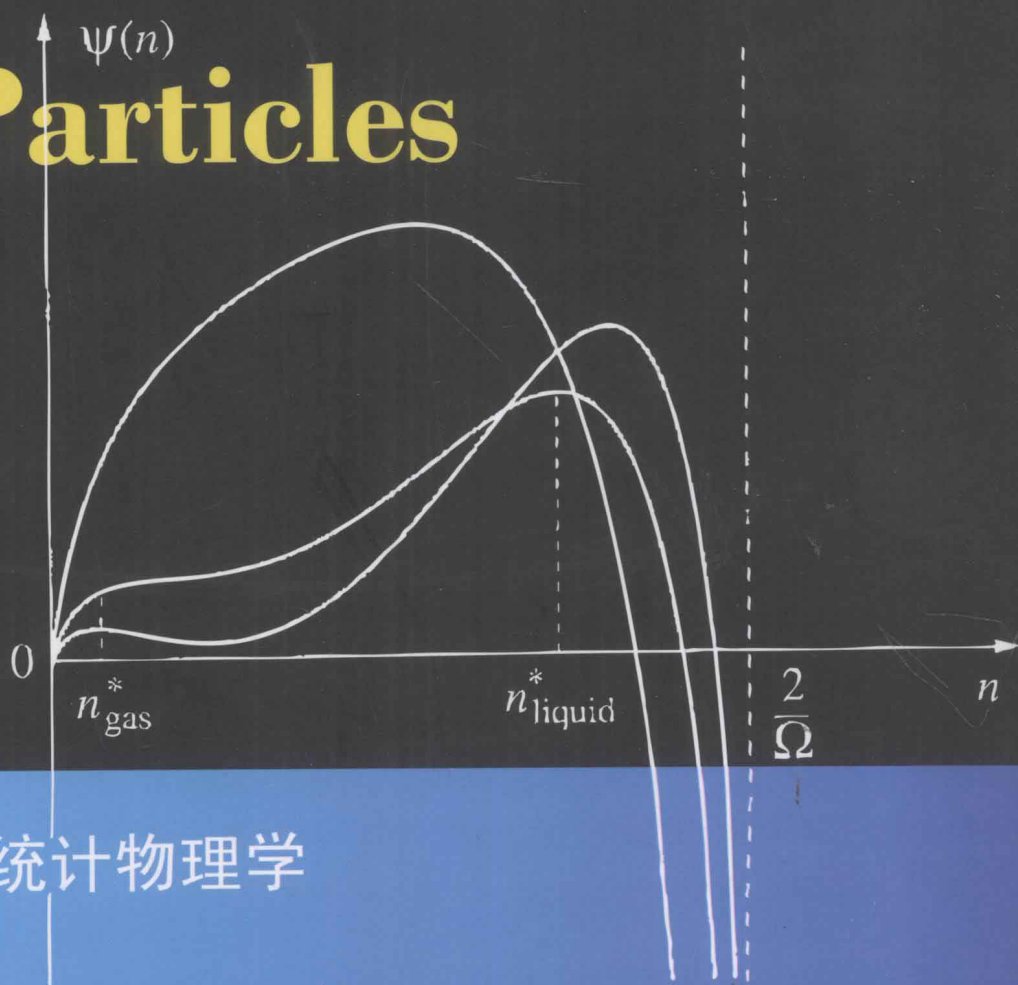


Mehran Kardar

Statistical Physics of Particles



粒子的统计物理学

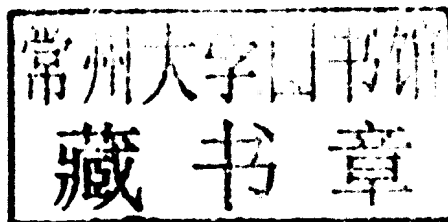
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图书在版编目 (CIP) 数据

粒子的统计物理学 = Statistical Physics of Particles:
英文/ (美) 卡达 (Kardar, M.) 著. —影印本.
—北京: 世界图书出版公司北京公司, 2010. 5
ISBN 978-7-5100-0565-7

