General introduction

Holy Entropy! It's boiling!
Mr Tompkins (G. Gamow [Gam65])

Historically, statistical mechanics (or thermostatistics) has been developed to give thermodynamics mechanical foundation. This program was more than successful, and thermostatistics has even been applied to models which was not studied by thermodynamics. Nowadays, statistical mechanics is used in almost (if not) all physical fields. It is even used outside physics, e.g. in economics and social sciences.

Thermodynamics deals with *extensive* systems composed of a very large (physically *infinite*) number of particles N. Hence, the tools developed in statistical mechanics are marked by these properties. In statistical mechanics the limit $N \to \infty$ for an extensive system is called the thermodynamical limit. As an example, phase transitions are defined as Yang-Lee singularities of the canonical potential of the considered system. It is easy to show that these singularities show up only at the thermodynamical limit. In other words, systems far from this limit, or "small" system, *cannot* exhibit the usual signals (Yang-Lee singularities) of phase transitions. Systems are considered to be "small" if the range of their forces is at least of the order of the size of the system.

Because the conventional signals rely on the thermodynamical limit they are absent in "small" systems. But does it mean that there is actually no phase transition at all in these systems?

In fact, in experiments (real or numerically simulated) one can observe that "small" systems do have some behaviors that would be called phase transitions if they were infinite. E.g. atomic clusters composed of a few hundreds of atoms have solid–like properties at low energies, then liquid–like at higher energies to eventually be a gas of atoms at high energies. Spin systems are "ordered" at small energies and completely "disordered" at very high energies. Nevertheless, in the conventional sense, these different macroscopic states and the intermediate stages between them cannot be called phases and phase transitions because the systems do not show any of the "correct" signals of phase transitions.

The facts mentioned above are clear indications that the phase transitions do not appear at the thermodynamical limit but only their usual signals. Therefore, it is natural to ask whether one can redefine phases and phase transitions without invoking the thermodynamical limit. Of course, these new definitions should converge to the usual ones in the limit $N \to \infty$, if it exists.

A thermostatistics of "small" systems has been developed by D.H.E. Gross and its collaborators for many years now [Gro01, Gro97]. In this theory, phases and phase transitions are defined by means of *local* properties of the *microcanonical entropy*, where the latter is a function of the *dynamically conserved* quantities of the system.

The microcanonical ensemble is based on the mechanical properties of the studied system. The entropy is defined by means of Boltzmann's principle and hence is a purely mechanical based quantity. Boltzmann's principle does not impose (or require) properties like extensivity or infinite number of particles. Hence, the microcanonical ensemble is the proper ensemble to study "small" systems. On the contrary, the canonical ensemble does not provide an accurate description of "small" systems, because it is based on assumptions (extensivity, small interactions with a heat bath) which are not true for these systems. The statistical descriptions of "small" systems, provided by the different ensembles, are not equivalent.

The aim of this thesis is, first to collect and summarize theoretical results, and convince the reader of the physical relevance of the microcanonical thermostatistics of "small" systems. Then, some concrete applications of this theory to different models of "small" systems are presented. It is shown that these systems have rich phase diagrams and that almost all their finite-size peculiarities are overlooked by the canonical ensemble.

This thesis is organized as follows.

The first part tries to give an almost exhaustive overview of the present status of the statistical mechanics of "small" systems from a theoretical point of view. This description is illustrated with some original applications to analytical entropy-models.

The first chapter is a remainder of notions that are used throughout this thesis. Most of them are known from standard statistical mechanics. However, some of them have to be redefined in order to be adapted to the peculiarities of "small" systems. The definitions of the microcanonical and canonical ensemble used in this work are given in sections 1.1 and 1.2. The choice of the microcanonical ensemble among the different statistical descriptions is discussed in section 1.3. Simple analytical entropy-models are introduced in sec. 1.4. They are mainly used in chap. 2. The microcanonical entropy of a gas in the van der Waals approximation is one of them. In chapter 2 the definitions of phases and phase transitions are given (sections 2.1, 2.2 and 2.3). The fact that these definitions apply to an ensemble of systems is stressed in sec. 2.4. Finally, alternative statistical descriptions of "small" (or non-extensive) systems are reviewed and compared with the one used in this work (sec. 2.5).

The two other parts show original results of studies of some "small" systems.

In part II, the liquid–gas transition of sodium clusters composed of a few hundreds of atoms is discussed. This work continues the one done by many authors of Gross' group.

In chapter 3 the transition is studied at atmospheric pressure. After a short introduction (sec. 3.1), the cluster model (sec. 3.2) and the numerical method (sec. 3.3) are described. The numerical results are shown in sec. 3.4. Caloric curves and their relation to the mass distribution of the system are discussed. The transition parameters are derived from the Maxwell construction. Finally, the scaling behavior of all these observable is described. The results are summarized in sec. 3.5.

In chapter 4 the system is studied at very high pressures. Here, the goal is to reach the critical point of the liquid-gas transition. In the introduction sec. 4.1, the bulk critical parameters are recalled. Then several attempts to observe a second order phase transition within the cluster models used in chap. 3 are presented. They all suggest that if the critical point of finite size sodium clusters it exits, then it is located at higher pressure than its bulk counter-part. In sec. 4.3 a new model for clusters is presented. It is inspired from lattice gas models. This models shows for the first time the critical point of the liquid-gas transition of sodium clusters. In this model the critical pressure is much higher compared to the critical pressure in the corresponding thermodynamical limit. The finite size critical pressure decreases with increasing total mass of the system.

The third and last part is devoted to self–gravitating systems. These systems are "small". They exhibit *negative* specific heat capacity regions for any number of particles. This fact has been pointed out to the astrophysical community by the seminal work of Antonov. The equilibrium properties of these systems have mainly be studied as a function of the total energy E. However, in astrophysical context, the energy is not the only relevant constant of motion. In this part of this thesis the influence of the conservation of total angular momentum L on the statistical properties of a self-gravitating system is presented.

In chapter 5 a very short introduction on the statistical description of self-gravitating systems is given. The assumptions that have to be made in order to make possible a statistical description of N–body systems interacting via Newtonian potential are briefly discussed. Contrary to previous works, no assumptions are made about the spatial symmetry of the mass distribution and a more "realistic" potential is used.

The study of this system is presented in chapter 6. First, some microcanonical definitions are given (sec. 6.1). Then the average and the dispersion of the linear momentum of a particle at a given position is discussed (sec. 6.2). A numerical method, suitable to integrate observables over the whole parameter space, is described in sec. 6.3. The numerical results are presented in sec. 6.4. The entropy, its derivatives (temperature, angular velocity) and observables probing the mass distributions are discussed for the whole parameter space. The definitions of phase transitions, given in chap. 2, are used in order to construct the phase diagram of the system. It is surprisingly rich, showing first order and many second order phase transitions. All the properties of astrophysical interest are lost in the canonical ensemble as shown in sec. 6.4.4. The results are summarized and an outlook on future works is given in sec. 6.5.

The main results of this thesis are collected and discussed in the general conclusions.