The Fundamental Concepts of Classical Equilibrium Statistical Mechanics

Sérgio B. Volchan

Abstract

A critical examination of some basic conceptual issues in classical statistical mechanics is attempted, with a view to understanding the origins, structure and status of that discipline. Due attention is given to the interplay between physical and mathematical aspects, particularly regarding the role of probability theory. The focus is on the equilibrium case, which is currently better understood, serving also as a prelude for a further discussion non-equilibrium statistical mechanics.

1 Introduction

It is a striking feature of the world that it has a multilevel structure. From subatomic particles to galaxies, there is a great variety of levels of reality, each with its own objects, properties and laws. The effort in dealing with such richness is reflected in the division of labor of the scientific enterprise, each discipline trying to map and understand some part of the complex whole.

Though the aforementioned levels are autonomous to a great extent, they are not totally independent. Therefore, once a reasonable understanding of phenomena at some of these levels is accomplished, there naturally arises the task of an interlevel investigation. It should address questions such as: how are levels organized with respect to each other, is there a natural hierarchy or structure of levels, how do new properties emerge from “lower” to “higher” levels, how can one explain higher levels in terms of the lower ones, etc? One could fairly say that the elucidation of the connections among levels of reality is a major test of the coherence of the scientific worldview and, besides functioning as a fine tuning for our theories, such a study not infrequently lead to new discoveries and further inquiries.

Now, one of the earliest and broadest level distinctions, of particular importance to physics, is that between the so-called macroscopic and microscopic levels. It

*Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Matemática, Rua Marquês de São Vicente 225, Gávea, 22453-900 Rio de Janeiro, Brasil volchan@mat.puc-rio.br
s, stems from the notion that, underlying the world of the visible and apparently homogeneous substances, there is a more “basic” reality consisting of a very large number of tiny invisible (and indivisible) discrete components. ¹

In principle, the microreality would be considered more basic in the sense that the directly observable phenomena would result from (or be explained by), the complicated motions and mutual arrangements of those components. This is essentially the “atomic hypothesis” (or atomism) which, together with mechanics and probability theory, are the main ingredients from which statistical mechanics emerged in the last half of the XIXᵗʰ century and the first decades of the XXᵗʰ, out of the efforts to provide a mechanical-atomistic foundation of thermodynamics.

Statistical mechanics can then be conceived of as a discipline (or, maybe, a set of techniques and prescriptions) whose aim is to serve as a bridge between the micro and macro levels. In its role as a level-connecting discipline, it acquired a peculiar flavor. So, in spite of having appeared in the somewhat narrow context of the study of gases, it is supposed to be very general to the point of being a sort of “super-theory”; for example it was instrumental in the advent of the quantum revolution, more specifically in Planck’s 1900 solution of the black-body radiation conundrum. Its ideas and techniques are frequently used (and sometimes abused) in such disparate areas as quantum field theory, turbulence, dynamical systems, image processing, neural networks, computational complexity theory, biology and finance. This is certainly linked to the pivotal role of probability theory, with its very general notions and theorems, in the framework of statistical mechanics.

Also, the mathematically rigorous analysis of specific statistical mechanical systems proposed in the physics literature turned out to be very difficult, even for some highly idealized models, like lattice gases. So statistical mechanics became also the battle ground par excellence for mathematical-physics, inspiring the creation of new concepts and techniques to deal with its problems. We think that statistical mechanics clearly illustrates the inestimable role of mathematical-physics in bringing precision and organization to a notoriously difficult subject. It is also interesting to witness once more how such rich, sophisticated and highly abstract mathematical machinery is needed even to formulate (not to mention solve) statistical mechanical problems on a rigorous basis. In any case, statistical mechanics has proven to be an indispensable and extremely rich tool of research in many-body physics, presenting many hard questions of physical, mathematical, conceptual, methodological and philosophical importance.

In this paper we intend to examine only a sample of issues in this already vast field, hoping to contribute to a better understanding of its role, structure and methods. We will focus mainly on fundamental concepts which seem to be at its core. Due attention is payed to the interplay between the physical-conceptual problems and the corresponding mathematical ideas, methods and theories used to formulate them in a rigorous fashion.

We will be mainly concerned with classical equilibrium statistical mechanics, leaving a discussion of the much more complicated (and more interesting) case of non-equilibrium statistical mechanics (whatever that might be) to another occasion. Although the two branches are historically and inextricably linked, the non-equilibrium case is, at the present stage of research, much less understood. Accordingly, a common research strategy has been to adapt some concepts from the former in trying to come to terms with the latter. ² In this sense, one can also say

¹More generally, it corresponds to the notion that a necessary aspect of any system is that it has components. [3]

²A case in point is the important (and delicate) notion of local equilibrium in non-equilibrium
that an acquaintance with the equilibrium situation might be a useful prerequisite to an understanding of non-equilibrium issues.

The paper is structured as follows. We first recall the main influences in the emergence of statistical mechanics and which strongly shaped its subsequent development. We then discuss with some detail the basic notions of the “ensemble” theory. Finally, we touch on the central and subtle topic of phase transitions, after which we make some concluding remarks.

2 Preliminaries

Without delving into the fascinating and rather convoluted history of the emergence of statistical mechanics, it is useful to summarize the main influences in its inception. This will provide a broader context that helps one grasp the sources of its main problems, aims and methods.

2.1 Thermodynamics

The first (and historically crucial) ingredient is of course, thermodynamics. In fact, the very idea of providing an atomistic-mechanical basis for it, can be taken as the point of departure of the statistical mechanical “program” (for example, in the guise of kinetic gas theory).

Thermodynamics, together with classical mechanics and electrodynamics, was one of the pillars of late nineteenth-century physics. It is an amazingly general phenomenological theory, concerning properties and processes of macroscopic systems (typically continuum media such as gases and fluids, but including reacting chemicals, magnetic systems, etc) regarding exchanges of heat, energy and matter. As such, it is an indispensable tool in many technological areas, particularly to engineering.

Notwithstanding the traditional textbook view of thermodynamics as a completed (and even stagnant) discipline, it is actually a very live research field, full of open problems and some ongoing controversies. In particular, one observes a sharp distinction of methodology and conceptual viewpoints between the rational-mechanics community and the mainstream physics community.

It was the unsatisfactory state of standard presentations of thermodynamics and the concomitant conceptual confusion, that has motivated the many attempts at a clarification of its foundations. Ideally, as suggested by David Hilbert, this con-statistical mechanics.

3 A history which is yet to be written. See however references 3, 12 and 16.

4 It is almost a scandal that one could complete a graduate program in theoretical physics without realizing the existence of such controversies and/or its modern developments.

5 We refer to the school led by W. Noll, the late C. Truesdell, J. Serrin and many others.

6 This curious (and unfortunate) lack of exchange between these research communities (and which deserved to be mended) would be an interesting case study in the sociology of science.

7 There is some similarity between the situation of the foundations of thermodynamics (particularly regarding its conceptual confusion), with that of quantum mechanics. So, thermodynamics had a rather influential but unsuccessful axiomatization in Carathéodory’s (1909) work, and the same can be said of von Neumann’s ill-fated axiomatization of quantum mechanics (1932). And, as it happened with the effort of clarification of thermodynamics, there has been recently an
ceptual elucidation should proceed through a careful axiomatization of the theory. At present, there is a variety of formulations, with different degrees of rigor and generality, but still no universal agreement. However, this does not mean the effort is worthless. Quite on the contrary, it signals that thermodynamics is a difficult and subtle discipline in need of conceptual clarification. A detailed critical review of the conceptual problems of thermodynamics is beyond the scope of this paper and in the following we limit ourselves to some general comments (see also ref. 51).

The usual presentations of thermodynamics discuss the three fundamental laws, starting from some basic concepts, say, of system, state and equilibrium. A thermodynamic system is characterized by its physico-chemical properties, like total mass and chemical composition, and also by a (real or hypothetical) boundary separating it from the environment with which it interacts. A system is closed when there is no exchange of matter, otherwise it is open. Usually the theory is formulated for closed ones. Also, a (closed) system is isolated when it does not interact with the exterior, i.e., there is no exchange of heat nor work is performed (it can be conceived of as a system enclosed by rigid adiabatic walls).

The thermodynamic state of the system is usually specified by a relatively small number of internal and external parameters (or state variables) (e.g., temperature, pressure, volume, internal energy and density for gases and fluids; magnetic field and magnetization for magnetic systems) that completely characterize the system in equilibrium. The equilibrium states of each system are completely determined by a set of independent parameters, say \( x_1, \ldots, x_n \), whose set of values constitute the \((n\text{-dimensional})\) state-space of the system. Any other parameter \( y \) is then given in terms of these by an equation state (or constitutive equation), \( y = f(x_1, \ldots, x_n) \). In particular, the quintessentially thermal parameter, temperature, characterizes equilibrium, which is the content of

- The Zeroth Law: a state of equilibrium exists; equality of temperature is a necessary condition for thermal equilibrium between two systems.

The simplest example of thermodynamic system is that of a one-component chemically inert homogeneous fluid (liquid or gas) in a container of volume \( V \) at temperature \( T \). Its state space could be taken as the two-dimensional set of points, say \((V, T)\), in the first quadrant. All other state variables can be obtained as functions of \((V, T)\) through the equation of state, for instance the pressure \( p = f(V, T) \). For example, for an ideal gas one has \( p = \frac{N k T}{V} \), where \( N \) is the number of molecules and \( k \) is Boltzmann’s constant; for the (non ideal) van der Waals gas \( p = \frac{N k T}{(V - b)} - a/V^2 \) (with suitable constants \( a \) and \( b \)).

The fundamental problem of classical thermodynamics might then be formulated as follows: given an isolated system in an initial equilibrium state, find the final equilibrium state to which the system relaxes, after some internal constraint had been lifted. Here, there is an implicit dynamical assumption (experimentally effort to reassess the foundations of quantum mechanics, for example, through a renewed version of the much neglected Bohmian approach.}

---

8The sixth problem in his famous list of 23 problems, proposed in 1900 at the Second International Congress of Mathematics in Paris, concerns the axiomatization of physical theories.

9In particular, if one intends to deduce thermodynamics from a more basic microscopic theory, it would be desirable to have a clear understanding and formalization of it.

10Which, in an axiomatic formulation, should figure among the primitive notions, that is, basic undefined concepts, a point is which rarely made explicit or even clearly discussed.

11Except, possibly, in the presence of phase transitions, see section 4.
supported), namely, that an isolated system, when left to itself, will eventually reach (“relax to”) an equilibrium state: this is the trend to equilibrium property. However, as there is as yet no reference whatsoever to a time parameter, the mention of dynamics at this stage seems to have only a motivational or heuristic purpose. In other words, classical thermodynamics would be concerned only with the outcome of the potentially very complex and violent happenings which the system experiences in its (time) evolution between the initial and final equilibrium states.

In any event, the First Law of Thermodynamics (Conservation of Energy) is then stated and taken to hold for any kind of thermodynamic “transformation” or “process”:

- The First Law: To every thermodynamic system there is associated a state variable, its internal energy $U$, such that in every infinitesimal transformation (“process”),

$$dU = dQ - dW,$$

where $dQ$ is the heat absorbed by the system and $dW$ the work performed by it (in particular, in an isolated system the internal energy is conserved).

Sometimes this is said to provide a definition of heat in terms of work, but if so, we would not be dealing with a law of nature but just a definition! In the usual formulations of thermodynamics, heat is a primitive concept, its inter-convertibility into work and internal energy being the crucial aspect of the first law.

While at this stage, a reference to “transformations” still does not cause much harm, things get increasingly confusing in the formulation of the Second Law, where the notions of reversible and irreversible processes explicitly appear.

- Second Law of Thermodynamics: There is a state variable, the entropy $S$, such that for reversible processes (in non-isolated systems), $dS = dQ/T$, where $T$ is the absolute temperature; in isolated systems, for irreversible processes, the entropy never decreases.

