

## Contents

Preface . . . . .	v
Introduction . . . . .	ix
Chapter 1	
Equilibrium Statistical Thermodynamics of Classical Systems . . . . .	1
§1. Distribution functions . . . . .	1
1.1. Distribution functions of systems of interacting particles. . . . .	1
1.2. Normalization . . . . .	3
§2. Liouville's equation . . . . .	5
2.1. Liouville's theorem on the invariance of extension in phase . . . . .	5
2.2. Liouville's equation . . . . .	8
2.3. The time evolution of distribution functions .	10
2.4. Entropy . . . . .	13
§3. Gibbsian statistical ensembles . . . . .	18
3.1. The microcanonical distribution . . . . .	20
3.2. The canonical distribution . . . . .	22
3.3. Gibbs' theorem on the canonical distribution. . . . .	25
3.4. The grand canonical distribution. . . . .	31
3.5. The distribution for the isobaric-isothermal ensemble . . . . .	35
§4. The connection between the Gibbsian distributions and the maximum of the information entropy . . . . .	38
4.1. The information entropy . . . . .	39
4.2. Extremal property of the microcanonical distribution. . . . .	41

4.3.	Extremal property of the canonical distribution. . . . .	42
4.4.	Extremal property of the grand canonical distribution. . . . .	43
§5.	Thermodynamic equalities. . . . .	46
5.1.	Quasi-static processes. . . . .	46
5.2.	Thermodynamic equalities for the micro-canonical ensemble . . . . .	47
5.3.	The virial theorem. . . . .	49
5.4.	Thermodynamic equalities for the canonical ensemble . . . . .	52
5.5.	Thermodynamic equalities for the grand canonical ensemble . . . . .	55
§6.	Fluctuations . . . . .	55
6.1.	Quasi-thermodynamic theory of fluctuations . . . . .	55
6.2.	The Gaussian distribution for the probability of fluctuations . . . . .	59

## Chapter 2

	Equilibrium Statistical Thermodynamics of Quantum Systems . . . . .	65
§7.	The statistical operator . . . . .	65
7.1.	The pure ensemble. . . . .	65
7.2.	The mixed ensemble and the statistical operator. . . . .	69
§8.	The quantum Liouville equation . . . . .	73
8.1.	The Liouville equation in the quantum case . . . . .	73
8.2.	The Schrödinger and Heisenberg pictures for statistical operators . . . . .	77
8.3.	The entropy operator . . . . .	78
8.4.	Entropy . . . . .	79
§9.	Gibbsian statistical ensembles in the quantum case . . . . .	82
9.1.	The microcanonical distribution . . . . .	83
9.2.	The canonical distribution . . . . .	85
9.3.	Gibbs' theorem on the canonical distribution. . . . .	87
9.4.	The grand canonical distribution. . . . .	93

9.5. Gibbs' theorem on the grand canonical distribution. . . . .	95
9.6. The distribution for the isobaric-isothermal ensemble . . . . .	99
§10. The connection between the Gibbsian distributions and the maximum of the information entropy (quantum case) . . . . .	100
10.1. Extremal property of the microcanonical distribution. . . . .	101
10.2. Extremal property of the canonical distribution. . . . .	102
10.3. Extremal property of the grand canonical distribution. . . . .	103
§11. Thermodynamic equalities. . . . .	105
11.1. Quasi-static processes. . . . .	105
11.2. Thermodynamic equalities for the microcanonical ensemble . . . . .	105
11.3. The virial theorem for quantum systems . . . . .	107
11.4. Thermodynamic equalities for the canonical ensemble . . . . .	108
11.5. Thermodynamic equalities for the grand canonical ensemble . . . . .	110
11.6. Nernst's theorem. . . . .	111
§12. Fluctuations in quantum systems . . . . .	115
12.1. Fluctuations in the canonical ensemble . . . . .	115
12.2. Fluctuations in the grand canonical ensemble . . . . .	116
12.3. Fluctuations in a generalized ensemble . . . . .	116
§13. Thermodynamic equivalence of the Gibbsian statistical ensembles . . . . .	119
13.1. Thermodynamic equivalence of the canonical and microcanonical ensembles . . . . .	121
13.2. Thermodynamic equivalence of the grand canonical and canonical ensembles . . . . .	125
§14. Passage to the classical limit of quantum statistics . . . . .	129
14.1. Passage to the limit for partition functions . . . . .	129
14.2. Passage to the limit for equilibrium statistical operators. . . . .	136

