STATISTICAL PHYSICS OF LIQUIDS AT FREEZING AND BEYOND

Exploring important theories for understanding freezing and the liquid–glass transition, this book is useful for graduate students and researchers in soft-condensed-matter physics, chemical physics, and materials science. It details recent ideas and key developments, providing an up-to-date view of current understanding.

The standard tools of statistical physics for the dense liquid state are covered. The freezing transition is described from the classical density-functional approach. Classical nucleation theory as well as applications of density-functional methods for nucleation of crystals from the melt are discussed, and compared with results from computer simulation of simple systems. Discussions of supercooled liquids form a major part of the book. Theories of slow dynamics and the dynamical heterogeneities of the glassy state are presented, as well as nonequilibrium dynamics and thermodynamic phase transitions at deep supercooling. Mathematical treatments are given in full detail so that readers can learn the basic techniques.

Shankar Prasad Das is Professor of Physics at Jawaharlal Nehru University, New Delhi. During the course of his career, he has made significant contributions to the field of slow dynamics in supercooled liquids and the glass transition.

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I dedicate this book to my parents,

Sudhir Kumar Das and Gita Rani Das

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Preface

This book is aimed at teaching the important concepts of the various theories of statistical physics of dense liquids, freezing, and the liquid–glass transition. Both thermodynamic and time-dependent phenomena relating to transport properties are discussed. The standard tools of statistical physics of the dense liquid state and the associated technicalities needed to learn them are included in the presentation. Details of some of the calculations have been included, whenever needed, in the appendices at the ends of chapters. I hope this will make the book more accessible to beginners in this very active field of research. The book is expected to be useful for graduate students and researchers working in the area of soft-condensed-matter physics, chemical physics, and the material sciences as well as for chemical engineers.

We now give a brief description of what is in the book. The first chapter reviews the basics of statistical mechanics necessary for studying the physics of the liquid state. Key concepts of equilibrium and nonequilibrium statistical mechanics are presented. The topics covered here have been chosen keeping in mind the theories and concepts covered in the subsequent chapters of the book. Following this introductory chapter, we focus on the physics of liquids near freezing. In Chapter 2, we demonstrate how the disordered liquid state as well as the crystalline state of matter with long-range order can be understood in a unified manner using thermodynamic extremum principles. Our primary focus in discussing the freezing transition here is the classical density-functional approach using the density as the order parameter. The model is constructed from a basic statistical-mechanical description of the equilibrium liquid close to the freezing point. It predicts the location (in terms of thermodynamic parameters such as temperature and density) of the transformation into the crystalline states coming from the liquid side. This is in contrast to the traditional lattice-instability theories of melting of the solid state. The approach is termed microscopic since it uses the two-body interaction between the particles in the classical Hamiltonian as the starting point.

After introducing the model for the broken symmetric state in terms of the inhomogeneous density function, we analyze the process of transformation from one phase to another. As the disordered liquid is quenched to a lower temperature at which the stable equilibrium state would be a crystal, the metastable liquid transforms into the state with long-range order through a nucleation process. A model for this transformation using a purely thermodynamic approach is given in terms of the classical nucleation theory. The latter is an important idea that is also applied in a somewhat different context in understanding the deeply supercooled state. Next, extensions of the density-functional theories introduced in the previous chapter are applied to identify the critical nucleus formation in the melt. Comparisons of the theories of freezing and nucleation with corresponding computer-simulation results are discussed at every step. Simulating nucleation of the crystalline phase from the melt has always been difficult. In recent years special techniques have been developed to study the formation and structure of the critical nucleus. We discuss these developments in Chapter 3.

In Chapter 4, we begin considering the supercooled state, i.e., liquid kept at metastable equilibrium at temperatures beyond the freezing point. Competition between supercooling into a metastable state and the process of crystallization as well as the standard phenomenology of the glassy state are discussed here. The computer models of the liquid developed to study various aspects of the supercooled state are also described in this chapter. Concepts of dynamical heterogeneities and growing length scales associated with the supercooled liquid are introduced at this point.

Next we turn to the discussion of the microscopic theories of the slow dynamics which develops in the supercooled liquid as it is increasingly supercooled. We present the theoretical developments in this field starting from the basics. Hence three chapters have been devoted to introducing the reader to the rather involved formalism necessary for treating this topics. The first, Chapter 5, presents the formulation of the basic equations of hydrodynamics for a set of slow modes in the many-body system. The dissipative equations are constructed using phenomenological arguments, and linear transport coefficients are defined. We introduce here the idea of generalizing hydrodynamic equations to short length scales in the dense liquid. In Chapter 6, we discuss the formulation of the nonlinear fluctuating hydrodynamics for several model systems. These equations control the dynamics of a set of slow modes in a manner that includes collective effects from semi-microscopic length scales. In Chapter 7, we present methods for formulating a renormalized theory of the dynamics. The effects of the nonlinear coupling of the slow modes are obtained in a systematic manner by using diagrammatic methods of quantum field theory. This Martin–Siggia–Rose (MSR) field-theoretic model obtains the dynamic density correlation function in terms of renormalized transport coefficients, which are themselves expressed self-consistently in terms of dynamic correlation functions. A new approach to studying the complex behavior of the supercooled liquid started with the idea of a nonlinear feedback mechanism on its transport properties from the coupling of slowly decaying correlation functions. That the renormalized dynamics for a compressible liquid obtains this model in a natural way is demonstrated in Chapter 7. The formalism also facilitates the analysis of the full implications of the nonlinearities in the equations of motion on the asymptotic dynamics. Chapters 5, 6, and 7 are technical and may be skipped by those not interested in understanding the construction of the mathematical models for the dynamics in full rigor. Some simpler deductions of the basic mode-coupling model are also presented in an appendix.

The above renormalized model gives rise to the idea of an ergodic–nonergodic (ENE) transition in which the long-time limit of the density correlation function freezes. This ENE transition, its implications for the dynamics, and supporting evidence from experiments and simulation are discussed in full detail in Chapter 8. The possible role of ergodicity-restoring mechanisms and removal of the sharp ENE transitions follows thereafter. Finally, we make a critical evaluation of the mode-coupling theory for structural liquids and its link with models of dynamics for mean-field systems. Up to this point the discussion of the dynamics is only in terms of equilibrium correlations. In Chapter 9 we deal with the nonequilibrium aspects of the glassy state. We present the modification of the standard results of equilibrium statistical mechanics, such as the fluctuation–dissipation theorem and the concept of effective temperatures for the glassy state. Related computer-simulation studies are presented. Theoretical models of nonequilibrium dynamics in terms of mean-field spin models are also worked out. The relaxation time for the supercooled liquid increases drastically as it is supercooled and eventually vitrification occurs when the liquid behaves like a frozen solid. Apart from having a characteristic large viscosity, the supercooled liquid shows a discontinuity in specific heat due to freezing of the translational degrees of freedom in the liquid. The difference of the entropy of the supercooled liquid from that of the solid having only vibrational motion around a frozen structure represents the entropy due to large-scale motion and is called the configurational entropy S_c of the supercooled liquid. Theoretical analysis of the rapid disappearance of S_c with supercooling (the so-called "entropy crisis") is essential for our understanding of the physics of the glass transition. The connections between structure and dynamics and the possibilities of an underlying thermodynamic phase transition in the deeply supercooled liquid are discussed in the last chapter of the book.

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