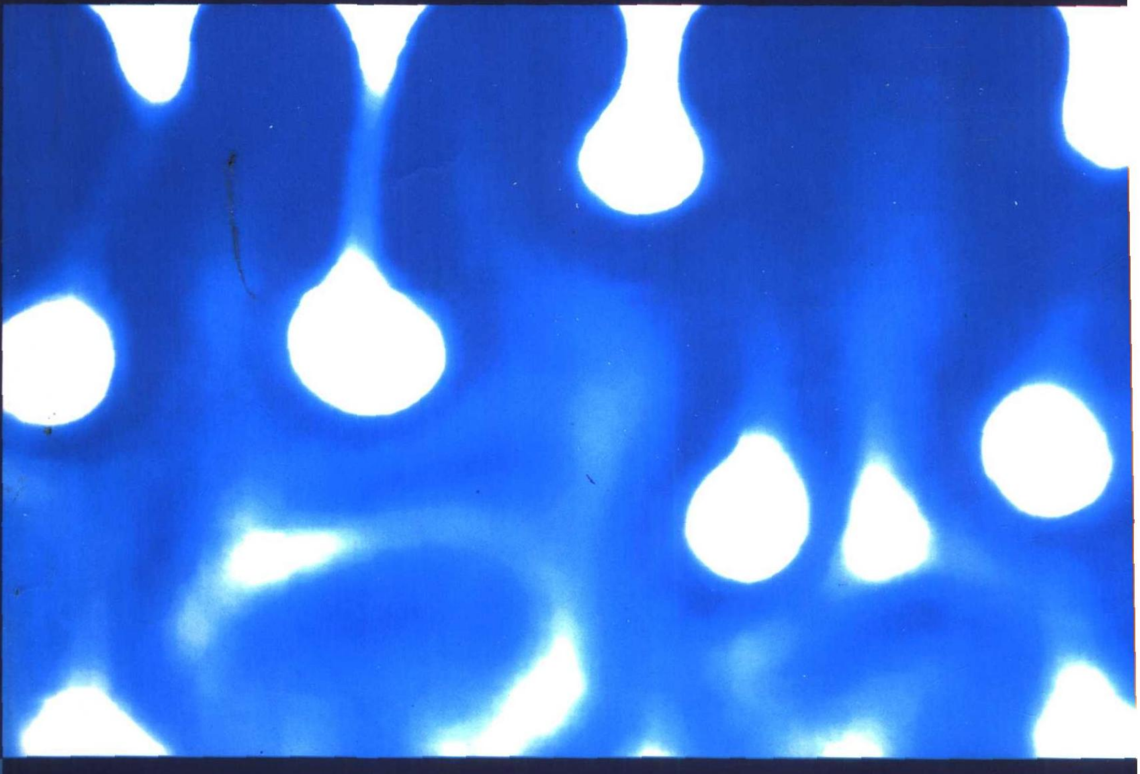
Akira Onuki

Phase Transition Dynamics

相变动力学



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Phase Transition Dynamics

Phase transition dynamics is of central importance in current condensed matter physics. Akira Onuki provides a systematic treatment of a wide variety of topics including critical dynamics, phase ordering, defect dynamics, nucleation, and pattern formation by constructing time-dependent Ginzburg–Landau models for various systems in physics, metallurgy, and polymer science.

The book begins with a summary of advanced statistical–mechanical theories including the renormalization group theory applied to spin and fluid systems. Fundamental dynamical theories are then reviewed before the kinetics of phase ordering, spinodal decomposition, and nucleation are covered in depth in the main part of the book. The phase transition dynamics of real systems are discussed, treating interdisciplinary problems in a unified manner. New topics include supercritical fluid dynamics, boiling near the critical point, stress–diffusion coupling in polymers, patterns and heterogeneities in gels, and mesoscopic dynamics at structural phase transitions in solids. In the final chapter, theoretical and experimental approaches to shear flow problems in fluids are reviewed.