I. ①粒… II. ①卡… III. ①基本粒子—统计
物理学—英文 IV. ①0414. 2

中国版本图书馆 CIP 数据核字 (2010) 第 036196 号

书 名: Statistical Physics of Particles

作 者: Mehran Kardar

中 译 名: 粒子的统计物理学

责任编辑: 高蓉 刘慧

出 版 者: 世界图书出版公司北京公司

印 刷 者: 三河国英印务有限公司

发 行: 世界图书出版公司北京公司 (北京朝内大街 137 号 100010)

联系电话: 010-64021602, 010-64015659

电子信箱: kjb@wpchj.com.cn

开 本: 16 开

印 张: 21

版 次: 2010 年 04 月

版权登记: 图字: 01-2010-0335

书 号: 978-7-5100-0565-7/O · 780

定 价: 55.00 元

Statistical Physics of Particles

Statistical physics has its origins in attempts to describe the thermal properties of matter in terms of its constituent particles, and has played a fundamental role in the development of quantum mechanics. It describes how new behavior emerges from interactions of many degrees of freedom, and as such has found applications outside physics in engineering, social sciences, and, increasingly, in biological sciences. This textbook introduces the central concepts and tools of statistical physics. It includes a chapter on probability and related issues such as the central limit theorem and information theory, not usually covered in existing texts. The book also covers interacting particles, and includes an extensive description of the van der Waals equation and its derivation by mean-field approximation. A companion volume, *Statistical Physics of Fields*, discusses non-mean field aspects of scaling and critical phenomena, through the perspective of renormalization group.

Based on lectures for a course in statistical mechanics taught by Professor Kardar at Massachusetts Institute of Technology (MIT), this textbook contains an integrated set of problems, with solutions to selected problems at the end of the book. It will be invaluable for graduate and advanced undergraduate courses in statistical physics. Additional solutions are available to lecturers on a password protected website at www.cambridge.org/9780521873420.

MEHRAN KARDAR is Professor of Physics at MIT, where he has taught and researched in the field of statistical physics for the past 20 years. He received his B.A. at Cambridge, and gained his Ph.D. at MIT. Professor Kardar has held research and visiting positions as a junior Fellow at Harvard, a Guggenheim Fellow at Oxford, UCSB, and at Berkeley as a Miller Fellow.

In this much-needed modern text, Kardar presents a remarkably clear view of statistical mechanics as a whole, revealing the relationships between different parts of this diverse subject. In two volumes, the classical beginnings of thermodynamics are connected smoothly to a thoroughly modern view of fluctuation effects, stochastic dynamics, and renormalization and scaling theory. Students will appreciate the precision and clarity in which difficult concepts are presented in generality and by example. I particularly like the wealth of interesting and instructive problems inspired by diverse phenomena throughout physics (and beyond!), which illustrate the power and broad applicability of statistical mechanics.

Statistical Physics of Particles includes a concise introduction to the mathematics of probability for physicists, an essential prerequisite to a true understanding of statistical mechanics, but which is unfortunately missing from most statistical mechanics texts. The old subject of kinetic theory of gases is given an updated treatment which emphasizes the connections to hydrodynamics.

As a graduate student at Harvard, I was one of many students making the trip to MIT from across the Boston area to attend Kardar's advanced statistical mechanics class. Finally, in *Statistical Physics of Fields* Kardar makes his fantastic course available to the physics community as a whole! The book provides an intuitive yet rigorous introduction to field-theoretic and related methods in statistical physics. The treatment of renormalization group is the best and most physical I've seen, and is extended to cover the often-neglected (or not properly explained!) but beautiful problems involving topological defects in two dimensions. The diversity of lattice models and techniques are also well-illustrated and complement these continuum approaches. The final two chapters provide revealing demonstrations of the applicability of renormalization and fluctuation concepts beyond equilibrium, one of the frontier areas of statistical mechanics.

Leon Balents, Department of Physics, University of California, Santa Barbara

Statistical Physics of Particles is the welcome result of an innovative and popular graduate course Kardar has been teaching at MIT for almost twenty years. It is a masterful account of the essentials of a subject which played a vital role in the development of twentieth century physics, not only surviving, but enriching the development of quantum mechanics. Its importance to science in the future can only increase with the rise of subjects such as quantitative biology.

