

# Physical Kinetics



# Physical Kinetics

By

Marian Apostol

Cambridge  
Scholars  
Publishing



Physical Kinetics

By Marian Apostol

This book first published 2020

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Copyright © 2020 by Marian Apostol

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN (10): 1-5275-4178-9

ISBN (13): 978-1-5275-4178-8

# Contents

<b>1</b>	<b>Preface</b>	<b>1</b>
<b>2</b>	<b>Introduction</b>	<b>7</b>
<b>3</b>	<b>Kinetics of Gases</b>	<b>25</b>
3.1	Boltzmann's kinetic equation . . . . .	25
3.2	Collision integral . . . . .	29
3.3	Solution of the Boltzmann equation . . . . .	31
3.4	Thermalization . . . . .	35
3.5	A particular case: constant and uniform force . . . . .	36
3.6	Other particular cases . . . . .	37
3.7	General case. Landau damping . . . . .	39
3.8	Calculation of the principal value . . . . .	42
3.9	Non-equilibrium entropy . . . . .	43
3.10	Approach to equilibrium . . . . .	44
3.11	Corrections to the thermodynamic potentials . . . . .	47
3.12	Interaction. Collective excitations . . . . .	49
3.13	van der Waals equation . . . . .	52
3.14	Kinetic approach for the non-ideal gas . . . . .	55
3.15	Sound . . . . .	56
<b>4</b>	<b>Transport in Gases</b>	<b>61</b>
4.1	Molecular kinetic theory. Transport . . . . .	61
4.2	Transport equation . . . . .	63
4.3	Thermopower . . . . .	66
4.4	General transport . . . . .	67
4.5	Brownian motion . . . . .	69
4.6	Diffusion equation . . . . .	72
4.7	Thermodiffusion . . . . .	74
4.8	Particle density . . . . .	75
4.9	Fluctuations. Einstein's kinetic equation . . . . .	77

## Contents

4.10	Molecular fluctuations . . . . .	80
4.11	Quantum-mechanical "diffusion" . . . . .	83
4.12	A general form of diffusion equation . . . . .	85
4.13	Ionized gases . . . . .	86
4.13.1	Plasma . . . . .	86
4.13.2	Electrical conduction . . . . .	87
4.13.3	Ambipolar diffusion . . . . .	90
4.13.4	Electrolytes . . . . .	91
4.13.5	Electrophoresis . . . . .	92
<b>5</b>	<b>Kinetics of Plasma</b>	<b>95</b>
5.1	Gaseous plasma . . . . .	95
5.2	Energy distribution in ionization . . . . .	103
5.3	Thermodynamic stability of the classical plasma . . . . .	105
5.4	The stability of matter . . . . .	114
5.5	The effect of the Debye screening length . . . . .	117
5.6	Plasma isotherms. Phase diagram . . . . .	120
5.7	Equation of motion . . . . .	128
5.8	Transverse field . . . . .	131
5.9	Surface plasmons . . . . .	132
5.10	Boltzmann equation for plasma . . . . .	134
5.11	Eigenfrequencies. Plasma oscillations . . . . .	136
5.12	External field . . . . .	140
5.13	Surface field. Penetration length . . . . .	142
<b>6</b>	<b>Phonons in Solids</b>	<b>149</b>
6.1	Phonons . . . . .	149
6.2	Phonon gas . . . . .	154
6.3	Second sound . . . . .	162
6.4	Thermoconductivity . . . . .	162
6.5	Anharmonic solids . . . . .	165
6.6	Temperature waves . . . . .	168
6.7	Sound attenuation . . . . .	169
6.8	Electron-phonon interaction . . . . .	170
6.9	Dimensionality effects . . . . .	172
<b>7</b>	<b>Fermi Liquid</b>	<b>175</b>
7.1	Quasiparticles . . . . .	175

## Contents

7.2	Interaction . . . . .	180
7.3	Effective mass . . . . .	194
7.4	Zero sound . . . . .	195
7.5	Paramagnetic susceptibility . . . . .	199
7.6	Thermodynamics . . . . .	200
<b>8</b>	<b>Electron Liquid</b>	<b>203</b>
8.1	Introduction . . . . .	203
8.2	Metallic cohesion . . . . .	204
8.3	Metals . . . . .	211
8.4	Electronic elementary excitations . . . . .	214
8.5	Effective electron mass . . . . .	216
8.6	Electronic properties. Plasmons . . . . .	217
8.7	Polarizability and diamagnetic susceptibility . . . . .	219
8.8	Electronic thermoconductivity . . . . .	220
8.9	Thermopower . . . . .	223
8.10	Electrical conductivity, 1 . . . . .	226
8.11	Electrical conductivity, 2 . . . . .	229
8.12	Hall effect . . . . .	231
8.13	Contact potential . . . . .	233
8.14	Galvanic cell . . . . .	235
8.15	Electrocapillarity . . . . .	236
8.16	Thermoelectricity . . . . .	237
8.17	Thermomagnetolectricity . . . . .	241
8.18	Electrodifusion . . . . .	243
8.19	Electrolysis . . . . .	245
<b>9</b>	<b>Magnetic Field</b>	<b>247</b>
9.1	Electrons in magnetic field . . . . .	247
9.2	Electron magnetism . . . . .	253
9.3	Heat capacity . . . . .	261
9.4	Quasi-classical description . . . . .	262
9.5	Magnetic oscillations . . . . .	265
9.6	Magnetic effects . . . . .	267
9.7	Magnetic transport . . . . .	271
9.8	Lateral thermoconductivity . . . . .	274
9.9	Lateral electrical conductivity and thermopower . . . . .	275

*Contents*

<b>10 Semiconductors</b>	<b>277</b>
10.1 Lifetime . . . . .	277
10.2 Transport coefficients . . . . .	280
10.3 Thermodynamics . . . . .	283
10.4 Magnetic transport . . . . .	286
<b>11 Electron-Phonon Interaction</b>	<b>289</b>
11.1 Introduction . . . . .	289
11.2 Renormalization of velocity . . . . .	293
11.3 Lifetime and interaction . . . . .	295
11.4 Ultrasound attenuation . . . . .	297
11.5 Sound absorption . . . . .	300
11.6 Electron lifetime . . . . .	301
11.7 Non-equilibrium phenomena . . . . .	302
<b>12 Superconductivity</b>	<b>305</b>
12.1 Introduction . . . . .	305
12.2 Cooper pair . . . . .	306
12.3 BCS theory . . . . .	308
12.4 The gap equation . . . . .	309
12.5 Critical temperature . . . . .	310
12.6 Thermal properties . . . . .	311
12.7 Acoustic attenuation . . . . .	312
12.8 Microwave absorption . . . . .	314
12.9 Nuclear spin relaxation rate . . . . .	314
12.10 Electron tunneling . . . . .	315
12.11 Josephson current . . . . .	317
12.12 Ginsburg-Landau theory . . . . .	318
12.13 Phase transition . . . . .	319
12.14 Meissner effect . . . . .	320
12.15 Flux quantization . . . . .	321
12.16 Coherence length . . . . .	322
12.17 Surface energy . . . . .	322
12.18 Comments and remarks . . . . .	323
12.19 Andreev reflection . . . . .	325
12.20 Comments on transport . . . . .	328
12.21 Concluding remarks . . . . .	331



