motions, the flows of physical quantities across these boundaries, and the development of a formalism to account for all of this. The formalism supports localization of those quantities that are properties of the particles, so the result was a local nonequilibrium thermodynamics in spacetime that can track both the forces between macroscopic bodies and the flows of conserved quantities between them.

The next concern was the problem of how to define the derivatives of thermodynamic quantities with respect to the macroscopic volume and temperature. Because the volume and temperature are not part of the Hamiltonian description of the system, it was necessary to find operators, acting at the particle level, which would map the analog of a physical quantity to an analog corresponding to its derivative with respect to volume or temperature. The phase average of the resulting analog is then identified as the thermodynamic quantity corresponding to the derivative of the original thermodynamic quantity.

Carrying this program through in the case of general particle distributions evolving in time eventually yielded a complete general nonequilibrium thermodynamics. The basic components of the resulting thermodynamics differ in some respects from those of standard equilibrium thermodynamics, but much of that structure is retained. Moreover, the quantities and relations defined in equilibrium thermodynamics are obtained from the general formalism when the underlying particle system is described by the equilibrium distribution.

## 2. Specific Problems in the Foundations of Thermodynamics

A careful examination of the catalog of results accepted as established in thermodynamics shows that many of them were demonstrated using questionable assumptions. Because these results are often quoted or applied without stating the assumptions used to obtain them, it is often not clear whether a particular use is justified in a particular setting. Some typical examples illustrating this problem will be reviewed next.

In the standard discussions of the relation of thermodynamics to statistical mechanics, the system $k$ under consideration is usually assumed to be isolated. If it is surrounded by other systems that are interacting with it, these other systems are either ignored or are represented by arbitrary potentials and

boundary conditions in the equations describing the $k$ system.[1] An evolution equation and a particle distribution are then attributed to the $k$ system and results are computed. This procedure ignores the fact that the other systems sharing a boundary with the $k$ system are also made of particles and are evolving, so the potentials associated with them should reflect this fact. The use of arbitrary external potentials and boundary conditions to describe the $k$ system means that we cannot tell if the predicted results are consistent with what would be expected in nature. In addition, the motion of the $k$ system boundaries and the conserved quantities exchanged through these boundaries are usually ignored as well.

The justification usually given for neglecting the exchange of physical quantities between systems is that the systems are "weakly interacting", so that the exchange of energy and momentum between them, while essential to establishing equilibrium, is otherwise unimportant to the evolution of the systems in time. This statement is generally untrue and in any case does not resolve the logical problem of how to deal with the interaction between systems in a way that is consistent with the fact that they are both parts of a larger system and governed by the mechanics of the larger system. This gap in the application of the standard theory affects the definition of the thermodynamic quantities involved and has contributed the budget of paradoxes associated with entropy, irreversibility, and recurrence.

Much analytical effort has been expended in attempting to answer these paradoxes and show how macroscopic irreversibility arises from microscopic equations of motion that are reversible in time.[2] Various explanations of how this happens have been given in terms of the "complexity" of macroscopic systems, the "great disparity between the macroscopic and microscopic scales", the "initial very low entropy condition of the universe", or the use of statistical methods and probability. These arguments employ statements such as "$S_B$ [Boltzmann's entropy] will *typically* increase in a way which *explains* qualitatively the evolution towards equilibrium of macroscopic systems", or refer to "systems with good ergodic properties", or draw conclusions of the form "It is therefore reasonable that", and so on. In many cases, the author puts crucial words within quotation marks that indicate some doubt about their use, meaning, or validity, in that context. Statements such as those in

[1] The work of Pierre Duhem [**1911**] is an exception. He considered an isolated system divided into interacting systems with boundaries that could move and discussed the relations between these subsystems as part of his study of the approach to thermodynamics from the standpoint of energetics.

[2] The examples mentioned in this paragraph are taken from the recent review article by Joel L. Lebowitz [**1999**] on statistical mechanics, but are representative of very many standard treatments of this issue.

the quotations above are all parts of a plausibility argument and not part of a logical or mathematical argument.[3]

Many of the problems in thermodynamic reasoning are connected with the entropy and the second law of thermodynamics. It is usually treated as axiomatic, for example, that the net entropy of the universe increases in the normal evolution of a particle system. To judge the correctness of such a statement, it is necessary to have a clear idea of the analog for the entropy, how its phase average representing the macroscopic entropy changes in time as the underlying particle system evolves, and what role either the entropy analog or the entropy actually plays, if any, in determining the course of history for a physical system. In the standard approach, the problem is approached piecemeal and not within the context of a guiding theory concerning the relation between the entropies of systems in interaction.

