P. Papon J. Leblond P. H. E. Meijer

# The Physics of Phase Transitions

**Concepts and Applications** 





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Tranlated from the French by S. L. Schnur

With 175 Figures



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### The Physics of Phase Transitions

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### Foreword

We learned in school that matter exists in three forms: solid, liquid and gas, as well as other more subtle things such as the fact that "evaporation produces cold." The science of the states of matter was born in the 19th century. It has now grown enormously in two directions:

- 1) The transitions have multiplied: first between a solid and a solid, particularly for metallurgists. Then for magnetism, illustrated in France by Louis Néel, and ferroelectricity. In addition, the extraordinary phenomenon of superconductivity in certain metals appeared at the beginning of the 20th century. And other superfluids were recognized later: helium 4, helium 3, the matter constituting atomic nuclei and neutron stars... There is now a real zoology of transitions, but we know how to classify them based on Landau's superb idea.
- 2) Our profound view of the mechanisms has evolved: in particular, the very universal properties of fluctuations near a critical point described by Kadanoff's qualitative analysis and specified by an extraordinary theoretical tool: the renormalization group.

Without exaggerating, we can say that our view of condensed matter has undergone two revolutions in the 20th century: first, the introduction of quantum physics in 1930, then the recognition of "self-similar" structures and the resulting scaling laws around 1970.

It would be naïve to make too much of these advances: despite all of this sophistication, we are still very unsure about certain points – for example, the mechanism governing superconducting oxides or the laws of the glass transition. However, a body of doctrines has been formed, and it is an important element of scientific culture in the year 2000.

This knowledge is generally expressed solely in works dedicated to only one sector. The great merit of the book by Drs. Papon, Leblond and Meijer is to offer a global introduction, accessible to students of physics entering graduate school. Of course, given the enormous expansion of the subject, many older readers will regret not finding their pet subject here (for example,

### VI Foreword

in my case demixing transitions involving linear polymers). However, the panorama is broad enough for the young public targeted here: I hope the book will guide them soundly.

I wish it great success.

Paris, France December 2001 P. G. de Gennes
Professor at the Collège de France
Director of the Ecole Supérieure de
Physique et Chimie Industrielles de Paris

### Preface

This book takes up and expands upon our teachings on thermodynamics and the physics of condensed matter at the School of Industrial Physics and Chemistry and Diplôme d'Etudes Approfondies in Paris and at the Catholic University of America in Washington D.C. It is intended for graduate students, students in engineering schools, and doctoral students. Researchers and industrial engineers will also find syntheses in an important and constantly evolving field of materials science.

The book treats the major classes of phase transitions in fluids and solids: vaporization, solidification, magnetic transitions, critical phenomena, etc. In the first two chapters, we give a general description of the phenomena, and we dedicate the next six chapters to the study of a specific transition by explaining its characteristics, experimental methods for investigating it, and the principal theoretical models that allow its prediction. The major classes of application of phase transitions used in industry are also reported. The last three chapters are specifically dedicated to the role of microstructures and nanostructures, transitions in thin films, and finally, phase transitions in large natural and technical systems. Our approach is essentially thermodynamic and assumes familiarity with the basic concepts and methods of thermodynamics and statistical physics. Exercises and their solutions are given, as well as a bibliography.

Finally, we would we like to thank J. F. Leoni who assisted in the preparation of the manuscript and the drawings and diagrams and Dr. S. L. Schnur who put much effort into translating the book as well as J. Lenz and F. Meyer from Springer-Verlag who provided helpful advice in publishing the book. We are also grateful to our colleague Prof. K. Nishinari, from Osaka City University, for his valuable comments on our manuscript.

Paris, France, Paris, France, Washington, D.C., U.S.A., December 2001 Pierre Papon Jacques Leblond Paul H. E. Meijer

# **Principal Notation**

Area
Magnetic induction
Specific heat at constant pressure
Specific heat at constant pressure per unit of mass
Specific heat at constant volume
Specific heat at constant volume per unit of mass
Intermolecular distance
Density of states
Elementary charge
Energy
Electric field
Free energy per unit of mass, radial or pair distribution function
Free energy (Helmholtz function)
Force
Free enthalpy per unit of mass or volume
Free enthalpy (Gibbs function)
Degeneracy factor
Enthalpy
Enthalpy per unit of mass or volume, Planck's constant
Magnetic field, Hamiltonian
Hamiltonian
Current density per unit of surface
Flux, grand potential
Wave vector
Boltzmann constant
Latent heat
Latent heat per unit of mass or volume, length
Mass
Molecular weight
Magnetization
Particle density $(N/V)$
Number of particles
Avogadro's number
Pressure

### Principal Notation XVIMomentum $\boldsymbol{p}$ POrder parameter, probability $\boldsymbol{P}$ Electric polarization Position variable qQuantity of heat Q,qDistance $\boldsymbol{r}$ Ideal gas constant REntropy per unit of mass or volume sSEntropy tTime TAbsolute temperature (Kelvin) $T_C$ Critical temperature UInternal energy Internal energy per unit of mass or volume, pair-potential uVVolume Velocity, variance vWNumber of states, work Probability distribution wConcentration xX Extensive variable Y Intensive variable (field) Coordination number zZPartition function, compressibility factor Volume expansion coefficient $\alpha$ B Reciprocal temperature parameter, 1/kTMagnetic susceptibility, helical pitch $\chi$ $\Delta, \delta$ Increase in a variable Elementary particle energy, $|T - T_C|/T_C$ ε Surface tension $\gamma$ Viscosity $\eta$ Ξ Grand partition function Θ Debye temperature κ Compressibility $\lambda$ Wavelength, thermal conductivity de Broglie thermal wavelength Λ Chemical potential $\mu$ Frequency $\nu$ $\rho$ Density Relaxation time $\tau$ Acentric factor, frequency $\Psi$ Thermodynamic potential, wave function ξ Correlation length $\Omega$ Grand potential $\Omega(E)$ Number of accessible states

Avogadro's number	$N_0$	$6.02205 \times 10^{23}$
Boltzmann's constant	k	$1.38066 \times 10^{-23} J~K^{-1}$
Gas constant	R	$8.31141 J K^{-1} mole^{-1}$
Planck's constant	h	$6.62618 \times 10^{-34}~\mathrm{J~s}$
Standard atmosphere	$p_0$	$1.01325\times 10^5 Nm^{-2}$
Triple point of water	$T_0$	273.16  K
Electron charge	e	$1.60219\times 10^{-19}~{\rm C}$
Electron mass	$m_e$	$9.10953\times 10^{-31}~\rm kg$
Bohr magneton $(eh/4\pi m_e)$	$\mu_B$	$0.927408\times 10^{-23} A\ m^2$
kT at 300 K	_	$4 \times 10^{-21} J = 1/40 \text{ eV}$

Energy: 1 Joule =  $10^7 \text{ ergs} = 0.2389 \text{ cal} = 9.48 \times 10^{-4} \text{ btu}$ 

Pressure: 1 Pascal = 1 Newton  $m^{-2} = 10^{-5} bar = 10 dynes cm^{-2}$ 

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