## Chapter 3

Irreversible Processes Induced by Mechanical Perturbations . . . . .	141
§15. Response of a system to external mechanical perturbations . . . . .	141
15.1. Linear response of a system (case of classical statistics) . . . . .	143
15.2. Linear response of a system (case of quantum statistics) . . . . .	154
15.3. Nonlinear response of a system . . . . .	160
15.4. Effect of an alternating electric field. Electrical conductivity . . . . .	167
15.5. Effect of an alternating magnetic field. Magnetic susceptibility . . . . .	173
§16. Two-time Green functions . . . . .	174
16.1. Retarded, advanced, and causal Green functions . . . . .	175
16.2. Spectral representations for the time correlation functions . . . . .	179
16.3. Spectral representations and dispersion relations for the Green functions . . . . .	184
16.4. Sum rules . . . . .	191
16.5. Symmetry of the Green functions . . . . .	193
§17. Fluctuation-dissipation theorems and dispersion relations . . . . .	196
17.1. Dispersion relations, sum rules, and Onsager's reciprocity relations for the generalized susceptibility . . . . .	196
17.2. The Callen-Welton fluctuation-dissipation theorem for the generalized susceptibility . . . . .	201
17.3. Linear relations between the fluxes and forces. Kinetic coefficients and their properties . . . . .	203
17.4. Order of the limits $V \rightarrow \infty, \epsilon \rightarrow 0$ in the kinetic coefficients . . . . .	209
17.5. Increase of energy under the influence of external mechanical perturbations . . . . .	212
17.6. Entropy production . . . . .	218
§18. Systems of charged particles in an alternating electromagnetic field . . . . .	220

18.1 Dielectric permittivity and conductivity . . . . .	220
18.2. Symmetry properties and dispersion relations . . . . .	231
18.3. System of particles with spin in an electromagnetic field . . . . .	232
18.4. System of particles with a dipole moment . . . . .	234
Chapter 4	
The Nonequilibrium Statistical Operator	237
§19. Conservation laws . . . . .	242
19.1. Local conservation laws for the case of classical mechanics . . . . .	242
19.2. Local conservation laws for the case of quantum mechanics . . . . .	248
19.3. The virial theorem for the nonuniform case . . . . .	255
19.4. Conservation laws for a mixture of gases or liquids . . . . .	258
19.5. Conservation laws for a system of particles with internal degrees of freedom . . . . .	263
§20. The local-equilibrium distribution . . . . .	266
20.1. The statistical operator and distribution functions for local-equilibrium systems . . . . .	267
20.2. Thermodynamic equalities . . . . .	277
20.3. Fluctuations in a local-equilibrium ensemble . . . . .	279
20.4. Critical fluctuations . . . . .	287
20.5. Absence of dissipative processes in a local-equilibrium state . . . . .	294
§21. Statistical operator for nonequilibrium systems . .	301
21.1. The nonequilibrium statistical operator . . . . .	302
21.2. Physical meaning of the parameters . . . . .	311
21.3. The meaning of local integrals of motion . . . . .	313
§22. Tensor, vector, and scalar processes. The equations of hydrodynamics, thermal conduction, and diffusion in a multicomponent fluid . . . . .	317
22.1. Transport processes in a multicomponent fluid. The statistical operator . . . . .	317

22.2.	Linear relations between the fluxes and thermodynamic forces . . . . .	322
22.3.	Onsager's reciprocity relations . . . . .	327
22.4.	Entropy production in nonequilibrium processes. . . . .	331
22.5.	Tensor, vector, and scalar processes. Thermal conduction, diffusion, thermal diffusion, the Dufour effect, and shear and bulk viscosity . . . . .	337
22.6.	Transport processes in a one-component fluid. The thermal-conduction equation and the Navier-Stokes equation . . . . .	346
22.7.	Transport processes in a binary mixture. Thermal conduction, diffusion, and cross effects . . . . .	349
22.8.	Another choice of thermodynamic forces . . . . .	353
§23.	Relaxation processes . . . . .	360
23.1.	General theory . . . . .	360
23.2.	Relaxation of nuclear spins in a crystal . . . . .	369
23.3.	Spin-lattice relaxation of conduction electrons in semiconductors in a magnetic field . . . . .	374
23.4.	Energy exchange between two weakly inter- acting subsystems . . . . .	377
23.5.	Rates of chemical reactions . . . . .	386
§24.	The statistical operator for relativistic systems and relativistic hydrodynamics . . . . .	395
24.1.	The relativistic statistical operator . . . . .	395
24.2.	Thermodynamic equalities . . . . .	397
24.3.	The equations of relativistic hydrodynamics .	400
24.4.	Charge transport processes . . . . .	409
§25.	Kinetic equations	411
25.1.	Generalized kinetic equations . . . . .	411
25.2.	Nonideal quantum gases . . . . .	419
25.3.	The kinetic equation for electrons in a metal . . . . .	421
§26.	The Kramers-Fokker-Planck equations . . . . .	424
26.1.	General method . . . . .	425
26.2.	Particular cases . . . . .	433
§27.	Extremal properties of the nonequilibrium statistical operator . . . . .	435

27.1.	Extremal properties of the quasi-equilibrium distribution . . . . .	436
27.2.	Derivation of the nonequilibrium statistical operator from the extremum of the information entropy . . . . .	439
27.3.	Connection between the nonequilibrium and quasi-equilibrium statistical operators . . . . .	442
27.4.	Generalized transport equations . . . . .	445
27.5.	Generalized transport equations and Prigogine's and Glansdorff's criteria for the evolution of macroscopic systems . . . . .	448
Appendix I	Formal Scattering Theory in Quantum Mechanics . . . . .	453
Appendix II	MacLennan's Statistical Theory of Transport Processes . . . . .	461
Appendix III	Boundary Conditions for the Statistical Operators in the Theory of Nonequilibrium Processes and the Method of Quasi-Averages .	465
References	.....	471