Foundations of Statistical Mechanics

Volume I:
Equilibrium Theory

Fundamental Theories of Physics

by

Walter T. Grandy, Jr

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Equilibrium Theory

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Preface

In a certain sense this book has been twenty-five years in the writing, since I first struggled with the foundations of the subject as a graduate student. It has taken that long to develop a deep appreciation of what Gibbs was attempting to convey to us near the end of his life and to understand fully the same ideas as resurrected by E.T. Jaynes much later. Many classes of students were destined to help me sharpen these thoughts before I finally felt confident that, for me at least, the foundations of the subject had been clarified sufficiently.

More than anything, this work strives to address the following questions: What *is* statistical mechanics? Why is this approach so extraordinarily effective in describing bulk matter in terms of its constituents? The response given here is in the form of a very definite point of view—the principle of maximum entropy (PME). There have been earlier attempts to approach the subject in this way, to be sure, reflected in the books by Tribus [*Thermostatics and Thermodynamics*, Van Nostrand, 1961], Baierlein [*Atoms and Information Theory*, Freeman, 1971], and Hobson [*Concepts in Statistical Mechanics*, Gordon and Breach, 1971]. Despite these efforts the bulk of writers on the subject, though diminishing in number, still fail to appreciate that statistical mechanics is a special case of a general reasoning process that appears to be optimal when insufficient information is available. This point of view was implicit in Boltzmann's later writings, and certainly was made explicit by Gibbs. The lasting contributions by these fathers of the subject lie with development of new methods of analysis, not in the discovery of new physics. Unfortunately, the exciting new physics was just coming to life as they passed from the scene.

It is apparent that the subjects of statistical mechanics and thermodynamics can mean many things to many different people. Indeed, the subjects tend to arouse deep emotions in a way unfamiliar to other areas of physics. One need only recall the tribulations of Robert Mayer circa 1840 in attempting to establish the first law of thermodynamics in conjunction with energy conservation: for his efforts he was ostracized in the community, his medical practice ruined, and even his attempts at suicide ended in failure! Planck recorded his own despair in his scientific autobiography. Similarly, the maximum-entropy principle, though advocated in one form or another since Boltzmann, continues to be pilloried in some quarters, and even characterized as 'muddleheaded' and 'nonsense'. Although a distinct minority, there nevertheless are those whose very vocal response to any new attempts at deeper insight in this area is scalding and charged with emotion—and to whose discomfort this volume will no doubt contribute immensely. Much of the rhetoric has already been answered by Jaynes in his collected works on these topics [*E.T. Jaynes: Papers on Probability, Statistics and Statistical Physics*, Reidel, 1983], so that little more in the way of polemic will be offered here.

Rather, a great deal of space is devoted to discussing what statistical mechanics is, and is not. For this reason the reader may encounter in the early chapters a number of topics deemed elementary for what is generally a somewhat advanced book, but the author has found it necessary to re-examine such topics in order to maintain a certain coherence in the discussion. Consequently, the first three chapters can be, and in fact have been used as a basis for undergraduate lectures. But the whole is directed toward the advanced undergraduate and graduate student, with a general emphasis on quantum statistical mechanics.

The topics treated throughout the book have been chosen to elucidate the *foundations* of the subject—that, after all, is the major thrust of the work. But the foundations can hardly be made clear without a number of detailed applications. Some of the latter tend to be a bit different than found in the usual textbook, and may possibly yield some new insights.

Unquestionably the student will not find here *all* the tools needed in order to carry out professional research in the field. For example, numerical techniques, such as the Monte-Carlo method, are essentially mentioned only in passing, and path-integral methods do not receive even that much notice. It is not the intent of the work to provide the wealth of calculational detail to be found in Fetter and Walecka [*Quantum Theory of Many-Particle Systems*, McGraw-Hill, 1971], say. Rather, an attempt is made to provide some answers to the questions raised at the beginning, from what some may consider a non-standard view. If the book serves to generate some non-standard thought along these lines as well, one of its purposes will have been achieved. In addition, it is also meant to serve as a foundation for Volume II, in which the much more exciting topics of nonequilibrium phenomena are addressed.

