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Classification of Phase Transitions and Ensemble Inequivalence, in Systems with Long Range Interactions

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Systems with long range interactions in general are not additive, which can lead to an inequivalence of the microcanonical and canonical ensembles. The microcanonical ensemble may show richer behavior than the canonical one, including negative specific heats and other non-common behaviors. We propose a classification of microcanonical phase transitions, of their link to canonical ones, and of the possible situations of ensemble inequivalence. We discuss previously observed phase transitions and inequivalence in self-gravitating, two-dimensional fluid dynamics and non-neutral plasmas. We note a number of generic situations that have not yet been observed in such systems.

KEY WORDS: Long range interaction; phase transition; bifurcation; ensemble equivalence.

1. INTRODUCTION

In a large number of physical systems, any single particle experiences a force which is dominated by interactions with far away particles. For instance, in a system with algebraic decay of the inter-particle potential $V(r) \sim_{r\to\infty} 1/r^{\alpha}$, when α is less than the dimension of the system, the interaction is long range (such interactions are sometimes called "non-integrable"). Such long range interacting systems are not-additive, as the interaction of any macroscopic part of the system with the whole is not negligible with respect to the internal energy of the given part.

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The main physical examples of non-additive, long range interacting systems are: astrophysical self-gravitating systems,[3,9,13,20,28,31,34,39,43] two-dimensional or geophysical fluid dynamics,[11,32,33,37] and certain plasma physics models.[17,25] Spin systems[5,21] and toy models[2] with long range interactions have also been widely studied.

As a consequence of the lack of additivity, peculiar thermodynamic behaviors are likely to be observed in such Hamiltonian systems. For instance, the usual proof of the validity of the canonical ensemble, for a system in contact with a thermostat, or for a part of a bigger isolated system, uses explicitly this additivity property. Hertel and Thirring[18] provided a toy model, mimicking self-gravitating dynamics, which displays inequivalence between canonical and microcanonical solutions, with negative specific heat regions in the microcanonical ensemble. Negative specific heat and ensemble inequivalence, previously known to astrophysicists, were then found in various fields: plasma physics,[25,38] 2D fluid dynamics[7] and geophysical fluid dynamics.[15] These examples show that new types of phase transitions are found in long range interacting systems.

A natural question then arises: do we know all possible behaviors stemming from long range interactions, and, if not, what are the possible phenomenologies? The aim of this article is to answer the question by providing a *classification* of all microcanonical and canonical phase transitions, in long range interacting systems, with emphasis on situations of ensemble inequivalence. Although we restrict here to long range interacting systems, we want to stress that these systems are not the only ones for which ensemble inequivalence may occur.[12] Let us note also that the deep link between ensemble inequivalence and dynamical non-linear stability issues has been recently recognized,[16] which provides a further incentive for this study.

In order to formalize the problem, we first argue, in Section 2, that the mean field approach is exact, in the limit of a large number of particles, for most systems with long range interactions. In this mean field context, the microcanonical equilibrium is defined by the maximization, with respect to an order parameter, of an entropy with an energy constraint. The canonical equilibrium is then given by the minimization of the associated free energy. The study of phase transitions is thus reduced to the study of the singularities of these two variational problems, while the study of ensemble inequivalence is reduced to comparing the equilibrium states in both ensembles.

We propose a classification of all singularities, convexity changes, and convexification properties of entropy functions, independently of the underlying physical problem; it uses the tools of singularity theory, along the lines of the works of Varchenko[42] and Aicardi,[1] on the classification of phase transitions for binary mixtures, in classical thermodynamics. We thus classify all microcanonical and canonical phase transitions, their mutual link, and all situations of ensemble inequivalence.

In Section 3, we carry on this program when one internal (the energy for instance) and one external parameter are varied; we then review the transitions already found in the (known to us) literature, by studying actual N-body systems. We will see that the classification identifies many new possibilities besides the well-known negative specific heat regions. In Section 4, we give a similar classification and comparison with the existing literature for systems with a parity symmetry.

In all this work, we study the possible inequivalence of ensembles, when only one dynamical constraint is taken into account. This is valid for inequivalence between the microcanonical and the canonical ensembles, or between the canonical and grand canonical ensembles, for instance. We briefly discuss the generalization to several constraints in the conclusion.

2. MEAN FIELD STATISTICAL MECHANICS AND ENSEMBLE INEQUIVALENCE

2.1. Microcanonical and Canonical Equilibrium States

A model will be said to have long range interactions when any single particle experiences a force for which a macroscopic number of particles contribute, and such that the contribution of closest particles is negligible when the number of particles N goes to infinity. The statistical equilibrium states of such systems are generically described by mean-field variational problems. We first give some heuristic justification of this statement, before referring to rigorous proofs for specific models.

The energy of such systems can be approximated, in the large N limit, by the energy of a coarse-grained variable m which may be a scalar, a vector or a field ($H \sim_{N\to\infty} Nh\,(m)$). The description of equilibrium structures then amounts to compute the probability $P(m)$ of this coarse-grained field. This probability is characterized by an entropy function or functional in the large N limit: $\log\left(P\,(m)\right) \sim_{N\to\infty} Ns\,(m)$. As a result, the microcanonical equilibrium state $m_m$and entropy of the system $S(E)$, for a given energy E, are the solutions of the maximization of the entropy function (functional) s with the energy constraint (this general approach is explained in ref. 15:

$$S(E) = \sup_m \{s(m) \mid h(m) = E\} = s(m_m). \tag{1}$$

The points where the supremum is reached defines $m_m(E)$, the microcanonical equilibrium state at energy E. We suppose that it exists;[4] however it is not necessarily unique.

