An Introduction into Thermodynamics

An Introduction into Thermodynamics

By

Marian Apostol

Cambridge
Scholars
Publishing

An Introduction into Thermodynamics

By Marian Apostol

This book first published 2025

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

ISBN: 978-1-0364-5602-3
ISBN (Ebook): 978-1-0364-5603-0

Contents

1 Foreword 1

2 Introduction 7

3 Temperature and Heat 13
3.1 Entropy . . . 13
3.2 Temperature and heat . . . 15
3.3 Gibbs distribution . . . 20
3.4 Fluctuations . . . 23
3.5 Thermodynamic inequalities . . . 29
3.6 Le Chatelier's principle . . . 31
3.7 Particle distribution . . . 32
3.8 Mechanical variables . . . 34

4 Thermodynamics 39
4.1 Thermal equilibrium . . . 39
4.2 Thermodynamic relations . . . 41
4.3 The Carnot cycle . . . 43
4.4 The Joule-Thomson process . . . 44
4.5 Virial theorem . . . 45

5 Applications I 47
5.1 Ideal classical gas . . . 47
5.2 Fermi gas . . . 52
5.3 Bose gas . . . 56
5.4 Condensation of matter and the real gas . . . 60
5.5 Liquids . . . 61
5.6 Cohesion of matter. Solids . . . 62
5.7 Plasma, colloids and electrolytes . . . 67
5.8 Quark-gluon plasma and condensation to nuclear matter 69
5.9 Superconductivity . . . 70

5.10 Superfluidity 71
5.11 Entropy of earthquakes 73
5.12 Phase coexistence 74
5.13 Pulse thermoelectricity 78

6 Magnetic Phase Transitions 81
6.1 Ferromagnetism 83
6.2 Ferrimagnetism and antiferromagnetism 87
6.3 First-order magnetic phase transition 90
  6.3.1 Introduction 90
  6.3.2 Normal phase 91
  6.3.3 Magnetic phase 93
  6.3.4 External field 95
6.4 Fluctuations 96

7 Magnetocaloric Effect 99
7.1 Adiabatic expansion/compression 99
7.2 Adiabatic demagnetization/magnetization 100
7.3 Vicinity of a phase transition 103

8 Applications II 107
8.1 Einstein solid model 107
8.2 Debye theory 108
8.3 Vapour pressure of solids 110
8.4 Gaseous mixture, thermal equilibrium 112
8.5 Condensation of matter 114
8.6 Dilute solutions 120
8.7 Strong electrolytes 122
8.8 The law of mass action 125
8.9 Saha's equation 127
8.10 Surface tension 128
8.11 Metals, insulators, semiconductors 130
8.12 Galvanic cell 133
8.13 Crystal lattice vibrations 134
8.14 Absence of classical magnetism 138

9 Kinetics 141
9.1 Boltzmann's equation and H function 141

9.2 Transport in gases 143
9.3 Fluctuations 148
9.4 Brownian motion 149
9.5 Black-body radiation 153

10 Fluctuations and Dissipation 161
10.1 Thermodynamic fluctuations 161
10.2 Approach to equilibrium 163
10.3 Correlation functions 166
10.4 Fluctuating harmonic oscillator 170
10.5 Susceptibility 173
10.6 The fluctuation-dissipation theorem 174
10.7 Several variables 177
10.8 Calculation of α 180
10.9 Current fluctuations 181
10.10Brownian motion 182
10.11Electromagnetic fluctuations 185
10.12Sound fluctuation and dissipation 187
10.13Density fluctuations 188
10.14Fluctuations in fluids and electromagnetic fluctuations 190

11 Statistical Seismology 191
11.1 Introduction 191
11.2 Background seismicity 192
11.3 Time-magnitude correlations 194
11.4 Temporal correlations 198
11.5 Concluding remarks 201
11.6 Appendix 202
  11.6.1 Energy accumulation law 202
  11.6.2 Time probability 203
  11.6.3 Time-magnitude correlations 204
  11.6.4 Temporal correlations 205

12 Entropy of Earthquakes 207
12.1 Introduction 207
12.2 Gutenberg-Richter statistical distributions 210
12.3 Fitting the data 213
12.4 Entropy of earthquakes 215

12.5 Shannon entropy 218
12.6 Fluctuations 221
12.7 Analysis of Vrancea seismic activity 223
12.8 Concluding remarks 229

Index **231**

1 Foreword

Thermodynamics is known in Theoretical Physics by two things. On one side, it is notoriously difficult in its conceptual basis, and, on the other side, it is the most general, therefore powerful, discipline of Theoretical Physics. This is a strange situation, which calls for an explanation: how is it that we, humans, are in the possession of such a powerful tool, and still we do not understand it very well?

Some believe that Thermodynamics is a self-standing subject of study, others believe that it should be derived from a statistical mechanics. Einstein was convinced that "...thermodynamics is the only physical theory of universal content,...which ... will never be overthrown", therefore, it is perfect and eternal; but, of course, such an absolute thing is, by its own definition, pretty non-intelligible. Landau thought that "although the general statements of Thermodynamics can be formulated non-statistically, ...all the concepts and quantities of Thermodynamics follow most naturally, simply and rigorously from statistical concepts, ...and ... their application to specific cases always requires the use of statistical physics"; which sounds somewhat self-contradictory.

Some authors present the situation in a dramatic style: "...Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. ...Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously." (David Goodstein, in *States of Matter*, Dover, 1975).

