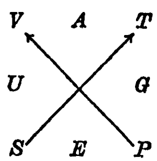
(a)	(b)
$U = U(S, V)\ (\mathrm{d}U = \mathrm{d}Q - P\,\mathrm{d}V)$	$U = U(S, M)\ (\mathrm{d}U = \mathrm{d}Q + H\,\mathrm{d}M)$
$E = E(S, P) = U + PV$	$E = E(S, H) = U - HM$
$G = G(T, P) = U - TS + PV$	$G = G(T, H) = U - TS - HM$
$A = A(T, V) = U - TS$	$A = A(T, M) = U - TS$

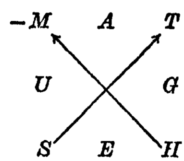
$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \mathrm{d}U = T\,\mathrm{d}S + H\,\mathrm{d}M \Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

$$\mathrm{d}E = T\,\mathrm{d}S + V\,\mathrm{d}P \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \mathrm{d}E = T\,\mathrm{d}S - M\,\mathrm{d}H \Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \mathrm{d}G = -S\,\mathrm{d}T - M\,\mathrm{d}H \Rightarrow \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

$$\mathrm{d}A = -S\,\mathrm{d}T - P\,\mathrm{d}V \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \mathrm{d}A = -S\,\mathrm{d}T + H\,\mathrm{d}M \Rightarrow \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M$$





Comparison of thermodynamic relations for (a) fluid systems and (b) magnetic systems. Note that the two are related by the substitutions $V \rightarrow -M$ and $P \rightarrow H$.

Summary of definitions of critical-point exponents for fluid systems

Exponent	Definition	Conditions ϵ	$P-P_c$	$\rho-\rho_c$	Quantity
α'	$C_V \sim (-\epsilon)^{-\alpha'}$	<0	0	0	Specific heat at constant volume $V = V_c$
α	$C_V \sim \epsilon^{-\alpha}$	>0	0	0	
β	$\rho_L - \rho_G \sim (-\epsilon)^{\beta}$	<0	0	$\neq 0$	Liquid–gas density difference (or shape of coexistence curve)
γ'	$K_T \sim (-\epsilon)^{-\gamma'}$	<0	0	$\neq 0$	Isothermal compressibility
γ	$K_T \sim \epsilon^{-\gamma}$	>0	0	0	
δ	$P - P_c \sim \lvert\rho_L - \rho_G\rvert^{\delta} \operatorname{sgn}(\rho_L - \rho_G)$	0	$\neq 0$	$\neq 0$	Critical Isotherm
ν'	$\xi \sim (-\epsilon)^{-\nu'}$	<0	0	$\neq 0$	Correlation length
ν	$\xi \sim \epsilon^{-\nu}$	>0	0	0	
η	$G(r) \sim \lvert r\rvert^{-(d-2+\eta)}$	0	0	0	Pair correlation function (d = dimensionality)
Δ'_ℓ	$\frac{\partial^\ell G}{\partial P^\ell} \equiv G^{(\ell)} \sim (-\epsilon)^{-\Delta'_\ell} G^{(\ell-1)}$	<0	0	0	Successive pressure derivatives of the Gibbs potential $G(T, P)$
$\Delta_{2\ell}$	$\frac{\partial^{2\ell} G}{\partial P^{2\ell}} \equiv G^{(2\ell)} \sim \epsilon^{-2\Delta_{2\ell}} G^{(2\ell-2)}$	>0	0	0	