Phase Transition Dynamics provides a comprehensive treatment of the study of phase transitions. Building on the statics of phase transitions, covered in many introductory textbooks, it will be essential reading for researchers and advanced graduate students in physics, chemistry, metallurgy and polymer science.

AKIRA ONUKI obtained his PhD from the University of Tokyo. Since 1983 he has held a position at Kyoto University, taking up his current professorship in 1991. He has made important contributions to the study of phase transition dynamics in both fluid and solid systems.

Preface

This book aims to elucidate the current status of research in phase transition dynamics. Because the topics treated are very wide, a unified phenomenological time-dependent Ginzburg–Landau approach is used, and applied to dynamics near the critical point. Into the simple Ginzburg–Landau theory for a certain order parameter, we introduce a new property or situation such as elasticity in solids, viscoelasticity in polymers, shear flow in fluids, or heat flow in ^{4}He near the superfluid transition. By doing so, we encounter a rich class of problems on mesoscopic spatial scales. A merit of this approach is that we can understand such diverse problems in depth using universal concepts.

The first four chapters (Part one) deal with static situations, mainly of critical phenomena, and introduce some new results that would stand by themselves. However, the main purpose of Part one is to present the definitions of many fundamental quantities and introduce various phase transitions. So it should be read before Parts two and three which deal with dynamic situations. Chapter 5 is also introductory, reviewing fundamental dynamic theories, the scheme of Langevin equations and the linear response theory. Chapter 6 treats critical dynamics in (i) classical fluids near the gas–liquid and consolute critical points and (ii) ^{4}He near the superfluid transition. Chapter 7 focuses on rather special problems in complex fluids: (i) effects of viscoelasticity on composition fluctuations in polymer systems; and (ii) volume phase transitions and heterogeneity effects in gels. Chapters 8 and 9 (in Part three) constitute the main part of this book, and consider the kinetics of phase ordering, spinodal decomposition, and nucleation. Motions of interfaces and vortices are examined in the Ginzburg–Landau models. Chapter 10 focuses on dynamics in solids, including phase separation, order–disorder and martensitic transitions, shape instability in hydrogen–metal systems, and surface instability in metal films. These problems have hitherto been very inadequately studied and most papers are difficult to understand for those outside the field, so it was important to write this chapter in a coherent fashion, though it has turned out to be a most difficult task. I believe that many interesting dynamical problems remain virtually unexplored in solids, because such phenomena have been examined either too microscopically in solid-state physics without giving due respect to long-range elastic effects or with technologically-oriented objectives in engineering. Chapter 11 is on shear flow problems in fluids, a topic on which a great number of theoretical and experimental papers appeared in the 1980s and 1990s. This book thus covers a wide range of phase transition dynamics. Of course, many important problems had to be omitted.

I have benefited from discussions with many people working in the fields of low-temperature physics, statistical physics, polymer science, and metallurgy. Particularly useful suggestions were given by H. Meyer, Y. Oono, K. Kawasaki, T. Ohta, M. Doi, T. Hashimoto, H. Tanaka, M. Shibayama, T. Miyazaki, T. Koyama, and Y. Yamada. Thanks are due to R. Yamamoto, K. Kanemitsu, and A. Furukawa for drawing some of the figures. It is with deep sadness that I record the deaths of T. Tanaka and K. Hamano. It is a great pleasure to be able to acknowledge their memorable contributions to Chapters 7 and 11, respectively. Finally, I apologize to my students, colleagues, and family, for any difficulty they may have experienced because I have been so busy with this extremely time-consuming undertaking.