Fact is that Thermodynamics is a beautiful science, and we, humans, as attracted as we could be by it, are also a bit intimidated by it, as always in the presence of beauty.

However, the fundamental concept of Thermodynamics, we may say its secret, is relatively easy to be discovered. This is the main aim of the present book.

We can imagine a body with a large, very large, number of degrees of freedom, and a very large number of corresponding states, consisting, usually, of a very large number of identical particles; or sufficiently homogeneous to be considered as consisting of a very large number of identical parts, called particles. This is almost always true for macroscopic bodies. At every moment the body is in any of such states. Therefore, we may imagine that the body exhausts the number of its possible states, which, under these conditions, may be thought as being the maximum number of possible states. This is nothing else but the celebrated principle of the so-called maximal entropy. Obviously, being in one state, out of a large number of states at every moment, we have no other choice but to speak about the motion of the body as a probabilistic motion. Now, suppose that we give to the body an amount of energy, called temperature, namely a temperature amount T to any new state acquired by the body, in number of ΔG; obviously, the body will impart the total amount of acquired energy $T\Delta G$ to all its states G, such that the increase of energy will be $\Delta E = T\Delta G/G$. The integration of this equation gives G and the probability $1/G$ for the body to be in a state. The result is precisely the Gibbs distribution. If we denote $\Delta G/G = \Delta S$ and call it entropy, we arrive immediately to Boltzmann probabilistic theory of heat ($dE = TdS$). Henceforth, the derivation of all the thermodynamic concepts, quantities, rules and laws is straightforward. This process is presented in this book. As we can see, the solution which allows the understanding and clarifies the matters is the introduction of the new concept of temperature. We get used with it by studying particular thermodynamic processes.

We understand immediately the reversible (equilibrium), irreversible and adiabatic thermodynamic transformations; we introduce the various thermodynamic potentials and show how they get their minimum values in equilibrium. We derive the Gibbs-Duhem equation and establish the theorem of the small increments. We determine the equilibrium conditions, the thermodynamic inequalities and discuss in detail the fluctuations. Indeed, having probabilities, we can only have mean values of the physical quantities, and, of course, the so-called statistical deviations, or fluctuations. The basic laws of Thermodynamics are derived immediately, with special discussion of the Carnot cycle of the thermal engine and the Joule-Thomson process. A great deal of attention is given, as it is appropriate, to the number of particles as statistical variable, the so-called canonical and grand-canonical ensembles, partition functions and particle distributions, with the quantum statistics as immediate particular cases.

We can only get used with the new thermodynamic concepts of temperature and entropy by studying applications. There is an enormous number of applications of Thermodynamics. Probably we do not err too much if we say that they are in an infinite number. Some are old and well known, but what is very interesting is that we are able to derive new, original applications, a situation not very common with such an old and well-established scientific discipline. For example, recently it was introduced in science the entropy of earthquakes, and it was shown that the seismicity is an irreversible process, as expected. The book has two large sections of thermodynamic applications, including, besides well-known theories of the ideal classical gas, quantum Fermi and Bose-Einstein gases, superconductivity and superfluidity, original applications to condensation of matter and the real gas, cohesion and aggregation of matter, theory of liquids, plasma, colloids and electrolytes, quark-gluon plasma, pulse transport. All these are original, developed theories, which cannot be given in their entirety, so only a description is suitable, which we hope, though quite concise, is sufficiently clear, exhaustive and proper. Other, more particular applications are described in detail.

Further on, the book continues with a detailed application to the magnetocaloric effect, which is included, on one hand, due to its very special theoretical character, and, on the other hand, due to its very useful application in refrigerators. Moreover, the theory becomes very interesting in the close proximity of a phase transition, usually obscured, to some extent, in current presentations. The problem of the phase transitions in Thermodynamics is notoriously difficult.

Indeed, in a phase transition the body passes from a normal phase, above a transition temperature, to an ordered phase, called condensed phase, below that transition temperature. The ordered phase has zero entropy, therefore it is not a thermodynamic phase. Consequently, the thermodynamic properties in the close neighbourhood of the transition temperature remain undetermined. A transition to an ordered phase exhibits usually infinite fluctuations. The thermodynamic potentials, or their derivatives, exhibit singularities at the transition temperature. Such singularities cannot arise from finite quantities, except in the thermodynamic limit, *i.e.* in the limit of an infinite body. It follows that, in order to describe a phase transition, we need to introduce new characterizations of the condensed phase, we need to define it to some extent. This is accomplished for example by the notion of mean field, or the concept of condensation. We can estimate the transition temperature, by using an order parameter, as in Landau's theory of phase transitions, or in some particular models; the behaviour of the order parameter is not governed by thermodynamics, but, instead, it is governed by general rules of equilibrium of higher-order arbitrary functionals of thermodynamic potentials. The book extends the previously known theory of condensation to first-order magnetic transitions. Also, the ferromagnetism and antiferromagnetism are presented. Once the ordered phase is determined, its parameters may vary, so we have elementary excitations (called Goldstone modes) with their own thermodynamic properties, an example of emergent dynamics. There exists another method of calculating the thermodynamic quantities in the neighbourhood of the transition temperature, called renormalization group. By this method we eliminate successively parts of the degrees of freedom, by averaging over them, until the iteration gives the same result (fixed point), so we get the transition temperature; it is an approximate procedure. It is worth noting that during such iterations we get higher-order functionals for thermodynamic potentials. Series expansion in the neighbourhood of the transition temperature exhibits characteristic powers with fractional exponents, called critical indices. The critical temperatures do not differ much from those obtained by other specific models, while the critical exponents are difficult to be measured experimentally.