*Contents*

<b>13 Superfluidity</b>	<b>333</b>
13.1 Introduction . . . . .	333
13.2 Landau's theory . . . . .	338
13.3 Wavefunction of the condensate . . . . .	347
<b>14 Pulse Thermoelectricity</b>	<b>353</b>
14.1 Figure of merit . . . . .	353
14.2 Pulsed thermoelectricity . . . . .	358
14.3 Basic ingredients . . . . .	360
14.4 Thermal and charge pulses . . . . .	362
14.5 Heat and electric flows . . . . .	364
14.6 Thermoelectricity of pulses . . . . .	368
14.7 "Flying" pulses . . . . .	370
14.8 Power in external circuit . . . . .	373
14.9 Conclusions . . . . .	375
<b>15 Liquids</b>	<b>377</b>
15.1 Introduction . . . . .	377
15.2 Local vibrations . . . . .	377
15.3 Statistics . . . . .	380
15.4 Low temperature . . . . .	384
15.5 Summarizing remarks . . . . .	386
15.6 Transport properties . . . . .	387
15.7 Non-equilibrium . . . . .	391
<b>16 Density Oscillations in Water</b>	<b>393</b>
16.1 Introduction . . . . .	393
16.2 Plasmons . . . . .	395
16.3 Two ionic species . . . . .	396
16.4 Polarization . . . . .	397
16.5 Dielectric function . . . . .	399
16.6 Cohesion and thermodynamics . . . . .	401
16.7 Debye screening . . . . .	402
16.8 Sound anomaly . . . . .	403
16.9 Another sound . . . . .	404
16.10 Multi-component plasma . . . . .	405
16.11 Structure factor . . . . .	407
16.12 Asymmetric interaction . . . . .	409

*Contents*

16.13	Summarizing remarks . . . . .	412
16.14	Molecular mixtures . . . . .	413
<b>Index</b>		<b>427</b>

# 1 Preface

Bodies with many degrees of freedom, in particular with many particles, exhibit certain patterns of their physical quantities, which can be viewed as a motion in space and time. The breakthrough into the nature of this motion was made by Maxwell in 1859, who showed, for gases, that this motion is a statistical motion which implies probabilities. This is a distinct type of motion, different from mechanical motion, or from other forms of motion like the elastic, fluid, electromagnetic or quantum-mechanical motions. Nevertheless, there was, and still is, a continuous attempt to derive the statistical motion from mechanical motion, or to reduce it to mechanical motion, such that Statistical Physics is often called Mechanical Statistics. In spite of Maxwell, founders of Statistical Physics like Boltzmann, Gibbs or Einstein persisted in connecting the statistical motion with the mechanical motion. The confusion is fuelled by the presence of the mechanical motion in statistical motion. The problem would rather be to see the compatibility of the statistical motion with the mechanical motion. This is the problem of Kinetics, to be developed in the present book. This rather misleading line of thought arose from the evolution equation for the distribution function  $F$ , which, instead of being written as

$$\frac{dF}{dt} = \frac{\Delta F}{\Delta t} = -\gamma[F - F(t = \infty)] \quad , \quad (1.1)$$

is usually written as

$$\frac{dF}{dt} = C(\Delta F) \quad , \quad (1.2)$$

where  $C(\Delta F)$  is the so-called collision integral ( $\Delta F = F - F(t = \infty)$ ).<sup>1</sup> Equation (1.1) is an evolution equation, from the moment  $t = 0$ , when  $F = F(t = 0)$  to  $t = \infty$ . The approximation used in the first equality

---

<sup>1</sup>Equation (1.1) has been used by Debye for molecular relaxation (P. Debye, *Polar Molecules*, Chem. Catalog Co., Inc., NY (1929)).

## 1 Preface

in equation (1.1) is valid for a sudden decrease of the function  $F$ . Indeed, the time  $\tau = 1/\gamma$  is the collision time of the particles (in the general sense of interaction), which is much shorter than any relevant time at our scale. It is related to the particle mean free path  $\Lambda$  and the particle (thermal) velocity  $v$ . The solution of equation (1.1) is

$$F = F(t = 0)e^{-\gamma t} + F(t = \infty)(1 - e^{-\gamma t}) \quad , \quad (1.3)$$

which shows that we may view  $F(t = 0)$  as the initial non-equilibrium distribution and  $F(t = \infty)$  as the final equilibrium distribution. Therefore, equation (1.1) embodies the principle of statistical (thermal) equilibrium, which is the basic principle of Statistical Physics. In fact, since  $\tau$  is very short in comparison with  $t$  (large  $\gamma$ ), the equilibrium is established much faster (than  $t \rightarrow \infty$ ).

The collision integral  $C(\Delta F)$  does not include necessarily (*i.e.* without additional ingredients) the principle of equilibrium, although it includes collisions, vanishes at equilibrium and in spite that the collisions are represented by probabilities (which remain undefined; Stosszahlansatz). The usual arguments that equation (1.2) would imply an increase of entropy (Boltzmann's  $H$ -theorem) in the evolution towards equilibrium are valid only at equilibrium, when the entropy is stationary.

Equation (1.1) can also be written as  $dF/dt = -\gamma f$ , where  $f = \Delta F = F - F(t = \infty)$  is the deviation of the distribution from its equilibrium value. If we keep  $\gamma f \neq 0$  in equation (1.1) (or  $C(\Delta F) \neq 0$  in equation (1.2)), we admit that we are not at equilibrium. Equation (1.1) shows how the ensemble tends to equilibrium. (As long as  $C(\Delta F)$  is not determined in a form similar with  $-\gamma f$ , equation (1.2) does not show the approach to equilibrium). Inasmuch as we write  $\gamma = 1/\tau$  and  $\tau = \Lambda/v$ , we admit that the approach to equilibrium is governed by collisions. But these collisions are not determined in the mechanical sense, they are determined in a statistical sense, through  $\Lambda$  and  $\tau$  which are purely statistical concepts, such that the statistical motion remains a distinct motion, not derivable from the mechanical motion. If we attribute to the molecular collisions a mechanical sense, we have not anymore, for instance, an ideal gas, but a gas with interaction. We should realize that the equilibrium is achieved, locally, much faster than our time scale. Therefore, we need to use in Kinetics (local)

## 1 Preface

equilibrium evolution equations. This approach was recognized by Landau in connection with the collisionless plasma, where  $\gamma = 0^+$  and  $\gamma \rightarrow 0^+$ ; it led to the Landau damping.<sup>2</sup> We emphasize that  $\gamma$  is not small as a consequence that  $\tau = 1/\gamma$  is large; on the contrary,  $\tau$  is short. We take the parameter  $\gamma$  zero because we are at local equilibrium.