Summary of definitions of critical-point exponents for magnetic systems

Exponent	Definition	Conditions ϵ	H	M	Quantity
α'	$C_H \sim (-\epsilon)^{-\alpha'}$	<0	0	0	specific heat at constant magnetic field
α	$C_H \sim \epsilon^{-\alpha}$	>0	0	0	
β	$M \sim (-\epsilon)^{\beta}$	<0	0	$\neq 0$	zero-field magnetization
γ'	$\chi_T \sim (-\epsilon)^{-\gamma'}$	<0	0	$\neq 0$	zero-field isothermal susceptibility
γ	$\chi_T \sim \epsilon^{-\gamma}$	>0	0	0	
δ	$H \sim \lvert M\rvert^{\delta} \operatorname{sgn}(M)$	0	$\neq 0$	$\neq 0$	critical isotherm
ν'	$\xi \sim (-\epsilon)^{-\nu'}$	<0	0	$\neq 0$	correlation length
ν	$\xi \sim \epsilon^{-\nu}$	>0	0	0	
η	$\Gamma(r) \sim \lvert r\rvert^{-(d-2+\eta)}$	0	0	0	pair correlation function (d = dimensionality)
Δ'_ℓ	$\frac{\partial^\ell G}{\partial H^\ell} \equiv G^{(\ell)} \sim (-\epsilon)^{-\Delta'_\ell} G^{(\ell-1)}$	<0	0	0	successive field derivatives of the Gibbs potential $G(T, H)$
$\Delta_{2\ell}$	$\frac{\partial^{2\ell} G}{\partial H^{2\ell}} \equiv G^{(2\ell)} \sim \epsilon^{-2\Delta_{2\ell}} G^{(2\ell-2)}$	>0	0	0	

INTRODUCTION TO
PHASE TRANSITIONS AND CRITICAL PHENOMENA

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TO IDAHLIA

PREFACE

THIS monograph is intended to serve as an introduction to the interdisciplinary field of phase transitions and critical phenomena. It is a short book, and is not designed to review all of the recent developments in this rapidly-developing area. I have attempted, however, to provide an introduction that is sufficiently thorough that much of the current research literature can profitably be read.

The subject matter concentrates almost exclusively upon phenomena near the *liquid–gas* and *ferromagnetic* critical points, and the analogies between fluid and magnetic transitions are emphasized throughout the book. The decision not to treat in detail the phase transitions that occur in a wide variety of other systems was made in order that the novice reader (not familiar with, say, superfluidity) should appreciate the concepts underlying current research in critical phenomena.

I assume as background some familiarity with elementary thermodynamics and statistical mechanics, and I also assume that the reader has some notion of what a phase transition is. Therefore Chapters 1 and 2 are designed to provide a brief review and to establish the notation to be used; they may certainly be omitted by a number of readers. Likewise the chapters in Part III concerning the 'classical' van der Waals, mean field, and Ornstein–Zernike theories may be read quickly or else skipped altogether. Conversely, the material presented in certain of the appendices, and in Chapters 12–15, is more compact and is intended for the advanced student.

The material treated in this monograph proved to be adequate for a one-term course on phase transitions and critical phenomena given at MIT. I have also used the manuscript to supplement an introductory course in thermodynamics and statistical mechanics, and I found the material in Chapters 2–6 and 10–11 particularly useful. For those who may consider using portions of this book as supplementary material for courses in solid state physics or applied mathematics, I would recommend Chapters 6–9, 11, and 13–15. In so far as it has proved feasible, I have attempted to keep the chapters reasonably independent of one another so that the reader may skip about in the text if he wishes.

Since phase transitions and critical phenomena form an interdisciplinary field involving the work of chemists, mathematicians, physicists, and engineers, it has not been possible to find a notation that all classes of readers will find natural. To help in this respect, I have provided a list of symbols and their definitions in the 'notation guide' which follows the list of contents.

In writing this monograph I have continually regretted the fact that my aim of writing a short book has not permitted me to treat as many topics as I would otherwise have desired. Therefore, in the lists of *Suggested further reading* appearing at the ends of each chapter I have provided references to particularly readable works which should serve to extend the text along the lines I would have liked to. The bibliography at the end of the book includes only the articles referred to in the text; a considerably more extensive bibliography will appear in my companion volume, *Readings in Phase Transitions and Critical Phenomena.*

