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Phase Transitions of Simple Systems

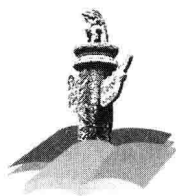
简单系统相变

(影印版)

[俄] 斯米尔诺夫 (B. M. Smirnov) 著
[美] 贝里 (R. S. Berry)



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By Boris M. Smirnov and R. Stephen Berry

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序 言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础,同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天,物理学不仅囿于基础科学和技术应用研究的范畴,而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到,改革开放三十多年来,随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展,我国物理学取得了跨越式的进步,做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下,近年来物理学相关书籍也呈现百花齐放的良好态势,在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看,尽管国内各出版社相继推出了一些质量很高的物理教材和图书,但系统总结物理学各门类知识和发展,深入浅出地介绍其与现代科学技术之间的渊源,并针对不同层次的读者提供有价值的教材和研究参考,仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展,特别是展现近年来中国物理学家的研究水平和成果,北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”,试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家,确保了整套丛书的权威性和前瞻性。

这套书系内容丰富,涵盖面广,可读性强,其中既有对我国传统物理学发展的梳理和总结,也有对正在蓬勃发展的物理学前沿的全面展示;既引进和介绍了世界物理学研究的发展动态,也面向国际主流领域传播中国物理的优秀专著。可以说,“中外物理学精品书系”力图完整呈现近现代世界和中国物理

科学发展的全貌,是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是,在把西方物理的精华要义“请进来”的同时,也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻,引进和翻译世界物理的经典著作和前沿动态,可以满足当前国内物理教学和科研工作的迫切需求。另一方面,改革开放几十年来,我国的物理学研究取得了长足发展,一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域,使世界对中国物理学的过去和现状有更多的深入了解,不仅充分展示出中国物理学研究和积累的“硬实力”,也向世界主动传播我国科技文化领域不断创新的“软实力”,对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是,“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20世纪以来,中国物理界诞生了很多经典作品,但当时大都分散出版,如今很多代表性的作品已经淹没在浩瀚的图书海洋中,读者们对这些论著也都是“只闻其声,未见其真”。该书系的编者们在这方面下了很大工夫,对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值,不仅可以很好地保护和传承我国物理学的经典文献,充分发挥其应有的传世育人的作用,更能使广大物理学人和青年学子亲身体会我国物理学研究的发展脉络和优良传统,真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在2006年中国科学技术大会上指出,“加强基础研究是提升国家创新能力、积累智力资本的重要途径,是我国跻身世界科技强国的必要条件”。中国的发展在于创新,而基础研究正是一切创新的根本和源泉。我相信,这套“中外物理学精品书系”的出版,不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣,也将进一步推动其他相关基础科学更好更快地发展,为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任

中国科学院院士,北京大学教授

王恩哥

2010年5月于燕园

Preface

Thermodynamic concepts of aggregate states and their phase transitions developed during the 19th Century and are now the basis of our contemporary understanding of these phenomena. Thermodynamics gives an universal, macroscopic description of the equilibrium properties of phase transitions independent of the detailed nature of the substances. However understanding the nature of phase transitions at the microscopic level requires a different approach, one that takes into account the specifics of the interparticle interactions. In this book, we lay the groundwork that connects the microscopic phenomena underlying phase changes with the macroscopic picture, but in a somewhat restricted way. We deal only with systems in which electronic excitations are not important, only with atomic systems, and only with homogeneous systems. We also restrict our analysis to systems in which only pairwise interactions need be included, and, in many parts of the treatment, to systems in which one need consider only the interactions between nearest neighbor atoms. In establishing these restrictions, we can be guided by the solid and liquid states of inert gases and the phase transitions between them, although the subsequent analysis is relevant and applicable for a series of other physical systems.

To study the behavior of a system of many interacting identical particles, we work extensively with its potential energy surface (PES), a surface in a many-dimensional space whose independent variables are the monomer coordinates or some transformation thereof. A central property of any multidimensional PES is its large number of local minima. We can think of the evolution of a system described by this surface as the trajectory taken by the system as it passes from the neighborhood of one local minimum to another. At moderate and low temperatures, the system remains in each of these neighborhoods for a time long compared with the period of atomic oscillations. This allows us to distinguish two forms of the system's excitation: thermal or vibrational excitation corresponds to the energy of oscillations of individual atoms; configurational excitation is that associated with location and change of location among the neighborhoods of the local minima of the PES. From this

perspective, a phase transition corresponds to a change of the configurational excitations of the system.

The approach treats both bulk systems and small systems, and their differences and similarities. One can gain insights into the properties of bulk phase transitions by seeing how they evolve from the equilibria of phase-like forms of systems of only tens of atoms, for example. Some of the information comes from analysis of simple model systems; some comes from simulations, by molecular dynamics for example; some, especially for bulk systems, comes from experimental data.