Statistical Physics of Fields builds on the foundation laid by the *Statistical Physics of Particles*, with an account of the revolutionary developments of the past 35 years, many of which were facilitated by renormalization group ideas. Much of the subject matter is inspired by problems in condensed matter physics, with a number of pioneering contributions originally due to Kardar himself. This lucid exposition should be of particular interest to theorists with backgrounds in field theory and statistical mechanics

David R Nelson, Arthur K Solomon Professor of Biophysics Harvard University

If Landau and Lifshitz were to prepare a new edition of their classic *Statistical Physics* text they might produce a book not unlike this gem by Mehran Kardar. Indeed, Kardar is an extremely rare scientist, being both brilliant in formalism and an astoundingly careful and thorough teacher. He demonstrates both aspects of his range of talents in this pair of books, which belong on the bookshelf of every serious student of theoretical statistical physics

Kardar does a particularly thorough job of explaining the subtleties of theoretical topics too new to have been included even in Landau and Lifshitz's most recent Third Edition (1980), such as directed paths in random media and the dynamics of growing surfaces, which are not in any text to my knowledge. He also provides careful discussion of topics that do appear in most modern texts on theoretical statistical physics, such as scaling and renormalization group.

H Eugene Stanley, Director, Center for Polymer Studies, Boston University

This is one of the most valuable textbooks I have seen in a long time. Written by a leader in the field, it provides a crystal clear, elegant and comprehensive coverage of the field of statistical physics. I'm sure this book will become "the" reference for the next generation of researchers, students and practitioners in statistical physics. I wish I had this book when I was a student but I will have the privilege to rely on it for my teaching.

Alessandro Vespignani, Center for Biocomplexity, Indiana University

Preface

Historically, the discipline of *statistical physics* originated in attempts to describe thermal properties of matter in terms of its constituent particles, but also played a fundamental role in the development of quantum mechanics. More generally, the formalism describes how new behavior emerges from interactions of many degrees of freedom, and as such has found applications in engineering, social sciences, and increasingly in biological sciences. This book introduces the central concepts and tools of this subject, and guides the reader to their applications through an integrated set of problems and solutions.

The material covered is directly based on my lectures for the first semester of an MIT graduate course on statistical mechanics, which I have been teaching on and off since 1988. (The material pertaining to the second semester is presented in a companion volume.) While the primary audience is physics graduate students in their first semester, the course has typically also attracted enterprising undergraduates, as well as students from a range of science and engineering departments. While the material is reasonably standard for books on statistical physics, students taking the course have found my exposition more useful, and have strongly encouraged me to publish this material. Aspects that make this book somewhat distinct are the chapters on probability and interacting particles. Probability is an integral part of statistical physics, which is not sufficiently emphasized in most textbooks. Devoting an entire chapter to this topic (and related issues such as the central limit theorem and information theory) provides valuable tools to the reader. In the context of interacting particles, I provide an extensive description of the van der Waals equation, including its derivation by mean-field approximation.

An essential part of learning the material is doing problems; an interesting selection of problems (and solutions) has been designed and integrated into the text. Following each chapter there are two sets of problems: solutions to the first set are included at the end of the book, and are intended to introduce additional topics and to reinforce technical tools. Pursuing these problems should also prove useful for students studying for qualifying exams. There

are no solutions provided for a second set of problems, which can be used in assignments.

I am most grateful to my many former students for their help in formulating the material, problems, and solutions, typesetting the text and figures, and pointing out various typos and errors. The support of the National Science Foundation through research grants is also acknowledged.

Statistical Physics of Particles, 1st ed. (978-0-521-87342-0) by Mehran Kardar
first published by Cambridge University Press 2007

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Thermodynamics

1.1 Introduction

Thermodynamics is a *phenomenological description of properties of macroscopic systems in thermal equilibrium*.