A large number of people have generously assisted with the preparation of the manuscript. First and foremost of these is my wife, Idahlia, to whom this volume is dedicated. I am deeply moved by the prodigious efforts of my research students, who have spent many hours of work on the manuscript. Particular sections were either written or re-written by Gerald Paul, Sava Milošević, Richard Krasnow, Charles Gordon, Frederic Harbus, Harvey Botman, and Jørgen Randers. Alexander Hankey solved all the exercises in the original lecture notes, and many of his solutions are incorporated into the present manuscript. David Njus prepared the drawings, and by his alertness and ingenuity in many cases improved their pedagogical value. The entire manuscript was also read carefully by Kenneth Ogan, Arthur Cook, Jill Punsky, Koichiro Matsuno, Jeffrey Golden, Nihat Berker, Douglas Karo, Stephen Schwartz, Judith Herzfeld, David Lambeth, Howard Lee, and Richard Lucash. The subject index, author index, and notation guide were kindly prepared by J. Punsky, S. Milošević, and K. Matsuno respectively.

I wish to express my appreciation to many of my professional colleagues who have supplied me with information and help in the preparation of this book. I have the particular pleasure of thanking Drs. A. J. Guttmann, P. C. Hohenberg, and J. B. Lastovka and Professors G. B. Benedek, H. Z. Cummins, M. H. Edwards, R. B. Griffiths, B. Jancovici, E. H. Lieb, J. D. Litster, J. E. Mayer, G. Sposito, G. Stell, K. Stierstadt, and L. Tisza for their thoughtful criticisms of the lecture notes from which this monograph has developed. I am also greatly indebted to Professor Robert B. Griffiths and to four former teachers, Professors Max Delbrück, Thomas A. Kaplan, Charles Kittel, and J. H. Van Vleck, for setting extremely high examples of intellectual honesty and clarity.

It is a pleasure to thank Professor Charles Kittel and the Physics Department of the University of California, Berkeley, for their hospitality during the academic year 1968–1969, and to thank the Miller Institute for Basic Research in Science for financial support in the form of a postdoctoral fellowship. This monograph developed from a set of lecture notes prepared for 'Physics 290g', spring quarter, 1969. To the students and faculty who attended these lectures, and to those MIT students who attended various sets of lectures given at this institution, I wish to express my gratitude for many stimulating discussions which contributed significantly to my own understanding of the subject.

I want to thank Mrs. Vera Sarantakis, Mrs. Janet Pollock, and Miss Susan J. Leonard for their diligence and patience in typing the final manuscript, and to thank a countless number of secretaries at Berkeley for having typed portions of the original lecture notes.

I am greatly indebted to the staff of the Oxford University Press for their gracious assistance in so many ways. I am also deeply appreciative of the warm advice and thorough criticism of the early manuscript by one of the series editors, Dr. Walter Marshall. Were it not for his encouragement, the original lecture notes would never have developed into the present monograph.

Severe self-criticism, even as I study the final page proof, means that I must resist an urge to re-write the treatment of several topics that I now realize can be explained more clearly and precisely. I do hope that readers who notice these and other imperfections will communicate their thoughts to me.

Cambridge, Massachusetts H. E. S.

January 1971

CONTENTS

NOTATION GUIDE

For those cases in which a symbol has more than one meaning, we list the chapter(s) in which the symbol is used. Symbols are not listed here if they occur only in the immediate context of a statement defining them, and conventional mathematical symbols are not listed. The abbreviation c.p.e. denotes 'critical-point exponent'. The reader should notice that all inequalities are written in the form $x \geq y$; that we have denoted the four thermodynamic potentials by U, E, G, and A; that, while in most cases we use the same symbol for analogous fluid and magnetic quantities, the correlation functions are denoted respectively by $G(\mathbf{r})$ and $\Gamma(\mathbf{r})$; that different symbols are used for time-dependent quantities (e.g., $G(\mathbf{r})$ and $\mathscr{G}(\mathbf{r}, t)$); that for magnetic systems we adhere to the relation $G(T, H) = -kT \ln Z(T, H)$ (Wannier 1966); that the energy of parallel spins is $-J$ except in Chapter 6 (where it is $-2J$), and that small arrows (►) denote equations referred to frequently.