As a text, the book forms the basis for a solid one-semester introductory course at the senior/graduate level. Although a number of problems have been included, they have been chosen mainly to illustrate the discussion in the text. Many more standard problems, particularly of the detailed calculational variety, are known and available to most lecturers in statistical mechanics.

I have attempted to include copious and detailed references, including those relevant to the historical record. Moreover, this is one aspect which is somewhat novel to the literature of physics, in that an attempt has been made to verify and supply the *titles* of all referenced works. Unfortunately, after all is said and done there are still a few missing—but not many. Aside from scholarly interest, my aim is to encourage such practice in this field, because it is eminently useful to the reader—and sometimes even to the writer!

There are numerous people who have contributed to the completion of this work, either directly or indirectly. Although it is not possible to provide detailed acknowledgment here, a few nevertheless will have to bear public exposure. It is only stating the obvious when I point to the extraordinary influence Ed Jaynes has had on my thoughts about the foundations of statistical mechanics. His friendship, good humor, and collegiality over many years have been greatly appreciated.

I have long been indebted to Franz Mohling for initially stimulating my interest in statistical mechanics and continuing to generate enthusiasm through thoughtful debate. I shall forever regret that he died without seeing this finished product, for I believe that he had come to share a great many of the views expressed here. After insisting that I stop climbing mountains and finish my dissertation, he climbed one too many himself.

Locating and identifying many older references would have been significantly more tedious without the generous assistance of Professor Lewis Pyenson, Université de Montréal, for which I am grateful. Professor John Skilling of Cambridge University provided thoughtful criticism of Chapter 2; no doubt some criticisms remain, but it is a better discussion for having suffered his scrutiny. Finally, it is customary at this point to thank typists and editors for their heroic efforts—but there are none! This entire book was *typeset* by the author using the marvelous typesetting program TEX developed by Donald Knuth. On the one

hand, availability of computerized typesetting with microcomputers has introduced a great deal of flexibility on the part of authors in producing highly technical books of this kind. On the other hand, the publisher is now granted significant absolution, so that essentially any and all defects are solely my responsibility.

W.T. Grandy, Jr.

Laramie, Wyoming
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Chapter 1

Introduction

Phenomenological thermodynamics consists primarily of a set of empirical rules and relations which, for more than one hundred fifty years, has provided a correct description of many of the macroscopic properties of bulk matter. Although the rules evolved some during this period, once the concept of energy and its conservation was grasped, as well as that of entropy, the rules quickly achieved their present form. With the advent of a serious particulate view of matter, however, it was realized that the thermodynamic rules were possibly only manifestations of the fundamental physical laws governing interactions among the basic constituents of matter; that is, atoms and molecules. Thus, one of the objectives of what Gibbs first called *statistical mechanics* is to provide an acceptable and fundamental explanation of phenomenological thermodynamics, in both the physical and philosophical senses. In addition, one might hope to go further and describe *all* physical properties of bulk matter in this way.

A second objective of such an undertaking emerges in the form of an inverse problem. That is, by constructing microscopic models of the underlying analytical dynamics which lead to prediction of observable macroscopic quantities, one obtains a means for testing the models of microscopic interactions themselves. In a sense, an understanding of few-body behavior can be gleaned from the many-body problem by inversion.

Realization of these objectives is not necessarily straightforward, of course, and the way is littered with pitfalls. For example, although we have a reasonable understanding of the classical two-body problem, even eighteenth-century Newtonian physicists knew the three-body problem to be intractable insofar as exact solutions are concerned. In this century we have been compelled to conclude likewise for the one- and two-body quantum problems, and quantum field theory would have us extend our frustration to the vacuum as well! Hence, we already know that the meaning to be given to the term 'exact solutions' must be considered carefully.