A dynamical aspect of the theory apparently enters the picture the moment the notion of “process” is mentioned. The trouble again is that, while by process one usually means a change of states in time, there is no explicit time parameter in the previous discussion: after all, one is dealing only with equilibrium states, which are supposedly time-independent. Besides, in real systems, for instance fluids, a change from an equilibrium state to another inevitably involves some (at least local) space and time inhomogeneity; therefore the basic quantities describing the system become time-dependent fields, so that during the process, the state space of the system is no longer a finite-dimensional manifold as before, but an infinite-dimensional one.

It is also not quite clear what is meant by a reversible process. In principle, it is a process that could be undone, that is, to which there is associated another process consisting in the reversed order of states in time. It seems that classical equilibrium thermodynamics deals only with these kind of processes which, on the other hand, are sometimes said not to be, strictly speaking, processes at all, but just “sequences of states of equilibrium”. Also, one usually depicts such “processes” as paths in state-space, supposed sufficiently smooth so that some path-integrals can be performed, and it would seem natural that these paths should be parametrized by time!

---

12 A similar mistake is sometimes made in some textbook presentation of newtonian mechanics, where Newton’s second law is said to provide definition of force, which is in fact a primitive concept there.
A common way out of this confusion is to say that reversible processes are only idealizations of real processes, which are always irreversible (in particular, not representable in general as smooth paths in state space). For heuristic purposes, so goes the argument, one can consider this idealization as a good approximation to real (time-dependent) processes in the limit of zero rates. These so-called “quasi-static processes” are conceived of as evolving through “infinitely slow and sufficiently small steps” in such a way that at each instant the system immediately relaxes to an equilibrium state. They are not only heuristic devices, however, but are crucial calculation tools. For example, to calculate the entropy change between two equilibrium states one imagines a reversible process connecting those same two states. But the feasibility, in principle, of this procedure, is rarely discussed: should it not either be proven or clearly taken as a hypothesis for each thermodynamic system (say, as a “state-accessibility” property)? In any case such notions are very rarely treated with the care they deserve. \(^{13}\)

It therefore seems that, as is the case with mechanics, a distinction should be clearly made between two branches of thermodynamics: classical equilibrium thermodynamics, which is really thermostatics, concerned only with equilibrium states and their properties (like stability, etc) and where time plays no fundamental role; this is what textbooks’ discussions of the three laws probably refer to. And general non-equilibrium thermodynamics, dealing with time-dependent phenomena including, but going beyond, equilibrium states \(^{14}\) and explicitly involving the concepts of time, processes and dynamics. That this is a much more complicated and less developed branch, and whether there is (or there could be) a unified treatment of it, are extremely important but separate issues.\(^{14}\)

Now, for a simple fluid, the First Law joined to the first part of the Second Law implies that for infinitesimal reversible processes the fundamental equation of equilibrium thermodynamics for homogeneous fluids (or Gibbs relation) reads:

$$dS = \frac{dU + p\,dV}{T}.$$  

One of the tasks of equilibrium statistical mechanics would be to somehow derive this fundamental macroscopic relation from microscopic principles. On the other hand, to study transport phenomena such as diffusion, viscous flow, conductivity, and also to (hopefully) elucidate the trend to equilibrium issue, one needs to enter the realm of out-of-equilibrium systems.

In sum, thermodynamics is an incredibly successful theory, in spite of having been marred by a long history of conceptual problems. It is an interesting, rich an live theory with many open problems. Still, it is a phenomenological theory (or of black-box kind) in the sense that there is no hint about the underlying mechanism that could explain the thermodynamic laws in terms of more basic (i.e., microscopic) constituents. The aim (or should one say dream?) of statistical mechanics is to provide a unified microscopic explanation of equilibrium and non-equilibrium thermodynamics. This leads us to the next ingredients in the formation of statistical mechanics.

\(^{13}\)A rare example of a clear-cut and mathematically precise treatment of such “quasi-static processes” (of course in the context of time-dependent changes of state, i.e., processes properly speaking) can be found in Ref. 38.

\(^{14}\)Which, by the way, should be obtained as special states, not only stationary (i.e., time-independent) but also such that temperature is uniform throughout the system. \(^{11}\).
2.2 Atomism, Mechanics, Kinetic Theory and Probability

Of the these ingredients, atomism was an ancient philosophical doctrine, while mechanics came to age at the scientific revolution, having attained its zenith in the developments of analytical mechanics during the mid-XIX\textsuperscript{th} century. As for kinetic theory, it is a kind of blending of these two previous ingredients plus the somewhat surprising role of probability, with the aim of providing a mechanical-atomistic explanation of the behavior of gases. Let us briefly discuss these contributions.

The atomic theory of matter, or atomism, is one of the most daring and fruitful ideas of the early Greek philosophers. \textsuperscript{15} Though totally speculative and qualitative in its origins, it turned out to be (at least in general lines) the accepted viewpoint of modern physics. Of course, we can only say that with the hindsight of 2500 years of enduring controversy and painstaking research. And, in fact, the actual atomic structure of matter is much more complicated than could have ever been conceived in the fifth century B.C.: first and foremost, atoms are not really indivisible, having a complex internal structure, the understanding of which demands mastering the sophisticated mathematical and conceptual apparatus of quantum mechanics and relativity theory.

In our “post-atomic” era, in which atoms can be photographed using electron-tunneling microscopes and even manipulated individually with the help of laser tweezers, their reality is an almost banal fact. Even so, it should not prevent us from appreciating the boldness and innovation of atomism. \textsuperscript{16} The very notion that observable properties of things could be explained through the complex arrangements of some hypothetical (invisible) discrete material entities was extremely controversial (to begin with, it was quite counterintuitive). \textsuperscript{17}

It is therefore not surprising that very soon after its proposal, the atomic theory had a rival, rather commonsensical, continuum theory (a byproduct of the stoic school), according to which the continuous substances provided the foundations for all natural phenomena, without the need of invoking invisible entities. \textsuperscript{18} We can already discern here the seeds of the future quarrel between the atomists and the so-called “energeticists” in the last half of the XIX\textsuperscript{th} century, over the existence of atoms. \textsuperscript{9} That controversy happened in the context of the then new kinetic theory of gases, greatly advanced by Maxwell and Boltzmann.

Kinetic theory is an attempt to use the atomic theory of matter and mechanics to explain the thermodynamic behavior of gases, being an early reductionistic program of physics. \textsuperscript{19} Starting with the pioneering paper by Clausius entitled “The kind of

\textsuperscript{15}Particularly associated to Democritus of Abdera, fifth century B.C. and also to some ancient Hindu sources.

\textsuperscript{16}In R. P. Feynman’s eloquent words \textsuperscript{19}: “If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis...or atomic fact...”

\textsuperscript{17}Today, however, we recognize the procedure of postulating the existence of some material invisible entities in order to explain complex phenomena, as one of the hall-marks of modern science. Of course, with the crucial proviso that the hypothesized entities should not be inscrutable, having in each case to be subjected to careful experimental (even if very indirect) testability.

\textsuperscript{18}This idea would find its modern counterpart in the various field theories of physics, like continuum mechanics, hydrodynamics, electromagnetism, etc. Incidentally, as in any deep theory, these ones contain plenty of “unobservables”. \textsuperscript{4}

\textsuperscript{19}Note the prominent status and role of mechanics, even at a time when the field theories of
motion we call heat” (1857), gases were pictured as being made of a huge number microscopic particles or molecules (of the order of $2.7 \cdot 10^{19}$ per cubic centimeter at 1 atm and $0^\circ$C). In the simplest model, the particles are taken as tiny rigid balls (of size of the order $10^{-8}$ cm), interacting according to the laws of classical mechanics, namely, through elastic collisions. These collisions would somehow provide the basis for an explanation of macroscopic phenomena; for instance, the pressure of a gas would be the result of the collisions of particles with the container walls. In this way one would ultimately be able to explain the laws of thermodynamics, providing a “the mechanical theory of heat”.

This program had some startling initial successes in the work of Maxwell (for example, his prediction that fluid viscosity is independent of density, for low-density fluids). It was further developed by Boltzmann, amid a growing resistance from the anti-atomists. Particularly important was the proposal of the Maxwell-Boltzmann transport equation describing the time evolution of the distribution function $f(r, v, t)$, where $f(r, v, t) \, d^3r \, d^3v$ is interpreted as the number of gas particles in the volume $d^3r \, d^3v$ around $r$ and $v$ at the time $t$. Namely:

$$\frac{\partial f(r, v, t)}{\partial t} + v \cdot \nabla f(r, v, t) = Q(f, f),$$

where the right-hand term (the so-called collision term) summarizes the effects of collisions.

This is probably the very first (integro-) differential equation for the time-evolution of a probability density (after normalization). This equation was “deduced” by Boltzmann, for the case of dilute gases, from heuristic considerations of binary particle collisions, plus some additional hypothesis on the initial conditions (the famous “molecular chaos hypothesis”). From this equation Boltzmann obtained his startling “H-theorem”, which seemed to provide for the first time a derivation of the relaxation of a gas to equilibrium. This, however, attracted sharp criticisms and generated a lot of controversy, particularly in connection to the so-called “irreversibility problem/paradox”.

Without entering into a detailed discussion of such issues, to which we intend return in another occasion (in the the context of non-equilibrium problems), we observe a very important novelty: the introduction (others would say intrusion) of probabilistic considerations into mechanical problems.

One should bear in mind that, although probability was by then a somewhat familiar topic, it nonetheless had a very confusing status. Some people thought it was part of physics, others that it just consisted of some set of guiding rules for “reasoning under uncertainty” or gambling, and yet others thought that it provided general principles for organizing large chunks of data (with the emergence of the fields of statistics, insurance and demography).

Probabilistic concepts had undergone great developments since its beginnings in 1654, in the famous correspondence of Pascal and Fermat on the division of stakes in physics, in particular electromagnetism, were gaining acceptance. The weight of the mechanistic viewpoint is clearly seen by the fact that Maxwell himself tried to interpret the electromagnetic fields as mechanical vibrations of an hypothetical ether.

---

20 As mentioned before, one has to remember that at that time the existence of atoms was far from being universally accepted. It was Einstein’s 1905 work on Brownian motion (using statistical mechanical ideas!) which finally settled the issue.

21 In the ensuing debate, among other things, Boltzmann proposed his famous ergodic hypothesis.
games of chance. A great impetus came from the need to understand the statistical regularities observed in certain “random” phenomena involving a large number of trials (or repetitions) of similar occurrences. For example, the stabilization of the relative frequency of heads in coin-tossing games (a manifestation of the Law of Large Numbers) and the ubiquity of the normal (or Gaussian) distribution (connected to the Central Limit Theorem), ranging from the errors in astronomical measurements through the height of conscripts in the military. 22. However, probability was not as yet a theory proper, but rather a collection of more or less general results.

It was only in 1933 that it finally reached maturity with the axiomatization provided by A. N. Kolmogorov 23 in his classical treatise, 26 which greatly helped in clarifying its nature. In the first place it became clear, once and for all, that probability theory, like geometry and analysis, is a branch of pure mathematics, not of physics. As such, it has many possible models (in the set-theoretic sense, i.e., examples or realizations in mathematics) and many different interpretations in applications to the factual sciences. 6 In particular, one need not be ab initio committed to any given interpretation, be it subjectivistic (as degrees of belief), frequentist (stabilization of frequencies of repeated trials), the propensity view or any other. As a matter of fact, once the formal structure of the theory have been elucidated, the adequacy of any suggested interpretation, vis-a-vis some intended application, could be better examined, criticized and justified.

The great insight of Kolmogorov was to notice that, besides the standard “elementary” probability theory, that is, that part dealing with discrete arrangements of many objects (usually under the hypothesis of equal probability) and which essentially reduces to (usually very intricate) combinatorics, there is a more general part which included some well-known classical cases involving so-called continuous distributions. He noticed that the adequate unifying framework would be provided by the then recently created measure theory. 7 That is the theory proposed in Henri Lebesgue’s 1905 doctorate thesis, which is a generalization of the concepts of length, area and volume. 24

We next describe the main ideas in the precise formulation of the statistical mechanics program.