Two types of problems are usually solved in Kinetics. In one type, we are interested in the slight perturbations produced in the equilibrium distribution by an external force. In these problems the kinetic equation (1.1) is solved by neglecting the small term  $\gamma\Delta F$  and treating  $\gamma$  as  $\gamma \rightarrow 0$ . This approach means that the ensemble is at local equilibrium (but not at global equilibrium). Mechanical motion produced by external forces coexists with the statistical motion. The macroscopic phenomena imply much longer times than the relaxation time  $\tau$ , such that, practically, they take place at equilibrium. The other type of problems is the transport. The standard approach is to use various ansatzes for the collision term  $C(\Delta F)$  and solve equation (1.2) for  $F$ , as if the ensemble were not at equilibrium; then, fluxes (flows) are computed with the solution  $F$ , which depends on the spatial derivatives of the thermodynamic parameters, to get the transport laws. However, the transport time is of the order  $l/v$ , where  $l$  is the dimension of the macroscopic sample. Therefore, the transport time is much longer than the relaxation time, and the transport takes place at local (but not global) equilibrium. Consequently, the appropriate approach is to leave aside the term  $\gamma\Delta F$  in equation (1.1) and to use the fact that the transport is made at local equilibrium. The statistical equilibrium is governed by probabilistic collisions (interactions) and the macroscopic phenomena are governed by local statistical equilibrium.

In transport equations time and spatial partial derivatives of the distribution may appear, or derivatives of the parameters of the distribution, or derivatives of quantities connected with the distribution. In the time partial derivatives of the type  $\partial F/\partial t$  we may replace  $\Delta F$  by  $F$  and  $\Delta t$  by  $\tau$ , since these variations are sudden variations produced by particle collisions; likewise, in spatial derivatives we may use  $\Lambda$ . Usually, the variations  $\Delta F$  are small (as  $\tau$  is), but even for larger

---

<sup>2</sup>L. Landau, "On the vibrations of the electronic plasma", ZhETF **16** 574 (1946) (J. Phys. USSR **10** 25 (1946)).

## 1 Preface

variations we may use such a procedure, as long as the contributions of the time and spatial derivatives compensate each other (as in the continuity equation), or are compensated by external forces, such that the equation of local equilibrium  $dF/dt = 0$  is preserved. The approximations  $\tau\partial/\partial t = 1$  and  $\Lambda\partial/\partial x = 1$  are not always useful; first-order differential equations, or equations which imply second-order spatial derivatives at most, are useful for the evolution of the physical quantities.

This book exhibits several original points. First, it derives the Boltzmann equation from atomic motion, making use extensively of Landau's concept of elementary excitations. Second, it includes external forces, besides the statistical motion, wherever relevant. The transport is treated at local equilibrium, according to the quasi-general evidence. In Kinetics we are at the limits of the Theoretical Physics, because we have to be content only with estimations of partially defined concepts like lifetime and mean freepath of elementary excitations; this makes Kinetics a particularly difficult (and intriguing) subject in the realm of Theoretical Physics, probably the most interesting one. This book presents the kinetic theory of the classical gas and the transport in classical gas. Special attention is devoted to the classical plasma, which raises a problem. The problem in classical plasma is the relation between the thermal equilibrium of the electrons, on one hand, and the ions, on the other. The Coulomb forces, and the correlations they produce, make the classical plasma a classical gas of interacting ions dressed with electrons, via the Debye-Huckel screening. This way, once correlated with the ions, the electrons acquire a special dynamics. The thermodynamics of a classical plasma is that of a gas of interacting dressed ions, which may exhibit condensed phases, like a liquid phase or a solid phase. The phonons in solids are a particularly interesting subject. Besides describing the thermoconductivity of a perfect lattice, this book emphasizes the role played by the anharmonic interactions in the phonon lifetime. Landau's fruitful concept of elementary excitations, quasiparticles and collective modes, is introduced especially in (normal) Fermi liquid, where the interaction is discussed in detail. The electron liquid is presented in connection with the cohesion of metals, and the transport in the magnetic field and in semiconductors is described. Special attention is devoted to

## 1 Preface

the electron-phonon interaction, where an interesting particular case of non-equilibrium transport appears (the drag effect).<sup>3</sup> Except for such particular cases, the non-equilibrium transport, besides being irrelevant to a large extent, requires additional, particular hypotheses which are not related to a general, consistent method. Basic features of the superconductivity and superfluidity are presented, emphasizing the relation of the transport with the condensed phases. A special kind of thermoelectricity, consisting of flying pulses of charge and heat, is described. A consistent model of classical liquids is also presented, together with its transport properties. Finally, the sound anomaly in water is clarified and the role played by the kinetic modes (densitons) is discussed.

There exist subjects which have been omitted in the treatment presented in this book, or described succinctly. Among them there are the magnetic resonance phenomena, the neutron transport, the ballistic transport, the electrodynamics of metals, plasmas in magnetic field, the electrolytes, chemical reactions, hydrodynamics, low-dimensional statistical ensembles. Most of these subjects do not exhibit new transport concepts or circumstances, having the general aspect of applications of the transport theory (in many cases routine applications).

---

<sup>3</sup>T. Holstein, "Theory of ultrasonic absorption in metals: the collisions-drag effect", *Phys. Rev.* **113** 479 (1959).





## 2 Introduction

If Physics would be viewed as a set of provinces (disciplines), Statistical Physics would be the Queen: the Queen of Physics. It distinguishes itself not only by its power, richness and elegance, but especially by raising a deep problem. And Physical Kinetics, to be dealt with in this book, should be called the Crown Jewel, because it incorporates this very deep statistical problem. The fundamental problem raised by Statistical Physics originates in the fact that it identifies a distinct type of motion (statistical motion), probably the most general form of motion; the characteristic note of this motion, as compared with other types of motion, is the problem.