The thermodynamic entropy is the phase average of a particle-based analog in the Theory of Interacting Systems. This implies immediately that some of the standard assumptions concerning the entropy are not valid in the Theory of Interacting Systems. A simple example is the requirement that the entropy is an extensive quantity proportional to the number of particles in a system. However, the entropy analog selected in TIS is proportional to the logarithm of the $\mathcal{N}_k$ particle system distribution—just as it was for Gibbs. It is shown in the book that the entropy, obtained in the general theory as the phase average of this analog, is an extensive quantity only when the system distribution factors into a product of one-particle distributions. Similarly, the entropy associated with this analog is not a homogeneous function of the macroscopic parameters describing the system and does not meet other thermodynamic requirements that are sometimes imposed. Moreover, in the general TIS theory the entropy can be time dependent, there are no sources of entropy internal to a system, and there are no entropy currents. There is also no "entropy balance equation". On the other hand, the entropy defined in the TIS version of Boltzmann's equation presented in Part III is an extensive quantity and an entropy current is defined as well.

For a purely macroscopic or phenomenological thermodynamics, it is necessary to use some assumptions about the nature of thermodynamic processes in order to prove the second law. As an example, the proof of the second law in the survey of thermodynamics by Martin Bailyn [**1994**] will be reviewed.[4]

[3]Some of the arguments of this type raised by Boltzmann are discussed in Part III of the book. Other plausibility arguments are discussed in connection with ergodicity in EIS and QTS.

[4]Bailyn [**1994**] has presented an authoritative and detailed survey of the standard theories of thermodynamics in their historical context that will be used as a reference on a number of occasions. The remarks below should not be construed as a criticism of Bailyn's excellent work in presenting thermodynamics. His statements reflect faithfully the thermodynamic reasoning typical in the field.

As part of the proof, Bailyn uses the concept of *local thermodynamic equilibrium,* LTE, which he, p. 133, defined as "situations where macroscopic changes are much slower than microscopic changes." Bailyn, [**1994**], p. 135, presented this as a general principle of thermodynamics: "We take the point of view that thermodynamic processes involve LTE states generally ...." He went on to use this idea in his proof of "the entropy inequality form of the second law," i.e., the form of the second law that states that $\Delta S \geq \int dQ/T$. As part of the proof, he required that the system process pass through two LTE states that can be connected by a reversible process. If the process does not contain any LTE states, he, p. 136, acknowledged that the proof fails, but stated that in this case "the process is hardly thermodynamic."

The problem with this argument is that there is no independent way of knowing when, if ever, a system state meets the criteria of being an LTE state and, if so, whether these states can be connected by a reversible process. Because there is no independent way of knowing if there are any LTE thermodynamic processes and when they occur, this proof is not sufficient in a practical sense to demonstrate that the theorem is valid for real systems. Rejecting an ordinary process as "hardly thermodynamic" because it does not match these assumptions simply shows the conceptual gaps in the theory. Moreover, leaving such processes out of consideration opens the door to the possibility that these processes may violate the entropy inequality being proved.

As a second example, consider the entropy change in an ideal gas undergoing free expansion from an initial volume $V_i$ to a final volume $V_f$. Bailyn [**1994**], pp. 127–128, obtained the standard result $\Delta S = k_B \mathcal{N}_k \ln(V_f/V_i)$. Similarly, he, pp. 141–143, obtained $\Delta S = C_{k,\mathrm{P}} \ln[T_2/T_1]$ for a reversible heat flow that raises the temperature $T_1$ of a system to $T_2$ under the assumption that the heat capacity at constant pressure, $C_{k,\mathrm{P}}$, is constant. To obtain these results requires the integration of macroscopic quantities between finite limits. The problem with this phenomenological procedure is that there is no way of knowing whether or not such an integration, which in this case is the mathematical representation of a thermodynamic process in a system moving between two volumes or temperatures, is warranted by the behavior of the underlying particle system.

Careful treatments of thermodynamic derivations state the limitations or basic assumptions on which the derivation is based. This has the consequence that qualifications such as (Bailyn, p. 169) "provided again that the motions are sufficiently slow and smooth enough for $dQ/T$ to be identified with $dS$" are often found in the proofs of thermodynamic theorems. Leaving aside the problems of determining how slow these motions must be and how we would know if the condition is fulfilled, qualifications such as this one should appear in every theorem or formula associated with the standard approach to thermodynamics in which there is change. Strictly speaking, of course,

no change can really be justified because the standard equilibrium formalism does not support it.