A special attention is given in this book to kinetics and the relationship between fluctuations and dissipation. Physical kinetics deals with transport, where we have local equilibrium but not a global one. The main concept in transport is the mean freepath. There exists a vast amount of transport phenomena. In this book we discuss in detail the transport in gases. A fluctuation is a deviation of the thermodynamic ensemble from its equilibrium state. During this deviation the ensemble thermalizes the involved energy, by friction, *i.e.* by dissipation, in order to be able to return to equilibrium. Apart from thermodynamic fluctuations, we introduce the gaussian distribution of entropy, the relaxation and transport coefficients, and establish the relaxation equations which govern the fluctuations. A great deal of progress was recorded when it was noticed, to a large extent surprisingly, that these equations, and their solutions, are recovered by linear response functions, or correlation functions, results included in the so-called theorem of fluctuation-dissipation. This theorem and its applications are discussed in detail in the book. Additional comments on hydrodynamic and electromagnetic fluctuations are included.

After reviewing Thermodynamics as largely as possible, it is perhaps wise to look back to its fundamental assumption, namely the realization of every state out of all the possible states. This assumption of thermodynamic equilibrium is not at all in conjunction with what Mechanics tells us. A mechanical ensemble of particles move along some states, as determined by the mechanical equations of motion from the initial conditions. These mechanical states depend on the initial conditions, so they cannot exhaust in any way the much larger set of all possible states. Moreover, a mechanical ensemble may come back to its initial state, in virtue of the reversible character of the mechanical motion, or it may pass very close to a previously visited state, such that the ensemble will move reversibly, or oscillatory, but in no case irreversibly as Thermodynamics claims. These were historical objections raised against Thermodynamics, and this problem of thermodynamic equilibrium remains unsolved. Thermodynamics, with its probabilistic motion, is a distinct science.

2 Introduction

As it happens with any chapter of Theoretical Physics, Thermodynamics, besides its magnificent understanding of the natural phenomena, carries also the danger of a series of misconceptions, perpetuated in textbooks and everywhere. For instance, Wannier believes that it would not be advisable to touch the fundamentals when speaking about Thermodynamics, but rather to resort to various "lighter" assumptions, theoretical, experimental, or whatever, whichever looks more convenient (G. H. Wannier, *Statistical Physics*, Dover, NY (1966)); otherwise it would be difficult.

One thinks that we are forced to use statistical methods in Thermodynamics because we are not able, and also would be useless, to solve the equations of motion of the small particles of the macroscopic bodies; these equations are too numerous, and too complex to be dealt with. It is assumed that the basis of Thermodynamics is Mechanics, and the inappropriate term of Statistical Mechanics is widely used. Pauli pays tribute to this misconception, obviously very reluctantly, in his own characteristic style (W. Pauli, *Statistical Mechanics*, *Pauli Lectures on Physics*, vol. 4, Dover, NY (1973)). We have not a manageable solution even for the classical motion of three bodies. Fermi is more reasonable when he says that for such large ensembles the motion of the individual particles is less important, and we have to focus ourselves on the average properties (E. Fermi, *Thermodynamics*, Dover (1936)). Fact is that an honest and clear look at Thermodynamics shows that we have to admit that the particle motion in large bodies is statistical; the position and momentum, or the quantum-mechanical states, are statistical variables, *i.e.* they take some, permissible and necessary, values according to a probability; probability which, without other special constraints, is a random, purely chaotical probability. This great, and perhaps unexpected insight, was gained by Boltzmann, and his few great precursors, like Bernoulli, Kroenig, Maxwell, and, especially, Clausius. Aristotle with the Theory of Luck and Bad Chance chapter in his Physics two thousand years ago was vindicated. The constraints needed to fix up the external conditions are compatible with the laws of other theories of motion, including Mechanics, but they are not constitutive to Thermodynamics. They are just compatible. In a relentless attempt to bring empty novelties there are authors who make a distinction between Statistical Mechanics, or even Statistical Physics, and Thermodynamics, viewing the latter as a mere chapter of the former. Fact is, again, that the discipline is Thermodynamics and its treatment, methods are statistical; though I may admit that the denomination of Statistical Physics looks acceptable (L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5 (*Statistical Physics*), Elsevier, Oxford (1981)). The object of study of Thermodynamics is the transformation of heat in mechanical work. Later on, due to the power of its statistical methods, Thermodynamics was extended to include phase equilibrium and phase transitions, and even the evolution towards equilibrium; the latter chapter becomes Physical Kinetics, a discipline in itself, due to its very large ambitus and richness of extremely minute, detailed and very particular and surprisingly enlightening knowledge it brings.

The difficulties in grasping Thermodynamics, generated by our misconceptions about it, have their good side. Of course, as any good side, it comes at a price. The price is that we immerse ourselves into philosophycal considerations; we fall down into philosophy. The good, precious part is that all these considerations are in fact delightful, subtle and elevating analyses, true intellectual feats (H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, Wiley, NY (1985)).