Let us consider a motion, *i.e.* a change in time from a physical (*i.e.* measurable) state to other physical states (a state is the set of values of measurable quantities). We may imagine that in a long duration of time  $T$  the motion spends some time  $\Delta T$  in a state; or we may imagine that  $\Delta N$  out of many identical motions  $N$  take up the same state at any moment; or, also, we may imagine that we have many times ( $N$ ) the same motion and  $\Delta N$  times this motion takes up the same state. Obviously,  $\Delta T/T$  or  $\Delta N/N$  is a probability, so we have a distribution of probability. Then, we can compute the mean values of any physical quantity (depending on states); and the deviations from these mean values. Thus, we are able to have some knowledge about that motion, providing, of course, we know the probability distribution. Such a motion would be a statistical motion, its realization a statistical ensemble and the determination of the probability distribution (statistical probability) would be the main task (problem) of Statistical Physics. The temporal ensemble defined above was employed by Einstein; the state ensembles originate with Boltzmann and, especially, Gibbs.

At this point the fundamental problem of the Statistical Physics appears: does such a statistical probability exist? Because, we note that

## 2 Introduction

the probability defined above is independent of time, while the motion depends on time. It is not obvious that statistical distributions exist. Statistical distributions, *i.e.* probability distributions which are independent of time, are specific for motions at statistical (thermal) equilibrium. The problem is cast now in the question whether statistical (thermal) equilibrium exists. Various plausible, reasonable arguments were brought in favour of the existence of the thermal equilibrium, for various physical ensembles, especially for gases. None is a proof of its existence. Thermal equilibrium is a postulate of Statistical Physics, one of the greatest principle of Physics. We may imagine probability distributions which depend on time, and we may devise evolution equations which, possibly, may bring these distributions to statistical distributions. This is a very popular misconception related to Physical Kinetics, perpetuated not as much by laymen, as by experts. In many instances the Physical Kinetics seems to prove the evolution towards equilibrium; in all these cases the arguments are misleading circular arguments, which presuppose the existence of the thermal equilibrium, or mistake the mechanical motion for statistical motion. The evolution equations of the Physical Kinetics show only that various other motions (like mechanical, quantum-mechanical, elastic, fluid, electromagnetic motion) are compatible with statistical motion.

It is worth noting that the statistical motion is not a deterministic motion, in the sense that the states in terms of which the statistical distribution is defined do not change in time. In the context of a deterministic motion the existence of the thermal equilibrium is sometimes called the "ergodic hypothesis" (or "quasi-ergodic hypothesis").<sup>1</sup>

Statistical distributions should depend only on the statistical motion and some external parameters; in the absence of other conditions, there is no reason to differentiate between the states; we note that the states are statistical coordinates. Consequently, we may admit that each available state has the same probability  $w = 1/\Gamma$ , where  $\Gamma$  is the total number of states. This is sometimes called the "hypothesis of molecular chaos". We may imagine a partition of any two sub-sets  $\Gamma_1$  and  $\Gamma_2$  of the  $\Gamma$  states; this is called a partition in two "sub-systems",

---

<sup>1</sup>See, for instance, E. Fermi, "Beweis, dass ein mechanisches Normalsystem im allgemeinen quasi-ergodisch ist", Z. Phys. **24** 261 (1923); E. Fermi, J. Pasta and S. Ulam, "Studies of non linear problems", Los Alamos Report No. 266, LA-1940, Los Alamos (1955).

## 2 Introduction

or two "sub-ensembles", or a motion partition (the sub-systems were introduced by Gibbs). Since the motion is the same and if the relevant external parameters are the same, the probabilities of the partition states are  $w_1 = 1/\Gamma_1$  and  $w_2 = 1/\Gamma_2$  and the equality  $w = w_1 w_2$  is valid. This is called the statistical independence. It follows that the function  $\ln w$  is an additive function of "sub-systems". For an infinitesimal number of states the probability is  $dw = \rho d\Gamma$ , where  $\rho$  is the probability density; its  $\ln$  is additive. Being constant in time,  $\rho$  may be related to other constants of motion, like, for instance, energy, momentum or angular momentum; the latter are additive, so  $\ln \rho$  may be a linear combination of these additive integrals of motion, with coefficients which are to be viewed as external parameters. In particular, we should have  $\ln \rho = \alpha - \beta \mathcal{E}$ , where  $\mathcal{E}$  is the energy of the motion associated with the states which define the probability density and  $\alpha$  and  $\beta$  are (constant) coefficients; it follows  $\rho \sim e^{-\beta \mathcal{E}}$ . This is Gibbs's statistical distribution; of course, it should be normalized, such that  $\int d\Gamma \rho = 1$ ; for quantum-mechanical states  $d\Gamma$  is the multiplicity of the state, and  $w \sim \rho$ ; the integration over  $\Gamma$  is replaced by summation over states. It is reasonable to assume  $\beta > 0$ , for stability. This connection indicates that the statistical motion may coexist with the mechanical motion. If the ensemble is a number  $\mathcal{N}$  of identical particles, then we may set  $\alpha = \text{const} + \beta \mu \mathcal{N}$ , where  $\mu$  is another coefficient; and the normalization should include integration (summation) with respect to  $\mathcal{N}$ . The existence of the parameters  $\alpha$  ( $\mu$ ) and  $\beta$  may show that the motion is not isolated in fact, it is not closed. The existence of the energy  $\mathcal{E}$  and the number of particles  $\mathcal{N}$  show, to some extent, that the motion is closed. This is a very interesting particularity of the statistical motion. Motion with distribution  $\sim e^{-\beta \mathcal{E}}$  is called canonical motion, that with distribution  $\sim e^{\beta(\mu \mathcal{N} - \mathcal{E})}$  is called macro-canonical (or grand-canonical) motion. Of course, such distributions are for motions which possess energy and particle numbers.

If the statistical motion is associated with classical mechanical motion, *i.e.* if the classical mechanical motion is present, the definition of the states includes the dynamical variables  $p$  and  $q$ , where  $p$  denotes momenta and  $q$  denotes the coordinates; then,  $\rho \sim e^{-\beta \mathcal{E}(p,q)}$  and the mean value of any physical quantity  $f(p, q)$  is given by  $\bar{f} = \int dpdq \rho(p, q) f(p, q)$ ; the dynamical variables are coordinates of the

## 2 Introduction

phase space ( $\Gamma$  includes points  $(p, q)$ ) and the state ensemble is called phase ensemble. If the quantum-mechanical motion is present, then  $\rho = \rho_n \sim e^{-\beta \mathcal{E}_n}$ , where  $n$  denotes the quantum-mechanical state (in the energy representation); and the probability is  $w_n = \rho_n$ . The quantities  $\rho_n$  may be viewed as the diagonal elements of a matrix  $\rho$ , which is called the statistical matrix; what we measure in quantum-mechanical motion is the quantum-mechanical mean value  $(\rho f)_{nn}$ , which, in the energy representation is  $\rho_n f_{nn}$ ; the statistical mean value is given by  $\bar{f} = \sum_n (\rho f)_{nn} = \text{tr}(\rho f)$ . Summation (integration) over other statistical variables, if present, should be included (*e.g.*, the particle number). Since  $\rho$  is diagonal in the energy representation we may see that the quantum-mechanical motion is statistically independent in this representation; we may infer that the statistical character of the statistical motion and the statistical character of the quantum-mechanical motion coincide in the energy representation. In other representations this is not true. In general, the statistical character of the quantum-mechanical motion is distinct from the statistical character of the statistical motion. The energy plays a special role in this context.