Imagine yourself as a post-Newtonian physicist intent on understanding the behavior of such a simple system as a container of gas. How would you proceed? The prototype of a successful physical theory is classical mechanics, which describes the intricate motions of particles starting from simple basic laws and employing the mathematical machinery of calculus. By analogy, you may proceed as follows:

- Idealize the *system* under study as much as possible (as is the case of a point particle). The concept of mechanical work on the system is certainly familiar, yet there appear to be complications due to exchange of heat. The solution is first to examine *closed systems*, insulated by *adiabatic walls* that don't allow any exchange of heat with the surroundings. Of course, it is ultimately also necessary to study *open systems*, which may exchange heat with the outside world through *diathermic walls*.
- As the state of a point particle is quantified by its coordinates (and momenta), properties of the macroscopic system can also be described by a number of *thermodynamic coordinates or state functions*. The most familiar coordinates are those that relate to mechanical work, such as pressure and volume (for a fluid), surface tension and area (for a film), tension and length (for a wire), electric field and polarization (for a dielectric), etc. As we shall see, there are additional state functions not related to mechanical work. The state functions are well defined only when the system is in *equilibrium*, that is, when its properties do not change appreciably with time over the intervals of interest (observation times). The dependence on the observation time makes the concept of equilibrium subjective. For example, window glass is in equilibrium as a solid over many decades, but flows like a fluid over time scales of millennia. At the other extreme, it is perfectly legitimate to consider the equilibrium between matter and radiation in the early universe during the first minutes of the Big Bang.

- Finally, the relationship between the state functions is described by the laws of thermodynamics. As a *phenomenological* description, these laws are based on a number of empirical observations. A coherent logical and mathematical structure is then constructed on the basis of these observations, which leads to a variety of useful concepts, and to testable relationships among various quantities. The laws of thermodynamics can only be justified by a more fundamental (microscopic) theory of nature. For example, statistical mechanics attempts to obtain these laws starting from classical or quantum mechanical equations for the evolution of collections of particles.

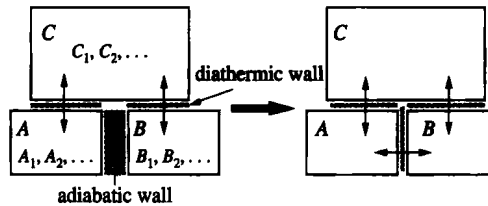
1.2 The zeroth law

The zeroth law of thermodynamics describes the transitive nature of thermal equilibrium. It states:

If two systems, A and B, are separately in equilibrium with a third system, C, then they are also in equilibrium with one another.

Despite its apparent simplicity, the zeroth law has the consequence of implying the existence of an important state function, the *empirical temperature* Θ , such that systems in equilibrium are at the same temperature.

Fig. 1.1 Illustration of the zeroth law: systems A and B, which are initially separately in equilibrium with C, are placed in contact with each other.



Let the equilibrium state of systems A, B, and C be described by the coordinates $\{A_1, A_2, \dots\}$, $\{B_1, B_2, \dots\}$, and $\{C_1, C_2, \dots\}$, respectively. The assumption that A and C are in equilibrium implies a constraint between the coordinates of A and C, that is, a change in A_1 must be accompanied by some changes in $\{A_2, \dots; C_1, C_2, \dots\}$ to maintain equilibrium of A and C. Denote this constraint by

$$f_{AC}(A_1, A_2, \dots; C_1, C_2, \dots) = 0. \quad (1.1)$$

The equilibrium of B and C implies a similar constraint

$$f_{BC}(B_1, B_2, \dots; C_1, C_2, \dots) = 0. \quad (1.2)$$

Note that each system is assumed to be separately in mechanical equilibrium. If they are allowed also to do work on each other, additional conditions (e.g., constant pressure) are required to describe their joint mechanical equilibrium.

Clearly we can state the above constraint in many different ways. For example, we can study the variations of C_1 as all of the other parameters are changed. This is equivalent to solving each of the above equations for C_1 to yield ¹

$$\begin{aligned} C_1 &= F_{AC}(A_1, A_2, \dots; C_2, \dots), \\ C_1 &= F_{BC}(B_1, B_2, \dots; C_2, \dots). \end{aligned} \quad (1.3)$$

Thus if C is separately in equilibrium with A and B , we must have

$$F_{AC}(A_1, A_2, \dots; C_2, \dots) = F_{BC}(B_1, B_2, \dots; C_2, \dots). \quad (1.4)$$

