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Boris M. Smirnov · R. Stephen Berry

Phase Transitions of Simple Systems

With 81 Figures and 32 Tables

Springer

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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, R. Stephen Berry
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