Also, we note that the existence of the conserved energy (and other integrals of motion) does not mean necessarily that the mechanical motion is integrable in terms of any dynamical variables  $(p, q)$ , or any type of states  $n$ . However,  $\ln \rho$  remains proportional to the energy, because the coordinates  $p, q$  are not treated as dynamical variables, but as statistical variables (coordinates); this amounts to say again that the statistical motion is distinct from the mechanical motion.

We can see that by admitting the existence of the statistical equilibrium we are able to derive the statistical distributions. In the course of derivation we characterized the statistical motion by molecular chaos ("molecular-disorder", Boltzmann) and statistical independence. We note that the states, the energy, the particle number are statistical variables.

Let us assume that the statistical motion consists of a number  $N$  of identical statistical motions; a physical quantity  $f$  may be written as the sum  $f = \sum_{i=1}^N f_i$  of all these "sub-motions"; then the mean value  $\bar{f}$  is proportional to  $N$  and the root mean square deviation  $\delta f = \sqrt{(\Delta f)^2} = \sqrt{\sum_{ij} \overline{\Delta f_i \Delta f_j}}$  is proportional to  $\sqrt{N}$ , because of

## 2 Introduction

the statistical independence; it follows  $\delta f/\bar{f} \sim 1/\sqrt{N}$  and, for large  $N$ , this ratio is zero.  $\delta f$  is called fluctuation. Therefore, statistical knowledge is useful for statistical motions with a large (macroscopic) number of degrees of freedom (states), when the fluctuations are small (vanishing); *i.e.*, the statistical variables are sharply distributed about their mean values. The extension of the statistical motion to one particle in an ensemble is a limiting case (we note that  $\rho$  and  $\Gamma$  may fluctuate).

Let us introduce the quantity  $\mathcal{S} = -\ln \rho$  and require, in accordance with the molecular chaos, its maximum mean value in certain conditions; for instance, for a given mean energy and a mean particle number; *i.e.*, let us require the maximum of

$$-\int d\Gamma \rho \ln \rho + \alpha \int d\Gamma \rho \mathcal{N} - \beta \int d\Gamma \rho \mathcal{E} ; \quad (2.1)$$

we get immediately the statistical distribution  $\rho = e^{\alpha \mathcal{N} - \beta \mathcal{E}}$ . The quantity  $\mathcal{S} = -\ln \rho$  is called entropy, its mean value

$$S = \bar{\mathcal{S}} = -\int d\Gamma \rho \ln \rho \quad (2.2)$$

is also called entropy; at equilibrium  $\mathcal{S} = S = \ln \Gamma$  and  $\partial S/\partial E = \beta$ . Therefore, at equilibrium the entropy is stationary, as a reflection of the molecular chaos. Since the molecular chaos is absolute, any deviation from equilibrium would mean a regular, ordered pattern, which would decrease the entropy; therefore, the evolution (long time in the temporal ensemble) is towards an increase of the entropy, towards equilibrium; out of equilibrium (in non-equilibrium) the entropy is smaller than at equilibrium. This is the law of increase of entropy. It is equivalent with the principle of thermal equilibrium. Statistical Physics may equally well be constructed starting from the principle of increase of entropy.  $-S$  is called Boltzmann's  $H$  function.<sup>2</sup> Processes where the entropy is constant (equilibrium processes) are reversible processes, those where the entropy increases are irreversible processes.

---

<sup>2</sup>L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen uber Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).

## 2 Introduction

Among the reversible processes those which are adiabatic are special; an adiabatic process is characterized by a parameter  $\lambda$  which varies slowly in time, *i.e.* its time derivative  $d\lambda/dt$  is small; we may expand the small derivative  $dS/dt$  of the entropy with respect to time in powers of  $d\lambda/dt$ ; this expansion should start with the second power of  $d\lambda/dt$ , because  $dS/dt > 0$ ; *i.e.*,  $dS/dt = A(d\lambda/dt)^2$  ( $A > 0$ ). It follows that  $dS/dt$  is much smaller than  $d\lambda/dt$ , *i.e.* the adiabatic processes may take place and the entropy remains practically constant. The adiabatic processes are reversible to a good approximation. Of course, a reversible process is not necessarily adiabatic.

Let us write the statistical distribution as

$$\rho = e^{c+\beta\mu\mathcal{N}-\beta\mathcal{E}} \quad , \quad (2.3)$$

where  $c$  is a normalization constant,

$$e^{-c} = \int d\Gamma e^{\beta\mu\mathcal{N}-\beta\mathcal{E}} = Z = 1 \quad ; \quad (2.4)$$

$e^{-c}$  is denoted by  $Z$ ; it is called partition function. Let us differentiate the normalization condition  $\int d\Gamma \rho = 1$ , with  $\rho$  given by equation (2.3), with respect to  $\beta$  and other external parameters  $\lambda$  which may enter the expression of the energy; we note that in such variations we assume the existence of the equilibrium, *i.e.* we consider equilibrium processes; we get

$$d(c - \beta E + \beta\mu N) = -\beta dE + \beta \frac{\partial E}{\partial \lambda} d\lambda + \beta \mu dN \quad , \quad (2.5)$$

where  $E = \bar{\mathcal{E}}$  and  $N = \bar{\mathcal{N}}$  are mean values; on the left in equation (2.5) we have an exact (total) differential; let us introduce the notation

$$d(c - \beta E + \beta\mu N) = -\beta dQ \quad ; \quad (2.6)$$

then, equation (2.5) becomes

$$dE = \frac{\partial E}{\partial \lambda} d\lambda + dQ + \mu dN \quad ; \quad (2.7)$$

here, we may view  $\lambda$  as volume  $V$ ,  $-\partial E/\partial \lambda$  as pressure  $p$  and  $dQ$  as heat. Statistical Physics identifies the heat as a form of energy.

## 2 Introduction

$\mu$  is an energy associated with the presence of a particle; it is called chemical potential.