## 3 Equilibrium Statistical Mechanics

Statistical mechanics main aim is to deduce the “collective”, “emergent” or “macroscopic” behavior of a system composed of a large number of microscopic interacting

---

22Interestingly, the discovery of such statistical regularities in social affairs, such as demography, seemed to corroborate Adolphe Quetelet’s program of a “social physics”, and, apparently, these ideas percolated into the physical sciences, being one of the few occasions when the mutual influence was in this direction. 50

23There was some previous proposals, but none has got such immediate and universal acceptance from the mathematical community as Kolmogorov’s.

24This theory is the culmination of some internal developments in classical mathematical analysis, linked to the clarification of the notion of function, Fourier series and integration theory. In particular it gave an extension of the Riemann integral, having many desirable properties. Specifically, it allows, under very general conditions, to take limits inside the integral sign, for sequences of functions, as in the classical monotone convergence theorem and dominated convergence theorem. In its general abstract version, measure theory strongly influenced virtually all branches of mathematics.
particles. We note that there is nothing mysterious regarding emergent properties: these are just properties of the system which the individual components lack, e.g., temperature for a particle system.

The main idea is that, in equilibrium, the microscopic dynamical details are not important or relevant, and the macroscopic properties appear as certain averages with respect to a suitable family of probability measures on phase-space: the so-called ensembles. Here, a crucial link with statistics is the fact that one is dealing with systems consisting of an extremely large number of microscopic components.

3.1 The Microscopic Model

In classical statistical mechanics the microscopic model of a fluid in a container consists of \( N \) identical and structureless (point) particles with mass \( m \), located in a subset \( \Lambda \subseteq \mathbb{R}^3 \) and evolving according to the laws of classical mechanics. \(^{25}\)

Though admittedly a caricature of microphysics, this model is still more realistic than the one provided by lattice models, at least for fluids. In fact, lattice systems are highly idealized pictures of microphysics, more appropriate for describing crystalline systems, where the atomic motions are so restricted that it is a good approximation to suppose that they can only occupy the sites of a lattice. Moreover, in contrast to the Hamiltonian dynamics of classical mechanical particles, lattice systems don’t have a natural dynamics, which is usually imposed in an ad hoc fashion (and usually taken to be intrinsically stochastic). \(^{26}\)

That said, one has to recognize that most of our detailed knowledge of statistical mechanics comes from the study of lattice systems, which is one of the greatest achievements of modern mathematical-physics. It is a huge research field, with a long history of successes, based on a rigorous analysis of diverse idealized models. Moreover, it is a fundamental source (as well as a test field) of a variety of ideas and concepts which are at the core of our understanding of statistical mechanics. \(^{32},^{22},^{49}\)

Ultimately, of course, a physically realistic model should begin from a quantum mechanical formulation (say, non-relativistic) for the basic atomic-molecular model. However, for historical reasons (i.e., kinetic theory) some of the first rigorous results were achieved within the classical framework, even within the rigid ball model. Far from trivial, it is nonetheless somewhat simpler and surprisingly adequate. \(^{10}\) As J. Lebowitz remarked \(^{29}\)

Why this crude classical picture (a refined version of that held by some ancient Greek philosophers) gives predictions that are not only qualitatively but in many cases also highly accurate, is certainly far from clear to me...

In the chosen model, the microstate of the system consists of the positions and momenta of all particles, that is, of a point \( \omega = (\mathbf{q}, \mathbf{p}) = (\mathbf{q}_1, \mathbf{p}_1, \ldots, \mathbf{q}_N, \mathbf{p}_N) \) in the system’s phase-space (or state-space) \( \Omega_{N,\Lambda} = (\Lambda \times \mathbb{R}^d)^N \).

\(^{25}\)In the somewhat misleading jargon of statistical mechanics, these models are referred to as “continuous” models, as they allow particles to move in the space continuum \( \mathbb{R}^3 \), in contrast with “discrete” lattice-gas models, in which particles can only occupy the discrete sites of a lattice. Of course, both are discrete models of the microworld, in line with the atomistic viewpoint.

\(^{26}\)This would not be too problematic, however, as long as one is dealing with equilibrium statistical mechanics which, as we will see, ignores the details of dynamics. This seems to justify some kind of “model-independence” of the results of statistical mechanics which in turn would further justify the study of idealized models.
Suppose, for simplicity, that \( \Lambda = \mathbb{R}^3 \). The time-evolution (or dynamics) of the system is given by Hamilton’s equations:

\[
\begin{align*}
\frac{dq_i(t)}{dt} &= -\frac{\partial H(q(t), p(t))}{\partial p_i(t)} \\
\frac{dp_i(t)}{dt} &= -\frac{\partial H(q(t), p(t))}{\partial q_i(t)},
\end{align*}
\]

(1)

plus the initial data \((q(0), p(0)) = (q_0, p_0)\) (for convenience, we took \(t_0 = 0\)).

Here, the Hamiltonian (or total energy) \( H(\omega) = H_{N,\Lambda}(\omega) \) of the system is a real-valued function on phase-space given by

\[
H(q, p) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} \varphi(|q_i - q_j|),
\]

where \( m > 0 \) is the mass of each particle and \( \varphi(\cdot) \) is a central pair-potential interaction energy.

If \( \varphi \) is sufficiently smooth (say, twice continuously differentiable), and short-ranged, then standard ordinary differential equations theory guarantees the existence and uniqueness of local solutions. That is, functions \( p(t) = p(q_0, p_0; t), q(t) = q(q_0, p_0; t) \), defined for some finite open time interval \( a < t < b \), which are differentiable functions of the initial data \((q_0, p_0)\) and of time, satisfying equations (1). Moreover, the solution can be extended to a global one, i.e., for \(-\infty < t < +\infty\). It thus defines a trajectory or orbit (i.e., a smooth curve) in phase-space.

So, for each \( t \in \mathbb{R} \) one defines a dynamical flow \( T_t \), taking each initial data \((q, p)\) to its \( t \)-evolved image under the dynamics,

\[
T_t : \mathbb{R}^{3N} \times \mathbb{R}^{3N} \mapsto \mathbb{R}^{3N} \times \mathbb{R}^{3N} \quad (q, p) \mapsto (q(t), p(t)) = T_t(q, p),
\]

(2)

the set \( \{T_t : t \in \mathbb{R}\} \) being a one-parameter group of transformations, i.e.

\[
\begin{align*}
T_0 &= 1 \\
T_t.T_s &= T_{t+s} \\
T_t^{-1} &= T_{-t}
\end{align*}
\]

(3)

As is well known, Hamiltonian flows (even local ones) have the following two fundamental properties:

---

27 That the initial data are an integral part of the dynamical description of a mechanical system, though a trivial observation, is useful bearing in mind, particularly regarding the question of reversibility in kinetic theory.

28 We will consider only this class of separable Hamiltonians, that is, for which the momenta and position variables are segregated in different terms. More general non-separable Hamiltonians can be very important; for example in the two-dimensional vortex model in fluid dynamics one deals with the non-separable Hamiltonian

\[
H(p, q) = -\frac{1}{8\pi} \sum_{i,j=1, i \neq j}^{N} a_i a_j \ln[(q_i - q_j)^2 + (\frac{p_i}{a_i} - \frac{p_j}{a_j})^2],
\]

where the \( a_j \)'s are some parameters.
1. Energy is an integral of motion: for all $t$,

$$H(T_t(q, p)) = H(q, p);$$

2. Liouville’s theorem: Lebesgue measure (volume) $\lambda_N$ on phase-space is invariant, i.e., for every measurable set $A$, and for all $t$

$$\lambda_N(T_t^{-1}A) = \lambda_N(A),$$

where

$$\lambda_N(A) \equiv \int_A \Pi_{i=1}^N d^3q_i \, d^3p_i.$$

Liouville’s theorem is an extremely important fact: it says that there is a natural invariant measure around, namely Lebesgue measure on phase space, which is crucial to the ensemble theory. Energy conservation implies that the orbits are restricted to the energy surface defined by $H(q, p) = E$, where $E$ is the initial energy of the system.\textsuperscript{29}

The basic dynamical issues can be more involved in the case of singular potentials (e.g., in celestial mechanics), where even global existence of the flow is not warranted due, for example, to so-called collision singularities. However, for gases one typically works with the Lennard-Jones potential, a semi-empirical potential of the form

$$\varphi(r) = \varphi_0 \left[ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right],$$

with strength $\varphi_0$ ($r_0$ is the point of minimum of the potential). This is a popular choice of potential giving a qualitatively realistic description of molecular interaction for inert gases: strong short range repulsion and weak long range attraction. Being bounded from below, there is no catastrophic collision singularities. Alternatively, one can work with hard-spheres which move freely and interact only through elastic collisions. An additional complication is the confinement issue, namely that particles are supposed to be restricted to a bounded region (container) $\Lambda \subset \mathbb{R}^3$.

Though a bit harder to establish, the main properties of the flow can be obtained for those cases also. The details, though very important for the dynamical foundations of statistical mechanics, are not so relevant to the ensemble theory of equilibrium statistical mechanics, which is the focus of this paper. As we will see, in this context the dynamics is, so to speak, swept under the rug, once the ensembles are identified to certain invariant probability measures on phase-space.

### 3.2 The ensembles

One might at first get the impression that there is a kind of built-in duality in the foundations of classical statistical mechanics, reflected in its very name, which juxtaposes two apparently antithetical concepts: mechanics and probability (or statistics). That is, though starting from a microscopic system of interacting newtonian particles, there soon appears, as if by fiat, a statistical or probabilistic ingredient, which is supposedly alien from the classical world.

\textsuperscript{29}If there are additional conserved quantities, the motion is of course restricted to the intersection of the corresponding surfaces. We observe that if the energy surface is a compact set the existence of an invariant measure for the dynamics follows from Krylov-Bogolyubov’s theorem.
The justification of that situation begins with the standard operational argument: it is impossible to know the microstate of such huge particle systems (as one cannot, in practice, simultaneously measure each and every particle’s position and momentum); moreover, so the argument goes, even if the microstate were accurately known, it would be hopeless to solve a system of the order of \(10^{23}\) differential equations. In sum, one has to use other means to study such systems and that is where statistics comes to the rescue.\(^{30}\)

Although it has a grain of truth, this rationale is somewhat confusing and has to be qualified in many respects. First of all, it mixes theoretical, epistemological and even methodological concepts, which should be kept separated. For example, our inability to measure the initial data with infinite precision is certainly an unavoidable fact, having very important methodological consequences bearing on the experimental analysis of models and the limits on predictability (for example, in meteorological systems and chaotic dynamical systems). However, such issues do not refer to the physical system the equations are supposed to model, which doesn’t care about human limitations. Besides, imprecision in measurement happens even for systems of few particles, so it is not intrinsically linked to the large numbers involved in statistical mechanics.

As for the “solvability” issue of the dynamical equations (although not that important for equilibrium statistical mechanics), similar observations could be made: the solvability of equations is an important mathematical (not physical) question. But in order to state it correctly, one has to carefully and rigorously explain what it means to solve or “integrate” a certain system of differential equations (for example, a series solution qualifies or not?). Once in possession of such a notion and also of a way to survey the collection of all differential equations of a given kind (e.g., with the aid of a topological notion of size), one can then proceed to examine whether “most” of the equations are solvable, or whether a particular one is.\(^{31}\)

Furthermore, the claim that it is hopeless to solve a huge system of equations is not correct in all generality and depends on the integrability properties of the system. So, for example, a Hamiltonian system consisting of an arbitrary number of harmonic oscillators is perfectly solvable and one can write down the solutions explicitly.\(^{32}\)

It is frequently stated that while microscopic systems are very “complex” (by which it is usually meant having a great number of degrees of freedom), macroscopic systems are much simpler, being described by very few variables and equations. This drastic “decimation” of degrees of freedom, characterizing the passage from the microscopic to the macroscopic description, suggests the use of an averaging procedure, and hence of statistics. This viewpoint is much more sensible, focusing as it does on the role of statistics as a level-bridging ingredient, connecting the micro and macro realities.