Most scientists undoubtedly accept the reductionist hypothesis which asserts that all natural phenomena are ultimately explainable in terms of the fundamental laws of physics. But this does not mean, in Rutherford's jocular phrase, that "all science is either physics or stamp collecting" (e.g., Blackett, 1962; Mayr, 1982). That is, reductionism does not imply a 'constructionist' hypothesis, a point emphasized quite strongly by Anderson (1972). Vitalism has proved a bankrupt notion in biology, yet one would have difficulty predicting the remarkable properties of DNA and the complexity of protein synthesis from quantum mechanics alone. Similarly, and on a more basic inanimate level, no one has ever succeeded in deriving the crystal lattice directly from the Schrödinger equation. Rather, at all levels of matter there exist *organizing principles* differing in scale and complexity, but nevertheless standing on their own. Thus, in another and deeper sense, statistical mechanics seeks to uncover the organizing principles governing the structure and behavior of macroscopic, or bulk matter.

The present chapter is devoted to summarizing much of the early work in the subject, as well as to providing a concise history of these efforts. We begin most appropriately with a review of some formal aspects of classical mechanics.

A. Physical Foundations

Perhaps the most efficient way to describe formally a mechanical system possessing s degrees of freedom is through the introduction of generalized coordinates $(q_1,\dots,q_s)$, along with the corresponding set of generalized velocities $\{\dot{q}_i\}$. By means of the Lagrangian function, which in the simplest problems is given as

$$L(q,\dot{q}) = T - U, \tag{1-1}$$

in terms of the system kinetic and potential energies, the equations of motion for the system can be written in the Euler-Lagrange form:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \qquad i = 1,2,\dots,s. \tag{1-2}$$

Subscripts on coordinates will generally be omitted when it is desired to denote the entire set of s quantities.

While quite general, and a distinct advance over the Newtonian formulation, the Lagrangian method lacks a certain symmetry. Thus, it is found convenient to introduce generalized momenta

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \tag{1-3}$$

and then carry out a Legendre transformation defined by the generating function

$$\mathrm{H}(q,p) \equiv \sum_{i=1}^{s} p_i \dot{q}_i - L(q,\dot{q}). \tag{1-4}$$

This defines the Hamiltonian function H which, as with L, is presumed time independent in the sense that it does not depend on time *explicitly*. In terms of H the equations of motion (1-2) now take the canonical form

$$\dot{q}_i = \frac{\partial \mathrm{H}}{\partial \mathrm{p_i}}, \qquad \dot{p}_i = -\frac{\partial \mathrm{H}}{\partial \mathrm{q_i}}, \qquad i = 1,\dots,s. \tag{1-5}$$

Define the Poisson bracket for arbitrary phase functions $u(q,p)$, $v(q,p)$ as

$$[u,v] \equiv \sum_{i}^{s}\left[\frac{\partial u}{\partial q_i}\frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i}\frac{\partial v}{\partial q_i}\right], \tag{1-6}$$

so that the equation of motion for any such function is just

$$\frac{du}{dt} = [u,v] + \frac{\partial u}{\partial t}. \tag{1-7}$$

In particular, for the choice $u = \mathrm{H}$,

$$\frac{d\mathrm{H}}{\mathrm{dt}} = 0, \tag{1-8}$$

because H is time independent. If, in addition, all forces are conservative (derivable from potential functions depending only on the coordinates q), then H is the total system energy: $H = T + U = E$.

As in most of theoretical physics, it is intuitively pleasing to construct a geometrical description of mechanical systems. This is readily achieved by defining a Euclidean space of $2s$ dimensions in terms of all possible numerical values of the q_i and p_i, which is called Γ-space, or *phase space*. Any fixed set of real values $(q_1, \ldots, q_s, p_1, \ldots, p_s)$ constitutes a possible state of the system and is represented by an image point in Γ. As the system develops in time from an initial state, the image point traces out a trajectory in phase space. All possible paths consistent with relativistic limitations comprise the set of kinematically possible trajectories (kpt), although here the discussion will be limited to nonrelativistic mechanics.

