

Fundamentals of Statistical and Thermal Physics

F. Reif

Carnegie Mellon University



Contents

Preface vii

1 Introduction to statistical methods

1

RANDOM WALK AND BINOMIAL DISTRIBUTION

- | | | |
|-----|---|----|
| 1·1 | <i>Elementary statistical concepts and examples</i> | 4 |
| 1·2 | <i>The simple random walk problem in one dimension</i> | 7 |
| 1·3 | <i>General discussion of mean values</i> | 11 |
| 1·4 | <i>Calculation of mean values for the random walk problem</i> | 15 |
| 1·5 | <i>Probability distribution for large N</i> | 17 |
| 1·6 | <i>Gaussian probability distributions</i> | 21 |

GENERAL DISCUSSION OF THE RANDOM WALK

- | | | |
|-------|---|----|
| 1·7 | <i>Probability distributions involving several variables</i> | 25 |
| 1·8 | <i>Comments on continuous probability distributions</i> | 27 |
| 1·9 | <i>General calculation of mean values for the random walk</i> | 31 |
| *1·10 | <i>Calculation of the probability distribution</i> | 35 |
| *1·11 | <i>Probability distribution for large N</i> | 37 |

2 Statistical description of systems of particles

47

STATISTICAL FORMULATION OF THE MECHANICAL PROBLEM

- | | | |
|-----|---|----|
| 2·1 | <i>Specification of the state of a system</i> | 48 |
| 2·2 | <i>Statistical ensemble</i> | 52 |
| 2·3 | <i>Basic postulates</i> | 53 |
| 2·4 | <i>Probability calculations</i> | 60 |
| 2·5 | <i>Behavior of the density of states</i> | 61 |

INTERACTION BETWEEN MACROSCOPIC SYSTEMS

2-6 Thermal interaction	66
2-7 Mechanical interaction	68
2-8 General interaction	73
2-9 Quasi-static processes	74
2-10 Quasi-static work done by pressure	76
2-11 Exact and "inexact" differentials	78

3 Statistical thermodynamics

87

IRREVERSIBILITY AND THE ATTAINMENT OF EQUILIBRIUM

3-1 Equilibrium conditions and constraints	87
3-2 Reversible and irreversible processes	91

THERMAL INTERACTION BETWEEN MACROSCOPIC SYSTEMS

3-3 Distribution of energy between systems in equilibrium	94
3-4 The approach to thermal equilibrium	100
3-5 Temperature	108
3-6 Heat reservoirs	108
3-7 Sharpness of the probability distribution	108

GENERAL INTERACTION BETWEEN MACROSCOPIC SYSTEMS

3-8 Dependence of the density of states on the external parameters	112
3-9 Equilibrium between interacting systems	114
3-10 Properties of the entropy	117

SUMMARY OF FUNDAMENTAL RESULTS

3-11 Thermodynamic laws and basic statistical relations	122
3-12 Statistical calculation of thermodynamic quantities	124

4 Macroscopic parameters and their measurement

128

4-1 Work and internal energy	128
4-2 Heat	131
4-3 Absolute temperature	133
4-4 Heat capacity and specific heat	139
4-5 Entropy	148
4-6 Consequences of the absolute definition of entropy	145
4-7 Extensive and intensive parameters	148