---

\(^{30}\)This kind of argument seems to have been borrowed from the highly influential operational philosophy of standard quantum mechanics. It is also to blame for conveying the misleading idea that the microstate of the (classical) system is a probability measure instead of a point in phase space.

\(^{31}\)An illuminating example is the three-body problem in celestial mechanics: it is non-integrable (i.e., cannot be algebraically solved), though it has a convergent series solution (hence an analytic solution) whose rate of convergence is too slow to be useful to understand the long-time behavior of the system!\(^{13}\)

\(^{32}\)Another, less trivial, example is the Toda lattice system which, though highly non-linear, is completely integrable.
We remark, however, that while some macroscopic systems (for example, homogeneous fluids) do have a relatively simple description in equilibrium, they can be extremely complicated in the non-equilibrium case, as testified by the (poorly understood) phenomena of turbulence. There, the motion is described by time-dependent fields, that is, infinite-dimensional vectors, so that the decimation mentioned above is illusory. Moreover, such fields satisfy certain non-linear partial differential equations which are, at present, beyond mathematical tractability.

3.2.1 The Boltzmann-Gibbs Principle

It was Boltzmann who gave the clearest view of the situation of statistical mechanics, while struggling to answer the criticisms of his results on kinetic theory. His insight begins with the following simple but crucial observation: let $F$ be a “physically relevant” state-function, that is, a function $F : \Omega_{\Lambda,N} \rightarrow \mathbb{R}$ on phase-space to which there is a corresponding macroscopic variable (typical examples are the ones associated with the conservation laws, like energy and momentum). Let $F$ be a given equilibrium value of that macroscopic variable. Now, there are usually very many different microscopic states $\omega \in \Omega_{\Lambda,N}$ compatible with the given macroscopic value. For example, there are many different microstates associated with the same value of total energy. It then makes sense to consider the subset $\Gamma_F = \{ \omega \in \Omega_{\Lambda,N} : F = F(\omega) \}$ of phase-space, consisting of all those microstates, as they are the ones putatively relevant to the micro-macro change of description.

It is then quite natural to ask oneself about the relative “sizes” of such subsets with respect to the whole phase-space, in order, for example, to assess their “relevance” as compared to any other subset. One possible notion of size is the relative volume in phase space, as defined by the Lebesgue measure which, by Liouville’s theorem, is invariant under the dynamics. In this way one focuses in the “fraction” of states in phase-space corresponding (or relevant) to the given value of the associated macrovariable. This amounts to nothing more than “counting” phase-space points, that is, a sort of (continuous) “combinatorial” estimate of certain subsets, using relative volume as the yardstick.

As such, there is no “chance mechanism” involved here, no more than when comparing volumes of geometrical figures. Nor is necessarily involved any notion of “choosing states at random” or of “ignorance” about the state of the system. Now, in the case of a compact phase-space, its total volume being finite, one can normalize the Lebesgue measure and we end up with a probability measure $P$ on phase-space (or on the energy surface); hence all the relevant techniques and results of probability theory apply.

Boltzmann and Gibbs then made a bold hypothesis: they proposed as the fundamental postulate of equilibrium statistical mechanics that, for any physically relevant state-function $F : \Omega_{\Lambda,N} \rightarrow \mathbb{R}$, the corresponding macroscopic equilibrium value is given by its expected (or mean) value) with respect to a suitable invariant probability measure $P$.

---

33 Note also that similar qualms could be raised here regarding “practical measurability” of the precise state of the fluid: the situation is even worse because fields, being an infinite component vectors, cannot be measured completely not only in practice but in principle. However this never prevented the study of fluid dynamics.

34 See, for example, the Clay Mathematical Institute’s million dollars prize for a proof of existence and smoothness for the Navier-Stokes equation.
bility measure $\mathbf{P}$ on phase-space, i.e.,

$$ F = \langle F \rangle_{\mathbf{P}} = \int_{\Omega_{\Lambda,N}} F(\omega) \mathbf{P}(d\omega), $$

at least when the number of particles $N \to +\infty$ (more on that later).

Each such $\mathbf{P}$ is a member of a so-called ensemble. We emphasize that the procedure of taking averages is not necessarily linked to any random mechanism: it might just mean that details are unimportant.

Of course, such a principle requires many clarifications and raises many questions. Which are the “suitable” probability measures and why? Are they unique? Which are the (class of) relevant state-variables? What does the limit $N \to \infty$ mean?

Let us begin with some nomenclature. As we have seen, from the viewpoint of modern mathematical-physics, an ensemble is just a family $\mathcal{E}$ of invariant probability measures on phase space. More precisely, each $\mathbf{P} \in \mathcal{E}$ is indexed by some macroscopic (thermodynamic) parameters (e.g., volume, energy), adequate to describe the physical situation of the (equilibrium) system under study. An ensemble element is sometimes referred to as a “statistical state” of the system, which probably means that such measures are to be identified with the macrostates of the system. We submit that this is misleading and should be avoided: as discussed before, the microscopic state is a point of phase-space while the macroscopic state, for example, of a homogeneous fluid is, say, a pair of temperature and pressure values. So neither the macroscopic nor the microscopic state are measures. So, what is the status of such measures? As each member of an ensemble refers to both the microscopic level (being a probability measure on phase-space) and to the macroscopic level (being indexed by the relevant macroscopic state-parameters), it can be viewed as the fundamental level-linking concept establishing the connection of the micro to the macro descriptions.

The requirement of invariance of the probability measures seems quite natural when dealing with systems in equilibrium; and as will be apparent, in equilibrium statistical mechanics, once an ensemble is chosen, the microscopic dynamical details are essentially forgotten in all the subsequent calculations of thermodynamic quantities. The microscopic interactions are, of course, fundamental as will be testified by the crucial role played by the potential in the following.

By Liouville’s theorem, one obvious choice of invariant measure is the Lebesgue measure (that is, volume) in phase-space. But, of course one could ask why not choose another invariant measure, if any? And, more importantly, is there a microscopic dynamical justification of the Boltzmann-Gibbs postulate? What would it be like? Those are perhaps the most difficult foundational questions of statistical mechanics and which necessarily bear on a deeper level of analysis, namely on non-equilibrium statistical mechanics. In spite of some advances, this is still an essentially open question. Hence, a more “pragmatic” justification of the postulate (besides its coherence) is that it works fine in many physical applications, so that it is vindicated by its very success.

Notice that, though in probability theory one usually begins with a probability measure and then proceeds to define the expectation or average, one could take the opposite path; that is (in case the sample space is compact Hausdorff space), beginning with a non-negative linear functional $\langle \cdot \rangle$ on continuous functions, it can be proved that there is a probability measure that represents this functional: this is the Riesz-Markov representation theorem.
Concerning the actual form of the postulate, notice that besides the total particle number $N$ and total volume $V = |\Lambda|$, some other physically relevant state-variables are:

- density (and specific volume): $\rho = \frac{N}{V} = \frac{1}{v}$;
- total kinetic energy: $K(\omega) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$;
- total potential energy: $\Phi(\omega) = \sum_{i<j} |q_i - q_j|$;
- total energy: $H(\omega) = K(\omega) + \Phi(\omega)$;
- momentum change (impulse) per unit time and per unit surface area transferred to container walls by collisions of particles when in state $\omega$: $P(\omega)$.

So, according to the Boltzmann-Gibbs postulate, for a given $P \in E$, the corresponding macroscopic variables (at the parameter values associated to $P$) are given by the mean values,

- mean density: $\rho = \langle \rho \rangle_P = \int_{\Omega_{\Lambda,N}} \rho P(d\omega) = \frac{N}{V}$;
- mean kinetic energy $K = \langle K \rangle_P = \int_{\Omega_{\Lambda,N}} K(\omega) P(d\omega)$;
- mean potential energy $\Phi = \langle \Phi \rangle_P = \int_{\Omega_{\Lambda,N}} \Phi(\omega) P(d\omega)$;
- mean total energy: $U = \langle H \rangle_P = \int_{\Omega_{\Lambda,N}} H(\omega) P(d\omega)$;
- mean pressure: $p = \langle P \rangle_P = \int_{\Omega_{\Lambda,N}} P(\omega) P(d\omega)$.

Note that these quantities are in general functions of $N$, $\Lambda$ and other parameters indexing the ensemble measures.

A crucial property required of an ensemble is that it correctly describes the equilibrium thermodynamics of the system. In the case of homogeneous fluids, this can be made precise by the following definition:

**Definition 3.1.** An ensemble is called orthodic if taking an infinitesimal change in the parameters indexing each of its elements, the corresponding variations of the macroscopic variables $U$, $p$, $V$ and $T$ defined above, are such that

$$\frac{dU + p \, dV}{T}$$

is an exact differential, at least when $N \to +\infty$, $V \to \infty$ with $\frac{N}{V} \to$ constant. Here $T = \frac{2}{3k} \kappa$, where $k$ is Boltzmann’s and $\kappa$ the mean kinetic energy density.
Orthodicity is a natural requirement. In fact, for such an ensemble, the macroscopic variables can be identified to the familiar thermodynamic variables satisfying the known thermodynamical relations; so in particular, the absolute temperature \( T \) would be interpreted as average kinetic energy per particle. Moreover, orthodicity guarantees that there is a function \( S \) of the macroscopic state variables (say, of \((p, V)\) or \((U, V)\)), which can be interpreted as the thermodynamic entropy of the system. This function is such that the fundamental equation of classical equilibrium thermodynamics (for homogeneous fluids), namely Gibbs relation,

\[
dS = \frac{dU + p dV}{T},
\]

is satisfied.

Summarizing, the fundamental postulate of equilibrium statistical mechanics, the so-called *Boltzmann-Gibbs Principle*, is the claim that the equilibrium thermodynamics of a (simple fluid) system is described (in the sense just discussed) by an orthodic ensemble.

Let us recall the three main classes of ensembles: *microcanonical*, *canonical* and *grand-canonical*.

### 3.2.2 The Microcanonical Ensemble

The microcanonical ensemble is the one suitable for isolated systems. The phase-space is reduced to the *energy surface*: \( \Omega_{\Lambda,N,U} = \{ \omega \in \Omega_{\Lambda,N} : H(\omega) = U \} \), which is a compact set (if the potential is bounded from below), invariant under the dynamics.

The corresponding invariant measure on \( \Omega_{\Lambda,N,U} \) cannot simply be the full phase-space volume measure, because the energy surface (being a set of codimension one) has Lebesgue measure zero. The alternative is to use the “Lebesgue measure cut to the energy surface”, \([25]\) defined as follows.

First, let us assume that the phase-space is “symmetrized”, that is, we identify any two microstates which differ by a permutation of particles (in other words, consider the identical particles to be indistinguishable). Then, if \( \nabla H(\omega) \) is non-zero on the energy surface, for any measurable set \( A \) on the surface the following limit exists: \([25]\)

\[
\nu_{\Lambda,N,U}(A) \equiv \lim_{\Delta U \to 0} \frac{1}{\Delta U} \int_{A \cap J_U} \frac{1}{N!} d\lambda_N = \frac{1}{N!} \int_A \frac{d\sigma(x_U)}{\| \nabla H(x_U) \|}.
\]

where \( J_U = \{ \omega \in \Omega_{\Lambda,N} : U \leq H(\omega) \leq U + \Delta U \} \) and \( \sigma(\cdot) \) is the area measure on the energy surface. Moreover, being a limit of invariant measures, the measure \( \nu_{\Lambda,N,U} \) is also invariant (the factor \( N! \) accounts for the symmetrization of Lebesgue measure \([36]\)).

\[\text{36} \]Strictly speaking, let \( \pi : (\Lambda \times \mathbb{R}^3)^N \to \Omega_{\Lambda,N} \) be the natural projection taking each ordered point \((q, p)\) to the corresponding unordered one, namely \( \pi(q, p) = \{q, p\} \). So, if \( \lambda_N \) is the usual Lebesgue-measure on (the \( \sigma \)-algebra of) \((\Lambda \times \mathbb{R}^3)^N\), the corresponding symmetrized Lebesgue-measure \( \lambda \) on \( \Omega_{\Lambda,N} \) is defined by \( \lambda_N(A) = \frac{1}{N!} \lambda_N(A) \), for any \( A \) in the corresponding \( \sigma \)-algebra \( \mathcal{M}_{\Lambda,N} \). This is usually shortened by writing \( d\lambda_N = \frac{1}{N!} d\lambda_N \). Note that the Hamiltonian is symmetric under permutation so that it is in fact a function of the unordered pair \( \{q, p\} \).
Then, by definition, the microcanonical ensemble is the family of invariant probability measures \( P_{\Lambda,N,U}^{mc} \), parametrized by \( \Lambda, N \) and \( U \), such that, for any measurable set \( A \subset \Omega_{\Lambda,N,U} \),

\[
P_{\Lambda,N,U}^{mc}(A) = \frac{\nu_{\Lambda,N,U}(A)}{Z_{\Lambda,N,U}},
\]

where the normalization factor

\[
Z_{\Lambda,N,U} = \nu_{\Lambda,N,U}(\Omega_{\Lambda,N,U}),
\]

is called the microcanonical partition function. The partition function is just the total \( \nu \)-measure of the new phase-space \( \Omega_{\Lambda,N,U} \), and it can be viewed as a (continuous) “counting” of all available microstates of the system. \(^{37}\)

The microcanonical ensemble is orthodic in the thermodynamic limit which is a kind of “infinite-volume limit” of the system. At this stage, this limit appears to be a technical question only, and we will discuss some of its physical justifications in the next section. Let us, however, describe the main aspects involved in its procedure.