The equations of motion (1–5) restrict the kpt to a smaller set of dynamically possible trajectories (dpt), such that the state of the system at any one time uniquely determines its state at any later time. That is, in an isolated system described by a Hamiltonian the equations of motion are first-order differential equations. Hence, the dpt do not intersect one another, and through each point of Γ there passes one and only one dpt.

In a more geometrical sense, the point P_0 in Γ at time t_0 is mapped into a new point P_t at time t by the equations of motion. Equations (1–5) induce a mapping of the space Γ onto itself in a continuous and one-to-one way, owing to the time-reversal invariance of Hamilton's equations. These mappings form a one-parameter group of automorphisms of phase space such that the motion is stationary. Canonical transformations form the covariance group of the theory and, as is well known, the entire description is invariant under the Galilean group. Of course not every mapping of the space onto itself constitutes a motion corresponding to Eqs.(1–5). Rather, only those transformations are to be admitted which map dpt into other dpt.

Occasionally it is useful to consider subspaces $\mathcal{M}$ of Γ, some of which have the property that every point of $\mathcal{M}$ is mapped into another point in $\mathcal{M}$ by the equations of motion. When this is the case, $\mathcal{M}$ is said to be an invariant subspace of Γ, or an invariant manifold. We shall presume that all manifolds in Γ, invariant or not, are measurable.

Consider now any manifold $\mathcal{M}_0$ mapped into another manifold $\mathcal{M}_t$ during a time interval t by the equations of motion. Then we have (Liouville, 1838)

Liouville's Theorem. *The measure of the set $\mathcal{M}_t$, for any t, coincides with the measure of the set $\mathcal{M}_0$.*

That is, the measure of measurable point sets in Γ is an invariant of the equations of motion.

This theorem is so important that it is worth stating in a more explicit way. The measure of the manifold $\mathcal{M}_0$ in phase space is just the ***phase volume***

$$\Omega_0 \equiv \int_{\mathcal{M}_0} dq\, dp, \tag{1–9}$$

where the multiple integral is over all values of all the q_i and p_i in $\mathcal{M}_0$. (When limits are omitted the integration is presumed to be over all of Γ.) During time t the manifold $\mathcal{M}_0$ is carried into the manifold $\mathcal{M}_t$ with phase volume

$$\Omega_t = \int_{\mathcal{M}_t} dq\, dp, \tag{1–10}$$

and Liouville's theorem states that

$$\Omega_t = \Omega_0 \,. \tag{1–11}$$

It is left as an exercise to show that an equivalent statement is that the Jacobian of the transformation of the coordinates (q_i, p_i) at time t_0 to those at time t is identically unity.

Liouville's theorem leads one, in a way which will only become clear later, to an important relation between the dynamical properties of a large system and their experimental manifestations. An essential quantity in this connection is the total phase volume compatible with experimentally observable conditions. The equation

$$\mathrm{H}(q,p) = E \tag{1–12}$$

for a conservative system defines a surface of constant energy in Γ. We shall almost always consider only such cases in which E has a finite lower bound throughout Γ, which can arbitrarily be taken as zero, and the surfaces of constant energy will be labeled S_E. These surfaces are presumed closed, and the volume contained therein finite and simply connected. As a consequence the surfaces S_E can be viewed as hyperspheres in Γ. The mappings induced by Eqs.(1–5) leave the surfaces of constant energy, as well as the domain contained within two such surfaces, invariant.