Another significant problem with the standard formalism is called the *Gibbs' paradox.* Gibbs computed the entropy change due to the mixing of dissimilar particles (entropy of mixing) when two systems of different types of particles are combined into one system. When he applied this formula to a situation in which two systems containing identical particles are combined, he found an entropy change of the same magnitude as expected for the entropy of mixing when the two systems contain different particles. This contradicted his feeling that the entropy should not change in the latter case, because the total entropy of the system made by combining two portions of a gas of the same particles should be the same as the sum of the entropies of the portions of gas.

In order to evade this paradox and obtain the proper behavior for the entropy, Gibbs made a distinction between what he called *generic* and *specific* phases. A specific phase function is a function that takes a value for a particular particle arrangement. A generic phase function is an average of a specific phase function over each member of the set of $\mathcal{N}_k!$ possible permutations of the particles. The computation of the entropy as the expectation value of the entropy analog was deemed by Gibbs to be a generic phase computation, because the entropy met his requirement when it was divided by $\mathcal{N}_k!$. This is equivalent to dividing Gibbs' entropy analog by $\mathcal{N}_k!$ before the phase averaging and calling this new function the entropy analog. While dividing either the thermodynamic entropy or the entropy analog by $\mathcal{N}_k!$ does evade Gibbs' paradox, it is an arbitrary modification of either the phase averaging procedure or of the entropy analog without any other justification for doing it. Later writers have tried to justify the division by $\mathcal{N}_k!$ in terms of quantum particle symmetrization, but this is inappropriate for the classical theory.[5] In addition, these writers and others have often added other superfluous quantum ideas to the classical theory, such as a minimum size for cells in phase space, and used this to insert factors proportional to $h^{\mathcal{N}_k}$ into the classical formalism without justification.

The use of such arbitrary assumptions and qualifications indicates that there is a basic problem at the root of the standard approach to thermodynamics. This problem has the consequence that the existing macroscopic formalisms and proofs, based on these assumed microscopic underpinnings, are often not compatible with the mechanics of the underlying particle system. In the TIS version of thermodynamics presented in the book, the axioms and theorems of thermodynamics are direct mathematical consequences of the classical mechanics of the underlying particles in conjunction with the phase averaging procedure. Only those relations that follow from this procedure

[5]The controversy over dividing the quantum entropy by $\mathcal{N}_k!$ is discussed in detail in QTS.

have general validity and only these are accepted in TIS. For this reason, the qualifications and limitations mentioned above are not needed.

## 3. The Reduction of Thermodynamics to Statistical Mechanics

The previous discussion has indicated that a number of issues need to be considered in the reduction of the thermodynamics of interacting macroscopic systems to statistical mechanics. A review of these issues indicates that an adequate reduction must be concerned with

- establishing the relation between the microscopic and macroscopic levels of description;
- finding the proper statistical mechanical analogs for thermodynamic quantities, especially the entropy, temperature, and pressure;
- reconciling the reversibility and recurrence properties of the underlying particle mechanics with the irreversibility of thermodynamics;
- proving the existence of reversible processes;
- defining equilibrium and stationary particle distributions and corresponding macroscopic equilibrium and stationary states;
- defining various other special system distributions, such as the absolute zero and microcanonical distributions;
- working out the correct employment and interpretation of the components of the theory, including the thermodynamic derivatives with respect to time, temperature, and volume;
- showing that the equilibrium theory follows from the general theory when the underlying system distribution is the equilibrium distribution;
- placing Boltzmann's equation within the framework of the general theory; and
- establishing the theory on a mathematically rigorous foundation.

Each of these issues will be addressed in the Theory of Interacting Systems.

The Theory of Interacting Systems avoids the problems of the standard theory by employing several innovations. The first is an explicit concern with the proper use and interpretation of the statistical elements of the theory from the outset. Second, each of the interacting systems is treated on an equal footing in the formalism—although one may be singled out for study. Third, there is an explicit treatment of the boundary and the quantities transmitted through it. A major advantage of this symmetric treatment of the collection of systems and their boundaries is that it allows an adequate understanding of how the entropy of the collection changes in time.

