

Equilibrium Statistical Physics

(2 n d E d i t i o n)

平衡统计物理学

(第二版)

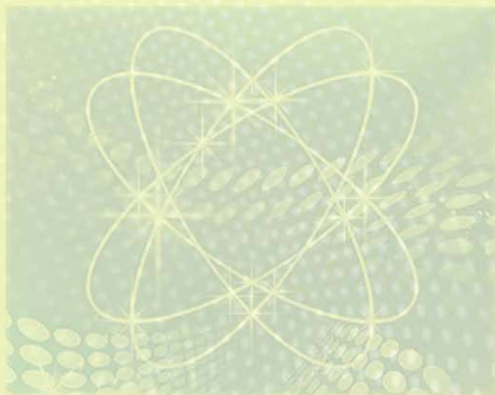
(英文影印版)

Michael Plischke

(Simon Fraser University, Canada)

Birger Bergersen

(University of British Columbia, Canada)



复旦大学出版社

研究生前沿教材书系

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图书在版编目(CIP)数据

平衡统计物理学(第二版) = Equilibrium Statistical Physics(2nd Edition)/
〔加〕普里斯科,〔加〕伯格森著. —上海:复旦大学出版社,2006.11
(研究生前沿教材书系)
ISBN 7-309-05200-5

I. 平… II. ①普…②伯… III. 平衡状态(热力学)-统计物理学-
研究生-教学参考资料-英文 IV. 0414.21

中国版本图书馆 CIP 数据核字(2006)第 121623 号

Equilibrium Statistical Physics(2nd Edition)

Michael Plischke, Birger Bergersen

First edition published in 1989 by Prentice-Hall, Inc.

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本书由(新加坡)世界科技出版公司 授权出版英文影印版

著作权合同登记号 图字:09-2006-682

平衡统计物理学(第二版)

〔加〕M. 普里斯科 〔加〕B. 伯格森 著

出版发行 复旦大学出版社

上海市国权路 579 号 邮编 200433

86-21-65642857(门市零售)

86-21-65118853(团体订购) 86-21-65109143(外埠邮购)

fupnet@fudanpress.com http://www.fudanpress.com

责任编辑 梁 玲

总 编 辑 高若海

出 品 人 贺圣遂

印 刷 浙江省临安市曙光印务有限公司

开 本 787×960 1/16

印 张 33.75

版 次 2006 年 11 月第二版第一次印刷

印 数 1—3 100

书 号 ISBN 7-309-05200-5/O·372

定 价 50.00 元

如有印装质量问题,请向复旦大学出版社发行部调换。

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Michael Plischke

加拿大 Simon Fraser 大学物理系主任,教授。芝加哥 Loyola 大学物理学学士,Yale 大学物理学硕士,Yeshiva 大学物理学博士,长期从事凝聚态物理研究,并给硕士生和本科生讲授统计力学。*Equilibrium Statistical Physics* 和 *Physics and Chemistry of Disordered Systems* 等是其代表性的著作。

Birger Bergersen

加拿大 British Columbia 大学物理和天文系荣誉退休教授。给硕士生和本科生讲授热力学和统计物理长达 30 多年,*Equilibrium Statistical Physics* 一书就是其重要的学术著作。

内 容 简 介

这是针对从事物理、化学和材料科学的研究生和高年级本科生的专业需求编写的统计物理教材。早在1980年,作者们发现由K. G. Wilson率先将重整化群方法引入临界现象并取得成功之后,凝聚态物理的研究进入了飞速发展的黄金时代,因此认为研究生的早期教学工作应当反映这方面的动态。为此于1989年率先由Prentice-Hall出版公司出版了反映这方面特色的《平衡统计物理学》,1994年经过修订,转到World Scientific出版了本书第一版,1999年出版了第二版,现在呈现在读者面前的是2003年的版本。

