

STATISTICAL MECHANICS OF SOLIDS

Louis A. Girifalco

OXFORD
UNIVERSITY PRESS

2000

Contents

1 The Basics of Thermodynamics 1

- 1.1 The existence of equilibrium and state functions 1
- 1.2 Empirical temperature scales 2
- 1.3 The ideal gas temperature 2
- 1.4 The mechanical equivalent of heat 3
- 1.5 Walls and the zeroth law of thermodynamics 4
- 1.6 Spontaneous, reversible, and irreversible processes 5
- 1.7 Work and the dependence of work on the path 6
- 1.8 The first law of thermodynamics 8
- 1.9 Heat capacity, energy, and enthalpy 9
- 1.10 The second law of thermodynamics and entropy 10
- 1.11 Free energies and equilibrium conditions 14
- 1.12 Thermodynamic potentials and Legendre transformations 16
- 1.13 Chemical potentials 20
- 1.14 Conditions of phase equilibria and stability 21
- 1.15 Euler's theorem and the Gibbs–Duhem equation 24
- 1.16 Reciprocity relations of Maxwell 26
- 1.17 Useful differential relations 27
- 1.18 Equations of state and heat capacity relations 28
- 1.19 Magnetic systems 31
- Exercises 32

2 Principles of Statistical Mechanics 34

- 2.1 Definitions for statistical mechanics 34
- 2.2 Thermodynamic state 35
- 2.3 Comparison of microscopic and macroscopic state 36
- 2.4 The relation between microscopic and macroscopic state 37
- 2.5 System and environment 38
- 2.6 Quantum states of macroscopic systems 39
- 2.7 Time averages 40
- 2.8 Ensembles 41
- 2.9 The canonical ensemble 42
- 2.10 The canonical most probable distribution 44
- 2.11 Summary of definitions of probabilities 47

- 2.12 The canonical ensemble and thermodynamics 48
- 2.13 Statistical entropy and the second law of thermodynamics 54
- 2.14 The semiclassical approximation 56
- 2.15 The grand canonical ensemble 60
- 2.16 The pressure ensemble 63
- 2.17 Fluctuations 64
- Exercises 67

3 Particle Statistics 69

- 3.1 Entropy and number of complexions 69
- 3.2 Particle distribution functions 71
- 3.3 Particle statistics and thermodynamics 74
- 3.4 The ideal gas 76
- 3.5 Particle statistics from the grand canonical ensemble 81
- 3.6 Representations of the density of states 84
- 3.7 Maxwell's velocity distribution 86
- 3.8 Two-dimensional ideal gas 87
- 3.9 Independent particles and subsystems 88
- Exercises 90

4 The Harmonic Crystal 92

- 4.1 The harmonic model 92
- 4.2 The monatomic linear chain and normal mode analysis 93
- 4.3 Partition function and free energy of the harmonic crystal 101
- 4.4 General heat capacity equations 104
- 4.5 The Einstein model 106
- 4.6 Superposition of Einstein oscillators 107
- 4.7 The Debye model 108
- 4.8 Debye energy and heat capacity 112
- 4.9 Relation between Einstein and Debye characteristic temperatures 115
- 4.10 Comparison of Debye theory with experiment 116
- 4.11 The phonon gas 119
- Exercises 121

5 Anharmonic Properties and the Equation of State 124

- 5.1 The crystal potential energy 124
- 5.2 Anharmonic properties and the Gruneisen assumption 129
- 5.3 Heat capacity at constant pressure 134
- 5.4 Debye theory and the Gruneisen assumption 134
- 5.5 Vibrational anharmonicity 136
- 5.6 Theory of the Gruneisen parameter 137
- Exercises 141

6 Free Electron Theory in Metals and Semiconductors 143

- 6.1 Free electrons in metals 143
- 6.2 Statistics for the electron gas 144

6.3	The distribution of free electrons	145
6.4	Thermodynamic properties of the free electron gas	148
6.5	Electronic heat capacity in metals	152
6.6	Equation of state of the free electron gas	153
6.7	Thomas–Fermi theory	155
6.8	Review of results of band theory	159
6.9	Impurity levels in semiconductors	162
6.10	Electron distribution in intrinsic semiconductors	163
6.11	Electron statistics in extrinsic semiconductors	167
6.12	Mass action laws for extrinsic semiconductors	171
6.13	Relation between Fermi level and impurity concentration	173
	Exercises	175

7 Statistical-Kinetic Theory of Electron Transport 177

7.1	Free electrons in external fields and temperature gradients	177
7.2	The statistical-kinetic method	180
7.3	The Boltzmann transport equation	181
7.4	Formal flux equations	185
7.5	The electrical conductivity of metals	186
7.6	Thermal conductivity and the Wiedemann–Franz law	188
7.7	The isothermal Hall effect	192
7.8	Electrical conductivity in semiconductors	196
	Exercises	201