First, one considers an increasing and sufficiently regular space-filling sequence of regions \(^{38}\) \( \{ \Lambda_i \}_{i \geq 1} \), that is \( \Lambda_i \subset \Lambda_{i+1} \) and \( \cup_{i \geq 1} \Lambda_i = \mathbb{R}^3 \) (this is indicated by writing \( \Lambda \uparrow \mathbb{R}^3 \)). At the same time, let \( \{ N_i \}_{i \geq 1} \) and \( \{ U_i \}_{i \geq 1} \) be increasing sequences of energies and particle numbers, respectively, such that \( v_i = V_i/N_i \to v = 1/\rho \) and \( u_i = U_i/N_i \to u, \) as \( i \to \infty \). Then, the following limit exists: \(^{20,34}\)

\[
s(u,v) = \lim_{\Lambda \uparrow \mathbb{R}^3, \nu \to u, \frac{V}{N} \to v} \frac{1}{N} k \ln Z_{\Lambda,N,U},
\]

where \( k \) is Boltzmann’s constant.

Notice Boltzmann’s famous formula for thermodynamic entropy as proportional to the logarithm of the “number” of microstates: \( S(U,V) = k \ln Z_{\Lambda,N,U} \), so \( s(u,v) \) is naturally interpreted as the entropy density (or specific entropy).

Moreover, the function \( s(u,v) \) satisfies Gibbs’ relation:

\[
ds = \frac{du + p dv}{T}.
\]

Here, \( T = \frac{2}{3k} \kappa \), where \( \kappa \) is the limit microcanonical average kinetic energy density,

\[
\kappa(u,v) = \lim_{\Lambda \uparrow \mathbb{R}^3, \nu \to u, \frac{V}{N} \to v} \frac{K}{N} >_{\Lambda,N,U}^{mc} = \lim_{\Lambda \uparrow \mathbb{R}^3, \nu \to u, \frac{V}{N} \to v} \frac{1}{N} \sum_{i=1}^{N} \frac{p_i^2}{2m} >_{\Lambda,N,U}^{mc}.
\]

Note that this is a kind of (weak) “law of large numbers”, as one is calculating an asymptotic (“large \( N \)” ) limit of sums of random variables, in this case, the particle’s kinetic energy \( p_i^2/2m \). \(^{39}\)

\(^{37}\)Its original german name is Zustandsumme or “sum over states”.

\(^{38}\)Boxes will do, but very general shapes are possible, as long as the rate of increase of surface area to volume ratio is suitably controlled.

\(^{39}\)Unfortunately the situation is much more complicated than the classical laws of large numbers, which usually pressuposes independence. Here, due to various constraints on the motion, one cannot expect the random variables to be independent.
We also have the limit average pressure,
\[ p = p(u, v) = \lim_{\Lambda \to \mathbb{R}^3, \frac{\Lambda}{|\Lambda|} \to u, \frac{\Lambda}{|\Lambda|} \to v} \mathcal{P}^{\text{inc}}_{\Lambda, N, U}. \]

So, if \( T = T(u, v) \) is interpreted as the absolute temperature and \( s(u, v) \) as the specific entropy, then (assuming differentiability) as \( ds = \frac{\partial s}{\partial u} du + \frac{\partial s}{\partial v} dv \), it follows that \( \frac{\partial s}{\partial u}(u, v) = \frac{1}{T(u, v)} \) and \( \frac{\partial s}{\partial v}(u, v) = \frac{p(u, v)}{T(u, v)} \). By eliminating \( u \) in these relation, one could obtain the equation of state of the fluid: \( p = f(T, \rho) \) (in principle at least, though by no means a trivial task in practice \([20, 21, 43]\)).

We observe that there are two separate issues involved here: orthodicity and the thermodynamic limit. It turns out that for the microcanonical ensemble orthodicity only holds in the thermodynamic limit, \([20]\) which is then a prior issue. In fact, the most difficult part of the above results is the proof of the existence of the limit \( s(u, v) \), in terms of which the other limit quantities can be expressed. For this reason the question of existence of this limit is sometimes referred to as the problem of the thermodynamic limit at the thermodynamical quantities level.

As would be expected, the existence proof of such limit will necessarily require some hypothesis on the interaction potential \( \varphi(\cdot) \). We see here an interesting interplay (even if coming out of an apparently purely technical issue), of the micro-macro change of description: for the microcanonical ensemble to provide the correct macroscopic description, one needs to impose some restrictions on possible types of microscopic interactions.

The restrictions typically are:

(a) **stability**: there is a constant \( B > 0 \) such that in every space configuration \( \mathbf{q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N) \) we have
\[
\Phi(\mathbf{q}) = \sum_{i<j} \varphi(|\mathbf{q}_i - \mathbf{q}_j|) \geq -BN;
\]

(b) **temperedness**: there are constants \( C > 0, R > 0 \) and \( x > 0 \) such that
\[
\varphi(|\mathbf{q}_i - \mathbf{q}_j|) \leq \frac{C}{|\mathbf{q}_i - \mathbf{q}_j|^{3+x}}, \quad \text{for} \quad |\mathbf{q}_i - \mathbf{q}_j| > R.
\]

These requirements are designed so that the thermodynamic limit exists. The stability condition avoids a possible collapse of the system \(^{40}\) due to the accumulation of particles in arbitrarily small regions of space, as a result of a too strong short-range attraction (see also subsection 3.2.4). Temperedness assures a sort of “localizability” of the interaction by avoiding a too slow long-range decay.

\(^{40}\)For technical reasons one sometimes needs an even stronger restriction, namely superstability: a potential is superstable if there are two constants \( a > 0 \) and \( b > 0 \) such that:
\[
\Phi(\mathbf{q}_1, \ldots, \mathbf{q}_N) \geq -bN + \frac{aN^2}{|\Lambda|}
\]
for all \( \mathbf{q}_i \in \Lambda \). A typical example is the Lennard-Jones potential.
Stability and temperedness are satisfied by the Lennard-Jones potential, however, the important cases of the Coulomb and gravitational potentials do not satisfy these requirements. This situation is partially mitigated by superposing a (purportedly more realistic) hard-core potential to them. That is, a potential such that \( \varphi(r) \rightarrow +\infty \) as \( r \rightarrow a+ \), (being smooth otherwise), where \( a \) is the particle’s diameter. Now, as particles are kept a minimum distance apart, stability is restored, but not temperedness. Another potential satisfying the requirements, and which is amenable to calculations, is the so-called hard-sphere potential, describing billiard ball particles (freely moving particles interacting only through elastic collisions). Temperedness is automatic as this is a finite-range potential. The exception of gravitational and electrostatic potentials might signal a different (and more complex) thermodynamic behavior for such systems.\(^{41}\)

### 3.2.3 The Canonical Ensemble

This is the ensemble describing a system in contact with a heat reservoir at a fixed temperature. Each element of the ensemble is a probability measure \( P_{\Lambda,N,\beta}^{\text{can}} \), for \( \beta > 0 \), whose density with respect to Lebesgue measure is

\[
\frac{1}{Z_{\Lambda,N,\beta}} e^{-\beta H(q,p)},
\]

where the canonical partition function is

\[
Z_{\Lambda,N,\beta} = \int_{\Omega_{\Lambda,N}} e^{-\beta H(q,p)} \frac{1}{N!} \Pi_{i=1}^{N} d^3q_i d^3p_i.
\]

It can be checked that

\[
T \equiv \frac{2}{3k} < \frac{K}{N} >_{\Lambda,N,\beta}^{\text{can}} = \frac{2}{3k} < \frac{1}{N} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} >_{\Lambda,N,\beta}^{\text{can}} = \frac{1}{k \beta},
\]

so that the parameter \( \beta \) is essentially the inverse absolute temperature. Also, the average internal energy \( U \) and the average pressure \( p \) are given by

\[
U = -\frac{\partial \ln Z_{\Lambda,N,\beta}}{\partial \beta}
\]

and

\[
p = \frac{1}{\beta} \frac{\partial \ln Z_{\Lambda,N,\beta}}{\partial V}.
\]

Curiously, it turns out that the canonical ensemble is orthodic, even without taking the thermodynamic limit. One can then verify that the thermodynamic free energy \( F = U - T S \), is given by \( F = F_N(\beta, \Lambda) = -\frac{1}{\beta} \ln Z_{\Lambda,N,\beta} \).

\(^{41}\)See, for example the odd thermodynamical behavior of stars and, more spectacularly, of black-holes.
The thermodynamic limit can also be performed for this ensemble, under the stability and temperedness conditions. So, for example one can prove the existence of the specific canonical free-energy in the thermodynamic limit:

\[ f_{\text{can}}(\beta, v) = \lim_{\Lambda \uparrow \mathbb{R}^3, N \to v} \frac{F_N(\beta, \Lambda)}{N}, \]

in terms of which many quantities can be calculated, e.g., the canonical specific internal energy \( u_{\text{can}} = \frac{\partial f_{\text{can}}}{\partial \beta}(\beta, v) \), as well as the canonical pressure \( p_{\text{can}} \), specific entropy \( s_{\text{can}} \), specific volume and the temperature.

3.2.4 The Grand-Canonical Ensemble

While the two previous ensembles dealt with systems with a fixed total number of particles, the grand-canonical ensemble describes a system in a region \( \Lambda \), with fixed temperature, but with variable number of particles. The phase-space is now \( \Omega_{\Lambda,N} = \bigcup_{N \geq 0} \Omega_{\Lambda,N} \), where \( \Omega_{\Lambda,N} \) is the set of states with exactly \( N \) particles; in particular \( \Omega_{\Lambda,0} \) consists of only one point: the empty (no-particle) or “vacuum” state.

The reference measure \( \lambda \) is such that for any measurable set \( A \), we have \( \lambda(A) = \sum_{N \geq 0} \lambda_N(A \cap \Omega_{\Lambda,N}) \), where by convention \( \lambda_0(\Omega_{\Lambda,0}) = 1 \). Then, the grand-canonical ensemble is the family of probability measures \( P_{\text{gc}}^{\Lambda,\beta,\mu} \), parametrized by \( \beta > 0 \) and \( \mu \in \mathbb{R} \), whose density with respect to \( \lambda \) is given by

\[
\frac{1}{Z_{\Lambda,\beta,\mu}} e^{-\beta(H(\omega)-\mu N_{\Lambda}(\omega))},
\]

where the grand-canonical partition function is

\[
Z_{\Lambda,\beta,\mu} = \int_{\Omega_{\Lambda}} e^{-\beta(H(\omega)-\mu N_{\Lambda}(\omega))} \lambda(d\omega).
\]

In the above, when the system is in a state \( \omega \) with exactly \( N \) particles, i.e., \( N_{\Lambda}(\omega) = N \), then the Hamiltonian is \( H(\omega) = H_{\Lambda,N}(\omega) \). Hence, the partition function can be written as a series,

\[
Z_{\Lambda,\beta,\mu} = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N!} \int (\Lambda \times \mathbb{R}^3)^N e^{-\beta H_N(p,q)} \prod_{i=1}^N d^3 q_i \prod_{i=1}^N d^3 p_i,
\]

\[
= 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} \int_{\Lambda^N} e^{-\Phi(q)} \prod_{i=1}^N d^3 q_i = \Xi_{\Lambda,\beta,z},
\]

where the integration with respect to the momentum variables is already performed \(^{42}\) and \( z = e^{\beta \mu} \left( \frac{2\pi m}{\beta} \right)^{3/2} \) is called “fugacity” or “activity” (which is approximately proportional to the density for dilute gases \(^{20,24,43}\)).