One particularly illustrative phenomenon is the apparent paradox that, while bulk systems show sharp phase transitions and satisfy the Gibbs phase rule, with two phases in equilibrium at only one pressure if the temperature is fixed, atomic clusters can coexist in two or more phases over a range of temperatures and pressures. The analysis presented here shows how the behavior of bulk systems evolves from the behavior of very small systems, as the number of particles comprising the system grows larger. In the course of the analysis, one encounters surprises that resolve themselves when one comes to understand some of the tacit assumptions underlying traditional development of thermodynamics and kinetics for bulk systems. We learn, by examining microscopic behavior as well as traditional properties such as caloric curves, how the fundamentals of thermodynamics remain valid even when some of those tacit assumptions are not.

Much of the development is based on the model of a simple dense material consisting of particles and voids. We introduce the void as an elementary configurational excitation. In a lattice, a void is very much like a vacancy, but here, “void” implies that the neighbors of the vacancy can relax to a stable form. In an amorphous material, the void need not have a specified shape and may even change its size. The void concept, together with the distinction between configurational and vibrational degrees of freedom, opens the way to analytic and combinatorial approaches to elucidating the phase behavior of small and large systems alike. The liquid and solid, for example, differ in the density of their voids. In small systems, they can coexist over a range of conditions because the solid is stabilized by its low energy with few voids, and the liquid is stabilized by its high entropy with many voids.

This book, devoted as it is to various aspects of the nature of the phase transitions in simple systems, addresses some aspects of the kinetics of phase changes as well as their thermodynamics and equilibrium properties. We hope that this approach will enable colleagues to go further, to extend these ideas to more complex systems, and to apply them in the expanding field of nanoscale materials.

Chicago,
Moscow,
August 2007

R. Stephen Berry
Boris M. Smirnov

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Introduction

To consider phase states and phase transitions, we must look first to thermodynamic concepts. According to classical thermodynamics, the phase or aggregate state of an ensemble of interacting atoms or molecules is a uniform spatial distribution of atoms or molecules that is restricted by boundaries. A transition between two phases of a macroscopic system has a stepwise character and results from variation of thermodynamic parameters, typically (but not necessarily) the temperature. Most commonly, the variable controlling the phase and phase change is an intensive variable. A thermodynamic description of phase transitions has advantages and disadvantages. The advantage of this description is its universal character; it is suitable for many kinds of systems with different interactions between atoms or molecules. But for this reason, a thermodynamic description of aggregate states and phase transitions is formal and does not allow one to exhibit the nature of phenomena under consideration at a microscopic level.

Computer simulation of clusters and bulk ensembles of interacting atoms opens the possibility for us to understand the nature of the phase transitions at that molecular level. But the microscopic character of this phenomenon depends on the form of interatomic interaction. In analyzing this phenomenon from the microscopic standpoint, we will consider ensembles of atoms interacting via a pairwise force; this corresponds to the simplest model and, apart from ionic materials such as alkali halide, represents the predominant interaction. This allows us to understand at a level deeper than the phenomenological that thermodynamics gives us, the nature of an aggregate state of an ensemble of interacting atoms. This approach provides a microscopic description to connect the true phase transition between equilibrium states with related phenomena, in particular, with the glass transition.

A real example of a system with pairwise interaction between atoms is a condensed inert gas. Indeed, because the atoms of inert gases have completed electron shells, the exchange interaction between such atoms and hence the short-range interatomic forces are repulsive in this case. Hence at equilibrium interatomic distances in condensed inert gases, the interaction potential of

two atoms is small in comparison with typical electronic energies. As a result, interactions between two atoms do not influence the interactions of these atoms with other atoms in condensed inert gases. In other words, two-body interactions dominate the behavior of such systems; we can neglect three-body and higher interactions and retain a reasonably accurate picture of the behavior of such systems.

Next, because the exchange interaction between two atoms is dominated by electron coordinates near the axis connecting the atoms, the pairwise character of interaction is conserved at high pressures, and is primarily a repulsive interaction. Therefore inert gases are objects that satisfy models based on a pairwise interaction. Consequently, in the following discussion, we make use of the properties of condensed inert gases in detail. We restrict our discussion only to the “heavy” inert gases Ne, Ar, Kr and Xe, whose atoms may be considered as classical particles under the conditions of phase changes. Ignoring quantum effects simplifies the analysis of an ensemble of identical particles yet retains the essential characteristics of such systems. The study of a bulk ensemble of classical atoms together with known properties of inert gases gives rich insights about these atomic systems and their phase transitions. Moreover we bring the properties of bulk systems into a common context with their very small counterparts, the nanoscale particles and clusters composed of the same inert gas atoms.