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Contents

Part one

Statics

1

Spin systems and fluids

To study equilibrium statistical physics, we will start with Ising spin systems (hereafter referred to as Ising systems), because they serve as important reference systems in understanding various phase transitions [1]–[7].[1] We will then proceed to one- and two-component fluids with short-range interaction, which are believed to be isomorphic to Ising systems with respect to static critical behavior. We will treat equilibrium averages of physical quantities such as the spin, number, and energy density and then show that thermodynamic derivatives can be expressed in terms of fluctuation variances of some density variables. Simple examples are the magnetic susceptibility in Ising systems and the isothermal compressibility in one-component fluids expressed in terms of the correlation function of the spin and density, respectively. More complex examples are the constant-volume specific heat and the adiabatic compressibility in one- and two-component fluids. For our purposes, as far as the thermodynamics is concerned, we need equal-time correlations only in the long-wavelength limit. These relations have not been adequately discussed in textbooks, and must be developed here to help us to correctly interpret various experiments of thermodynamic derivatives. They will also be used in dynamic theories in this book. We briefly summarize equilibrium thermodynamics in the light of these equilibrium relations for Ising spin systems in Section 1.1, for one-component fluids in Section 1.2, and for binary fluid mixtures in Section 1.3.

1.1 Spin models

1.1.1 Ising hamiltonian

Let each lattice point of a crystal lattice have two microscopic states. It is convenient to introduce a spin variable s_i, which assumes the values 1 or -1 at lattice point i. The microscopic energy of this system, called the Ising spin hamiltonian, is composed of the exchange interaction energy and the magnetic field energy,

$$\mathcal{H}\{s\} = \mathcal{H}_{\rm ex} + \mathcal{H}_{\rm mag}, \tag{1.1.1}$$

where

$$\mathcal{H}_{\rm ex} = -\sum_{<i,j>} J s_i s_j, \tag{1.1.2}$$

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[1] References are to be found at the end of each chapter.

$$\mathcal{H}_{\text{mag}} = -H \sum_i s_i. \tag{1.1.3}$$

The interaction between different spins is short-ranged and the summation in $\mathcal{H}_{\text{ex}}$ is taken over the nearest neighbor pairs i, j of the lattice points. The interaction energy between spins is then $-J$ if paired spins have the same sign, while it is J for different signs. In the case $J > 0$ the interaction is ferromagnetic, where all the spins align in one direction at zero temperature. The magnetic field H is scaled appropriately such that it has the dimension of energy. At zero magnetic field the system undergoes a second-order phase transition at a critical temperature T_c. The hamiltonian $\mathcal{H}$ mimics ferromagnetic systems with uniaxial anisotropy.

In the case $J < 0$, the interaction is antiferromagnetic, where the neighboring paired spins tend to be antiparallel at low temperatures. Let us consider a cubic lattice, which may be divided into two sublattices, A and B, such that each lattice point and its nearest neighbors belong to different sublattices. Here, we define the staggered spin variables S_i by

$$S_i = s_i \quad (i \in A), \qquad S_i = -s_i \quad (i \in B). \tag{1.1.4}$$

Then, $\mathcal{H}_{\text{ex}}$ in terms of $\{S_i\}$ has the positive coupling $|J|$ and is isomorphic to the ferromagnetic exchange hamiltonian.

The Ising model may also describe a phase transition of binary alloys consisting of atoms 1 and 2, such as Cu–Zn alloys. If each lattice point i is occupied by a single atom of either of the two species, the occupation numbers n_{1i} and n_{2i} satisfy $n_{1i}+n_{2i} = 1$. Vacancies and interstitials are assumed to be nonexistent. If the nearest neighbor pairs have an interaction energy ϵ_{KL} $(K, L = 1, 2)$, the hamiltonian is written as

$$\mathcal{H}\{n\} = \sum_{<i,j>} \sum_{K,L} \epsilon_{KL} n_{Ki} n_{Lj} - \sum_i \sum_K \mu_K n_{Ki}, \tag{1.1.5}$$

where μ_1 and μ_2 are the chemical potentials of the two components. From (1.1.4) we may introduce a spin variable,

$$s_i = 2n_{1i} - 1 = 1 - 2n_{2i}, \tag{1.1.6}$$

to obtain the Ising model (1.1.1) with

$$J = \frac{1}{4}(-\epsilon_{11} - \epsilon_{22} + 2\epsilon_{12}), \qquad H = \frac{1}{2}(\mu_1 - \mu_2) - \frac{z}{4}(\epsilon_{11} - \epsilon_{22}), \tag{1.1.7}$$

where z is the number of nearest neighbors with respect to each lattice point and is called the coordination number.