5 Simple applications of macroscopic thermodynamics

152

PROPERTIES OF IDEAL GASES

5-1 Equation of state and internal energy	153
5-2 Specific heats	158

5.3 Adiabatic expansion or compression	158
5.4 Entropy	160
GENERAL RELATIONS FOR A HOMOGENEOUS SUBSTANCE	
5.5 Derivation of general relations	161
5.6 Summary of Maxwell relations and thermodynamic functions	164
5.7 Specific heats	166
5.8 Entropy and internal energy	171
FREE EXPANSION AND THROTTLING PROCESSES	
5.9 Free expansion of a gas	175
5.10 Throttling (or Joule-Thomson) process	178
HEAT ENGINES AND REFRIGERATORS	
5.11 Heat engines	184
5.12 Refrigerators	190
6 Basic methods and results of statistical mechanics	201
ENSEMBLES REPRESENTATIVE OF SITUATIONS OF PHYSICAL INTEREST	
6.1 Isolated system	201
6.2 System in contact with a heat reservoir	202
6.3 Simple applications of the canonical distribution	206
6.4 System with specified mean energy	211
6.5 Calculation of mean values in a canonical ensemble	212
6.6 Connection with thermodynamics	214
APPROXIMATION METHODS	
6.7 Ensembles used as approximations	219
*6.8 Mathematical approximation methods	221
GENERALIZATIONS AND ALTERNATIVE APPROACHES	
*6.9 Grand canonical and other ensembles	225
*6.10 Alternative derivation of the canonical distribution	229
7 Simple applications of statistical mechanics	237
GENERAL METHOD OF APPROACH	
7.1 Partition functions and their properties	237
IDEAL MONATOMIC GAS	
7.2 Calculation of thermodynamic quantities	259
7.3 Gibbs paradox	243
7.4 Validity of the classical approximation	246

THE EQUIPARTITION THEOREM

- 7-5 *Proof of the theorem* 248
7-6 *Simple applications* 250
7-7 *Specific heats of solids* 255

PARAMAGNETISM

- 7-8 *General calculation of magnetization* 257

KINETIC THEORY OF DILUTE GASES IN EQUILIBRIUM

- 7-9 *Maxwell velocity distribution* 262
7-10 *Related velocity distributions and mean values* 265
7-11 *Number of molecules striking a surface* 269
7-12 *Effusion* 273
7-13 *Pressure and momentum transfer* 278

8 Equilibrium between phases or chemical species 288**GENERAL EQUILIBRIUM CONDITIONS**

- 8-1 *Isolated system* 289
8-2 *System in contact with a reservoir at constant temperature* 291
8-3 *System in contact with a reservoir at constant temperature and pressure* 294
8-4 *Stability conditions for a homogeneous substance* 296

EQUILIBRIUM BETWEEN PHASES

- 8-5 *Equilibrium conditions and the Clapeyron equation* 301
8-6 *Phase transformations and the equation of state* 306

SYSTEMS WITH SEVERAL COMPONENTS; CHEMICAL EQUILIBRIUM

- 8-7 *General relations for a system with several components* 312
8-8 *Alternative discussion of equilibrium between phases* 316
8-9 *General conditions for chemical equilibrium* 317
8-10 *Chemical equilibrium between ideal gases* 319

9 Quantum statistics of ideal gases 331**MAXWELL-BOLTZMANN, BOSE-EINSTEIN, AND FERMI-DIRAC STATISTICS**

- 9-1 *Identical particles and symmetry requirements* 331
9-2 *Formulation of the statistical problem* 335
9-3 *The quantum distribution functions* 338
9-4 *Maxwell-Boltzmann statistics* 343
9-5 *Photon statistics* 345
9-6 *Bose-Einstein statistics* 348
9-7 *Fermi-Dirac statistics* 350
9-8 *Quantum statistics in the classical limit* 351

IDEAL GAS IN THE CLASSICAL LIMIT

- 9-9 *Quantum states of a single particle* 353
9-10 *Evaluation of the partition function* 360
9-11 *Physical implications of the quantum-mechanical enumeration of states* 363
*9-12 *Partition functions of polyatomic molecules* 367

BLACK-BODY RADIATION

- 9-13 *Electromagnetic radiation in thermal equilibrium inside an enclosure* 373
9-14 *Nature of the radiation inside an arbitrary enclosure* 378
9-15 *Radiation emitted by a body at temperature T* 381

CONDUCTION ELECTRONS IN METALS

- 9-16 *Consequences of the Fermi-Dirac distribution* 388
*9-17 *Quantitative calculation of the electronic specific heat* 393

10 Systems of interacting particles 404**SOLIDS**

- 10-1 *Lattice vibrations and normal modes* 407
10-2 *Debye approximation* 411

NONIDEAL CLASSICAL GAS

- 10-3 *Calculation of the partition function for low densities* 418
10-4 *Equation of state and virial coefficients* 422
10-5 *Alternative derivation of the van der Waals equation* 426

FERROMAGNETISM

- 10-6 *Interaction between spins* 428
10-7 *Weiss molecular-field approximation* 430