Suppose the system in question is isolated and known to have a total energy E. It is useful to consider the total phase volume contained within the corresponding surface S_E,

$$\Omega(E) = \int \theta[E - \mathrm{H}(q,p)]\, dq\, dp, \tag{1–13}$$

where $\theta(x)$ is the unit step-function. This volume is a monotonic increasing function of E. The differential phase volume is called the *structure function*,

$$g(E) \equiv \frac{d\Omega}{dE} = \int \delta[E - \mathrm{H}(q,p)]\, dq\, dp. \tag{1–14}$$

It will be seen subsequently that $g(E)$ plays a crucial role in the macroscopic description of mechanical systems with many degrees of freedom. Although it does not follow from any of the foregoing, it is usually presumed that $g(E)$ is also a monotonic increasing function of E.

Calculation of the structure function is rather difficult in general, and it is often easier to calculate first its Laplace transform, which we shall call the *partition function*:

$$Z(\beta) = \int_0^\infty g(E) e^{-\beta E}\, dE\,, \tag{1–15}$$

where β is a real parameter. This is called the 'generating function' by Khinchin (1949), but it does indeed represent a kind of partitioning of phase space. An alternative expression is obtained by substitution of Eq.(1–14) into Eq.(1–15):

$$Z(\beta) = \int e^{-\beta \mathrm{H}(q,p)}\, dq\, dp\,, \tag{1–16}$$

which often proves useful in calculations.

The parameter β has no immediate physical significance for a system with few degrees of freedom, but it will assume considerable meaning later for large systems. For now we note that if the structure function itself is needed, and $Z(\beta)$ is known, one can invert the Laplace transform by extending β to the complex plane. Then

$$g(E) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} Z(\beta) e^{\beta E}\, d\beta\,, \tag{1–17}$$

where c is chosen so that the contour lies to the right of all singularities of $Z(\beta)$.

Some insight into the meaning of $g(E)$ can be gained from its defining equation (1–14). On the one hand, because $g(E)$ is always non-negative, $Z(\beta)$ is logarithmically convex and monotonic decreasing in β. It appears, therefore, that $Z(\beta)$ does not possess a great deal of interesting structure. On the other hand, Eq.(1–14) describes $g(E)$ as a 'density of phase', such that its integral yields the total phase volume contained within the hypersphere defined by the total energy E. In this sense $g(E)$ describes the relevant geometric structure of the phase space for a particular mechanical system. Although the present discussion is directed specifically toward classical systems, it is useful to digress for a moment and consider the quantum-mechanical analog of this function.

Envision a physical volume in the shape of a cube of side L, with volume $V = L^3$, containing a single particle. The behavior of this particle can be described, partially, in terms of plane-wave eigenfunctions of linear momentum with quantum numbers $\mathbf{p} = \hbar\mathbf{k}$, where $\mathbf{k}$ is the wavenumber. Imposition of periodic boundary conditions has the effect of restricting wavenumber values to the discrete set

$$\mathbf{k} = (2\pi/L)\mathbf{n} = (2\pi/L)(\mathbf{i}n_x + \mathbf{j}n_y + \mathbf{k}n_z)\,, \tag{1–18}$$

where the vector $\mathbf{n}$ has components $0, \pm1, \pm2, \ldots$. The single-particle energy then has the possible values

$$E = \hbar^2 k^2/2m, \qquad k^2 = \frac{(2\pi)^2}{L^2}(n_x^2 + n_y^2 + n_z^2). \tag{1–19}$$

Observe that, except for the very lowest energies, the energy states possess an enormous degeneracy owing to the extraordinary number of ways a perfect square can be represented by the sum of the squares of three integers. This suggests possible utility in defining a density of energy states, and direct calculation from the above yields the expression

$$g(E) = \frac{\Delta n}{\Delta E} = \frac{2^{5/2}\pi m^{3/2} V}{h^3} E^{1/2}. \tag{1–20}$$