To study the phase changes of an ensemble of classical particles, one can separate excitations of such systems into two groups. The first group relates to thermal motion of particles, specifically their oscillations in the total system; the second group consists of configurational excitations, which include diffusion and translational motions because the high density of the systems require configurational excitation for translational motion to be possible. Phase transitions are closely related to configurational excitation of a particle ensemble, and therefore configurational excitation is the principal object of study of this book. At zero temperature the first, vibrational excitations disappear; hence it is convenient to study the configurational excitation of an ensemble of classical particles at zero (vibrational) temperature, to be free from thermal motion of particles. An effective way to characterize the behavior of such a system is to cast that behavior in terms of motions on its potential energy surface (PES) in a many-dimensional space of particle coordinates. The important property of the PES, that is the basis of understanding of the nature of configurational excitation, is that the PES has many local minima which are separated by barriers. Just this fact allows us to separate the thermal and configurational degrees of freedom. Indeed, assuming a typical barrier height is large compared to thermal energy, we find that an ensemble has many oscillations near a given local minimum of the PES before the transition to the neighboring minimum. The first kind of excitations are motions within the region of a single local minimum on the many-dimensional surface; the second kind correspond to motions from one local minimum to another.

Classical thermodynamics, being intrinsically phenomenological, does not allow us to understand phases and phase transitions at the microscopic level. Fortunately, it is possible to study a simple ensemble of classical particles with pairwise interaction to reach a level of understanding at that level. Indeed, we define a phase as a group states of configurational excitations with similar excitation energies if these excitations are realized with roughly similar probabilities. For the dense particle ensembles under consideration, in the present context we have only two phase states, the solid or ordered state and the liquid or disordered state. Of course, one can go to a more detailed description to recognize different solid structures as different phases, and, for small systems at least, distinguish liquid character or liquid-like phases in terms of the behavior of different shells. We shall study these problems in detail later.

By analyzing some phenomena exhibited by an ensemble of classical atoms from the standpoint of the local minima of the PES, we obtain a depend understanding of these phenomena. In reality, one can simplify the concept of the PES by introducing voids as elementary configurational excitations. If we assume individual voids to be identical, the void concept simplifies the understanding and description of the properties of the phase states.

It is convenient to start the void concept from formation of vacancies in a crystal structure of classical particles. Suppose the system contains n particles and v voids. Indeed, assume the number of classical particles of an ensemble $n + v$ is so large that surface particles of this particles give a negligible contribution to its parameters. In the ground configurational state these particle form a close-packed crystal structure, face-centered cubic or hexagonal, that follows from the pairwise interaction between the particles. Each internal particle of this structure has 12 nearest neighbors. In order to prepare a configurationally excited cluster consisting of n particles and v internal vacancies, v internal particles are removed to the outside. If newly-formed vacancies do not border one another (i.e. a number of vacancies $v < n/12$), this system is stable and its state corresponds to a local minimum of the PES. At large excitation ($v > n/12$) such a state is unstable; the system formed by removing atoms and creating site vacancies relaxes by shrinking under its own attractive van der Waals forces. As a result, vacancies are converted into voids. These are free spaces between particles that vary their shape and size in time. We consider and use average parameters of voids. Of course, during relaxation, vacancies can join into bubbles – large empty constituents inside a system of particles. However usually (and in any case, for condensed inert gases) vacancies convert into voids and not into large bubbles. Moreover, the number voids is equal approximately to the number of initial vacancies. This method of generation of voids inside a particle ensemble is convenient for the void analysis.

Describing the phase state of a system of identical classical particles within the framework of the void concept simplifies our understanding of various phenomena connected with configurational excitation and phase transitions. In

particular, displacement of elementary configurational excitations in terms of voids describes some key properties and phenomena in these systems. A void can transfer to a neighboring site; this is precisely the transition between two neighboring local minima of the PES. Because neighboring local minima of the PES are separated by barriers, this transition has an activation character, so it proceeds only slowly at low temperature. A sum of transitions between local minima of PES, each considered as the motion of independent voids, determine diffusion of voids inside the particle ensemble. Naturally the diffusion coefficient of voids decreases sharply with decreasing temperature. Hence at low temperatures, one can prepare an unstable configurational state of this system with voids frozen inside it. The transition into a stable configuration state consists of diffusion of voids to the boundaries, and since this time is long, these states are characterized by long lifetimes at low temperatures. These states are total analogous with glassy states, so we have a possibility to analyze the glassy states for simple systems.

Because the phase states of a system of classical particles differ by the presence or absence the voids inside the system, a phase transition is characterized by displacement of those voids. Hence, growth of nuclei of a new phase inside the system, the nucleation process, can be considered as a result of diffusion of voids in a space separated into two regions by the phase boundary. Considering the growth of nuclei of a new phase as a result of diffusion of voids allows us to analyze some aspects of this phenomenon in a simple manner.

Thus, this book is devoted the analysis of ensembles of classical particles with pairwise interaction between particles and configurational excitations of these ensembles which include the phase transitions and adjacent phenomena. Because we consider simple systems, ensembles of classical particles with pairwise interaction and not at low particle densities, this allows us to describe these phenomena in a simple manner that conserves the strictness of the analysis.

**Thermodynamics of Ensembles
of Classical Particles**