1.1.2 Vector spin models

Many variations of spin models defined on lattices have been studied in the literature [8]. If the spin $s_i = (s_{1i}, \ldots, s_{ni})$ on each lattice point is an n-component vector, its simplest hamiltonian reads

$$\mathcal{H}\{s\} = -\sum_{<i,j>} J s_i \cdot s_j - H \sum_i s_{1i}. \tag{1.1.8}$$

The first term, the exchange interaction, is assumed to be invariant with respect to rotation in the spin space. The magnetic field H favors ordering of the first spin components s_{1i}. The model with $n = 2$ is called the xy model, and the model with $n = 3$ the Heisenberg model. It is known that the static critical behavior of the three-dimensional xy model is isomorphic to that of ^{4}He and ^{3}He–^{4}He mixtures near the superfluid transition, as will be discussed later. However, there are many cases in which there is some anisotropy in the spin space and, if one direction is energetically favored, the model reduces to the Ising model asymptotically close to the critical point. Such anisotropy becomes increasingly important near the critical point (or *relevant* in the terminology of renormalization group theory). As another relevant perturbation, we may introduce a long-range interaction such as a dipolar interaction.

1.1.3 Thermodynamics of Ising models

Each microscopic state of the Ising system is determined if all the values of spins $\{s\}$ are given. In thermal equilibrium, the probability of each microscopic state being realized is given by the Boltzmann weight,

$$P_{\text{eq}}(\{s\}) = Z^{-1} \exp(-\beta\mathcal{H}\{s\}), \tag{1.1.9}$$

where

$$\beta = 1/T. \tag{1.1.10}$$

In this book the absolute temperature multiplied by the Boltzmann constant $k_B = 1.381 \times 10^{-16}$ erg/K is simply written as T and is called the temperature [1], so T has the dimension of energy. The normalization factor Z in (1.1.9) is called the partition function,

$$Z = \sum_{\{s\}} \exp(-\beta\mathcal{H}\{s\}), \tag{1.1.11}$$

where the summation is taken over all the microscopic states. The differential form for the logarithm $\ln Z$ becomes

$$d(\ln Z) = -\langle\mathcal{H}\rangle d\beta + \beta\langle\mathcal{M}\rangle dH = -\langle\mathcal{H}_{\text{ex}}\rangle d\beta + \langle\mathcal{M}\rangle dh, \tag{1.1.12}$$

where the increments are infinitesimal,

$$h = \beta H = H/T, \tag{1.1.13}$$

and $\mathcal{M}$ is the sum of the total spins,[2]

$$\mathcal{M} = \sum_i s_i. \tag{1.1.14}$$

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[2] In this book the quantities, $\mathcal{H}$, $\mathcal{M}$, $\mathcal{N}$, ... in script, are fluctuating variables (dependent on the microscopic degrees of freedom) and not thermodynamic ones.

Hereafter $\langle\cdots\rangle$ is the average over the Boltzmann distribution (1.1.9). The usual choice of the thermodynamic potential is the free energy,

$$F = -T \ln Z, \tag{1.1.15}$$

and the independent intensive variables are T and H with

$$dF = -SdT - \langle\mathcal{M}\rangle dH, \tag{1.1.16}$$

where $S = (\langle\mathcal{H}\rangle - F)/T$ is the entropy of the system.