Symbol	*Meaning*	*Page*	*Used only in chapter*
$a\,[a']$	c.p.e. for thermal conductivity $T > T_c\,[T < T_c]$	203	
$\mathscr{a}, \mathscr{b}$	parameters in van der Waals equation	68	
$A(T, V)\,[A(T, M)]$	Helmholtz potential for fluid [magnet]	22	
$\mathscr{A}\,[\mathscr{A}']$	coefficient for specific heat, $T > T_c\,[T < T_c]$	44	
a_ϵ, a_H	scaling parameters	181	
a_M, a_S	scaling parameters	274	
a_ℓ, b_ℓ, c_ℓ	coefficients of series expansions	137, 148	9
$b\,[b']$	c.p.e. for shear viscosity, $T > T_c\,[T < T_c]$	203	
B	coefficient of Botch–Fixman correction	225	
$\mathscr{B}$	coefficient for order parameter	10, 42	
$B_S(y)$	Brillouin function	81	
$c\,[c']$	c.p.e. for bulk viscosity $T > T_c\,[T < T_c]$	203	
$\mathscr{C}\,[\mathscr{C}']$	coefficient for K_T, χ_T for $T > T_c\,[T < T_c]$	43	
C	Curie constant	3, 83	
$C(\mathbf{r})$	'direct' correlation function	102	7
$\hat{C}(\mathbf{q})$	Fourier transform of $C(\mathbf{r})$	102	7
C_H	specific heat for constant magnetic field	32, 35	
C_M	specific heat for constant magnetization	35	
C_P	specific heat for constant pressure	25	
C_V	specific heat for constant volume	25	
C_V°	specific heat for non-interacting limit	75	

Symbol	*Meaning*	*Page*	*Used only in chapter*
d	dimensionality of lattice	46	
D	dimensionality of spin	111	
$\mathscr{D}$	coefficient for critical isotherm	43	
D_S	sound wave damping constant	211	
D_T	thermal diffusivity	211	
D_ℓ	$(mn)^{-1}(\frac{4}{3}\eta+\zeta)$	211	
e	energy density	275	
e_1	energy density measured from its equilibrium value	276	
$E(S, P)$ $[E(S, H)]$	enthalpy for fluid [magnet]	22	
$\mathscr{E}$	electric field	206, 288	
$f(x)$, $F(x)$	arbitrary functions	—	
$\mathscr{F}$	shape function	234	
g	Landé factor	80	
$\mathbf{g}$	momentum density	274	
$g(\ell)$	number of graphs with ℓ lines	142	
$G(T, P)$ $[G(T, H)]$	Gibbs potential for fluid [magnet]	22	
$\bar{G}$	Gibbs potential per particle	92	
$G(\mathbf{r})$	static pair correlation function, fluid	46, 95	
$\mathscr{G}_{nn}(\mathbf{r}, t) = \mathscr{G}(\mathbf{r}, t)$	density–density correlation function	204	
$\mathscr{G}_{hn}(\mathbf{r}, t)$	heat density–number density correlation function	278	
h	Planck's constant	94	7
h	tanh $(\bar{\mu}H/2kT)$	84	6
h	dimensionless magnetic field, site model	131, 191	8, 12
h	heat energy density	276	App. D
$\mathscr{h}$	scaled magnetic field	186	
H	magnetic field	8	
$\tilde{h}$	effective magnetic field, cell model	192	12
$\mathscr{H}$	Hamiltonian	80	
$\mathscr{H}^{(D)}$	Hamiltonian for isotropically-interacting D-dimensional spins	111	
H_c°	kT_c/m_0	43	
H_{eff}	effective magnetic field	82	
$\tilde{H}$	$\bar{\mu}SH/kT$, normalized magnetic field	88	
i, j, k, m, n	lattice sites	—	
$I(\mathbf{q})$	intensity of scattered radiation, static case	99	
$\mathscr{I}(\mathbf{q}, \omega)$	intensity of scattered radiation, dynamic case	209	
$I^\circ(\mathbf{q})$	intensity of scattered radiation in non-interacting limit	99	
I_B	intensity of Brillouin component	213	
I_R	intensity of Rayleigh component	213	
J or J_{ij}	exchange energy	90, 111	
$\mathscr{J}$	J/kT	92	
$\mathscr{J}_c$	J/kT_c	152	