The determination of the probability of finding an ensemble in a certain state is a problem in Thermodynamics. It is thought that an isolated ensemble has a certain number of available states, and this number should be a maximum in certain conditions. Actually, we prefer to work with the logaritm of this number, because it is additive, and we want to relate it in some way to some physical, additive quantity. This is the entropy, and the maximum condition would be the law of increase of entropy. This is sufficient to get the Gibbs distribution, a fact too often overlooked. Instead, one introduces the idea of two ensembles, such that our ensemble is in contact with another one, much bigger, called thermal bath (Landau and Lifshitz cited above; R. K. Pathria, *Statistical Mechanics*, Butterworth-Heineman, Oxford (1972)). Though leading to the same result, this construction is not necessary. Moreover, since this hypothesis does not appear to be always fulfilled by the experimental situation, or by theoretical considerations, Gibbs invented a "mental" infinite multitude of similar ensembles, which share energy, or other relevant physical quantities, which again is unnecessary and unphysical. Others believe that the Gibbs distribution could be derived by a "most probable distribution" of sharing energy among a large number of identical ensembles, which, though leading to the Gibbs distribution, again it is not necessary; it is not a most probable distribution, it is a maximization of entropy with constraints (E. Schroedinger, *Statistical Thermodynamics*, Cambridge University Press, London (1948)). The difficulty resides in the way we understand the probability for a body which, we thought, moves mechanically. The solution is that the body does not move mechanically, classically or quantum-mechanically, it moves probabilistically; and the maximum condition gives us a unique solution to the problem.

Let us take a point-like particle with mass m, moving circularly with angular velocity ω at distance r, with velocity $v = \omega r$. The energy $mv^2/2$ of this particle is conserved. There exist an infinity of states with different ω and different r, such that $v = \omega r$ is constant; or at least a finite, large number of states for a particle moving in a container. There is no reason to assume that the particle visits every one of these states, as Thermodynamics assumes. Let us assume that we have N point-like particles with mass m, enclosed in an isolated container with perfectly reflecting walls. We assume that the particles collide elastically with one another. Let us assume that $N-1$ particles are fixed, and let us follow the trajectory of one particle. It will take many positions, with many values of the momentum, but it will certainly not exhaust all possible position-momentum mechanical states, not even in a very long time. Now let us assume that the other $N-1$ particles move. We increase the chance for one particle to visit many more states as before, including the particle permutations, especially for large values of N. But there is no obvious reason for any one particle, or the whole ensemble, to visit all the available states, not even in a sufficiently long time, or an infinite time, or for an infinite N. Thermodynamics assumes precisely that all the available states are visited, with equal probabilities in this case, of an isolated (micro-canonical) ensemble. This would be called the ergodic hypothesis. The situation is not changed for a canonical, or macro-canonical ensemble. As reasonable as it may appear, the hypothesis of a perfect, probabilistic chaos is special, and it is not supported by mechanical theory. Thermodynamics introduces in Physics a new hypothesis regarding the motion.

The difficulties in relating Thermodynamics to Mechanics led even to an axiomatic presentation of Thermodynamics (see C. Carathéodory, "Untersuchungen ueber die Grundlagen der Thermodynamik", Math. Ann. **67** 355 (1909)), a situation similar to Quantum Mechanics. This only shows that we give up the understanding of Thermodynamics (and Quantum Mechanics).

An interesting problem in Thermodynamics occurs in connection with correlations and interaction. A well-known example is provided by the van der Waals equation for the non-ideal (real) gas. The excluded volume (or the finite volume of the particles) reflects certain correlations, and they should be taken carefully into account, since they bring important contributions to the sum over states. A similar situation occurs in liquids, electrolytes and colloids. It is too often that such correlations, like the excluded volume, are treated in a sloppy manner. Also, quantum correlations are fundamental for the Fermi and Bose gases. The interaction effects is a different problem. Small corrections to thermodynamic quantities can be estimated by expanding the Gibbs distribution in powers of interaction, and retaining only a few terms. A somewhat similar situation is related to the quantum corrections, which, with respect to the classical contribution, are generated by the quantum-mechanical kinetic energy; since the latter is proportional to $\hbar^2$, the first-order quantum corrections to the free energy are proportional to $\hbar^2$. Quantum correlations generated by the symmetry of the wavefunctions are exponentially small, but those related to the quantum delocalization bring additional terms to the free energy, proportional to $\hbar^3$. In general, the interaction may have appreciable effects, leading to the condensation (aggregation) of matter, in condensed phases like liquids, solids, superconducting or superfluid phases. In general, we need first to solve for the effects of the interaction, in order to define the ensuing condensed phases, then get the elementary excitations of these phases, and only thereafter calculate the thermodynamics of these elementary excitations. In this respect we note that the particles in liquids and even gases should be viewed as (one-particle) elementary excitations (besides other, low-lying, one-particle or collective elementary excitations). A special problem of interaction occurs in plasma, and to some extent electrolytes and colloids, as well as in phase mixtures in general. The solution of this interaction problem consists in reducing it to correlations, which can be treated thermodynamically in the evaluation of the sum over states. For instance, in plasma the interaction generates electrons correlated around ions, through a Debye length, such that we may treat separately, to a satisfactory extent, the phase of the correlated electrons and that of the ions surrounded by electrons. In other cases, interaction, non-thermodynamic modes, can affect appreciably the effective interaction and the correlations generated by it, like in concentrated electrolytes (ionic liquids), where the screening length becomes very large.