全书共分11章,前两章分别复习热力学和统计系统理论,这部分内容既是读者学习后面各章的基础,也是为了本科期间没有接触过热力学和统计物理的学生设计的。两章都有大量习题,可以帮助读者加深理解。后面各章分别讲述平均场和朗道理论、致密气体和液体、临界现象的二维伊辛模型、级数展开、标度律、重整化群方法等。第七章介绍动力学模拟方法。八、九、十、十一各章介绍统计物理最活跃的应用领域:聚合物和薄膜、量子流体、线性响应理论、无序系统等。由于本书的后半部分涉及二次量子化的概念,因此在附录中补充了占有数表象的内容。本书每章都有不少的习题,越到后面各章,习题的难度越来越有挑战性。作者们还专门编写了《习题解答》,有需要的教师或读者可通过互联网(<http://www.worldscibooks.com/physics/4485.html>)查找。

第一版序言

在过去的 10 年时间里,我们两位作者都在各自的学校给研究生或高年级本科生讲授固定的统计力学课程。正是这段时间,由 K. G. Wilson 率先把重整化群的方法引入临界现象之中,这就大大地改变了我们对凝聚态物理的研究方法。自从重整化群引入相变的研究领域以来,发现这一方法在诸如多体理论、混沌、无序材料的导电性质,以及分形结构等等很多其他物理学领域都具有应用前景。由于它的影响是如此深刻,使得我们感到,当务之急是在研究生的早期阶段,就能将标度律、普适性、不动点、重整化变换等等在临界现象的范围内发展起来的、但又同很多其他领域密切相关的概念,引入到统计力学的教学之中。

在这本教科书中,我们在阐述统计力学的传统方法的同时,也介绍过去 20 年中新发展起来的技术。大多数研究生只讲授一门统计物理的课程,我相信现在这门课程必将在典型的本科生课程(通常只涉及无相互作用的,诸如理想气体和顺磁物质)和研究人员所必需的复杂概念之间构筑起桥梁。

我们在开始的两章里,简短地讨论一下热力学,复习一下统计力学的基础。我们假设研究生们以前已经接触过这两章的材料,因此我们的阐述相当简洁。不过我们挑选了大量的习题,有助于实现更好的复习。

第三章我们详尽地讲述平均场理论,开始讨论强相互作用系统。不少实例都分析得很细致。关于相变的普遍的朗道理论作了讨论,并把它应用到临界点、三重临界点、一级相变等领域。平均场理论和朗道理论的局限性也作了阐述,并且涨落的作用也根据朗道-京茨堡模型的框架给予讨论。

第四章涉及致密气体和液体的理论。液体理论中常用的许多

技巧已有较长历史并在其他书中已有很好的描述,但是我们还是认为液体理论依然十分重要,我们不应当忽视它们。传统的维里展开法也作了阐述,并且我们强调配对关联函数在理论和实验两方面的重要作用。我们是在用来计算配对关联函数和液体微扰论的 Ornstein-Zernike 方程的基础上,简洁地描述某些有用且依然流行的积分方程法。(Monte Carlo 和分子动力学)模拟法也引入介绍。在本章的最后一节,我们描述了平均场理论的一种有趣应用,亦即描述了液-汽界面的范德瓦尔斯理论,这是反映由于毛细作用波引起这一界面粗糙的一种简单模型。

第五、第六两章致力于连续相变和临界现象。第五章中我们讨论了基于方格点的二维伊辛模型的昂色格解,再用历史上极重要的临界现象理论——级数展开法继续讨论之。我们遵照 Kadanoff 的思想,建立了相变的标度理论,引进了临界行为的普适性概念,最后对具有连续对称性的二维系统相变的 Kosterlitz-Thouless 理论作出主要是定性的讨论。

第六章完全是用重整化群的方法来讨论相变,这里的概念对于一维、二维伊辛模型而言,从技巧上讲完全是通过直接计算引进的。我们讨论了重整化变换的不动点的作用,说明了理论上如何得出普适性的临界行为。Wilson 和 Fisher 的原始的 ϵ 展开法也作了讨论。这一节我们写得很细致,那是因为考虑到学生很可能缺乏场论的背景知识,为使他们尽量易于理解起见。

第七章我们转到量子流体,讨论理想玻色气体、弱相互作用玻色气体、超导电性的 BCS 理论,以及超导的唯象的朗道-京茨堡理论。我们对这些课题的处理方法,除了理想玻色气体之外,同平均场理论的精神十分一致,并对第三章中发展起来的很多形式提出了更富挑战性的应用。

