General conclusions

This thesis has been devoted to the study of phase transitions in "small" systems. A system where the range of the forces is at least of the order of the system size is considered to be "small".

These "small" systems cannot be considered as being at the thermodynamical limit, and are moreover non-extensive. Hence, the usual thermostatistics does not offer a satisfactory framework to study their equilibrium properties. As an example, in thermostatistics, phase transitions are defined by means of singularities of the canonical potential. These singularities cannot occur in finite-size systems, and extensivity is essential to define a proper canonical ensemble.

However, as recalled and many times illustrated in this thesis, one can define phases and phase transitions in the microcanonical ensemble by means of the topological properties of the entropy surface. The microcanonical ensemble is the proper ensemble to describe "small" systems. It is defined by means of the dynamical properties of the considered system. Extensivity and infinite number of particles are not required in order to define the microcanonical ensemble.

In this thesis new results from applications of the microcanonical thermostatistics to several "small" systems have been presented.

First, the liquid-gas phase transition of metal clusters has been studied for low and large microcanonical pressures.

At atmospheric pressure and for a certain range of enthalpy, the caloric curve is characterized by a *negative* heat capacity. In "small" systems, this signals a first order phase transition. This phase transition is divided into two parts (with increasing enthalpy). First, the big liquid cluster evaporates light fragments (monomers and dimers) over a relatively large enthalpy-range. Then, this time in a very narrow enthalpy region, the temperature drops down rapidly. There the mass distribution is reorganized completely. Before this fast transition, the mass distribution is composed by one big liquid cluster, embedded in a gas of light fragments. After this transition, there are no longer any very big liquid cluster, but on the contrary, there are several medium sized fragments (dimers, 4–mers and 8–mers). This particular mass selection is explained by the local maxima of their respective binding energy as a function of the cluster size. These irregularities are due to the electronic shell effects. After this fast transition, the caloric curve recovers a "normal" slope as a function of h, i.e. a *positive* heat capacity. Then, the fragments decay to monomers. In the present thesis, this region of the caloric curved has been called multifragmentation regime. At very high enthalpies, there are only monomers.

The multifragmentation is not accessible to a canonical description because it does not correspond to absolute minima of the free energy.

At the thermodynamical limit the multifragmentation regime vanishes, and the transition from a liquid to a gas occurs uniquely via evaporation.

At high pressures, the avoided volume to the clusters, NCC, plays a very important role by

(a) selecting the mass distribution with small NCC,

(b) giving the main contribution to the pressure via its derivative with respect to the volume of the system.

In a new model of metallic clusters, the critical point (second order phase transition) of the liquid–gas transition has been reached for the first time. Although, in this simplified model the critical parameters do not scale to their bulk values, the results confirm the preliminary ones obtained from the previous cluster model. E.g. the critical point of finite size cluster is located at higher pressure and density and at lower temperature than the bulk critical point.

In order to improve the quantitative estimates of the critical parameters, one should include some properties of the clusters that have been removed from the model in order to make possible these firsts numerical computations (e.g. highly excited clusters).

The other "small" system studied within the microcanonical thermostatistics is a model self–gravitating N-bodies. Due to the non saturation of the Newtonian gravitational potential, self–gravitating systems are "small". This model is studied as a function of the total energy E *and* of the total angular momentum L.

On average, all the particles of the system rotates around the center of mass of the system with the same angular velocity. The dispersion of the linear momenta is a function of the distance to the center of mass d. This dispersion increases from the center to the boundary.

By using the definitions of phases and phase transitions of "small" systems, one could construct the phase diagram of the considered self–gravitation system. At high energies, the system is in a pure gas phase (uniform mass distribution). For $L = 0$ and at low energy, the system is in a pure collapsed phase with a large concentration of particles at the center of mass (one cluster). For $L \neq 0$ and near the ground states, there are several pure phases. Their respective mass distributions are composed of *two* clusters. At small L the respective masses of the clusters are very different. At large L and near the ground state, the pure phase is made of two equal-size clusters located very close to the system boundary. All the pure phases are separated by a first order phase transition region. There are even several second order phase transitions. Although, they are not all of physical relevance, two of them, located at relatively high energies, might be of astrophysical importance. They deserve further studies.

All the pure phases with non-symmetric cluster masses, the first order and all second order phase transitions are overlooked if one fixes the intensive variables. It is even shown, that for a particular choice of the intensive parameters the partition sum *diverges* for some microcanonical values of these parameters.

Hence, throughout this thesis many examples of the deep insight provided by the microcanonical thermostatistics of "small" systems on the equilibrium properties of those systems have been given. They show that, contrary to the Schrödinger's pessimistic prediction [SCH46], the microcanonical entropy defined via Boltzmann's principle is not just only useful to study gases.