Contents

PART I Principles of statistical thermodynamics	1
ol The first law of thermodynamics	3
 1-1. Systems and state variables 4 1-2. The equation of state 7 1-3. "Large" and "small" systems; statistics of Gibbs versus Boltzmann 10 1-4. The First Law; heat, work, and energy 12 1-5. Precise formulation of the First Law for quasistatic change 17 Problems 23 	
2 Elementary statistical methods in physics	28
 2-1. Probability distributions; binomial and Poisson distributions 30 2-2. Distribution function for large numbers; Gaussian distribution 35 2-3. Statistical aspect of quantum mechanics 37 2-4. Statistics dealing with averages in time; virial theorem 42 Problems 47 	
3 Statistical counting in mechanics	50
 3-1. Statistical counting in classical mechanics; Liouville theorem and ergodic hypothesis 52 3-2. Statistical counting in quantum mechanics 57 Problems 61 	
vii	

17111	Contents
VIII	Contents

4	The Gibbs-Boltzmann distribution law	63	8-4. Particle versus system partition function; Gibbs paradox 1678-5. Grand ensemble formulas for Boltzmann particles 170
	 4-1. Derivation of the Gibbsian or canonical distribution 63 4-2. Elucidation of the temperature concept 68 4-3. The perfect gas; Maxwellian distribution 69 		Problems 173
	4-4. Energy distribution for small and large samples; thermodynamic		9 Quantum statistics of independent particles
	limit 73 4-5. Equipartition theorem and dormant degrees of freedom 75 Problems 81		 9-1. Pauli exclusion principle 175 9-2. Fermi-Dirac statistics 178 9-3. Theory of the perfect Fermi gas 182 9-4. Bose-Einstein statistics 185
5	Statistical justification of the Second Law	83	9-5. The perfect Bose gas; Einstein condensation 188
	 5-1. Definition of entropy; entropy and probability 83 5-2. Proof of the Second Law for "clamped" systems 88 5-3. The Ehrenfest or adiabatic principle 92 		Problems 190
	5-4. Extension of the Second Law to general systems 95		PART II Equilibrium statistics of special systems
	5-5. Simple examples of entropy expressions 100		10 Thermal properties of electromagnetic radiation
	5-6. Examples of entropy-increasing processes 106 5-7. Third Law of thermodynamics 111 Problems 114		10-1. Realization of equilibrium radiation; black body radiation 19510-2. Thermodynamics of black body radiation; laws of Stefan-Boltzmann and Wien 197
06	6 Older ways to the Second Law	117	10-3. Statistics of black body radiation; Planck's formula 203 Problems 208
	6-1. Proof by the method of Carnot cycles 118		
	6-2. Proof of Caratheodory 126 Problems 132		11 Statistics of the perfect molecular gas
07	 Thermodynamic exploitation of the Second Law; mass transfer problems 7-1. Legendre transformations and thermodynamic potentials 134 7-2. Thermodynamics of bulk properties; extensive and intensive variables 138 7-3. Equilibrium of two phases; equation of Clausius and Clapeyron 142 	134	 11-1. Decomposition of the degrees of freedom of a perfect molecular gas 211 11-2. Center-of-mass motion of gaseous molecules 213 11-3. Rotation of gaseous molecules 215 11-4. The rotational heat capacity of hydrogen 217 11-5. Vibrational motion of diatomic molecules 222 11-6. The law of mass action in perfect molecular gases 225 Problems 231
	7-4. Equilibrium of multiphase, multicomponent systems; Gibbs'		*12 The problem of the imperfect gas
	phase rule 145 7-5. Refined study of the two-phase equilibrium; vapor pressure of small drops 148 Problems 152		 12-1. Equation of state from the partition function 233 12-2. Equation of state from the virial theorem 235 12-3. Approximate results from the virial theorem; van der Waals' equation 239
8	 The grand ensemble; classical statistics of independent particles 8-1. Statistics of the grand ensemble 155 8-2. Other modified statistics; Legendre-transformed partition functions 160 8-3. Maxwell-Boltzmann particle statistics 164 	155	 12-4. The Joule-Thomson effect 241 12-5. Ursell-Mayer expansion of the partition function; diagram summation 244 12-6. Mayer's cluster expansion theorem 247 12-7. Mayer's formulation of the equation of state of imperfect gases 249