From  $S = -\overline{\ln \rho}$  we get  $S = -c + \beta E - \beta \mu N$  and

$$-dS = d(c - \beta E + \beta \mu N) = -\beta dQ ; \quad (2.8)$$

therefore, the entropy is a function of state (its differential is an exact differential) and  $T = 1/\beta$  is the temperature (hence the denomination "thermal" equilibrium). For  $T \rightarrow 0$ , when there exists only one state,  $\rho \rightarrow 1$  and  $S = -\overline{\ln \rho} \rightarrow 0$ ; this is called the "third principle of Thermodynamics" (the energy conservation would be the first, the law of increase of entropy the second). The entropy may increase, in an irreversible process, independently on the heat gained, so we have  $TdS \geq dQ$ . As regards the time  $\tau$  of measuring the temperature, we should have  $T\tau \gg \hbar$ , where  $\hbar$  is Planck's constant; otherwise, the quantum effects destroy the statistical equilibrium (*e.g.*, at very low temperatures or in very short times).

Equations (2.7) and  $dQ = TdS$  define the thermodynamic potentials; in addition,

$$cT = -T \ln Z = E - TS - \mu N ; \quad (2.9)$$

$\Omega = E - TS - \mu N$  is called the grand-canonical potential,  $F(V, T, N) = E - TS$  is the free energy ( $E = E(V, S, N)$ );  $W(p, S, N) = E + pV$  is the enthalpy. We note the useful relation  $\partial(\beta F)/\partial\beta = E$ . From

$$d(E + pV - TS) = Vdp - SdT + \mu dN = d\Phi , \quad (2.10)$$

where  $\Phi(p, T, N) = E + pV - TS$  is the Gibbs free energy ( $F$  is also called the Helmholtz free energy), it follows  $\Phi = \mu N$  (since  $V$  and  $S$  are proportional to  $N$ ); and  $E + pV - TS = \mu N$  implies  $\Omega(V, T, \mu) = E - TS - \mu N = -pV$ . We note that  $E + pV - TS - \mu N = 0$  at equilibrium and, in general, since the entropy increases and is stationary at equilibrium,  $E + pV - TS - \mu N \geq 0$ ; *i.e.*, the thermodynamic potentials have a minimum at equilibrium. Since the fluctuations are deviations from equilibrium mean values, we can use this expression for deriving their distribution; in order to do this, we should leave aside one contribution to this expression, say,  $\mu N$ , and take  $\Delta E + p\Delta V - T\Delta S > 0$  as defining the distribution  $\rho \sim e^{-\beta(\Delta E + p\Delta V - T\Delta S)}$  for the fluctuations  $\Delta E$ ,  $\Delta V$  and  $\Delta S$ ; note

## 2 Introduction

that the fluctuations are deviations of equilibrium type. If we take the derivative of

$$\int d\Gamma(\mathcal{E} - E)e^{-\beta\mathcal{E}} = 0 \quad (2.11)$$

with respect to the temperature we get the energy fluctuation  $\delta E = T(\partial E/\partial T)^{1/2}$ .

It is of the greatest importance to note the following circumstance. In canonical distribution  $\rho \sim e^{-\beta\mathcal{E}}$  the variable  $\mathcal{E}$  is the mechanical energy; this may induce the idea that the statistical motion would be a mechanical motion. In fact,  $\rho$  includes also the factor  $e^c$  ( $\rho = e^{c-\beta\mathcal{E}}$ ), which leads to  $d(c - \beta E) = -\beta dQ = -dS$  and

$$dE = -pdV + dQ \quad , \quad (2.12)$$

*i.e.* to the existence of another form of energy, distinct from the mechanical energy, which is heat. The occurrence of this new form of energy originates in the fact that  $\rho$  is a probability distribution, which should be normalized; *i.e.*, from the hypothesis of the molecular chaos and the principle of thermal equilibrium. It is this latter characteristic which is the distinctive feature of the statistical motion; and the existence of  $\mathcal{E}$  in the definition of the statistical distribution shows only that the statistical motion is compatible with the mechanical motion, that both motions may coexist. The existence of  $\mathcal{N}$  in the macro-canonical distribution also indicates the non-mechanical character of the statistical motion. The statistical character is embodied in the amount of heat which is  $dQ = TdS = Td \ln \Gamma$  (for a variation between infinitesimally-separated equilibrium states); we can see that it is the variation of the number of states which gives the heat. This is not a mechanical motion, since in a mechanical motion a state is occupied (gained) only by leaving behind (losing) an empty state.

The statistical distributions are derived above from the assumption of thermal equilibrium, characterized by statistical independence and molecular chaos. We may think that an external agent, probably endowed with similar characteristics, generates such a special kind of motion (statistical motion). Let us consider a motion with fixed energy  $E_0$  and fixed particle number  $N_0$ . Let us assume that it is possible to divide this motion into two parts, one larger, with various



## 2 Introduction

energies  $\mathcal{E}'$  and various particle numbers  $\mathcal{N}'$ , called "bath", and another, smaller, with various energies  $\mathcal{E}$  and various particle numbers  $\mathcal{N}$ . The probability distribution of the "0" motion will be proportional to  $\delta$ -functions,

$$\rho_0 \sim \delta(E_0 - \mathcal{E}' - \mathcal{E})\delta(N_0 - \mathcal{N}' - \mathcal{N}) \quad (2.13)$$

and the probability distribution of the smaller motion is of the form

$$\begin{aligned} \rho &= \int d\Gamma' d\mathcal{N}' \rho_0 \sim \\ &\sim \int d\Gamma' d\mathcal{N}' \delta(E_0 - \mathcal{E}' - \mathcal{E})\delta(N_0 - \mathcal{N}' - \mathcal{N}) = \\ &= \int d\Gamma' \delta(E_0 - \mathcal{E}' - \mathcal{E}) |_{\mathcal{N}'=N_0-\mathcal{N}} . \end{aligned} \quad (2.14)$$

In this expression we use  $d\Gamma' = (d\Gamma'/d\mathcal{E}')d\mathcal{E}' = (d\mathcal{S}'/d\mathcal{E}')e^{\mathcal{S}'}d\mathcal{E}'$ , where  $\mathcal{S}' = \mathcal{S}'(\mathcal{E}', \mathcal{N}')$ ; the main contribution to equation (2.14) comes from  $e^{\mathcal{S}'(E_0-\mathcal{E}, N_0-\mathcal{N})}$ ; the series expansion of  $\mathcal{S}'$  for  $\mathcal{E} \ll E_0$ ,  $\mathcal{N} \ll N_0$  gives the statistical distribution  $\rho \sim e^{\beta\mu\mathcal{N}-\beta\mathcal{E}}$ ; the assumption of thermal equilibrium is implicit, in the form of molecular chaos (and statistical independence), in the integration over the variables  $\Gamma'$  and  $\mathcal{N}'$  of the bath. The distribution given by equation (2.13) is called micro-canonical distribution.<sup>3</sup>