第八章主要讨论线性响应理论。涨落耗散定理、Kubo 形式、输运系数的昂色格关系等等都作了讨论。这一章我们始终把重点放在平衡现象——线性响应近似中,平衡关联函数发挥着主导的作用。诸如电子气的介电响应、海森伯铁磁体的元激发,以及相互作

用玻色流体的激发谱等等一系列形式的应用,都作了细致的讨论。对于通过线性化玻尔兹曼方程讨论输运的补充方法,也作了讨论。

第九章提供了无序材料物理学的介绍。我们讨论了无序对系统量子态的影响,通过对一维模型的具体计算,作为实例引进了定域电子态的概念。我们还介绍了渗滤理论,并且阐明它和热相变很相似。无序材料中相变的性质作了讨论,对于玻璃和自旋玻璃的相变,我们作了简洁、结论性的定性描述。这些专题都是当今重要的前沿研究阵地,但不要求我们的处理方法都达到十全十美。为了弥补本章的不足,我们在正文脚注中注明了近年关于这些专题的研究文献,而不像其他各章的文献那样笼统。

我们发现本书所涉及的内容既适用研究生作入门教材,如果作适当的筛选,也适合于高年级本科生作教材。对于已有统计力学初步基础、有量子力学背景,并且最好还学过某些固态物理的学生,其预备知识是相当充分了。二次量子化的概念在本书的后半部分用得很多,本书附录中对此有详尽的介绍。这里有必要提醒一下教师,尽管有些习题,尤其是头几章习题,的确比较简单,但越到后面相应的习题却有着相当的挑战性。

本书涉及的大多数课题都是近年来研究的热门课题。鉴于这个原因,我们发现必须列出期刊上出现的大量文献。尽我们的最大可能,去参考最新的评论性文章而不是仅仅采用原始的资料。

这本书的编写持续了好多年(中间还常常停顿下来),通过与很多同事的讨论,倾听他们的批评和建议,使我们得益匪浅。这其中特别是 Ian Affleck, Leslie Ballentine, Robert Barrie, John Berlinsky, Peter Holdsworth, Zoltán Rácz 以及 Bill Unruh 对我们的帮助特别多。我们的学生 Dan Ciarniello, Victor Finberg 及 Barbara Frisken 协助我们订正了差错,点出了模棱两可和含糊不清的地方。当然留下来的不足之处完全由作者承担。

Michael Plischke
Birger Bergersen

第二版序言

本书第一版出版至今已有 5 年时间,我们收到了来自我们各自学校和其他单位的朋友和同事们的很多有益的建议。同时,统计力学的研究领域也在持续地拓展。在第二版的写作过程中,我们将尽可能考虑这些方面的情况。两个版本的目标仍然相同:为物理、化学和材料科学的研究生提供统计物理中最佳的处理技巧。

尽管第二版的总体框架同第一版极为类似,但补充了许多重要内容。相当简略的计算机模拟方法,已大大地扩充并构成了单独的第七章。在经典流体的那章中,我们补充介绍了密度泛函法。关于聚合物和薄膜使我们新增了整整一章。在讨论临界现象时,我们纠正了第一版的重要疏忽,新增了关于有限大小标度律和唯象重整化群的一节。最后,我们拓广了对自旋玻璃的讨论并新增几道新的习题。我们还完成了习题解答手册,读者如有需求可向出版商索取。

无需赘言,凡是我们发现了的第一版中的差错,都已给予订正。这项任务大大地受益于很多人的帮助。尤其要感谢 Vinay Ambegaokar, Leslie Ballentine, David Boal, Bill Dalby, Zoltán Rácz, Byron Southern 以及 Philip Stamp。

Michael Plischke
Birger Bergersen
于加拿大温哥华

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Chapter 1

Review of Thermodynamics

This chapter presents a brief review of elementary thermodynamics. It complements Chapter 2, in which the connection between thermodynamics and statistical mechanical ensembles is established. The reader may wish to use this chapter as a short refresher course and may wish to consult one of the many books on thermodynamics, such as that of Callen[48] or Chapters 2 to 4 of the book by Reichl[216], for a more complete discussion of the material. The outline of the present chapter is as follows. In Section 1.1 we introduce the notion of state variables and equations of state. Section 1.2 contains a discussion of the laws of thermodynamics, definition of thermodynamic processes, and the introduction of entropy. In Section 1.3 we introduce the thermodynamic potentials that are most useful from a statistical point of view. The Gibbs–Duhem equation and a number of useful Maxwell relations are derived in Section 1.4. In Section 1.5 we turn to the response functions, such as the specific heat, susceptibility, and compressibility, which provide the common experimental probes of macroscopic systems. Section 1.6 contains a discussion of some general conditions of equilibrium and stability and we conclude, in 1.7, with a brief discussion of the thermodynamics of phase transitions and the Gibbs phase rule.