\(^{42}\)Of course one supposes the potential satisfies

\[
\int_{\Lambda^N} e^{-\Phi(q)} \prod_{i=1}^N d^3 q_i < \infty,
\]

for all \( N \geq 1 \), so that each term of the series is finite.
Still, the series above could diverge, in which case \( P_{\Lambda, \beta, \mu}(N_{\Lambda} < \infty) = 0 \), and hence \( P_{\Lambda, \beta, \mu}(N_{\Lambda} = +\infty) = 1 \). In words, the probability that there is an infinite number of particles in \( \Lambda \) would be one. In order to avoid such a collapse of infinitely many particles on any bounded region of space, one requires the convergence of the series, which in turn depends crucially on the potential.

In fact, stability is a sufficient condition, \(^{43}\) because in this case,

\[
\Xi_{\Lambda, \beta, z} = 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} \int_{\Lambda} e^{-\Phi(q)} \prod_{i=1}^{N} d^3q_i \leq 1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} |\Lambda|^N e^{N\beta B} = e^{z|\Lambda|\beta B},
\]

which is finite for all \( z \). Moreover, it follows that the grand-canonical partition function is a real analytic function of \( z \) and \( \beta \).

The grand-canonical ensemble is orthodic in the thermodynamic limit, with the grand-canonical pressure given, for fixed \( \beta > 0 \) and \( z > 0 \), by

\[
p_{gc}(\beta, z) = \lim_{\Lambda \uparrow \mathbb{R}^3} p_{\Lambda}(\beta, z) = \lim_{\Lambda \uparrow \mathbb{R}^3} \frac{1}{\beta |\Lambda|} \ln \Xi_{\Lambda, \beta, z}.
\]

and density

\[
\rho_{gc}(\beta, z) = \lim_{\Lambda \uparrow \mathbb{R}^3} \rho_{\Lambda}(\beta, z),
\]

where

\[
\rho_{\Lambda}(\beta, z) = \frac{< N_{\Lambda} >_{gc}}{|\Lambda|} = z\beta \frac{\partial p_{\Lambda}(\beta, z)}{\partial z}.
\]

At this point, there arises the natural question about the relation of the macroscopic variables, calculated at the thermodynamic limit, say, in the grand-canonical ensemble, to the corresponding quantities evaluated using the microcanonical and canonical ensembles. This is linked to the important problem of the equivalence of ensembles (at the quantities level), about which we limit ourselves to the following brief comments.

If, according to the Boltzmann-Gibbs Principle, one could choose any orthodic ensemble to describe the equilibrium behavior of a given system, and if one agrees to interpret the thermodynamic limit as a procedure to extract information about bulk properties of the system (disregarding boundary effects, inevitable when dealing with any real, hence finite, physical system), then one would expect that the choice of ensemble should not be crucial (except, of course, in calculational terms). That is, in the sense that they should describe the same thermodynamic behavior of the system under study, the ensembles should be equivalent (in the thermodynamic limit). This is indeed the case (in the absence of phase transitions), which is proven by verifying that the ensembles are related to each other through suitable re-parametrizations of the basic macroscopic variables. \(^{34}\)

As mentioned before, the three ensembles discussed above are not the only orthodic ensembles available. For example, one can create new ensembles by imposing fixed external boundary conditions, say, by imagining that there are particles at certain fixed positions outside the region \( \Lambda \), with which the particles inside can

\(^{43}\)It is also necessary. \(^{34}\)
The interaction potential of the system inside \( \Lambda \) has to be modified accordingly (see also sec. 4.3.1).

Then, working with the corresponding modified Hamiltonian, one can consider respectively, the microcanonical, canonical and grand-canonical ensembles with fixed external boundary conditions (thus the previous examples correspond to the case of free boundary conditions). Under suitable hypothesis on the distribution of the external particles, these can be shown to be orthodic in the thermodynamic limit (under stability and temperedness).

## 4 Thermodynamic Limit, Infinite-Volume Measures and Phase Transitions

There are many reasons for taking the thermodynamic limit. We have already seen a strong one, namely, to insure orthodicity of the main ensembles and, a fortiori, their equivalence. That is, in order to correctly describe the equilibrium thermodynamics of a fluid from microscopic principles, one needs to take the thermodynamic limit.

In any case, one would have expected the need of some kind of limiting procedure, when trying to establish (in a mathematically sound way) a bridge between two very different descriptions of the same system: that of the discrete (or granular) microscopic world of particles and that of the continuous (or homogeneous) macroscopic world of thermodynamics. A classical example of this discrete-continuum transition is found in mathematical analysis: in Cantor’s construction of the real number system, the passage from the discrete (an even dense) set of rational numbers \( \mathbb{Q} \) to the real number continuum \( \mathbb{R} \) is accomplished through classes of equivalence of Cauchy sequences; then any real number is conceived as a limit of rationals.

One can also view the need of the thermodynamic limit as reflecting the change of scales involved in the different descriptions, given the inherently vague micro-macro distinction in classical statistical mechanics. There, in fact, a system will qualify as “macroscopic” basically when it consists of a “very large number” of tiny (interacting) particles; but exactly how many? The usual order of magnitude is given by Avogadro’s number which, being so huge, suggests the radical idea of taking the limit of infinitely many particles in infinite volume. As the late mathematical-physicist R. Dobrushin observed, “infinity is a better approximation to the number \( 6.10^{23} \) than the number 100 \( (100 \ll 6.10^{23} \sim \infty) \)”.

And, curiously, it it is sometimes combinatorially easier to deal directly with infinity (as a unit whole) instead of keeping track of each component of a finite but huge system.

Of course, real physical systems have a finite number of particles, usually restricted to a bounded region. Hence, the thermodynamic limit certainly is an idealization (like so many others in the modeling of physical systems), justified as a procedure that allows, in the model at hand, to obtain an exact and precise treatment of bulk properties of such many-body systems (i.e., properties which would be

---

44 The external particle’s momenta are not important as the interaction potential is a function of positions only. Note also that the external particles could be assigned according to a given probability distribution, or with periodic boundary conditions, etc.

45 As explicitly recognized by Hilbert regarding kinetic theory.

46 *En passant*, the non-standard real numbers (hyperreals) can in turn be viewed as certain sequences of real numbers. For a discussion of continuity, discreteness and its relations with infinity and mathematical models, see Ref. 18.
not too sensitive on the finiteness of the system and of boundary effects). In particular, it opens up the possibility of studying, in a mathematically rigorous way, the very difficult and subtle notion of a phase transition, which is arguably the central problem of equilibrium statistical mechanics.

4.1 What is a phase transition?

Generally speaking, a phase-transition is a qualitative change in the properties of a macroscopic system when it changes from one to another of its phases. But what are the “phases” of a substance, e.g., a fluid? It is hard to find a precise definition in thermodynamics. Intuitively, they are the different homogeneous “forms” of that same substance, each with its characteristic physico-chemical properties and equation of state. Or else, they are the different “states of aggregation” of matter, an unmistakably microscopic viewpoint.

For a fluid, we have the familiar solid, gas and liquid phases, which are geometrically described by the set of states comprising certain sectors in the \((p,v)\) (or \((p,T)\)) state-space or phase diagram. These sectors seem to be separated by well-defined coexistence curves where two different phases can coexist at the same value of the thermodynamic parameters. Besides, at such curves the equation of state seems to break down due to the appearance of singularities or, more specifically, nonanalyticities, in some thermodynamic quantities, like pressure.

This is a picture corroborated by countless experiments (and numerical simulations) and which one would like to explain from statistical mechanics. However, this turned out to be an extremely difficult problem and, although there is a very detailed understanding of it for some lattice systems, is still essentially open for continuous models.

Now, even to start such an ambitious goal, one would surely need a precise notion of phase transition in the context of statistical mechanics. And the fact is that there are, at present, different notions of phase transitions around, usually suggested by some fundamental negative results, that is, concerning the absence of phase transition (see below).

If one examines the phase diagram of a fluid system, the situation at a point on the coexistence curve seems to indicate that the thermodynamic parameters (or state variables) do not uniquely specify the equilibrium “macrostate” of the system. It could be, for example, liquid or solid at the liquid-solid coexistence curve, with different proportions of each phase. Also, the crossing of such curves usually manifests itself through some “abrupt” (for example, discontinuous) change in some thermodynamic quantities. These observations are the basis of two popular notions of phase transition, that we briefly describe next.

4.2 Phase transitions as singularities of thermodynamic potentials

The idea is as follows. Many important thermodynamical quantities are obtained as derivatives of a thermodynamic potential with respect to the basic parameters of the chosen ensemble. Hence, the presence of a discontinuity on some such quantity signals that the potential is non-differentiable at some point, i.e., it is singular: such a point (in the parameter space) will be called a phase-transition point.

\[\text{With many different possible crystalline phases.}\]
In principle, this would provide a method to pin-point the values of the basic parameters at which a phase-transition occurs. One then loosely define a phase-transition as a singularity of the thermodynamic potential (due, for example, to the discontinuity or non-existence of some of its derivatives).

However, in finite volume the thermodynamic potentials are smooth functions of the basic parameters (being given as expectation values of the partition function). We have seen, for example, that the finite-volume grand-canonical partition function is a real analytic function of the basic parameters. Therefore, one needs to take the thermodynamic limit if one hopes to observe the appearance of a singularity. This provides yet another justification for taking the thermodynamic limit: it is needed in order to be able to have a sharp (mathematically precise) manifestation of a phase-transition.

In this way one would hope to study the structure of parameter-space (or phase diagram) by, say, separating the regions where there is or not a phase-transition. This approach has been more successful in providing proofs of absence of phase transitions. So, for example, there are classical results showing that in the thermodynamic limit the grand-canonical pressure $p_{gc}(\beta, z)$ is an analytic function of $(\beta, z)$ for sufficiently small values of inverse temperature $\beta > 0$ or of fugacity $z > 0$ (and for these so-called regular values the equivalence of ensembles holds). In other words, for sufficiently high temperatures and/or sufficiently low densities, there is no phase-transition.

The main defect of this approach is that it provides no clear physical mechanism to explain the appearance of the singularities. However, as at those values of the parameters the system would presumably be in the gas phase, there is at least a hint that particles would be so far apart that they could not interact strongly enough to begin forming “aggregates” (or “clusters”) which would eventually lead to the condensation process.

4.3 Phase transitions as non-uniqueness of infinite volume measures

This alternative approach to the description of phase transition is inspired by the above mentioned non-uniqueness of the “macrostate” at a coexistence curve. The precise formulation, however, is much more abstract: first of all, it proposes to work directly in an infinite-volume setting, leading to the notion of the thermodynamic limit at the level of (probability) measures.

At first, this is just an extension of the thermodynamic limit procedure (discussed in the last section for some specific quantities) to the whole set of local state-variables. Recall that a state-variable is a measurable function (say, bounded or integrable) $F : \Omega_\Lambda \to \mathbb{R}$ on phase-space.

Let $\Delta \subset \Lambda$ be an open bounded set. Then $F$ is said to be localized in $\Delta$ if it does not depend on position and momentum coordinates of particles lying outside of $\Delta$ (examples are kinetic energy, potential energy, etc).