We also consider the small change of the microscopic canonical distribution in (1.1.9) for small changes, $\beta \to \beta + \delta\beta$ and $h \to h + \delta h$. Explicitly writing its dependences on β and h, we obtain

$$P_{\text{eq}}(\{s\}; \beta + \delta\beta, h + \delta h) = P_{\text{eq}}(\{s\}; \beta, h) \exp\left[-\delta\mathcal{H}_{\text{ex}}\delta\beta + \delta\mathcal{M}\delta h + \cdots\right], \tag{1.1.17}$$

where $\delta\mathcal{H}_{\text{ex}} = \mathcal{H}_{\text{ex}} - \langle\mathcal{H}_{\text{ex}}\rangle$ and $\delta\mathcal{M} = \mathcal{M} - \langle\mathcal{M}\rangle$. To linear order in $\delta\beta$ and δh, the change of the distribution is of the form,

$$\delta P_{\text{eq}}(\{s\}) = P_{\text{eq}}(\{s\})\left[-\delta\mathcal{H}_{\text{ex}}\delta\beta + \delta\mathcal{M}\delta h + \cdots\right]. \tag{1.1.18}$$

Therefore, the average of any physical variable $\mathcal{A} = \mathcal{A}\{s\}$ dependent on the spin configurations is altered with respect to the change (1.1.18) as

$$\delta\langle\mathcal{A}\rangle = -\langle\mathcal{A}\delta\mathcal{H}_{\text{ex}}\rangle\delta\beta + \langle\mathcal{A}\delta\mathcal{M}\rangle\delta h + \cdots. \tag{1.1.19}$$

We set $\mathcal{A} = \mathcal{M}$ and $\mathcal{H}_{\text{ex}}$ to obtain

$$V\chi = \frac{\partial^2 \ln Z}{\partial h^2} = \frac{\partial\langle\mathcal{M}\rangle}{\partial h} = \langle(\delta\mathcal{M})^2\rangle, \tag{1.1.20}$$

$$\frac{\partial^2 \ln Z}{\partial\beta^2} = -\frac{\partial\langle\mathcal{H}_{\text{ex}}\rangle}{\partial\beta} = \langle(\delta\mathcal{H}_{\text{ex}})^2\rangle, \tag{1.1.21}$$

$$\frac{\partial^2 \ln Z}{\partial h\partial\beta} = \frac{\partial\langle M\rangle}{\partial\beta} = -\frac{\partial\langle\mathcal{H}_{\text{ex}}\rangle}{\partial h} = -\langle\delta\mathcal{M}\delta\mathcal{H}_{\text{ex}}\rangle, \tag{1.1.22}$$

where V is the volume of the system, χ is the isothermal magnetic susceptibility per unit volume, h and β are treated as independent variables, and use has been made of (1.1.12). Another frequently discussed quantity is the specific heat C_H at constant magnetic field defined by[3]

$$C_H = \frac{T}{V}\left(\frac{\partial S}{\partial T}\right)_H = \frac{1}{V}\left(\frac{\partial\langle\mathcal{H}\rangle}{\partial T}\right)_H. \tag{1.1.23}$$

Here we use $-(\partial\langle\mathcal{H}\rangle/\partial\beta)_H = (\partial^2 \ln Z/\partial\beta^2)_H$ to obtain

$$C_H = \langle(\delta\mathcal{H})^2\rangle/T^2 V. \tag{1.1.24}$$

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[3] In this book all the specific heats in spin systems and fluids have the dimension of a number density.