Symbol	*Meaning*	*Page*	*Used only in chapter*
$\mathbf{j}_e$	energy current density	275	
k	Boltzmann constant	3	
$\mathbf{k}_0$	wave vector of incident radiation	99	
$\mathbf{k}_S$	wave vector of scattered radiation	99	
K_S	adiabatic compressibility	26	
K_T	isothermal compressibility	3, 25	
K_T°	isothermal compressibility for an ideal gas	43	
L	length of cell in Kadanoff construction	191	12
$L_j(T)$	Landau expansion coefficient of the Helmholtz free energy	168	
ℓ_{jk}	expansion coefficient of $L_j(T)$	169	
ℓ	dummy index of summation; integer	—	
m	mass of a molecule	3	
$M = M(T, H)$	magnetization	8	
$M_H(T)$	constant-field magnetization	42	3, 4
$M_T(H)$	constant-temperature magnetization	62	4
M_0	$M(T = 0, H = 0)$	81	6
$\mathscr{m}$	scaled magnetization	186	
$\mathscr{M}$	magnetization operator	36	
$\mathscr{m}_0$	magnetic moment per spin	43	
n	N/V or $\langle n(\mathbf{r})\rangle$	26, 95	
$n(\mathbf{r})$	number density at point $\mathbf{r}$	94	
n_1	number density measured from its equilibrium value	276	
$\mathscr{n}$	N/N_A, number of moles	67	5
$\mathscr{n}$	index of refraction	206	13
N	total number of particles (or spins)	26	
N_A	Avogadro's number	67	
p	$(P - P_c)/P_c$, dimensionless pressure	74	5
P	pressure	1	
$\tilde{P}$	P/P_c, normalized pressure	72	
P_c	critical pressure	2	
P_c°	pressure of ideal gas at $\rho = \rho_c$, $T = T_c$	43	
$\mathscr{P}$	number of nearest neighbour pairs in a lattice	139	
$\mathscr{P}_D^N$	Padé approximant of order $[D, N]$	162	
q	coordination number ($\equiv$ number of nearest neighbours)	90	
$\mathbf{q}$	momentum transfer vector	99	
r	distance	46	
r_c	radius of convergence	153	
R	Debye persistence length	104	
$\mathscr{R}$	kN_A, ideal gas constant	67	
s_i	Ising spin on site i	91	
$\tilde{s}_\alpha$	magnetic moment of cell α	192	

Symbol	*Meaning*	*Page*	*Used only in chapter*
S	entropy	22	
S	spin quantum number	80	
$\mathbf{S}_i$	vector spin on site i	80	
$S_{nn}(\mathbf{q}) = S(\mathbf{q})$	static structure factor; Fourier transform of $G(\mathbf{r})$	100	
$\mathscr{S}_{nn}(\mathbf{q}, \omega) = \mathscr{S}(\mathbf{q}, \omega)$	dynamic structure factor; Fourier transform of $\mathscr{G}_{nn}(\mathbf{r}, t)$	205	
$\mathscr{S}^{\mathrm{L}}_{nn}(\mathbf{q}, \omega)$	Fourier–Laplace transform of $G_{nn}(\mathbf{r}, t)$	278	
t	time	204	
T	temperature	1	
$\tilde{T}$	T/T_c, normalized temperature	72	
T_c	critical temperature	2	
T_{c1}	critical temperature for divergence of susceptibility	119	
T_{c2}	critical temperature for spontaneous magnetization	119	
T_N	critical temperature for antiferromagnet	11	
T_λ	λ temperature for ^{4}He	19	
$\mathbf{T}$	stress tensor	275	App. D
$\mathbf{T}$	transfer matrix	132	8
u	$\exp(-4J/kT)$	158	9
$U(\mathbf{r})$	interparticle potential	76, 96	
$U(S, V)$ [$U(S, M)$]	internal energy for fluid [magnet]	22	
v	$(V - V_c)/V_c = \tilde{V} - 1$	74	5
v	$\tanh(J/kT)$	139	8, 9
v	c/κ, velocity of light in medium	206	13, 14
v_s	sound velocity	211	
V	volume	22	
V_c	critical volume	71	
$\bar{V}$	V/N	68	
$\tilde{V}$	V/V_c, normalized volume	72	
$\mathbf{v}_1$	velocity measured from its mean value	276	
w	transition probability per unit time	279	
x	$\bar{\mu}H/kT$	80	6
z	homogeneity parameter	235	15
z	$1 - \tanh(J/kT)$	164	9
Z	partition function	77	
Z_c	$P_cV_c/\mathscr{R}T_c$	72	
$\mathscr{Z}$	grand partition function	94	
α [α']	c.p.e. for C_H and C_V, $T > T_c$ [$T < T_c$]	44	
α	characteristic inverse time	283	App. E
α_P	coefficient of thermal expansion, $V^{-1}(\partial V/\partial T)_P$	26	
α_H	$(\partial M/\partial T)_H$	35	
α_M	$(\partial H/\partial T)_M$	36	

