# METHODS OF STATISTICAL PHYSICS

This graduate-level textbook on thermal physics covers classical thermodynamics, statistical mechanics, and their applications. It describes theoretical methods to calculate thermodynamic properties, such as the equation of state, specific heat, Helmholtz potential, magnetic susceptibility, and phase transitions of macroscopic systems.

In addition to the more standard material covered, this book also describes more powerful techniques, which are not found elsewhere, to determine the correlation effects on which the thermodynamic properties are based. Particular emphasis is given to the cluster variation method, and a novel formulation is developed for its expression in terms of correlation functions. Applications of this method to topics such as the three-dimensional Ising model, BCS superconductivity, the Heisenberg ferromagnet, the ground state energy of the Anderson model, antiferromagnetism within the Hubbard model, and propagation of short range order, are extensively discussed. Important identities relating different correlation functions of the Ising model are also derived.

Although a basic knowledge of quantum mechanics is required, the mathematical formulation is accessible, and the correlation functions can be evaluated either numerically or analytically in the form of infinite series. Based on courses in statistical mechanics and condensed matter theory taught by the author in the United States and Japan, this book is entirely self-contained and all essential mathematical details are included. It will constitute an ideal companion text for graduate students studying courses on the theory of complex analysis, classical mechanics, classical electrodynamics, and quantum mechanics. Supplementary material is also available on the internet at http://uk.cambridge.org/resources/0521580560/

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To the late Professor Akira Harasima

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Frontmatter
More information

# Contents

# Preface

This book may be used as a textbook for the first or second year graduate student who is studying concurrently such topics as theory of complex analysis, classical mechanics, classical electrodynamics, and quantum mechanics.

In a textbook on statistical mechanics, it is common practice to deal with two important areas of the subject: mathematical formulation of the distribution laws of statistical mechanics, and demonstrations of the applicability of statistical mechanics.

The first area is more mathematical, and even philosophical, especially if we attempt to lay out the theoretical foundation of the approach to a thermodynamic equilibrium through a succession of irreversible processes. In this book, however, this area is treated rather routinely, just enough to make the book self-contained.†

The second area covers the applications of statistical mechanics to many thermodynamic systems of interest in physics. Historically, statistical mechanics was regarded as the only method of theoretical physics which is capable of analyzing the thermodynamic behaviors of dilute gases; this system has a disordered structure and statistical analysis was regarded almost as a necessity.

Emphasis had been gradually shifted to the imperfect gases, to the gas–liquid condensation phenomenon, and then to the liquid state, the motivation being to be able to deal with correlation effects. Theories concerning rubber elasticity and high polymer physics were natural extensions of the trend. Along a somewhat separate track, starting with the free electron theory of metals, energy band theories of both metals and semiconductors, the Heisenberg–Ising theories of ferromagnetism, the Bloch–Bethe–Dyson theories of ferromagnetic spin waves, and eventually the Bardeen–Cooper–Schrieffer theory of super-conductivity, the so-called solid state physics, has made remarkable progress. Many new and powerful theories, such as

† The reader is referred to the following books for extensive discussions of the subject: R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford, 1938, and D. ter Haar, *Elements of Statistical Mechanics*, Rinehart and Co., New York, 1956; and for a more careful derivation of the distribution laws, E. Schrödinger, *Statistical Thermodynamics*, Cambridge, 1952.

the diagrammatic methods and the methods of the Green's functions, have been developed as applications of statistical mechanics. One of the most important themes of interest in present day applications of statistical mechanics would be to find the strong correlation effects among various modes of excitations.

In this book the main emphasis will be placed on the various methods of accurately calculating the correlation effects, i.e., the thermodynamical average of a product of many dynamical operators, if possible to successively higher orders of accuracy. Fortunately a highly developed method which is capable of accomplishing this goal is available. The method is called the cluster variation method and was invented by Ryoichi Kikuchi (1951) and substantially reformulated by Tohru Morita (1957), who has established an entirely rigorous statistical mechanics foundation upon which the method is based. The method has since been developed and expanded to include quantum mechanical systems, mainly by three groups; the Kikuchi group, the Morita group, and the group led by the present author, and more recently by many other individual investigators, of course. The method was a theme of special research in 1951; however, after a commemorative publication,† the method is now regarded as one of the more standardized and even rather effective methods of actually calculating various many-body correlation functions, and hence it is thought of as textbook material of graduate level.

Chapter 6, entitled 'The cluster variation method', will constitute the centerpiece of the book in which the basic variational principle is stated and proved. An exact *cumulant expansion* is introduced which enables us to evaluate the Helmholtz potential at any degree of accuracy by increasing the number of *cumulant functions* retained in the variational Helmholtz potential. The mathematical formulation employed in this method is tractable and quite adaptable to numerical evaluation by computer once the cumulant expansion is truncated at some point. In Sec. 6.10 a four-site approximation and in Appendix 3 a tetrahedron-plus-octahedron approximation are presented in which up to six-body correlation functions are evaluated by the cluster variation method. The number of variational parameters in the calculation is only ten in this case, so that the numerical analysis by any computer is not very time consuming (Aggarwal and Tanaka, 1977). In the advent of much faster computers in recent years, much higher approximations can be carried out with relative ease and a shorter cpu time.