Perhaps one of the most interesting subjects in thermodyamics is the phase transitions. Macroscopic bodies may exhibit discontinuities in their thermodynamic quantities at a certain transition (critical) temperature. It is believed that such discontinuities may be accounted for by exactly soluble models. The most celebrated example is the Ising model in two dimensions (L. Onsager, "Crystal statistics. I. A two-dimensional model with an order-disorder transition", Phys. Rev. **65** 117 (1944)). However, an exactly soluble model implies the exact calculation of the sum over states. The sum over states includes finite, continuous and differentiable functions. Singularities, which imply discontinuities, may only appear in infinite summations. If these singularities are going to be associated to phase transitions, we may expect that the phase transitions are due to an infinite number of degrees of freedom (C. N. Yang and T. D. Lee, "Statistical theory of equations of state and phase transitions. I. Theory of condensation", Phys. Rev. **87** 404 (1952); T. D. Lee and C. N. Yang, "Statistical theory of equations of state and phase transitions. II. Lattice gas and Ising model", Phys. Rev. **87** 410 (1952)); which is unphysical. Also, two- or one-dimensional bodies are unphysical, to a large extent. The discontinuities at the transition temperature appear as a consequence of having there two distinct phases. Therefore, the transition can be described by calculating two partition functions, not only one. Moreover, the correlations responsible for the phase transitions make the condensed phase to behave mechanically, so the thermodynamic qualities are lost. They are recovered only by the elementary excitations of the condensed phase. Thermodynamics has general, rather qualitative concepts, with a large applicability, whilst specific knowledge can only be obtained by calculations implying the particularities of the macroscopic bodies.

To summarize, Mechanics, classical or quantal, is not able to determine mechanical states of motion for an ensemble of many particles. Such macroscopic ensembles tend naturally to a state of maximal disorder, which is their thermodynamic equilibrium. The various states are visited with a probability, which is either the fraction of time spent in that state, or the frequency of that state in a large number of identical ensembles (in this latter case is perhaps better to use the term assembly for an individual realization of the thermodynamic set of assemblies, which may be called thermodynamic ensemble). These states are able to exchange a particular form of energy, which is called heat; the exchange is done in given conditions, governed by a parameter called temperature.

3 Temperature and Heat

3.1 Entropy

Let us consider an ensemble of N identical, independent particles, labelled by $i = 1, 2, ...N$, each having g_i states. The total number of states is

$$G = \prod_{i=1}^{N} g_i \ . \tag{3.1}$$

We intend to associate this number to an extensive physical quantity, so we use

$$S = \ln G = \sum_{i=1}^{N} \ln g_i \ . \tag{3.2}$$

We call this S entropy.

The particles may all be in the same unique state, *i.e.* $g_i = 1$, in which case $S = 0$. Then, we have a perfectly ordered ensemble, like a perfect crystalline solid, or a perfectly saturated ensemble of aligned magnetic moments. Also, some particles may have a different number of states, such that some particles are more ordered than others; there are many such inhomogeneous distributions, which may change in time. In that case we say that the ensemble is in a non-equilibrium state. We are interested in a unique, homogeneous state which remains the same in time, with a maximal disorder; this would be an equilibrium state. Obviously, such a state would maximize the entropy. However, the maximization of the entropy is meaningful only in some given conditions, which, reasonably, are a fixed number of states,

$$\sum_{i=1}^{N} g_i = const \ . \tag{3.3}$$

Then,

$$\sum_{i=1}^{N} \ln g_i - \alpha \sum_{i=1}^{N} g_i \tag{3.4}$$

has a maximum for

$$g_i = g = 1/\alpha \ , \tag{3.5}$$

where α is a given constant; and, indeed, the second derivative of S,

$$-\frac{N}{g^2} < 0 \ , \tag{3.6}$$

is negative at the maximum value; and the maximum is as narrow as $g \gg \sqrt{N}$. The ratio $\sqrt{N}/N$ is an indicative of how good the equilibrium is; for $N \gg 1$ it is very good. The deviation $\Delta g \simeq \sqrt{N}$ from the equilibrium value is a measure of the fluctuations.

It is believed that every isolated and constrained ensemble of the type described above evolves towards such an equilibrium state, with maximal entropy. This is an irreversible process. This is the law (principle) of increase of entropy. We owe it to Boltzmann.[1] We call such ensembles statistical ensembles. We note that the equilibrium state is not the "most probable state"; on the contrary, $dS = dG/G$ may be viewed as a probability, which is minimal at equilibrium; it is the most chaotical state under given conditions.

Note: For a statistical behaviour it is necessary to have a large number of available states; it is not necessary to have a large number of particles, or a large number of degrees of freedom. For instance, we may have one, small particle, with mass $m = 10^{-6}g$ $(1\mu g)$ and one degree of freedom, with positions in the range $\Delta x = 10^{-4}cm$ $(1\mu m)$ and velocities in the range $\Delta v = 10^4 cm/s$; this is a reasonable macroscopic particle, with a classical motion. We count the number of states as $\Delta g = \Delta p \Delta x / 2\pi\hbar$, which, in our case, is a very large number $\Delta g \simeq 1.5 \times 10^{20}$ (Planck's constant $h \simeq 6.62 \times 10^{-27} erg \cdot s$, $\hbar = h/2\pi \simeq 10^{-27} erg \cdot s$). However, for a small number of particles the fluctuations are large (equation (3.6)).

---

[1] L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen ueber Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).