We include here another remark. Let a statistical motion of  $\mathcal{N}_0$  identical particles have  $\Gamma_0$  states for each particle; let us consider a partition  $\mathcal{N}_0 = \mathcal{N}' + \mathcal{N}$ ,  $\Gamma = \Gamma' + \Gamma$ ; the entropy is

$$\mathcal{S}_0 = \ln(N_0\Gamma_0) = \ln(\mathcal{N}' + \mathcal{N}) + \ln(\Gamma' + \Gamma) ; \quad (2.15)$$

for  $\mathcal{N} \ll \mathcal{N}'$ ,  $\Gamma \ll \Gamma'$  a series expansion in equation (2.15) gives  $\mathcal{S}_0 = \mathcal{S}' + \mathcal{S}$ ,

$$\mathcal{S} = \text{const} \cdot \mathcal{N} + \text{const} \cdot \Gamma ; \quad (2.16)$$

for independent particles with energy  $\mathcal{E}$  the number of states  $\Gamma$  is proportional to  $\mathcal{E}$  (the surface of the momenta sphere), so we get

$$\mathcal{S} = \text{const} \cdot \mathcal{N} + \text{const} \cdot \mathcal{E} , \quad (2.17)$$

---

<sup>3</sup>J. W. Gibbs, *Elementary Principles in Statistical Mechanics (The Rational Foundation of Thermodynamics)*, Ch. Scribner's Sons, NY (1902) (Dover, NY (1960)).

## 2 Introduction

which leads to the statistical distribution. The assumption of thermal equilibrium, through statistical independence and molecular chaos, is implicit in this derivation.

During statistical motion, which passes from one state to another, other motions may be present, as, for instance, mechanical motion. In classical mechanics, the density  $\rho$  of the trajectories, which depends on coordinates and momenta (*i.e.* on the states), is left unchanged by the mechanical motion (so is the volume of the phase space defined by the trajectories); this is Liouville's theorem (the conservation of probabilities). Consequently, the statistical motion is not destroyed by the (classical) mechanical motion, and the two motions may coexist (are compatible). In quantum-mechanical motion, if the density matrix were diagonal in the energy representation, *i.e.* if it commutes with the hamiltonian, it is conserved. However, in general, this is not true. The quantum statistical distribution is unperturbed by the quantum-mechanical motion, because the mean statistical values need only mean quantum-mechanical values.

Arguments of the type given above are often used in the attempt to define the statistical motion. Actually, they are invalid. Indeed, it is claimed that, if  $\rho$  is a constant, then it obeys the equation of motion

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{H, \rho\} = 0 \quad , \quad (2.18)$$

or

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \frac{i}{\hbar}[H, \rho] = 0 \quad , \quad (2.19)$$

where  $\partial\rho/\partial t = 0$ ,  $\{\}$  is the Poisson bracket,  $[\ ]$  is the commutator,  $H$  is the hamiltonian and  $\hbar$  is Planck's constant; from these equations we would derive that  $\{H, \rho\}$  or  $[H, \rho]$  are zero, *i.e.* the distribution would be conserved. These equations are invalid, since the statistical distribution  $\rho$  does not obey the laws of the mechanical motion given above;  $\rho$  in the above equations is the trajectory (Liouville) distribution or the density matrix. The mechanical motion of the states (*i.e.* the motion of the dynamical variables  $p$ ,  $q$ , or quantum-mechanical states  $n$ ) is disrupted by the statistical, chaotical motion. In the statistical motion the states (in particular the coordinates  $p$ ,  $q$ ) are viewed as statistical variables (coordinates). We note again that this

## 2 Introduction

particular circumstance does not prevent the constant  $\ln \rho$  from being proportional to the constant energy  $\mathcal{E}$ , as shown above.

Finally, it is worth noting another feature of the statistical motion. This motion proceeds in time. The mean values tend to equilibrium mean values in a relaxation time. The deviations from mean values, *i.e.* the fluctuations, occur in longer times in non-equilibrium and in shorter times at equilibrium.

The main object of Statistical Physics is related to ensembles of many particles; these particles may be of various types, like fermions, bosons, radiation quanta, various elementary excitations; their mechanical motion may be classical or quantum-mechanical. Their Statistical Physics has many particularities; we limit ourselves here to give a general frame related to the statistical motion of the many-particle ensembles. If the particles do not interact (are free), their measurable physical quantities do not move; consequently, the ensemble does not have a statistical motion (except for the case where the ensemble has not been prepared in such a state by external agents; in which case an interaction is present). Therefore, in order to achieve a statistical motion and the statistical equilibrium the particles must interact. If a particle has at some instant an energy  $\varepsilon_{eq}$ , then, by interaction, it shares this energy with many other particles; after some time, when the statistical equilibrium is reached, the particles have a mean energy of the order of the temperature  $T$ ; therefore, we must have the inequality  $\varepsilon_{eq} > T$ . Since the existence of the energy scale  $\varepsilon_{eq}$  is a necessary condition for statistical equilibrium, we may call this energy equilibrium energy and endow it with the suffix *eq* from "equilibrium". At equilibrium, there exist fluctuations, and the fluctuation energy  $\delta\varepsilon_f$  should be lower than the temperature  $T$ , in order for the mean values to make sense; therefore, we have the inequalities  $\varepsilon_{eq} > T > \delta\varepsilon_f$ ; in addition, the uncertainty  $\delta\varepsilon_{ex}$  in the energy of the elementary excitations should be smaller than the fluctuation energy, in order for these excitations to be well defined. Of course, the mean spacing between the quantum states  $\delta\varepsilon_q$  should be very small, and finally, the energy  $\delta\varepsilon_{obs}$  involved in the measurement (observation) process should be the smallest. Therefore, we have the series of inequalities  $\varepsilon_{eq} > T > \delta\varepsilon_f > \delta\varepsilon_{ex} \gg \delta\varepsilon_q > \delta\varepsilon_{obs}$ . In the limit of a large number of particles the quantum-mechanical energies (and states) are not de-

## 2 Introduction

fined, and  $\delta\varepsilon_q$  may be left aside in these inequalities. By the general uncertainty relation  $\delta\varepsilon \simeq \hbar/\tau$ , these inequalities transform themselves in a succession of time inequalities  $\tau_{eq} < \tau_{th} < \tau_f < \tau_l \ll \tau_q < \tau_{obs}$ , where  $\tau_{eq}$  may be viewed as the time of destroying the equilibrium by interaction,  $\tau_{th}$  is the "thermal" time of establishing the equilibrium (determining the equilibrium),  $\tau_f$  is the fluctuation time,  $\tau_l$  is the lifetime of the elementary excitations,  $\tau_q$  is the time needed to establish the quantum levels and  $\tau_{obs}$  is the time of observation of all these phenomena.  $\tau_{eq}$  may be viewed also as the mean time of collisions between the particles. The mean freepath and the associated mean freetime in gases correspond to one-particle elementary excitations. All these estimations are made at equilibrium. We can see that the thermal equilibrium deviates fastest from equilibrium and comes back fastest, such that various observational processes are possible at equilibrium. The relaxation time is related to the observation time, and we can see that it is the longest.