Consider, in the grand-canonical ensemble (with fixed $\beta$ and $\mu$), for each local state-variable $F$, the limit,

$$< F >_{\Lambda, \beta, \mu}^{ge} = \lim_{\Lambda \uparrow \mathbb{R}^4} \int_{\Omega_\Lambda} F(\omega) \mathbf{P}^{ge}_{\Lambda, \beta, \mu}(d\omega),$$

for a suitable increasing sequence of space-filling volumes. Under certain restrictions on the potential (i.e., super-stability) it is possible to use standard compactness argu-
ments to prove that such limits exist, at least along certain subsequences. Moreover, if they exist, one can show (using a version of the Riesz-Markov theorem) that the $< F >^\text{ge}_\beta,\mu$, for all local $F$, determine a unique probability measure $P^\text{ge}_\beta,\mu$ on a certain infinite-volume phase-space $\Omega$, with

$$< F >^\text{ge}_\beta,\mu = \int_\Omega F(\omega) P^\text{ge}_\beta,\mu(d\omega),$$

so that they are expectations with respect to that measure.

Such probability measure is called an infinite-volume limit (or cluster) measure. There is an associated notion of (weak) convergence on the space of probability measures on $(\Omega,M)$, such that all the above can be summarized by saying that cluster measures are (weak) limits (as $\Lambda \uparrow \mathbb{R}^3$) of the corresponding finite-volume grand-canonical measures, thus: $P^\text{ge}_\Lambda,\mu \Rightarrow P^\text{ge}_\beta,\mu$.

Of course, there are many technical details involved here. To begin with, one needs to describe what is the infinite-volume phase-space $\Omega$. It will consist of all symmetrized (i.e., permutation-invariant) and locally finite sequences of particle’s position and momenta, the last requirement meaning that only a finite number of particles are allowed in any open bounded subset $\Lambda \subset \mathbb{R}^3$. 48

The above discussion was based on choosing the (finite volume free boundary) grand-canonical ensemble, and one could ask what happens if one begins with a different ensemble (possibly including those with boundary condition). This brings up again the question of the equivalence of ensembles, now at the level of measures which was recently dealt with rigorously. 24

4.3.1 The DLR-equation

At this point, one should mention yet another, more general and very elegant (and much less known) viewpoint, not directly involving limits: the so-called DLR equation. It is motivated by the following semi-rigorous reasoning. 48

Let $\nu_\Lambda$ denote the finite-volume grand-canonical measure (where, for simplicity, we do not write the parameters $\beta$ and $\mu$), that is:

$$\nu_\Lambda(d\omega) = \frac{1}{Z_\Lambda} e^{-\beta(H(\omega)-\mu N(\omega))} \lambda(d\omega).$$

Then, for any $\Delta \subset \Lambda$, we can identify the space $\Omega_\Lambda$ with the cartesian product $\Omega_\Delta \times \Omega_\Delta^c$ (where $\Delta^c = \Lambda - \Delta$), each state being denoted by $\omega = \omega_\Lambda = \{\omega_\Delta,\omega_\Delta^c\}$. Then the reference measure $\lambda$ can be identified with the product measure $\lambda_\Delta \otimes \lambda_\Delta^c$.

The Hamiltonian in $\Omega_\Lambda$ is then written as

$$H(\omega_\Lambda) = H(\omega_\Delta) + H(\omega_\Delta^c) + W(\omega_\Delta|\omega_\Delta^c),$$

48That is, for $\omega \in \Omega$, $\omega = \{\{q_i, p_i\}\}_{i \geq 1}$, then for any bounded open set $\Lambda \subset \mathbb{R}^3$, we have card{\{q_n\}_n} < $\infty$, where $\omega_\Lambda = \omega \cap (\Lambda \times \mathbb{R}^3)$, and card{\{A\}} means the cardinality of the set $A$. The space $\Omega$ is endowed with the topology of local convergence: a sequence $\omega_\Lambda = \omega_n = \{(q_i^n, p_i^n)\}_{i \geq 1}$ converges to $\omega = \{\{q_i, p_i\}\}_{i \geq 1}$ if $\lim_{n \to \infty} q_i^n = q_i$ and $\lim_{n \to \infty} p_i^n = p_i$, for some enumeration of position and momenta. More precisely, such that for all bounded open $A$ such that card{\{\omega_n \cap (\Lambda \times \mathbb{R}^3)\}} = card{\{\omega \cap (\Lambda \times \mathbb{R}^3)\}}.

Consider the natural projection $\pi_\Lambda : \Omega \to \Omega_\Lambda$, with $\pi_\Lambda(\omega) = \omega_\Lambda$. Then, a state-function $F$ is localized in $\Lambda$ if $F(\omega) = F(\omega')$ for all $\omega, \omega'$ such that $\pi_\Lambda(\omega) = \pi_\Lambda(\omega')$. 24
where
\[ W(\omega_{|\omega_{\Delta^c}}) = \sum_{(q_i, p_i) \in \omega_{\Delta}} \sum_{(q_j, p_j) \in \omega_{\Delta^c}} \varphi(|q_i - q_j|), \]
is the potential energy of interaction of particles inside \( \Delta \) with particles outside of it.

We then have,
\[ \nu_{\Lambda}(d\omega) = \nu_{\Lambda}(d\omega_{\Delta}, d\omega_{\Delta^c}) = \frac{1}{Z_{\Lambda}} e^{-\beta(H(\omega_{\Delta^c}) - \mu N(\omega_{\Delta^c}))} e^{-\beta(H(\omega_{\Delta}) + W(\omega_{\Delta^c}) - \mu N(\omega_{\Delta}))} \lambda_{\Delta}(d\omega_{\Delta}) \otimes \lambda_{\Delta^c}(d\omega_{\Delta^c}). \]

By Fubini’s theorem, for any bounded measurable state-function \( F \) on \( \Omega_{\Lambda} \), we have
\[ \int_{\Omega_{\Lambda}} \nu_{\Lambda}(d\omega) F(\omega_{\Lambda}) = \int_{\Omega_{\Delta^c}} \lambda(d\omega_{\Delta^c}) e^{-\beta(H(\omega_{\Delta^c}) - \mu N(\omega_{\Delta^c}))} Z_{\Lambda}(\omega_{\Delta^c}) \int_{\Omega_{\Delta}} g(d\omega_{\Delta}|\omega_{\Delta^c}) F(\omega_{\Delta}, \omega_{\Delta^c}), \]
where \( g(\cdot|\omega_{\Delta^c}) \) (sometimes called a Gibbs specification) is just the finite-volume grand-canonical probability measure on \((\Omega_{\Delta}, M_{\Delta})\), with boundary conditions \( \omega_{\Delta^c} \).

That is,
\[ g(d\omega_{\Delta}|\omega_{\Delta^c}) = \frac{1}{Z_{\Delta}(\omega_{\Delta^c})} e^{-\beta(H(\omega_{\Delta}) + W(\omega_{\Delta^c}) - \mu N(\omega_{\Delta}))} \lambda_{\Delta}(d\omega_{\Delta}), \]
with corresponding partition function \( Z_{\Delta}(\omega_{\Delta^c}) \).

In sum, we have:
\[ \int_{\Omega_{\Lambda}} \nu_{\Lambda}(d\omega_{\Lambda}) F(\omega_{\Lambda}) = \int_{\Omega_{\Delta^c}} \nu_{\Lambda}(\Omega_{\Delta^c}, d\omega_{\Delta^c}) \int_{\Omega_{\Delta}} g(d\omega_{\Delta}|\omega_{\Delta^c}) F(\omega_{\Delta}, \omega_{\Delta^c}), \]
where we used that \( \nu_{\Lambda}(\Omega_{\Delta^c}, d\omega_{\Delta^c}) = \int_{\Omega_{\Delta}} \nu_{\Lambda}(d\omega_{\Delta}, d\omega_{\Delta^c}). \)

Having in mind the infinite-volume limit, \( \Lambda \uparrow \mathbb{R}^3 \), this suggests the following definition: a probability measure \( P \) in \((\Omega, M)\) is called an infinite-volume Gibbs measure (or distribution) with interaction potential \( \varphi \), inverse temperature \( \beta \) and chemical potential \( \mu \) if, for every bounded set \( \Delta \in \mathbb{R}^3 \) and all localized functions \( F \), it satisfies the so-called DLR-equation (after Dobrushin, Lanford and Ruelle):
\[ \int_{\Omega} P(d\omega) F(\omega) = \int_{\Omega} P(d\omega) \int_{\Omega_{\Delta}} g(d\omega_{\Delta}|\omega_{\Delta^c}) F(\omega). \]

Now, \( \Delta^c = \mathbb{R}^3 - \Delta \) and we identify \( \Omega = \Omega_{\Delta} \times \Omega_{\mathbb{R}^3 - \Delta} \). 

Although a bit technically complicated, the idea is quite straightforward: an infinite-volume Gibbs measure is such that, when conditioned on events outside any

\[ ^{49} \text{An equivalent formulation is as follows: a probability measure } P \text{ on } (\Omega, M) \text{ is an infinite-} \]
given bounded region $\Delta$ and then restricted to events on $\Delta$, we get exactly a finite-volume grand-canonical distribution, with the corresponding boundary condition.

Under certain technical assumptions on the potential, it is known that every infinite-volume limit measure (in the sense discussed in the previous section) is a solution of the DLR-equation and, conversely, every infinite-volume Gibbs measure is the infinite-volume limit of a finite-volume grand-canonical measure with some (random) boundary conditions (for the delicate and difficult proofs of these results, see Ref. 46). Moreover, there always exists a solution of the DLR-equations.

It is quite possible that, for a given pair $(\beta, \mu)$, there exists more than one solution to the DLR-equation. However, it is proven (14, 46) that at sufficiently high temperature or low density there exists a unique solution of DLR-equations, which is translation-invariant (which is important because such measures would be interpreted as the “pure” phases of the macroscopic system). Moreover, this unique solution has exponential decay of correlations, which would mean that particles do not tend to form “clusters”, supposedly the mechanism working in gas condensation. 50 In conjunction with the analyticity properties of the thermodynamic potential, these results characterize the absence of phase-transition for that range of the parameters $(\beta, \mu)$.

Correspondingly, at those values of the parameters for which there exist more than one solution of the DLR-equation, a phase transition is said to occur. That is, the non-uniqueness of the infinite-volume Gibbs measure is taken to signal the occurrence of a phase-transition. For example, if $(\beta, \mu)$ belongs to the liquid-vapor coexistence line, one would expect the existence of only two extremal translation-invariant Gibbs measures, $P_l$ and $P_g$. 51 This is interpreted by saying that these measures describe the “pure” liquid and gas phases (respectively), so that any other translation-invariant Gibbs measure $P^{(b)}$, with boundary conditions denoted by $b$, is a convex combination of them, i.e.,

$$P^{(b)} = \alpha P_l + (1 - \alpha) P_g,$$

where $\alpha \in [0, 1]$ would depend on the boundary conditions $b$.

Each such $P^{(b)}$ is interpreted as a “mixture” of phases at coexistence, with clusters (maybe drops) of liquid amidst vapor and $\alpha$ being the “proportion” of liquid...
phase, $1 - \alpha$ that of the gas phase. As this proportion depends on the boundary conditions $b$, it appears that a phase transition can also be viewed as a kind of instability of the system, which becomes sensitive to the (infinite-volume) boundary condition chosen; in other words, it becomes highly correlated. 52

While this kind of scenario is basically proven in the case, for example, of the Ising model, 29 there is no corresponding results for continuous systems. That is, the problem of proving the existence of phase transitions for fluids, by showing the non-uniqueness of the infinite-volume Gibbs measures at suitable parameter values, is an essentially open problem. Only very recently there was a breakthrough, 47 with a proof of existence of the liquid-vapor phase transition for a continuous particle model interacting through a finite-range Kac-type potential. 53

We end this discussion by realizing that at present there is no consensus on what is (or should be) the appropriate definition of a phase transition, 54 and this is probably due to the fact that one does not quite understand the physical phenomenon itself. Note also that there is not a clear and complete understanding of the relationships among the different notions currently in use by physicists and mathematical physicists.