8 Order-Disorder Alloys 202

8.1	Order-disorder structures	202
8.2	The order-disorder transition	203
8.3	Description of the degree of order	204
8.4	The Order-disorder partition function	209
8.5	The Kirkwood method	213
8.6	The Bragg–Williams approximation	217
8.7	The second moment approximation	222
8.8	The quasi-chemical approximation	225
8.9	Comparison with experiment	230
	Exercises	232

9 Magnetic Order 234

9.1	Magnetic response	234
9.2	Paramagnetism of independent moments	236
9.3	Paramagnetism of free electrons	240
9.4	Ferromagnetism: mean field theory	242
9.5	The Ising model for ferromagnetism	245
9.6	Antiferromagnetism: mean field theory	248
9.7	Spin waves	251
	Exercises	256

10 Phase Equilibria 258

- 10.1 Phase equilibria in one-component systems 258
- 10.2 The van der Waals model 262
- 10.3 Sublimation 270
- 10.4 The liquid state 272
- 10.5 Communal entropy 276
- 10.6 Vibrations and melting 277
- 10.7 Melting 281
- 10.8 Regular solution theory of binary alloys 282
- Exercises 286

11 Critical Exponents and the Renormalization Group 288

- 11.1 Equivalent models 288
- 11.2 Critical points 289
- 11.3 Landau theory and the Kirkwood expansion 292
- 11.4 Fluctuations and correlation length 295
- 11.5 The monatomic Ising chain 298
- 11.6 Renormalization of the one-dimensional Ising model 302
- 11.7 The Kadanoff construction 305
- 11.8 The renormalization group 311
- 11.9 Scaling and the renormalization group 313
- 11.10 Numbers 316
- Exercises 317

12 Surfaces and Interfaces 318

- 12.1 Basic concepts 318
- 12.2 Thermodynamics of interfaces 322
- 12.3 Thermodynamics of adsorption on solid surfaces 325
- 12.4 Adhesion and cohesion 328
- 12.5 Critical point and critical exponent for surface tension 333
- 12.6 Monolayer adsorption: Langmuir isotherm 335
- 12.7 Monolayer adsorption: mobile layer 339
- 12.8 Multilayer adsorption: BET isotherm 340
- 12.9 Segregation of impurities at interfaces 345
- Exercises 346

13 The Theory of Random Flight 349

- 13.1 Introduction 349
- 13.2 The mean square total displacement 350
- 13.3 Random flight on a lattice 354
- 13.4 Reflecting and absorbing barriers 361
- 13.5 The Markoff method 363
- 13.6 The general solution 367
- 13.7 Self-similarity 370
- 13.8 The diffusion equation from random flights 371
- Exercises 373

14 Linear Polymer Chains 375

- 14.1 Polymer chains and random flight 375
- 14.2 Persistence length 376
- 14.3 Chain length fluctuations 379
- 14.4 Density in a polymer chain 381
- 14.5 Partition function of a polymer chain 381
- 14.6 Excluded volume 383
- 14.7 The force ensemble and chain elasticity 385
- 14.8 Elastomers 389
- 14.9 The Flory correction 395
- 14.10 Solutions and gels 395
- Exercises 401

15 Vacancies and Interstitials in Monatomic Crystals 403

- 15.1 Choice of ensemble 403
- 15.2 The vacancy concentration 404
- 15.3 The crystal free energy 407
- 15.4 Vacancies and thermodynamic functions 410
- 15.5 The vacancy formation functions 413
- 15.6 Vacancies, divacancies, and interstitials 418
- 15.7 Some numerical results 422
- Exercises 429

16 Point Defects in Dilute Alloys 431

- 16.1 General comments 431
- 16.2 The statistical count for substitutional defects 433
- 16.3 Defect concentration formulas for substitutional defects 435
- 16.4 Internal equilibria for substitutional defects 440
- 16.5 Quenched-in resistivity of dilute binary alloys 441
- 16.6 Some general theory 443
- 16.7 Thermodynamics of the dilute alloy 446
- Exercises 448

17 Diffusion in Simple Crystals 450

- 17.1 The empirical laws of diffusion 450
- 17.2 Transition probabilities and Fick's laws 452
- 17.3 Atomic jumps and the diffusion coefficient 455
- 17.4 The jump frequency in one dimension 457
- 17.5 Many-body theory of the jump frequency 460
- 17.6 The diffusion coefficient 466
- Exercises 467

Appendix 1 Combinatorial Problems in Statistical Mechanics 469**Appendix 2 The Method of Undetermined Multipliers 473****Appendix 3 Stirling's Approximation 477**

Appendix 4 Sums and Integrals 479

Appendix 5 Fermi Integrals 484

Appendix 6 Kirkwood's Second Moment 488

Appendix 7 The Generalized Lattice Gas 492

Appendix 8 Dyadics and Crystal Symmetry 495

Additional Readings 505

Index 509