However, according to the zeroth law there is also equilibrium between A and B , implying the constraint

$$f_{AB}(A_1, A_2, \dots; B_1, B_2, \dots) = 0. \quad (1.5)$$

We can select any set of parameters $\{A, B\}$ that satisfy the above equation, and substitute them in Eq. (1.4). The resulting equality must hold quite independently of any set of variables $\{C\}$ in this equation. We can then change these parameters, moving along the manifold constrained by Eq. (1.5), and Eq. (1.4) will remain valid irrespective of the state of C . Therefore, it must be possible to simplify Eq. (1.4) by canceling the coordinates of C . Alternatively, we can select any fixed set of parameters C , and ignore them henceforth, reducing the condition (1.5) for equilibrium of A and B to

$$\Theta_A(A_1, A_2, \dots) = \Theta_B(B_1, B_2, \dots), \quad (1.6)$$

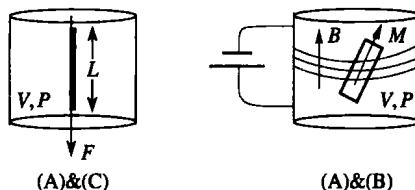
that is, equilibrium is characterized by a function Θ of thermodynamic coordinates. This function specifies the *equation of state*, and *isotherms* of A are described by the condition $\Theta_A(A_1, A_2, \dots) = \Theta$. While at this point there are many potential choices of Θ , the key point is the existence of a function that constrains the parameters of each system in thermal equilibrium.

There is a similarity between Θ and the force in a mechanical system. Consider two one-dimensional systems that can do work on each other as in the case of two springs connected together. Equilibrium is achieved when the forces exerted by each body on the other are equal. (Of course, unlike the scalar temperature, the vectorial force has a direction; a complication that we have ignored. The pressure of a gas piston provides a more apt analogy.) The mechanical equilibrium between several such bodies is also transitive, and the latter could have been used as a starting point for deducing the existence of a mechanical force.

¹ From a purely mathematical perspective, it is not necessarily possible to solve an arbitrary constraint condition for C_1 . However, the requirement that the constraint describes real physical parameters clearly implies that we can obtain C_1 as a function of the remaining parameters.

As an example, let us consider the following three systems: (A) a wire of length L with tension F , (B) a paramagnet of magnetization M in a magnetic field B , and (C) a gas of volume V at pressure P .

Fig. 1.2 Equilibria of a gas (A) and a magnet (B), and a gas (A) and a wire (C).



Observations indicate that when these systems are in equilibrium, the following constraints are satisfied between their coordinates:

$$\begin{aligned} \left(P + \frac{a}{V^2}\right)(V-b)(L-L_0) - c[F - K(L-L_0)] &= 0, \\ \left(P + \frac{a}{V^2}\right)(V-b)M - dB &= 0. \end{aligned} \quad (1.7)$$

The two conditions can be organized into three empirical temperature functions as

$$\Theta \propto \left(P + \frac{a}{V^2}\right)(V-b) = c \left(\frac{F}{L-L_0} - K \right) = d \frac{B}{M}. \quad (1.8)$$

Note that the zeroth law severely constrains the form of the constraint equation describing the equilibrium between two bodies. Any arbitrary function cannot necessarily be organized into an equality of two empirical temperature functions.

The constraints used in the above example were in fact chosen to reproduce three well-known equations of state that will be encountered and discussed later in this book. In their more familiar forms they are written as

$$\begin{cases} (P + a/V^2)(V-b) = Nk_B T & \text{(van der Waals gas)} \\ M = (N \mu_B^2 B)/(3k_B T) & \text{(Curie paramagnet)} \\ F = (K + DT)(L-L_0) & \text{(Hooke's law for rubber)} \end{cases} \quad (1.9)$$

Note that we have employed the symbol for Kelvin temperature T , in place of the more general empirical temperature Θ . This concrete temperature scale can be constructed using the properties of the ideal gas.