Chapter 7 deals with the infinite series representations of the correlation functions. During the history of the development of statistical mechanics there was a certain period of time during which a great deal of effort was devoted to the calculation of the exact infinite series for some physical properties, such as the partition function, the high temperature paramagnetic susceptibility, the low temperature

† *Progress in Theoretical Physics Supplement no. 115* 'Foundation and applications of cluster variation method and path probability method' (1994).

spontaneous magnetization, and both the high and low temperature specific heat for the ferromagnetic Ising model in the three-dimensional lattices by fitting different diagrams to a given lattice structure. The method was called the combinatorial formulation. It was hoped that these exact infinite series might lead to an understanding of the nature of mathematical singularities of the physical properties near the second-order phase transition. G. Baker, Jr. and his collaborators (1961 and in the following years) found a rather effective method called *Padé approximants*, and succeeded in locating the second-order phase transition point as well as the nature of the mathematical singularities in the physical properties near the transition temperature.

Contrary to the prevailing belief that the cluster variation type formulations would give only undesirable classical critical-point exponents at the second-order phase transition, it is demonstrated in Sec. 7.5 and in the rest of Chapter 7 that the infinite series solutions obtained by the cluster variation method (Aggarwal & Tanaka, 1977) yield exactly the same series expansions as obtained by much more elaborate combinatorial formulations available in the literature. This means that the most accurate critical-point exponents can be reproduced by the cluster variation method; a fact which is not widely known. The cluster variation method in this approximation yielded exact infinite series expansions for ten correlation functions simultaneously.

Chapter 8, entitled 'The extended mean-field approximation', is also rather unique. One of the most remarkable accomplishments in the history of statistical mechanics is the theory of superconductivity by Bardeen, Cooper, & Schrieffer (1957). The degree of approximation of the BCS theory, however, is equivalent to the mean-field approximation. Another more striking example in which the mean-field theory yields an exact result is the famous Dyson (1956) theory of spin-wave interaction which led to the $T^4$ term of the low temperature series expansion of the spontaneous magnetization. The difficult part of the formulation is not in its statistical formulation, but rather in the solution of a two-spin-wave eigenvalue problem. Even in Dyson's papers the separation between the statistical formulation and the solution of the two-spin-wave eigenvalue problem was not clarified, hence there were some misconceptions for some time. The *Wentzel theorem* (Wentzel, 1960) gave crystal-clear criteria for a certain type of Hamiltonian for which the mean-field approximation yields an exact result. It is shown in Chapter 8 that both the BCS reduced Hamiltonian and the spin-wave Hamiltonian for the Heisenberg ferromagnet satisfy the Wentzel criteria, and hence the mean-field approximation gives exact results for those Hamiltonians. For this reason the content of Chapter 8 is pedagogical.

Chapter 9 deals with some of the exact identities for different correlation functions of the two-dimensional Ising model. Almost 100 Ising spin correlation functions may be calculated exactly if two or three known correlation functions are fed into these identities. It is shown that the method is applicable to the three-dimensional Ising model, and some 18 exact identities are developed for the diamond lattice (Appendix 5). When a large number of correlation functions are introduced there arises a problem of naming them such that there is no confusion in assigning two different numbers to the same correlation function appearing at two different locations in the lattice. The so-called *vertex number representation* is introduced in order to identify a given cluster figure on a given two-dimensional lattice.

In Chapter 10 an example of oscillatory behavior of the radial distribution (or pair correlation) function, up to the seventh-neighbor distance, which shows at least the first three peaks of oscillation, is found by means of the cluster variation method in which up to five-body correlation effects are taken into account. The formulation is applied to the order–disorder phase transition in the super-ionic conductor AgI. It is shown that the entropy change of the first-order phase transition thus calculated agrees rather well with the observed latent heat of phase transition. Historically, the radial distribution function in a classical monatomic liquid, within the framework of a continuum theory, is calculated only in the three-body (super-position) approximation, and only the first peak of the oscillatory behavior is found. The model demonstrated in this chapter suggests that the theory of the radial distribution function could be substantially improved if the lattice gas model is employed and with applications of the cluster variation method.

Chapter 11 gives a brief introduction of the Pfaffian formulation applied to the reformulation of the famous Onsager partition function for the two-dimensional Ising model. The subject matter is rather profound, and detailed treatments of the subject in excellent book form have been published (Green & Hurst, 1964; McCoy & Wu, 1973).

Not included are the diagrammatic method of many-body problem, the Green's function theories, and the linear response theory of transport coefficients. There are many excellent textbooks available on those topics.

The book starts with an elementary and rather brief introduction of classical thermodynamics and the ensemble theories of statistical mechanics in order to make the text self-contained. The book is not intended as a philosophical or fundamental principles approach, but rather serves more as a recipe book for statistical mechanics practitioners as well as research motivated graduate students.

*Tomoyasu Tanaka*

# Acknowledgements

I should like to acknowledge the late Professor Akira Harasima, who, through his kind course instruction, his books, and his advice regarding my thesis, was of invaluable help whilst I was a student at Kyushu Imperial University during World War II and a young instructor at the post-war Kyushu University. Professor Harasima was one of the pioneer physicists in the area of theories of monatomic liquids and surface tension during the pre-war period and one of the most famous authors on the subjects of classical mechanics, quantum mechanics, properties of matter, and statistical mechanics of surface tension. All his physics textbooks are written so painstakingly and are so easy to understand that every student can follow the books as naturally and easily as Professor Harasima's lectures in the classroom. Even in the present day physics community in Japan, many of Professor Harasima's textbooks are best sellers more than a decade after he died in 1986. The present author has tried to follow the Harasima style, as it may be called, as much as possible in writing the *Methods of Statistical Mechanics*.

The author is also greatly indebted to Professor Tohru Morita for his kind leadership in the study of statistical mechanics during the four-year period 1962–6. The two of us, working closely together, burned the enjoyable late-night oil in a small office in the Kean Hall at the Catholic University of America, Washington, D.C. It was during this period that the cluster variation method was given full blessing.