3.2 Temperature and heat

At equilibrium the entropy is

$$S = \ln G = N \ln g \ . \tag{3.7}$$

Let us consider an equilibrium change dS in entropy, and multiply this change by a positive, constant parameter T, with dimensions of energy, called temperature; its meaning will be given later. We get an energy change

$$dE = dQ = TdS \ \ , \tag{3.8}$$

which we call heat. In such an equilibrium transformation we say that the ensemble is in thermal contact. Of course, such a transformation is reversible, *i.e.* dS may have either sign. If dS is zero ($S = const$) we have an adiabatic transformation, which is reversible.

It is worth noting that $dQ = TdS$ is $dQ = TdG/G$, which means that we give an energy (heat) TdG to the ensemble (or take that energy from the ensemble) and thereafter impart equally that energy to all the states, in number of G; so, we modify the energy of every state by dQ on average. Since dQ belongs to the whole ensemble, that means that the ensemble is at any moment in a given state, though not exactly, but with a certain probability, in order to agree with the fact (actually, a definition) that the energy is shared on average. Also, that means that the time we need to measure a thermodynamic quantity, and get its mean value, is much longer than the time spent by the ensemble to visit one state and pass from one state to another. We may think of states in mechanical, or quantum-mechanical terms, even if we do not know them; for heat it is sufficient to characterize them in terms of energy. Also, various other forms of energy can be included, characterized by some other variables which define states. Similarly, the entropy can be represented in terms of other parameters which define the number of states. The fundamental thing is the state probability.

The ensemble may have other distinct, independent parameters, which may vary in an equilibrium transformation. For example, from equation (3.7) we may have

$$d(N \ln g) = Nd(\ln g) + \ln g \cdot dN \ ; \tag{3.9}$$

for independent changes this equality may be written as

$$dS + \ln g \cdot dN \ . \tag{3.10}$$

This way, we get an additional energy change

$$dE = T \ln g \cdot dN = \mu dN \ , \tag{3.11}$$

where $\mu = T \ln g$ is called chemical potential. The change dN is an equilibrium, reversible transformation, where the ensemble is in chemical contact; and the chemical potential is constant during such a transformation. Finally, we may add the mechanical work $dE = W = -pdV$, done by the ensemble with constant pressure p on the surrounding bodies, by a volume change dV (mechanical contact); similarly, it is an independent equilibrium, reversible transformation. By collecting all these energy changes we get the energy conservation law

$$dE = -pdV + TdS + \mu dN \ ; \tag{3.12}$$

other similar contributions may be included, like, for instance, the work HdM done upon the magnetization M by the (parallel) magnetic field H. The partial derivatives p, T, μ are functions of V, S, N; they are called equations of state. The heat as energy was recognized first by Joule and Helmholtz.[2]

Equation (3.12) has very interesting properties; it can equivalently be written as

$$d(E + pV - TS) = Vdp - SdT + \mu dN \ . \tag{3.13}$$

In this equation V and S are extensive quantities, *i.e.* quantities proportional to N; while μ is not an extensive quantity, it is an intensive one. Consequently, equation (3.13) makes sense only if

$$\begin{aligned} d(E + pV - TS) &= Vdp - SdT + \mu dN = \\ &= d(\mu N) = \mu dN + N d\mu \ , \end{aligned} \tag{3.14}$$

---

[2] J. P. Joule, "Expériences sur l'identité entre le calorique et la force mécanique. Determination de l'équivalent par la chaleur dégagée pendant la friction du mercure", Compt. Rend. August 23 (1847); "On the mechanical equivalent of heat", Phil. Trans. Roy. Soc. London **140** 61 (1850); H. Helmholtz," Ueber die Erhaltung der Kraft. Eine physikalische Abhandlung", G. Reimer, Berlin (1847).

such that

$$d\mu = (V/N)dp - (S/N)dT \tag{3.15}$$

and

$$E + pV - TS - \mu N = 0 \ . \tag{3.16}$$

This relationship (known as Gibbs-Duhem equation) follows in fact immediately from the homogeneity of equation (3.12).

From equations (3.12), (3.15) and (3.16) we get several so-called thermodynamic potentials, like the (Helmholtz) free energy $F = E - TS$,

$$dF = -pdV - SdT + \mu dN \ \ , \tag{3.17}$$

the enthalpy $H = E + pV$,

$$dH = Vdp + TdS + \mu dN \ , \tag{3.18}$$

the Gibbs free energy $\Phi = E - TS + pV = \mu N$,

$$d\Phi = Vdp - SdT + \mu dN \ \ , \tag{3.19}$$

and the thermodynamic potential $\Omega = E - TS - \mu N = -pV$,

$$d\Omega = -pdV - SdT - Nd\mu \ . \tag{3.20}$$

In an irreversible process, *i.e.* a process during which the ensemble goes to equilibrium, the entropy increases, and the heat in equation (3.8) is such that

$$\delta Q < T\delta S \tag{3.21}$$

and, consequently,

$$\delta E + p\delta V - \mu\delta N < T\delta S \ . \tag{3.22}$$

From this equation we get the following inequalities:

$$\begin{gathered} \delta(E - TS)_{V,T,N} < 0 \ , \ \delta(E + pV)_{p,S,N} < 0 \ , \\ \delta(E + pV - TS)_{p,T,N} < 0 \ , \\ \delta(E - TS - \mu N)_{V,T,\mu} < 0 \ \ , \end{gathered} \tag{3.23}$$

i.e. the thermodynamic potentials have a minimum at equilibrium, a property which justifies their denomination of potentials.