Equivalently,

$$\frac{V\,\Delta p_x\,\Delta p_y\,\Delta p_z}{\Delta n} = h^3\,, \tag{1–21}$$

indicating that each state in phase space occupies a volume h^3. Note that Eq.(1–20) also leads to identification of a density of momentum states:

$$\frac{d^3 n}{d^3 k} = \frac{V}{(2\pi)^3}. \tag{1–22}$$

From this form one infers a well-known prescription for converting sums over states to integrals:

$$\sum_{n} \longrightarrow \frac{V}{(2\pi)^3}\int d^3k. \tag{1–23}$$

These density-of-states functions are able to provide almost exact descriptions of the system, except possibly at very low energies. But as L becomes very large even those states become well approximated and the entire discrete spectrum becomes continuous as $L \to \infty$. This is one version of the so-called infinite-volume limit, and provides a technique in which the mathematical description of a quantum-mechanical system can be made to appear rather similar to that of its classical counterpart.

Prior to providing some examples of mechanical systems and their descriptions in phase space, it will be found useful subsequently to mention here two further aspects of the geometric formulation. Consider a subset $\Delta\Omega$ of Γ containing a number of image points P_t at time t lying on dpt of the system. Then, for a closed system evolving under the equations of motion, it can be proved that for all t and all P_t in $\Delta\Omega$ there exists a T such that P_{t+T} is in $\Delta\Omega$. This is known as *Poincaré recurrence* (Poincaré, 1890), and means that every closed classical system with a finite number of degrees of freedom is almost periodic. In essence, if N is the number of degrees of freedom and ϵ the error of recurrence, then a large body of specific studies indicates that quite generally $T \sim \epsilon^{-N}$.

The second aspect we wish to mention concerns a property of the phase volume as a measure, originally due to Hopf (1932). Adopt a normalization such that $\Omega(E) = 1$. A system is defined as *mixing* if and only if, for a set $\mathcal{M}_t$ on S_E and *any* other set $\mathcal{Q}$ in S_E, both of positive measure, it is true that

$$\lim_{t\to\infty} \Omega(\mathcal{M}_t \bigcap \mathcal{Q}) = \Omega(\mathcal{M})\,\Omega(\mathcal{Q}). \tag{1–24}$$

That is, if a system is mixing it follows that in the limit $t \to \infty$ all the dynamically possible points in $\mathcal{M}_t$ are distributed uniformly over S_E, and a mixing system does not exhibit Poincaré recurrence in this limit. Sinai (1970) has demonstrated that a finite system ($N \geq 2$) of hard spheres in a box is mixing. We shall return to further discussion of these two results later.

It is useful to consider four specific examples so as to illustrate the application of the phase-space formalism. Subsequently we shall see that these have been well chosen in order to emphasize several features of interest to the later discussion.

Example 1. A spherical pendulum of length r and mass m restricted to the region below a horizontal plane through its pivot point is described by a Lagrangian

$$L = \frac{1}{2} m r^2 \dot{\phi}^2 \sin^2\theta - mgr(1-\cos\theta)\,, \tag{1–25}$$

where the zero of energy is taken at the equilibrium rest point, and g is the acceleration of gravity. Form the Hamiltonian, as in Eq.(1–4), and substitute into Eq.(1–16) to obtain the partition function:

$$Z(\beta) = \frac{4\pi^2 r}{\beta^2 g}(1 - e^{-\beta mgr}). \tag{1–26}$$

This is certainly a Laplace transform, so we can invert to obtain the structure function:

$$g(E) = \frac{4\pi^2 r}{g}\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}(1 - e^{-\beta mgr})e^{\beta E}\,\frac{d\beta}{\beta^2}. \tag{1–27}$$

The integrand has a second-order pole at the origin and we close the contour to the left. Evaluation is readily carried out by means of the residue theorem and one finds that

$$g(E) = \frac{4\pi^2 r}{g}\big[E - \theta(E - mgr)(E - mgr)\big]. \tag{1–28}$$

Example 2. A simple linear harmonic oscillator has Hamiltonian

$$\mathrm{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2\,. \tag{1–29}$$