**Historical note.** In *Hydrodynamica*, published between 1734-1738,<sup>4</sup> Daniel Bernoulli claimed explicitly that gases are composed of moving atoms and molecules, whose collisions with container's walls give pressure and their mean kinetic energy is proportional to the temperature and heat; this was the birth of the kinetic theory of gases. The merit of this book consists in the atomistic conception; its drawback is the association of the statistical motion with the mechanical motion. The atomistic conception introduces the notion of complex assemblies composed of many (identical) particles. Leaving aside that their mechanical motion may not be integrable (both classically and quantum-mechanically),<sup>5</sup> the probability distribution over the phase space of the coordinates  $q$  and momenta  $p$  is

$$\rho = \sum_i \delta(q - q_i(t))\delta(p - p_i(t)) \quad (2.20)$$

in classical motion, where the summation extends over the number of particles and  $q_i(t)$ ,  $p_i(t)$  describe the classical trajectory (trajec-

---

<sup>4</sup>D. Bernoulli, *Hydrodynamics*, Dover (1968).

<sup>5</sup>See, for instance, H. Poincare, *Les Méthodes Nouvelles de la Mécanique Celeste*, Gauthier-Villars, Paris (1892, 1893, 1899); M. Apostol, "The many-body theory: its logic along the years", J. Theor. Phys. **152** (2007); see also, F. Diacu, "The solution of the  $n$ -body problem", Math. Intell. **18** 66 (1996).

## 2 Introduction

tory distribution). The conservation of the particle number gives the equation of continuity

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) = 0 \quad , \quad (2.21)$$

where  $\mathbf{v} = (\dot{q}, \dot{p})$ ; if we assign the mechanical dynamics to the coordinates, we get

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \text{grad} \rho = \frac{\partial \rho}{\partial t} + \dot{q} \frac{\partial \rho}{\partial q} + \dot{p} \frac{\partial \rho}{\partial p} = \frac{\partial \rho}{\partial t} + \{H, \rho\} = 0 \quad , \quad (2.22)$$

where  $H$  is the hamiltonian; this equation is in fact  $d\rho/dt = 0$ . This is Liouville's theorem; with the Poisson bracket replaced by commutator, it is the equation of motion of the density matrix (which is not equal to zero, in general). The above equations are usually employed to show that the statistical distribution is an integral of motion (in the absence of the explicit time dependence); this would be the conservation of the probabilities (the conservation of the volume in the phase space is the conservation of the number of particles, or the number of states). In fact, equation (2.20) leads immediately to  $d\rho/dt = 0$ . We should note, however, that as long as  $p$  and  $q$  are dynamical variables, the definition of a probability in reference to them is meaningless, since for statistical distributions  $p$  and  $q$  are statistical coordinates. Similarly, for a quantum-mechanical motion the micro-canonical distribution (in the energy representation) may be taken as an equivalent of equation (2.20), which does not lead to statistical distribution without the additional assumption of molecular chaos (principle of statistical equilibrium). The statistical distribution is not given by equations like equation (2.20), but by  $\rho = 1/\Gamma$ , where  $\Gamma$  is the number of states ( $d\Gamma = 1$  for quantum-mechanical motion). This was the merit of Boltzmann, who, implicitly, identified thereby the statistical motion as a distinct kind of motion.

The notion of probability made its way into Statistical Physics with Maxwell, who, in 1859, derived the velocity distribution of the particles in a gas, by assuming a random motion (which amounts to a uniform distribution  $\rho = 1/\Gamma$ ).<sup>6</sup> He coined the term statistical mo-

---

<sup>6</sup>J. C. Maxwell, "Illustrations of the dynamical theory of gases. Part I. On the motions and collisions of perfectly elastic spheres", *Phil. Mag.* **19** 19 (1860) (4-th series).

## 2 Introduction

tion. Maxwell showed also that the viscosity does not depend on density, a result which enforced the atomistic theory.<sup>7</sup> "The path of each molecule must be so irregular that it will defy all calculations. However, according to the laws of probability theory, one can assume a completely regular motion instead of this completely irregular one".<sup>8</sup>

Since 1870, starting from Maxwell, in a long series of papers, Boltzmann enunciated the notion of statistical ensemble in terms of states (phase statistical ensemble) and claimed that  $H = -\ln \Gamma$  or  $H = \int d\Gamma \rho \ln \rho$  should decrease in time or be stationary (note that the function  $x \ln x$  is negative for  $0 < x < 1$ ); he related  $H$  to the entropy,  $H \sim -S$ .<sup>9</sup> If we accept that the change in time of the function  $H$  is caused by collisions, then, at equilibrium, the time reversal, or the combined time reversal and spatial inversion, leads to the principle of detailed balancing; more general, the unitarity of the scattering matrix leads to a similar conclusion;<sup>10</sup> making use of these results one can prove indeed that  $dH/dt \leq 0$  (and  $dS/dt \geq 0$ ).<sup>11</sup> This is the famous Boltzmann's " $H$ -theorem".<sup>12</sup> However, these arguments are valid at equilibrium, which restricts the result to  $dH/dt = 0$ . The law of increase of entropy follows from the principle of statistical equilibrium.

Indeed, serious objections have been raised to the proof of Boltzmann's  $H$ -theorem. For instance, the invariance under time reversal or, equivalently, the unitarity of the scattering matrix, used in de-

---

<sup>7</sup>J. C. Maxwell, "Illustrations of the dynamical theory of gases. Part II. On the process of diffusion of two or more kinds of moving particles among one another", *Phil. Mag.* **20** 21 (1860) (4-th series).

<sup>8</sup>A. Kronig, "Grundzuge einer Theorie der Gase", *Ann. Phys.* **175** 315 (1856).

<sup>9</sup>L. Boltzmann, "Weitere Studien über das Warmegleichgewicht unter Gasmolekülen", *Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe* **66** 275 (1872); "Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Warmegleichgewicht", *Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe* **76** 373 (1877).

<sup>10</sup>E. C. G. Stueckelberg, "Théorème H et unitarité de S", *Helv. Phys. Acta* **25** 577 (1952).

<sup>11</sup>See, for instance, L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 10, *Physical Kinetics* (E. Lifshitz and L. Pitaevskii), Elsevier, Oxford (1981).

<sup>12</sup>L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen über Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).