Also, let us assume that we add a small amount of energy to equation (3.12), of the form $\Lambda d\lambda$, where λ varies very slowly in time, such that the process of variation of λ is a (quasi-) equilibrium process. Then, it is obvious that the same energy amount should be added to all the thermodynamic potentials, and the expressions of their equilibrium changes remain valid; therefore, for constant corresponding variables, all the potentials acquire the same quantity $\Lambda d\lambda$, and Λ is given by the derivative of the potentials at constant corresponding variables. This is known as the theorem of small increments for the thermodynamic potentials.

Note: The entropy, temperature and heat as introduced above, including their relation with a probability, form the basis of Thermodynamics. In particular, emphasis shoud be placed on the notion of thermodyamic equilibrium. The main assumption of Thermodynamics is that the ensemble may be, with a certain probability, in any of all the available states, in given conditions. This is the condition of thermodynamic equilibrium. Here, at least, one contradiction with Mechanics appears. First, a mechanical ensemble has well determined solutions of motion for given initial conditions, and the corresponding states are by far less than all the possible states. Indeed, this is expected, because the mechanical states depend on the initial conditions. Consequently, the density of phase points in the phase space is constant in time, a basic result in Mechanics, known as Liouville's theorem. There is no sign that the phase density would decrease, in order to comply to the basic assumption of Thermodynamics of all available, possible states. There exists an interesting numerical experiment by Pasta, Ulam, Fermi of calculating the energy distribution of a set of coupled oscillators, which shows no sign of thermalization, *i.e.* equilibrium.[3] In mechanical motion the ensemble may exhibit Umkehreinwands, *i.e.* states previously visited may be visited again, due to the reversibility of the mechanical motion; in contrast with the thermodynamic assumption (Loeschmidt's paradox[4]). Also, a me-

---

[3] E. Fermi, J. Pasta and S. Ulam, "Studies of non-linear problems", Los Alamos Report 266, LA-1940, Los Alamos (1955).

[4] J. Loeschmidt, "Ueber den Zustand des Waermegleichgewichtes eines Systems

chanical ensemble may exhibit Wiederkehreinwands, *i.e.* it may pass very close to previously visited states (Zermelo's paradox, Poincare's recurrence theorem[5]). All these are historical mechanical objections raised against Thermodynamics, which, indeed, emphasize the distinct character of Thermodynamics in comparison with Mechanics. Of course, we may admit that a suitable arrangement, distribution, of initial conditions may result in a thermodynamic equilibrium state; but this does not solve the equilibrium problem, it only transfers it to the initial conditions. Fact remains that we are not able and do not know how to explain the existence of thermodynamic equilibrium. We can only take note that it exists and use it as a basic hypothesis for the development of Thermodynamics.

Similar distinctive basic notes appear for other disciplines of Theoretical Physics, like Electromagnetism, or Quantum Mechanics; but there they may be attributed to the distinctive character of the conditions of these new disciplines, the existence of the electromagnetic field, or the existence of small, atomic particles, such that we may expect differences with Mechanics, and between themselves. This is not the case for Thermodynamics, where we have no visible distinct circumstances, and we are inclined to admit that the motion is mechanical. As we can see, it is not.

Next, for a mechanical ensemble the states are defined by the set of canonical variables, namely momentum p and position r; or, by the set of quantum numbers n. The energy is conserved for any of these states. We can change the energy of a state only by changing the state. This is in contrast with Thermodynamics, where we can give energy to a state, or take energy from it (see equation (3.8)). Obviously, thermodynamic processes are not processes of mechanical motion. The mechanical states in Thermodynamics are only statistical variables which serve to define a probability.

A macroscopic body has quantum-mechanical states with, say, energy ε_n, where n is some quantum numbers, with a high degeneracy.

---

von Koerpern mit Ruecksicht auf die Schwerkraft. 1. Teil", Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe **73** 128 (1876).

[5] E. Zermelo, "Ueber einen Satz der Dynamik und die mechanische Waermetheorie", Ann. Phys. **57** 485 (1896); "Ueber mechanische Erklaerungen irreversibler Vorgaenge. Eine Antwort auf Hrn. Boltzmann's "Entgegnung"", Ann. Phys. **59** 793 (1896).

The spacing $\Delta\varepsilon_n$ between these states is extremely small; in fact, the states are not well-defined, neither the quantum numbers; they form a continuum. The essential ingredient in constructing Thermodynamics is the amount of energy T given to each state from a large number dG, which then is shared equally by all the states in the very large number G (the heat). As long as the quantum states are extremely dense, this process is possible, practically, for any amount of energy T. The transition from one approximate state to other approximate state, far away or in close proximity, is, practically, a classical process. We can construct Thermodynamics for a quantum-mechanical ensemble in this sense. For a fairly large number of particles (such as to have fairly small fluctuations) there exists an ultraviolet cutoff on the quantum states of the particles, given by $\hbar^2/ma^2$, where m is the particle mass and a is the mean separation distance between the particles. Higher energies, or momenta higher than $\hbar/a$, *i.e.* wavelengths shorter than a, are meaningless; they do not correspond to physical processes. We can easily see now that a temperature T smaller than $\hbar^2/ma^2$ can give heat, and Thermodynamics can be constructed in this case, providing, of course that T is still larger than $\Delta\varepsilon_n$. For higher temperature $T \gg \hbar^2/ma^2$ the Thermodynamics becomes classical.

