PREFACE

The phrase "thermal physics" will be understood here to embrace mainly *thermodynamics* and *statistical mechanics*. We will touch only incidentally upon such collateral subjects as the kinetic theory of gases, though the latter did contribute importantly to the historical development of *both* thermodynamics and statistical mechanics.

Statistical mechanics is (like kinetic theory) rooted in the dynamics of mechanical systems with many degrees of freedom,[1] but has things to say about such systems only when they are **states of thermal equilibrium**. And the things it has to say are *statistical* things, things about the *averaged* properties of the thermalized system. Thermodynamics provides us with a rich repertory of general *functional relationships among* those averaged properties.

Thermalization—the process

$$\text{disequilibrated state} \longrightarrow \text{state of thermal equilibrium}$$

—is a <u>mechanical process that takes place in dynamical time</u>. What are the physical preconditions to the *possibility* of such a process? How long does it take? How do we know it has been accomplished? Neither thermodynamics nor statistical mechanics has anything to say about the first two questions (those provide the subject matter of "ergodic theory") and, concerning the final question, thermodynamics invites us to work out implications of the assumption that thermalization has taken place and to compare those with the observed facts. Which is pretty much how we test *any* theoretical statement. And in the present instance we are aided by our commonsensical intuition: we may not know what thermal equilibrium means, in any deep sense, but—tentatively—we suppose ourselves able to recognize it when we meet it.

[1] Avogadro's number $N \approx 6.0221367 \times 10^{23}$ is the characteristic number.

A principal symptom (necessary, if not sufficient) of the thermalization of a system is the *time-independence of its gross features* (which we do not expect to be reflected in the underlying microphysics: think of the buzzing molecules in a thermalized box of gas). Since it is the business of statistical mechanics to describe those *gross* features it is perhaps not surprising that statistical mechanics, though rooted in dynamics, recognizes the existence of no t-variable. Nor does thermodynamics, which—though it does recognize the before/after distinction—is powerless to describe the temporal rate at which thermodynamic processes take place.[2]

Were we to undertake to describe the detailed micro-mechanics of a many-body system (a drop of fluid, let us say) our first step might be to write down a conjectured Hamiltonian

$$H(p_1, x_1, p_2, x_2, \ldots, p_N, x_N) \quad : \quad N \sim 10^{23}$$

and then to try (!) to solve . . . maybe Hamilton's canonical equations, maybe the Schrödinger equation. But solutions, even if they could be obtained, would provide bewilderingly much information, most (nearly all!) of which would lie beyond the limits of our observational capability (and all t-dependent aspects of which would have somehow to be discarded). Broad classes of distinct solutions would, to our gross senses and imperfect instruments, appear indistinguishable, and we would find ourselves powerless to set prescribed initial conditions with the exquisite precision required to distinguish one solution from another. We would have labored heroically to place ourselves in a situation where too much is almost as bad as nothing at all.

But *thermodynamic* analysis of the *thermalized* states of such a system assigns importance to only a handful of observationally accessible variables (things like temperature, pressure, volume), variables which—remarkably—are bound together in a self-consistently closed system of relationships.

Thermodynamics is recommended to our attention not only by its computational efficiency and its immediate relevance to what we observe, but also by the depth of its principles. It says little (relative to all that could—in principle—be said about a system with 10^{23} degrees of freedom) because, in the last analysis, it assumes little, but what it does say it says with implacable finality. Einstein summarized the situation with these words:

[2] This circumstance makes it sometimes a little hard for physicists to grasp what it is that thermodynamics is trying to accomplish, so habituated are we to a sequential view of the world: in classical/quantum mechanics, in electrodynamics . . . we look first to the equations of motion, from which we tickle conservation laws, variational principles and all the rest that makes up those subjects. Viewed in the light of this experience, thermodynamics may initially seem to have no clearly defined beginning/middle/end, no directed logical thread, to be confusingly "mesh-like," a crazy network of relations.

> *A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of a universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown . . .*

Einstein's point was underscored by Max Planck, who, it might be argued, was primarily a great thermodynamicist and only incidentally the father of quantum mechanics: he considered himself to have been *forced* to adopt the "quantum hypothesis"—forced to give up the "principle of continuity" which had been an essential feature of all prior physics, and thus to alter the course of all future physics—forced by the fact that the arguments that had led him to the blackbody spectrum had been *thermodynamic* in nature, and thus inescapable. He writes

> . . . *what I did can be described as simply an act of desperation. By nature I am peacefully inclined, and reject all doubtful adventures. But . . . a theoretical interpretation* [*of the thermodynamically deduced Planck distribution formula*]. . . *had to be . . . found at any cost, no matter how high . . . The two laws* [*of thermodynamics*], *it seems to me, must be upheld under all circumstances.*

Thermodynamics sprang historically from trains of thought that were uncontaminated by any reference to "systems with many microscopic degrees of freedom," arguments cultivated at a time when the "atomic hypothesis" was just that: a *hypothesis* of (it was widely imagined) dubious physical validity. And it can be developed today as an axiomatic system, free from any reference to an underlying microphysics. But Planck/Einstein held the pronouncements of thermodynamics to be inescapable, and its laws "deep," for reasons having to do not so much with thermodynamics itself (and certainly not with any specific system of axioms) as with its statistical underpinnings, which are so primitive (think of the Law of Large Numbers) as to defy contradiction.

In view of the latter circumstance it has become fashionable to dismiss thermodynamics as a mere *corollary* of statistical mechanics, a subject hardly worthy, therefore, of independent study. That position, in my view, is not quite fair to the facts . . . any more than it would be fair to the facts to describe classical mechanics as a mere "corollary" of quantum mechanics. For in point of practical fact it is by classical argument that (typically) we set up our quantum calculations, and by measurements that are (in at least their final stages) classical that discover whether those calculations have been fair to the physical facts. Similarly, thermodynamic notions enter essentially into the *construction* of statistical mechanics, and it is (typically, if not invariably) by thermodynamic measurement that statistical mechanical calculations establish contact with the facts of laboratory experience. I hold that the dialog between classical and quantum physics is much too rich, and latently too informative, to be casually dismissed. And that the dialog between thermodynamics and statistical mechanics is in many respects similar.

Accordingly (and contrary to established practice) I devote my initial chapters to a review of the fundamentals of classical thermodynamics, and look only after that work is reasonably complete to the principles of statistical mechanics.