5 Conclusions

In this paper we tried to examine some basic notions behind the structure of classical equilibrium statistical mechanics. We argued that statistical mechanics was born as a level-connecting discipline, in the specific context of the attempts to provide a mechanical-atomistic explanation of thermodynamics.

At least for the equilibrium case, the micro-macro link is effected through the Boltzmann-Gibbs prescription, with the help of additional hypothesis such as the thermodynamic limit. At the formal (mathematical) level this is accomplished through the crucial level-linking concept of the ensembles, that is, families of invariant probability measures on the microscopic phase-space, indexed by the macroscopic parameters. Probabilistic methods and notions (old and new) are essentially present, but they are not necessarily associated to any random mechanisms.

Incidentally, the need of such “extra” hypothesis as the thermodynamic limit, shows that the “reduction” of thermodynamics to statistical mechanics is not a simple matter. It requires the development of sophisticated mathematical-physical concepts and techniques, specially of a probabilistic sort, such as the notion of infinite volume Gibbs measures and the DLR-equation. Moreover, as the delicate and complicated issue of phase transitions shows, the statistical mechanical program is far from being completed, in spite of some enormous advances.

On the other hand, the very success of the ensemble method of equilibrium statistical mechanics have inspired its application not only to the study of many-body classical and quantum mechanics, but to many other fields dealing with systems

---

52There could also exist non-translation invariance Gibbs measures, which would correspond to phase coexistence favoring the formation of a separating interface.

53There is yet no corresponding proof for the case of Lennard-Jones potential, 29 not to mention the question of proving the existence of a crystalline (solid) phase. 66

54We should also mention the critical exponents viewpoint, a more phenomenological approach with a huge literature, and which tries to describe and classify the singular behavior of quantities close to a phase transition, with the associated notions of universality, scaling, renormalization, etc. 16 There is also a topological viewpoint of phase transitions, see ref. 8
with many interacting “microscopic” components from of which one hopes to deduce some corresponding “macroscopic” behavior through an averaging procedure.

The reasons for this “portability” of statistical mechanical methods, given the somewhat restricted context to which it was originally linked, are not quite clear. A crucial ingredient surely is the central role of probability theory in its framework, with its unifying language, methods and results. Another would be the relative simplicity of the recipe to be followed in such applications, which boils down to: in studying a system with a very large number of similar interacting components “in equilibrium”, apply the Boltzmann-Gibbs prescription, with a suitable Hamiltonian, a suitable notion of temperature, etc, and try to derive the consequences. This does not in any way mean that it is an easy task to derive useful, not to mention, meaningful results from this procedure.

But what justifies the use of the Boltzmann-Gibbs prescription, besides its practical successes. In many of the applications outside the original thermodynamic systems, different concepts of “entropy” are usually introduced, loosely interpreted as measuring “disorder”, and the Boltzmann-Gibbs prescription is “justified” by a variational principle which requires that the entropy should be maximized. Though such justifications might be satisfactory as far as some of these application go, and though there are variational principles also in the standard statistical mechanics, these will not provide an explanation for the Boltzmann-Gibbs principle from first principles.

It is an old dream of one of the founders of the field, Ludwig Boltzmann, that the ultimate justification of equilibrium statistical mechanics would lie at a deeper level, namely, at the basic non-equilibrium dynamics of the system. That is, one should somehow derive equilibrium statistical mechanics from a (still non-existent!) theory of non-equilibrium statistical mechanics. In spite of some important advances in this area, it still remains the basic foundational open problem of statistical mechanics and of physical science.

ACKNOWLEDGMENTS

This work was partially supported by FAPERJ, Projeto Cientista do Nosso Estado, E-26/151.905/2000.

References

1. BELL, J. L. (2001). The Art of The Inelligible, The Western Ontario Series in Philosophy of Science, vol. 63, Kluwer Academic Publishers, Dordrecht.

2. BRICMONT, J., DÜRR, D., GALLAVOTTI, G., GHIRARDI, F., PETRUCCIONI AND ZANGHĪ, N. eds., (2001). Chance in Physics. Springer.

3. BRUSH, S. G. (1994). The kind of motion we call heat, book 1, 3rd edn. North-Holland.

4. BUNGE, M. Foundations of Physics (1967). Springer-Verlag, New York.
5. Bunge, M. (1991). The power and limits of reductionism. In The Problem of Reductionism in Science, ed. E. Agazzi. Kluwer Academic Publishers, Dordrecht, pp. 31-49.

6. Bunge, M. (1988). Two faces and three masks of probability. In Probability in the Sciences, ed. E. Agazzi. Kluwer Academic Publishers, Dordrecht, p 27-49.

7. Bingham, N. H. (2000). Studies in the history of probability and statistics XLVI. Measure into probability: from Lebesgue to Kolmogorov. Biometrika 87, 145–156.

8. Casetti, L., Pettini, M. and Cohen E. G. D. (2003) Phase transitions and topology changes in configuration space. J. Statist. Phys., 111(5-6):1091-1123.

9. Cercignani, C. (1998). Ludwig Boltzmann, the man who trusted atoms. Oxford University Press.

10. Cohen, E. G. D. (1993). Kinetic theory: Understanding nature through collisions. Am. J. Phys., 61, (6), pp. 524-533.

11. Corry, L. (1997). David Hilbert and the axiomatization of physics (1894-1900). Arch. Hist. Exact Sci., 51, pp. 83-198.

12. Darrigol, O. and Renn, J. (2000). The Emergence of Statistical Mechanics. To appear in Sandro Petruccioli (ed.), Storia Della Scienza. Instituto della Enciclopedia Italiana.

13. Diacu, F. (1996). The solution of the n-body problem. Mathematical Intelligencer, vol. 18, no. 3, pp. 66-70.

14. Dobrushin, R. L., Sinai, Ya. G. AND Sukhov, Yu. M. (1989). Dynamical Systems of Statistical Mechanics and Kinetic Theories. In Dynamical Systems II, Encyclopedia of Mathematical Sciences, Vol. 2, ed. Ya. G. Sinai Springer-Verlag, pp. 207-254.

15. Dobrushin, R. L. (1997). A mathematical approach to the foundations of statistical mechanics. In Boltzmann’s legacy 150 years after his birth. Atti dei Convegni Lincei 131. Accademia Nazionali dei Lincei, Roma.

16. Domb, C. (1996). The Critical Point. Taylor&Francis.

17. Dorlas, T. J. (1999). Statistical Mechanics. IOP Publishing Ltd.

18. Fenstad, J. E. (1988). Infinites in mathematics and the natural sciences. In Contemporary Mathematics, vol. 69, American Mathematical Society, pp. 79-92.

19. Feynman, R. P., Leighton, R. B. AND Sands, M. (1977). The Feynman Lectures on Physics, vol I. Addison Wesley.

20. Gallavotti, G. (1999). Statistical Mechanics. Springer-Verlag.

21. Georgii, H.-O (1994). Large Deviations and the Equivalence of Ensembles for Gibbsian Particle Systems with Superstable Interaction. Probab. Th. Rel. Fields, 99, pp. 171-195.
22. Georgii, H.-O (1988). Gibbs Measures and Phase Transitions. de Gruyter Studies in Mathematics, Berlin.

23. Goldstein, S., Dürr, D. and Zanghi, N. (1996). Bohmian Mechanics as the Foundation of Quantum Mechanics. In Bohmian Mechanics and Quantum Theory: an Appraisal, ed. J.T. Cushing, A. Fine, and S. Goldstein, Boston Studies in the Philosophy of Science 184, Kluwer, pp. 21-44.

24. Griffiths, R. B. (1972). Rigorous results ad theorems. In Phase Transitions and Critical Phenomena, vol. 1, eds. C. Domb and M. S. Green, Academic Press, pp. 7-109.

25. Khinchin, A. I. (1949). Mathematical Foundations of Statistical Mechanics. Dover Publications, Inc., New York.

26. Kolmogorov, A. N. (1956). Foundations of the Theory of Probability. Chelsea Publishing Co., New York.

27. Kotecký, R. Phase transitions: on a crossroads of probability and analysis. In Highlights of Mathematical Physics, ed. A. Fokas, J. Halliwell, T. Kibble, B. Zegarlinski, American Mathematical Society, Providence, pp. 191-207.

28. Lanford, O. (1975). Time evolution of large classical systems, Lecture Notes in Physics, 38, Springer Verlag, pp. 1-111.

29. Lebowitz, J. L. (1999). Statistical mechanics: A selective review of two central issues. In Reviews of Modern Physics 71, No. 2, Special Issue in Honour of the Centennial of the American Physical Society, p. S347.

30. Lieb, E. and Yngvason, J. (2000). A Fresh Look at Entropy and the Second Law of Thermodynamics. Physics Today, 53, pp. 32-37.

31. Martin-Löf, A. (1979). Statistical Mechanics and the Foundations of Thermodynamics, Lecture Notes in Physics, 101 Springer-Verlag.

32. Minlos, R. A. (2000). Introduction to Mathematical Statistical Mechanics, University Lecture Series, vol 19. AMS.

33. Reed, M. and Simon, B. (1980). Functional Analysis. Academic Press, New York.

34. Ruelle, D. (1999). Statistical Mechanics: rigorous results. World Scientific Pub. Co.

35. Ruelle, D. (1988). Is our mathematics natural? The case of equilibrium statistical mechanics. Bull. Amer. Math. Soc. (N.S.) 19, no. 1, pp. 259–268.

36. Ruelle, D. (2002). Some ill-formulated problems on regular and messy behavior in statistical mechanics and smooth dynamics for which I would like the advice of Yasha Sinai. J. Statist. Phys., 108, nos. 5/6, pp. 723-728.

37. Serrin, J. (1991). The Nature of Thermodynamics. Atti. Sem. Mat. Fis. Univ. Modena, XXXIX, pp. 455-472.
38. Serrin, J. (1995). On the elementary thermodynamics of quasi-static systems and other remarks. In Thermoelastic problems and the thermodynamics of continua, ed. L. M Brock, AMD-Vol. 198, ASME, pp. 53-62.

39. Sommerfeld, A. Thermodynamics and Statistical Mechanics. Academic Press.

40. Spohn, H. (1991). Large Scale Dynamics of Interacting Particles. Springer-Verlag, New York.

41. Sylhavý, M. (1997). The Mechanics and Thermodynamics of Continuous Media. Springer-Verlag.

42. Thompson, C. J. (1988). Classical Equilibrium Statistical Mechanics. Oxford University Press, New York.

43. Toda, M, Kubo, R. and Saitô, N. (1998). Statistical Physics I, second edition. Springer.

44. Truesdell, C. (1984). Rational Thermodynamics. Springer-Verlag.

45. Truesdell, C. (1986). What did Gibbs and Carathéodory leave us about thermodynamics?. In New Perspectives in Thermodynamics, ed. J. Serrin, Springer-Verlag, pp. 101-124.

46. Petrina, D. Ya., Gerasimenko, V. I. and Malyshev, P. V. (1989). Mathematical Foundations of Classical Statistical Mechanics. Gordon and Breach.

47. Presutti, E. (2001). Liquid-vapour phase transitions. In XIIIth International Congress on Mathematical Physics (London, 2000) Int. Press, Boston, pp. 113-122.

48. Pulvirenti, M. (1981). Evoluzione Temporale di Sistemi Classici di Infiniti Particelle, Quaderni del C.N.R., Roma.

49. van Enter, A. C. D., Fernández R. and Sokal, A. D. (1993). Regularity properties and pathologies of position-space renormalization-group transformations: scope and limitations of Gibbsian theory. J. of Statist. Phys., 72, no.5-6, pp. 879-1167.

50. von Plato, J. (1994). Creating Modern Probability. Cambridge University Press.

51. Uffink, J. (2001). Bluff your way in the second law of thermodynamics. Stud. Hist. Phil. Mod. Phys., Vol. 32, No. 3, pp. 305-394.

52. Wick, D. (1995). The Infamous Boundary: Seven Decades of Heresy in Quantum Mechanics. Birkhäuser.