3.3 Gibbs distribution

From equation (3.7) we have $dS = dG/G$; the smallest dG is 1, such that the entropy change is of the form $\Delta G/G$. This means that $1/G$ may be viewed as a probability density, *i.e.* the ensemble may occupy various state ranges ΔG from G to $G + \Delta G$ with the probability $\Delta G/G$. Consequently, its variables are statistical variables, and their mean values are reached at equilibrium. For example, if we denote the states by α, the energy is a function of states $\mathcal{E}_\alpha$, and $E = \overline{\mathcal{E}_\alpha} = \frac{1}{G}\sum_\alpha \mathcal{E}_\alpha$. The mean force is $-gradE = -(\partial E/\partial V)_{S,N} dV/d\boldsymbol{r}$, whence we get the pressure $p = -(\partial E/\partial V)_{S,N}$ (since $dV = d\boldsymbol{r}d\boldsymbol{s}$, $d\boldsymbol{s}$ being the element of surface). Similarly, the entropy $\mathcal{S}$ is a function of states, and so on. We owe this probabilistic interpretation of the statistical ensembles to Maxwell and Gibbs.[6] It remains that we should know the dependence of the thermodynamic potentials on their corresponding variables (*e.g.*, $E(V,S,N)$), which amounts to knowing the equations of state.

This is done by using

$$d\mathcal{S} = \frac{dG}{G} = \frac{1}{T} d\mathcal{E} \ , \tag{3.24}$$

where we assume $V, N = const$. We denote $1/T$ by β, and close to equilibrium we may view $\beta = const$. We recall that we are sufficiently close to equilibrium, where S attains its maximum, for a large number of states and particles ($G, N \gg 1$, see above). We note that this equality implies an average, *i.e.* a probability, according to the above discussion, and $1/G$ for the probability means a maximal disorder, *i.e.* a maximal entropy. The integration of equation (3.24) leads to

$$\ln(G/G_0) = \beta(\mathcal{E} - E) \ , \tag{3.25}$$

where $S = \ln G_0$. It follows

$$G = G_0 e^{-\beta E} e^{\beta\mathcal{E}} = e^{S-\beta E} e^{\beta\mathcal{E}} \tag{3.26}$$

and the probability density

$$w = \frac{1}{G} = e^{\beta(E-TS)} e^{-\beta\mathcal{E}} \ . \tag{3.27}$$

In principle, this equation should be used wih discrete summation over states. However, we may also write

$$\begin{aligned} dw &= e^{\beta(E-TS)} e^{-\beta\mathcal{E}} dG/\delta G = \\ &= e^{\beta F} e^{-\beta\mathcal{E}} dG = e^{\beta(\Omega+\mu N)} e^{-\beta\mathcal{E}} dG \ , \end{aligned} \tag{3.28}$$

---

[6] 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); "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); J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (*The Rational Foundation of Thermodynamics*), Ch. Scribner's Sons, NY (1902) (Dover, NY (1960)).

with $\delta G = 1$. This is called the Gibbs distribution (for a canonical ensemble). Equation (3.28) is useful, because, by knowing the function $\mathcal{E}_\alpha$ and the density of states $dG/d\alpha$ for given V, N, we use the normalization condition of the probabilities $\int dw = 1$ and get the free energy F as a function of V, T, N. The sum

$$Z = e^{-\beta F} = \int e^{-\beta \mathcal{E}} dG \tag{3.29}$$

is called partition function (or sum over states).

If we use the probability density $\rho = w$ given by equation (3.28) we can check that $\overline{\mathcal{E}} = E$ and $-\overline{\ln \rho} = \overline{\mathcal{S}} = S$.

We may include the number of particles in equation (3.24),

$$\frac{dG}{G} = \frac{1}{T} d\mathcal{E} - \frac{\mu}{T} d\mathcal{N} \ , \tag{3.30}$$

and get

$$\ln(G/G_0) = \beta(\mathcal{E} - E) - \beta\mu(\mathcal{N} - N) \ , \tag{3.31}$$

$$G = e^{S - \beta(E - \mu N)} e^{\beta(\mathcal{E} - \mu\mathcal{N})} = e^{-\beta\Omega} e^{\beta(\mathcal{E} - \mu\mathcal{N})} \tag{3.32}$$

and

$$dw = e^{\beta\Omega} e^{-\beta(\mathcal{E} - \mu\mathcal{N})} dG d\mathcal{N} \ . \tag{3.33}$$

This is called the grand (macro)-canonical distribution;[7] its partition function is

$$Z = e^{-\beta\Omega} = \int e^{-\beta(\mathcal{E} - \mu\mathcal{N})} dG d\mathcal{N} \ . \tag{3.34}$$

If we associate a statistical variable to the volume, we can include a volume dependence in the statistical distribution.[8]

From the definition of the canonical sum over states we can see that the temperature T is a measure of the accessibility of the states; for high T the exponential $e^{-\beta\mathcal{E}}$ is large, for small T it is small. For $T \rightarrow 0$ no state is available anymore, except the one with the lowest,

---

[7] A closed, isolated ensemble with constant energy (volume, particle number, etc) is called a micro-canonical ensemble.

[8] M. Apostol, "A model for the thermodynamics of simple liquids", Physica **B403** 3946 (2008).