Contents ix

Con	

374

A	Contonia	
	12-8. Phase equilibrium between liquid and gas; critical phenomenon 251 Problems 255	
13	Thermal properties of crystals	257
	 13-1. Relation between the vibration spectrum and the heat capacity of solids 257 13-2. Vibrational bands of crystals; models in one dimension 260 13-3. Vibrational bands of crystals; general theory 267 13-4. Debye theory of the heat capacity of solids 272 13-5. Vapor pressure of solids 279 Problems 281 	
14	Statistics of conduction electrons in solids	283
	 14-1. The distinction of metals and insulators in Fermi statistics 284 14-2. Semiconductors: electrons and holes 288 14-3. Theory of thermionic emission 295 14-4. Degeneracy and non-degeneracy: electronic heat capacity in metals 298 14-5. "Doped" semiconductors: n-p junctions 303	
15	Statistics of magnetism	316
	15-1. Paramagnetism of isolated atoms and ions 317 15-2. Pauli paramagnetism 324 15-3. Ferromagnetism; internal field model 326 15-4. Ferromagnetism; Ising model 330 *15-5. Spin wave theory of magnetization 342 Problems 350	
* 16	Mathematical analysis of the Ising model	352
	 16-1. Eigenvalue method for periodic nearest neighbor systems 352 16-2. One-dimensional Ising model 354 16-3. Solution of the two-dimensional Ising model by abstract algebra 356 16-4. Analytic reduction of the results for the two-dimensional Ising model 363 	
17	Theory of dilute solutions	366
	 17-1. Thermodynamic functions for dilute solutions 367 17-2. Osmotic pressure and other modifications of solvent properties by the solutes 370 17-3. Behavior of solutes in dilute solutions; analogy to perfect gases 	

	17-4. Theory of strong electrolytes 377 Problems 383	
PAI	RT III Kinetic theory, transport coefficients and fluctuations	385
* 18	$\label{lem:kinetic} \textit{Kinetic justification of equilibrium statistics; Boltzmann transport equation}$	387
	 18-1. Derivation of the Boltzmann transport equation 388 18-2. Equilibrium solutions of the Boltzmann equation; Maxwellian distribution 392 18-3. Boltzmann's H-theorem 394 18-4. Paradoxes associated with the Boltzmann transport equation; Kac ring model 396 18-5. Relaxation rate spectrum for Maxwellian molecules 404 18-6. Formal relaxation theory of the Boltzmann equation 411 	
	Problems 415	
19	Transport properties of gases	416
	 19-1. Elementary theory of transport phenomena in gases 419 19-2. Determination of transport coefficients from the Boltzmann equation 424 19-3. Discussion of empirical viscosity data 429 Problems 432 	
20	Kinetics of charge carriers in solids and liquids	434
	 20-1. Kinetic theory of Ohmic conduction 434 20-2. Nature of the charge carriers in matter; Nernst relation 441 20-3. Nature of the electric carriers in metals; law of Wiedemann and Franz 442 20-4. Separation of carrier density and carrier velocity; Hall effect 448 Problems 453 	
*21	Kinetics of charge carriers in gases	455
	 21-1. Kinetics of the polarization force 456 21-2. "High field" velocity distribution of ions and electrons in gases 462 21-3. Velocity distribution functions for electrons; formulas of 	
	Davydov and Druyvesteyn 466	
22	Fluctuations and Brownian motion	472
	22-1. Equilibrium theory of fluctuations 473 22-2. Brownian motion 475	

Contents xi

22-3. Spectral decomposition of Brownian motion; Wiener-Khinchin theorem 479 Problems 484 *23 Connection between transport coefficients and equilibrium statistics 486 23-1. Nyquist relation 487 23-2. Kubo's equilibrium expression for electrical conductivity 492 23-3. Reduction of the Kubo relation to those of Nernst and Nyquist 496 23-4. Onsager relations 500 Problem 506

Supplementary Literature	507
Answers to Problems	511
Index	519