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(continued following index)

George D.J. Phillies

Elementary Lectures in Statistical Mechanics

With 51 Illustrations

Springer

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Preface

This volume is based on courses on Statistical Mechanics which I have taught for many years at the Worcester Polytechnic Institute. My objective is to treat classical statistical mechanics and its modern applications, especially interacting particles, correlation functions, and time-dependent phenomena. My development is based primarily on Gibbs's ensemble formulation.

Elementary Lectures in Statistical Mechanics is meant as a (relatively sophisticated) undergraduate or (relatively straightforward) graduate text for physics students. It should also be suitable as a graduate text for physical chemistry students. Physicists may find my treatment of algebraic manipulation to be more explicit than some other volumes. In my experience some of our colleagues are perhaps a bit over-enthusiastic about the ability or tendency of our students to complete gaps in the derivations.

I emphasize a cyclic development of major themes. I could have begun with a fully detailed formal treatment of ensemble mechanics, as found in Gibbs's volume, and then given material realizations. I instead interleave formal discussions with simple concrete models. The models illustrate the formal definitions. The approach here gives students a chance to identify fundamental principles and methods before getting buried in ancillary details.

There are lots of other good books on statistical mechanics. In reading them, I am often staggered by how much some of my colleagues know about statistical mechanics—far more than I do. I am even more staggered by their faith that students can learn that displayed knowledge in the space of a semester or two. I have tried to write a "you really should know much of this" book rather than a "behold my sublime genius and overwhelming knowledge" book. The last three Lectures do present a real research problem, drawn from my own papers, to convince students that they are now ready to read the primary literature for themselves.

I note two approaches for causing students to learn theory. In the first approach, held by a sufficiently large majority that its supporters oft refer to it as the "only approach," students are expected to learn primarily by solving problems. In the second approach, students learn primarily by wrestling with the words of the author. Students who respond to the second approach, while interested in seeing worked examples, tend to view homework problems as as obstacle which must be traversed before they can spend time learning the material. If you are a student, be warned!: Many people think they only need to ponder problems rather than working them; few people actually do need to ponder problems rather than working them.

These methods appear to me to represent underlying differences in how their supporters think. I myself learn from the latter method, but hope I have presented enough problems to satisfy students who need to work problems. The problems have a wide range of difficulty. The easiest problem requires a few lines of calculation; the final problem of the final Lecture has consumed hundreds of man-years of research without being solved. I also use homework problems to introduce significant results not seen elsewhere in the text, so a perusal of unworked problems may prove worthwhile. The concept of naming problems is due to Mr. Mark Swanson, who initially advocated the procedure as a method for tagging rules in large complex games.

On a parallel line, some students say "tell us what is true, not what is not true," while others find the mathematician's emphasis on elaborated counterexamples to be critical in sharpening their thinking about what a definition means. The mathematicians appear to have the better of this argument.

At a few points my development differs from some other modern works:

First, the material is arranged as "Lectures," not "Chapters." While some of the early Lectures have grown in writing, an hour-and-a-half presentation or two will cover almost any Lecture. The Lectures are grouped into five parts, covering (I) separable classical systems, (II) separable quantum systems, (III) systems of interacting particles and cluster expansions, (IV) correlation functions and dynamics, and (V) a research problem from the literature. Lectures are interleaved with "Asides." The Asides ease the passage between Lectures and supply material on the real foundations of statistical mechanics.

Second, I am a firm believer in dotting i's and crossing t's. For example, note Aside C and its treatment of the so-called Gibbs Paradox, which Gibbs did not view as involving a paradox. Some instructors mix results from the canonical and microcanonical ensembles without discussing logical consistency. I have tried, probably unsuccessfully, to avoid inconsistency here.

Third, in developing most of the material presented here, quantum mechanics has been reduced to its historically subordinate role. Most research in statistical mechanics of physical systems does not use quantum theory directly. Admittedly, if one wishes to compute the forces within a pair or cluster of atoms, quantum mechanics is indispensable. Similarly, to calculate the allowed vibration energies of a molecular system, one may well need quantum mechanics. However, interference effects are seldom obvious except at low temperatures. The correct counting of states of indistinguishable particles at normal densities and room temperature was obtained by Gibbs in the last century using a purely classical argument. In cold dense systems, quantum corrections can become large. Quantum effects are treated in Part II.

Fourth, I adhere rigorously to Gibbs [1] rather than Boltzmann [2] or Schroedinger [3] in asserting the primacy of the canonical over the microcanonical ensemble, not the other way around. I believe that this choice maintains pedagogical simplicity and keeps a direct connection between theory and reality.

Had I begun with the microcanonical ensemble, I would necessarily have begun with the elaborate demonstration that the microcanonical statistical weight for the whole of a large isolated physical system

$$W_j = 1/A \tag{0.1}$$

implies the canonical statistical weight

$$W_j = \exp(-\beta E_j)/Q \tag{0.2}$$

for a small part of the large isolated system. Real systems of fixed temperature are generally not small parts of equilibrium systems which have fixed energy, so this derivation is unphysical. This derivation also sacrifices the major advantage which Gibbs proved for his canonical ensemble approach, namely that his canonical ensemble is equally valid for small and large systems, while the transition from (0.1) to (0.2) is only useful for large systems.

From a logical-theoretical standpoint, equations 0.1 and 0.2 are equivalently desirable. Either gives a single new postulate beyond Newtonian and quantum mechanics. One may cultivate a preference for one or the other of these equations on such grounds as "simplicity," but I am writing science, not theology. Operationally, (0.2) is to be preferred to (0.1), in that the world contains many examples of thermostated systems (for which (0.2) is apparently exact), but no examples of isolated systems (for which (0.1) is believed to be correct [4].) Gibbs emphasizes that the canonical ensemble is as useful for systems containing few particles as it is for systems containing many particles, in contrast to the microcanonical ensemble, which is only applicable to many-particle systems.

Finally, I will remain entirely grateful to the colleagues, students (notably Susan Merriam, who read carefully the final draft), and the editorial staff at Springer-Verlag. Together, they found my typographic and algebraic errors, missing steps in proofs, weak homework problems that could be made better, ... and called these deficiencies to my attention. The remaining errors are all mine.

References

[1] J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, Yale University Press, New Haven, CT (1902).

[2] L. Boltzmann, *Lectures in Gas Theory*, Leipzig (1896), translated in S. G. Brush, *Kinetic Theory*, Oxford University Press, Oxford, (1965).

[3] E. Schroedinger, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, (1952).

[4] It is sometimes asserted that—since no process creates or destroys energy—the Universe as a whole forms an element of a microcanonical ensemble. However, the best estimate—when I wrote this footnote—is that the Universe is open, in the cosmological sense, and therefore infinite in extent. If the total energy content of the Universe be infinite, the assertion that the Universe's total energy content is not changed by any process is not significant. The energy content of an infinite universe, being infinite itself, cannot be said not to change. To put it another way, the usual argument that (0.1) implies (0.2) relies on the assumption that if the energy in a part of an isolated system is increased, the energy available for distribution over the remainder of the system must have been reduced. In a finite system, this assumption is an obvious consequence of energy conservation. In an infinite isolated system, increasing the amount of energy in a small part of the system has no effect on the amount of energy available to be distributed over the remainder of the system, so in an infinite system the usual arguments for proceeding from (0.1) to (0.2) are not valid.

George D. J. Phillies
Worcester, Massachusetts
June, 1999

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