Namely, C_H is proportional to the variance of the total energy. We also introduce the specific heat C_M at constant magnetization $\langle \mathcal{M} \rangle$ by

$$VC_M = T\left(\frac{\partial S}{\partial T}\right)_M = VC_H - T\left(\frac{\partial \langle \mathcal{M} \rangle}{\partial T}\right)_H^2 \Bigg/ \left(\frac{\partial \langle \mathcal{M} \rangle}{\partial H}\right)_T . \tag{1.1.25}$$

From $(\partial \langle \mathcal{M} \rangle / \partial \beta)_H = -\langle \delta \mathcal{H} \delta \mathcal{M} \rangle$ we obtain

$$C_M = \left[\langle (\delta \mathcal{H})^2 \rangle - \langle \delta \mathcal{H} \delta \mathcal{M} \rangle^2 / \langle (\delta \mathcal{M})^2 \rangle\right] / VT^2, \tag{1.1.26}$$

where $\delta \mathcal{H}$ may be replaced by $\delta \mathcal{H}_{\mathrm{ex}}$ because $\delta \mathcal{H} - \delta \mathcal{H}_{\mathrm{ex}} = -H \delta \mathcal{M}$ is linearly proportional to $\mathcal{M}$. It holds the inequality $C_H \geq C_M$. These two specific heats coincide in the disordered phase at $H = 0$ where $\langle \delta \mathcal{H} \delta \mathcal{M} \rangle = 0$. We shall see that C_M in spin systems corresponds to the specific heat C_V at constant volume in one-component fluids.

Positivity of C_M

Combinations of the variances of the form,

$$C_{AB} = \langle (\delta \mathcal{A})^2 \rangle - \langle \delta \mathcal{A} \delta \mathcal{B} \rangle^2 / \langle (\delta \mathcal{B})^2 \rangle \geq 0, \tag{1.1.27}$$

will frequently appear in expressions for thermodynamic derivatives. Obviously C_{AB} is the minimum value of $\langle (\delta \mathcal{A} - x \delta \mathcal{B})^2 \rangle = \langle (\delta \mathcal{A})^2 \rangle - 2x \langle \delta \mathcal{A} \delta \mathcal{B} \rangle + x^2 \langle (\delta \mathcal{B})^2 \rangle \geq 0$ as a function of x, so it is positive-definite unless the ratio $\delta \mathcal{A} / \delta \mathcal{B}$ is a constant. Thus we have $C_M > 0$.

1.1.4 Spin density and energy density variables

We may define the spin density variable $\hat{s}(\boldsymbol{r})$ by[4]

$$\hat{\psi}(\boldsymbol{r}) = \sum_i s_i \delta(\boldsymbol{r} - \boldsymbol{r}_i), \tag{1.1.28}$$

where $\boldsymbol{r}_i$ is the position vector of the lattice site i. Then $\mathcal{M} = \int d\boldsymbol{r} \hat{\psi}(\boldsymbol{r})$ is the total spin sum in (1.1.14). Through to Chapter 5 the equilibrium equal-time correlation functions will be considered and the time variable will be suppressed. For the deviation $\delta \hat{\psi} = \hat{\psi} - \langle \hat{\psi} \rangle$ of the spin density, the pair correlation is defined by

$$g(\boldsymbol{r} - \boldsymbol{r}') = \langle \delta \hat{\psi}(\boldsymbol{r}) \delta \hat{\psi}(\boldsymbol{r}') \rangle, \tag{1.1.29}$$

which is expected to decay to zero for a distance $|\boldsymbol{r} - \boldsymbol{r}'|$ much longer than a correlation length in the thermodynamic limit ($V \to \infty$). The Fourier transformation of $g(\boldsymbol{r})$ is called the structure factor,

$$I(\boldsymbol{k}) = \int d\boldsymbol{r} g(\boldsymbol{r}) \exp(i\boldsymbol{k} \cdot \boldsymbol{r}), \tag{1.1.30}$$

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[4] Hereafter, the quantities with a circumflex such as $\hat{\psi}, \hat{m}, \hat{n}, \ldots$ are fluctuating quantities together with those in script such as $\mathcal{H}, \mathcal{A}, \mathcal{B}, \ldots$. However, the circumflex will be omitted from Chapter 3 onward, to avoid **cumbersome notation**.