Symbol	*Meaning*	*Page*	*Used only in chapter*
β	$1/kT$	77	
β	c.p.e. for $\rho_L - \rho_G$ and $M(T, H = 0)$	10, 42	
β_G	c.p.e. for $\rho_c - \rho_G$	4	
β_L	c.p.e. for $\rho_L - \rho_c$	4	
$\tilde{\beta}$	β/β_c, reduced inverse temperature	153	9
$\gamma\,[\gamma']$	c.p.e. for K_T and χ_T, $T > T_c\,[T < T_c]$	3, 43	
$\Gamma(\mathbf{r})$	pair correlation function, magnet	45	
$\Gamma(\mathbf{r})$	dimensionless correlation function, fluid	102	7
Γ_B	half-width of Brillouin component	211	
Γ_R	half-width of Rayleigh component	211	
Γ_L	relaxation rate for longitudinal spin fluctuations	244	15
δ	c.p.e. for critical isotherm	3, 43	
δ_s	$H \sim M^{\delta_s}$, $S = S_c$	62	
$\Delta_{2\ell}[\Delta'_\ell]$	gap exponent, $T > T_c\,[T < T_c]$	50	
ϵ	$(T - T_c)/T_c$, normalized temperature	4, 10	
$\epsilon_T[\epsilon_\eta;\,\epsilon_s]$	crossover temperature between regions 1, 2 [2, 3; 3, 4]	254	
ζ	$S \sim -M^{\zeta+1}$, $T = T_c$	55	
ζ	bulk viscosity	203	
ζ_0	bulk viscosity far from critical point	247	
η	$G(r) \sim r^{-(d-2+\eta)}$, $T = T_c$	46	
η_E	$\Gamma_{EE}(r) \sim r^{-(d-2+\eta_E)}$, $T = T_c$	62	
η	shear viscosity	203	
η_0	shear viscosity far from critical point	247	
η^*	$\eta(q = \kappa, \Omega = \Omega_\eta^*)$	251	
θ	vapour pressure curvature exponent	51	
κ	$1/\xi$, inverse correlation length	105	
κ_0	coefficient of inverse correlation length	214	
λ	arbitrary critical-point exponent	39	3
λ	molecular field parameter	82	6
λ	wavelength	214	
λ_s	c.p.e. for singular part of function	41	
$\lambda_\pm$	eigenvalues of transfer matrix	132	
Λ	thermal conductivity	203	
Λ_0	thermal conductivity far from critical point	247	
Λ^*	$\Lambda(q = \kappa, \Omega = \Omega_T^*)$	251	
μ	chemical potential	33	
μ_B	Bohr magneton	80	
$\bar{\mu}$	$g\mu_B$	80	
$\nu\,[\nu']$	c.p.e. for correlation length for $T > T_c\,[T < T_c]$	46	
ξ	correlation length	5, 46	