The ideal gas temperature scale: while the zeroth law merely states the presence of isotherms, to set up a practical temperature scale at this stage, a reference system is necessary. The *ideal gas* occupies an important place in thermodynamics and provides the necessary reference. Empirical observations indicate that the product of pressure and volume is constant along the isotherms of any gas that is sufficiently dilute. The ideal gas refers to this *dilute* limit of

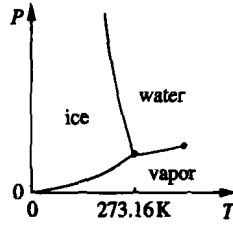


Fig. 1.3 The triple point of ice, water, and steam occurs at a unique point in the (P, T) phase diagram.

real gases, and the ideal gas temperature is proportional to the product. The constant of proportionality is determined by reference to the temperature of the triple point of the ice–water–gas system, which was set to 273.16 (degrees) kelvin (K) by the 10th General Conference on Weights and Measures in 1954. Using a dilute gas (i.e., as $P \rightarrow 0$) as thermometer, the temperature of a system can be obtained from

$$T(\text{K}) = 273.16 \times \left(\lim_{P \rightarrow 0} (PV)_{\text{system}} / \lim_{P \rightarrow 0} (PV)_{\text{ice-water-gas}} \right). \quad (1.10)$$

1.3 The first law

In dealing with simple mechanical systems, conservation of energy is an important principle. For example, the location of a particle can be changed in a potential by external work, which is then related to a change in its potential energy. Observations indicate that a similar principle operates at the level of macroscopic bodies *provided that the system is properly insulated*, that is, when the only sources of energy are of mechanical origin. We shall use the following formulation of these observations:

The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states, and not on the means by which the work is performed, or on the intermediate stages through which the system passes.

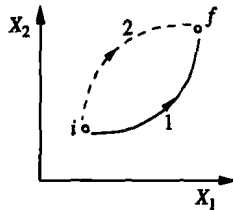


Fig. 1.4 The two adiabatic paths for changing macroscopic coordinates between the initial and final point result in the same change in internal energy.

For a particle moving in a potential, the required work can be used to construct a potential energy landscape. Similarly, for the thermodynamic system we can construct another state function, the internal energy $E(X)$. Up to a constant,

$E(\mathbf{X})$ can be obtained from the amount of work ΔW needed for an *adiabatic* transformation from an initial state \mathbf{X}_i to a final state \mathbf{X}_f , using

$$\Delta W = E(\mathbf{X}_f) - E(\mathbf{X}_i). \quad (1.11)$$

Another set of observations indicate that once the adiabatic constraint is removed, the amount of work is no longer equal to the change in the internal energy. The difference $\Delta Q = \Delta E - \Delta W$ is defined as the *heat* intake of the system from its surroundings. Clearly, in such transformations, ΔQ and ΔW are not separately functions of state in that they depend on external factors such as the means of applying work, and not only on the final states. To emphasize this, for a differential transformation we write

$$dQ = dE - dW, \quad (1.12)$$

where $dE = \sum_i \partial_i E dX_i$ can be obtained by differentiation, while dQ and dW generally cannot. Also note that our convention is such that the signs of work and heat indicate the energy *added* to the system, and not vice versa. The first law of thermodynamics thus states that to change the state of a system we need a fixed amount of energy, which can be in the form of mechanical work or heat. This can also be regarded as a way of defining and quantifying the exchanged heat.

A *quasi-static* transformation is one that is performed sufficiently slowly so that the system is always in equilibrium. Thus, at any stage of the process, the thermodynamic coordinates of the system exist and can in principle be computed. For such transformations, the work done on the system (equal in magnitude but opposite in sign to the work done by the system) can be related to changes in these coordinates. As a mechanical example, consider the stretching of a spring or rubber band. To construct the potential energy of the system as a function of its length L , we can pull the spring sufficiently slowly so that at each stage the external force is matched by the internal force F from the spring. For such a quasi-static process, the change in the potential energy of the spring is $\int F dL$. If the spring is pulled abruptly, some of the external work is converted into kinetic energy and eventually lost as the spring comes to rest.

Generalizing from the above example, one can typically divide the state functions $\{\mathbf{X}\}$ into a set of *generalized displacements* $\{\mathbf{x}\}$, and their conjugate *generalized forces* $\{\mathbf{J}\}$, such that for an infinitesimal quasi-static transformation²

$$dW = \sum_i J_i dx_i. \quad (1.13)$$

² I denote force by the symbol \mathbf{J} rather than \mathbf{F} , to reserve the latter for the free energy. I hope the reader is not confused with currents (sometimes also denoted by \mathbf{J}), which rarely appear in this book.