11 Magnetism and low temperatures 438

- 11-1 *Magnetic work* 439
11-2 *Magnetic cooling* 445
11-3 *Measurement of very low absolute temperatures* 452
11-4 *Superconductivity* 455

12 Elementary kinetic theory of transport processes 461

- 12-1 *Collision time* 463
12-2 *Collision time and scattering cross section* 467

12·3	Viscosity	471
12·4	Thermal conductivity	478
12·5	Self-diffusion	483
12·6	Electrical Conductivity	488

13 Transport theory using the relaxation time approximation 494

13·1	Transport processes and distribution functions	494
13·2	Boltzmann equation in the absence of collisions	498
13·3	Path integral formulation	502
13·4	Example: calculation of electrical conductivity	504
13·5	Example: calculation of viscosity	507
13·6	Boltzmann differential equation formulation	508
13·7	Equivalence of the two formulations	510
13·8	Examples of the Boltzmann equation method	511

14 Near-exact formulation of transport theory 516

14·1	Description of two-particle collisions	516
14·2	Scattering cross sections and symmetry properties	520
14·3	Derivation of the Boltzmann equation	523
14·4	Equation of change for mean values	525
14·5	Conservation equations and hydrodynamics	529
14·6	Example: simple discussion of electrical conductivity	531
14·7	Approximation methods for solving the Boltzmann equation	534
14·8	Example: calculation of the coefficient of viscosity	539

15 Irreversible processes and fluctuations 548

TRANSITION PROBABILITIES AND MASTER EQUATION

15·1	Isolated system	548
15·2	System in contact with a heat reservoir	551
15·3	Magnetic resonance	553
15·4	Dynamic nuclear polarisation; Overhauser effect	558

SIMPLE DISCUSSION OF BROWNIAN MOTION

15·5	Langevin equation	560
15·6	Calculation of the mean-square displacement	565

DETAILED ANALYSIS OF BROWNIAN MOTION

15·7	Relation between dissipation and the fluctuating force	567
------	--	-----

15·8	<i>Correlation functions and the friction constant</i>	570
*15·9	<i>Calculation of the mean-square velocity increment</i>	574
*15·10	<i>Velocity correlation function and mean-square displacement</i>	575

CALCULATION OF PROBABILITY DISTRIBUTIONS

*15·11	<i>The Fokker-Planck equation</i>	577
*15·12	<i>Solution of the Fokker-Planck equation</i>	580

FOURIER ANALYSIS OF RANDOM FUNCTIONS

15·13	<i>Fourier analysis</i>	582
15·14	<i>Ensemble and time averages</i>	583
15·15	<i>Wiener-Khintchine relations</i>	585
15·16	<i>Nyquist's theorem</i>	587
15·17	<i>Nyquist's theorem and equilibrium conditions</i>	589

GENERAL DISCUSSION OF IRREVERSIBLE PROCESSES

15·18	<i>Fluctuations and Onsager relations</i>	594
-------	---	-----

Appendices 605

A.1	<i>Review of elementary sums</i>	605
A.2	<i>Evaluation of the integral</i> $\int_{-\infty}^{\infty} e^{-z^2} dz$	606
A.3	<i>Evaluation of the integral</i> $\int_0^{\infty} e^{-z} z^n dz$	607
A.4	<i>Evaluation of integrals of the form</i> $\int_0^{\infty} e^{-az^2} x^n dx$	608
A.5	<i>The error function</i>	609
A.6	<i>Stirling's formula</i>	610
A.7	<i>The Dirac delta function</i>	614
A.8	<i>The inequality</i> $\ln x \leq x - 1$	618
A.9	<i>Relations between partial derivatives of several variables</i>	619
A.10	<i>The method of Lagrange multipliers</i>	620
A.11	<i>Evaluation of the integral</i> $\int_0^{\infty} (e^x - 1)^{-1} x^k dx$	622
A.12	<i>The H theorem and the approach to equilibrium</i>	624
A.13	<i>Liouville's theorem in classical mechanics</i>	626

Numerical constants 629

Bibliography 631

Answers to selected problems 637

Index 643