1.1 State Variables and Equations of State

A macroscopic system has many degrees of freedom, only a few of which are measurable. Thermodynamics thus concerns itself with the relation between a small number of variables which are sufficient to describe the bulk behavior of the system in question. In the case of a gas or liquid the appropriate variables are the pressure P , volume V , and temperature T . In the case of a magnetic solid the appropriate variables are the magnetic field $\mathbf{H}$, the magnetization $\mathbf{M}$, and the temperature T . In more complicated situations, such as when a liquid is in contact with its vapor, more variables are needed: the pressure P , temperature T , volume of liquid and gas V_L , V_G , interfacial area A , and surface tension σ . If the thermodynamic variables are independent of time, the system is said to be in a *steady state*. If, moreover, there are no macroscopic currents in the system, such as a flow of heat or particles through the material, the system is in *equilibrium*. Any quantity which, in equilibrium, depends only on the thermodynamic variables, rather than on the history of the sample, is called a *state function*. In subsequent sections we shall meet a number of such quantities. For a large system, the state variables can normally be taken to be either *extensive* (i.e., proportional to the size of the system) or *intensive* (i.e., independent of system size). Examples of extensive variables are the internal energy, the entropy, and the mass of the different constituents or their number, while the pressure, the temperature, and the chemical potentials are intensive. The postulate that quantities like the internal energy and entropy are extensive and independent of shape is equivalent to an assumption of additivity or, as we shall see in Section 2.1, of the existence of the *thermodynamic limit*. In the process of taking the thermodynamic limit, we let the size of the system become infinitely large, with the densities (of mass, energy, magnetic moment, polarization, etc.) remaining constant.

In equilibrium the state variables are not all independent and are connected by equations of state. The rôle of statistical mechanics is the derivation, from microscopic interactions, of such equations of state. Simple examples are the ideal gas law,

$$PV - Nk_B T = 0 \quad (1.1)$$

where N is the number of molecules in the system and k_B is Boltzmann's constant; the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right) (V - Nb) - Nk_B T = 0 \quad (1.2)$$

where a, b are constants; the virial equation of state

$$P - \frac{Nk_B T}{V} \left[1 + \frac{NB_2(T)}{V} + \frac{N^2 B_3(T)}{V^2} + \dots \right] = 0 \quad (1.3)$$

where the functions $B_2(T), B_3(T)$ are called virial coefficients; and in the case of a paramagnet, the Curie law,

$$M - \frac{CH}{T} = 0 \quad (1.4)$$

where C is a constant called the Curie constant. Equations (1.1), (1.2), and (1.4) are approximations, and we shall use them primarily to illustrate various principles. Equation (1.3) is, in principle, exact, but as we shall see in Chapter 4, calculation of more than a few of the virial coefficients is very difficult.

1.2 Laws of Thermodynamics

In this section we explore the consequences of the zeroth, first, and second laws of thermodynamics. The zeroth law can be thought of as the statement that matter in equilibrium can be assigned values for the temperature, pressure and chemical potentials, which in principle can be measured. Formally the law can be stated as:

If system A is in equilibrium with systems B and C then B is in equilibrium with C .

The zeroth law allows us to introduce universal scales for temperature, pressure etc.

Another way of looking at the zeroth law is through an analogy with mechanics. In equilibrium the forces are balanced. This implies that the intensive variables are constant throughout the system. In particular:

$$\begin{aligned} T &= \text{const.} \rightarrow \text{Thermal equilibrium} \\ P &= \text{const.} \rightarrow \text{Mechanical equilibrium} \\ \mu &= \text{const.} \rightarrow \text{Chemical equilibrium} \end{aligned}$$

As we shall see in the next chapter, the zeroth law has a fairly straightforward statistical interpretation and this will allow us to make contact between the thermodynamic and statistical description.