An important goal of this approach is to show explicitly the roots of all functions and formulas of thermodynamics in the underlying microscopic particle dynamics. This is the reason that each thermodynamic function is required in TIS to be the phase average of a specific analog phase function. The phase analog functions themselves use only the particle coordinate

and momentum phase variables and the particle interaction potential energy functions. The interaction potential energy functions, in turn, depend only on the distances between pairs of the particles. Because each quantity used in TIS thermodynamics is a phase average over a microscopically defined analog function, its time evolution is guaranteed to be consistent with the time evolution of the underlying particle system. In parallel with this, the fourth innovation is the use of specific operators to map thermodynamic functions to other thermodynamic functions representing their time, volume, and temperature derivatives. This allows the association of thermodynamic relations involving derivatives of the time, volume, or temperature with the underlying particle system.

As the fifth innovation, the structure of the theory is set up so that an explicit Galilean transformation of the frame of reference in phase space leads to an explicit transformation of the system thermodynamic quantities. The transformations of the thermodynamic entropy, pressure, and temperature, follow easily from the transformation properties of their analogs. For both physical and mathematical reasons, classical systems are limited to a finite number of particles and to bounded domains in phase space. This implies that all particle energies, momenta, and coordinates, have finite values at all times. The fact that these quantities are finite means that the relation between the energy of an isolated system and the energies of its component subsystems is always well defined. There is no loss of generality in this approach because all actual physical systems are bounded in this way. A mathematical formalism in which all physical quantities are bounded is more realistic than the usual one that allows integrations over unbounded energies and momenta. Finally, this approach leads to a number of mathematical relationships that are not well defined in the unbounded momentum and energy case.

In the development of the theory, there is a clear distinction between concepts that are macroscopic in origin, such as the volume of a system (with the associated concepts of its boundary and the motion of the boundary), and those with roots in the underlying microscopic particle dynamics. This distinction is important, for example, when considering the division of the microscopic energy flow through a boundary into the macroscopic concepts of heat flow and work flow. Special attention has also been paid to understanding the distinction between concepts that are mechanical in origin, such as particle number, momentum, angular momentum, and energy, and those that originate in thermodynamics: entropy, temperature, and pressure. The analog phase functions for momentum and energy, for example, depend on the momentum and energy of the microscopic elements. The analog phase functions for the entropy and temperature, on the other hand, reflect their non-mechanical origin in that each involves the system distribution in its definition.

The approach to the issues of irreversibility and recurrence taken here centers on the analysis of the boundary and how it modifies the evolution equation of the system. Thus, when the boundary is described stochastically, the system evolves irreversibly. On the other hand, when the particle interactions at the boundary are described exactly, the evolution of the system is reversible. The boundary formalism allows irreversible behavior for subsystems of an isolated system within the interacting systems approximation while not contradicting the reversible behavior of the isolated system as a whole. This point is reflected in the proof of Clausius's inequality in Chapter 9. The existence of reversible and equilibrium distributions and their relation to each other will also be shown within this formalism. Other specific system distributions and their properties are presented and discussed as well. Finally, as part of the examination of the mathematical foundations of the theory in Part IV, it is shown that the system equilibrium distribution is approached asymptotically from almost any initial distribution when the boundary conditions are constant.

## 4. Bibliography

The CIS bibliography contains a balance between older references to pioneers in the fields of thermodynamics and statistical mechanics and references to some of the new thinking in these areas.

## 5. References for this Prospectus

### References

[1994] Martin Bailyn, *A Survey of Thermodynamics*, AIP Press, New York, 1994.

[1911] Pierre Duhem, *Traité d'Energetique ou de Thermodynamique Générale*, in two volumes, Gauthier-Villars, Paris, 1911.

[1999] Joel Lebowitz, *Statistical Mechanics: A Selective Review of Two Central Issues*, printed as pp. 581–600 in B. Bederson, ed., *More Things in Heaven and Earth: A Celebration of Physics at the Millennium,* American Physical Society, Springer-Verlag, New York, 1999.

### 6. CIS Table of Contents

The Table of Contents for Classical Theory is given next. It shows the range of topics covered.

# CIS Table of Contents


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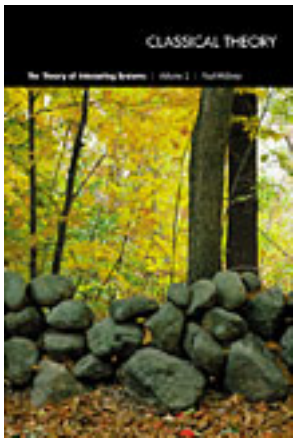


**The Theory of Interacting Systems**

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