With similar arguments, the canonical[5] equilibrium m_c, at inverse temperature β, is given by the minimization of the free energy functional:

$$F(\beta) = \inf_m \{-s(m) + \beta h(m)\} = -s(m_c) + \beta h(m_c) \tag{2}$$

We note that the usual free energy is $F(\beta)/\beta$. Nevertheless, for sake of simplicity, we will always call F the free energy.[6] The points where the infimum is reached defines $m_c(\beta)$, the canonical equilibrium state at inverse temperature β; we suppose that it exists, but as in the microcanonical case, it is not necessarily unique. In a canonical context, this reduction to a variational problem was already rigorously described for gravitating fermions in ref. 19, and in a more general setting in ref. 29.

Such a mean field description has been proposed for the point-vortex system,[(22)] two dimensional incompressible flows,[(32,35)] Quasi-geostrophic flows, rotating Shallow-Water model,[(11)],[7] self-gravitating systems,[(9,28,34,39)] plasma physics,[(17,25)] spin systems.[(2,5,21)] Some rigorous large deviations results, confirming this mean field description, have been rigorously obtained for a large class of long range interacting systems: two-dimensional or quasi-geostrophic models,[(15,30,36)] the point vortex model[(7,24)], spin systems.[(5)]

From now on, we call microcanonically stable, metastable and unstable state respectively a global maximum of problem (1) (that is a microcanonical equilibrium state), a local maximum of (1) which is not global, and a local minimum or a saddle point of (1). We define similarly canonically stable, metastable and unstable states with problem (2). In the following we will study generic properties of the two dual variational problems (1) and (2), independently of any specific system. The Lagrange multiplier result insures that, for a given energy E, a critical point of (1) is a

[4]the existence has to be proved for each case, using properties of the entropy functional $s(m)$, which is usually strictly concave.

[5]in systems with long range interaction, the canonical ensemble does not describe the fluctuations of a small subsystem. However, it can describe fluctuation of the whole system coupled to a thermostat with vanishingly small coupling.

[6]For negative temperature states, for instance in two dimensional turbulence, the functional $-s(m) + \beta h(m)$ must still be minimized, whereas the usual free energy should be maximized. Such a notation thus simplifies the discussion.

[7]The main peculiarity of models of two dimensional or quasi-geostrophic flows is the existence of an infinite number of conserved quantities (Casimirs), due to the continuous nature of the dynamics, and similar to the conserved quantity of a Vlasov dynamics.

critical point of (2) for some value of β, verifying $-ds+\beta dh=0$.[8] However the stability of this critical point (stable, metastable, unstable) may differ for the two variational problems. We will say that the microcanonical and canonical ensembles are equivalent at an energy E if it exists β such that $m_m(E)=m_c(\beta)$ (with $m_c(\beta)$ canonically stable). In the opposite case, we will say that the two ensembles are not equivalent. The problem of ensemble equivalence thus reduces to the study of the solutions of the two general variational problems (1) and (2). In the following paragraph, we recall the results linking ensemble equivalence and the concavity of $S(E)$.

2.2. Characterization of Ensemble Equivalence

It is classically known that ensemble equivalence is related to the concavity of the entropy $S(E)$ (for instance authors of ref. 24 use this property as a definition). If the entropy is twice differentiable and non concave at some point, both ensembles are obviously not equivalent, since the specific heat is always positive in the canonical ensemble.[9] More generally, ensemble inequivalence is completely characterized by the concavity of $S(E)$. The concave envelope of the $S(E)$ curve is defined as the boundary of the intersection of all closed half-spaces which contains the $S(E)$ curve. One can prove the three following points by convex analysis:[(15)]

1. a canonical equilibrium state at inverse temperature β is always a microcanonical equilibrium state for some energy E.

2. a microcanonical equilibrium state of energy E is also a canonical equilibrium state, for some inverse temperature β, if and only if the function S coincides, at the point E, with its concave envelope.

3. the second point can be refined: we consider an energy E at which S is regular (at least twice differentiable); then a microcanonical equilibrium state of energy E is a canonical stable or metastable state, for

[8] By definition, the microcanonical inverse temperature β is the Lagrange parameter β corresponding to the entropy maximum (it may be not uniquely defined, for instance at a first order microcanonical transition point). When S is differentiable, we have $\beta=s'(E)$. On the contrary, in the canonical ensemble, β is a parameter. If the two ensembles are equivalent at the energy E, then the canonical calculations with inverse temperature $\beta=s'(E)$ will yield the same equilibrium state and the energy E. When no confusion is possible, β will either refer to the microcanonical or to the canonical inverse temperature.

[9] The specific heat is defined in the canonical ensemble as $C_v^{\text{cano}}=-\beta^2 d^2F/d\beta^2$, and as $C_v^{\text{micro}}=-\beta^2/(d^2S/dE^2)$ in the microcanonical ensemble.

some inverse temperature β, if, and only if, the function S is locally concave around the point E (that is locally under its tangent).

A proof of points 1 and 2, in the context of long range interacting systems, from the variational problems (1) and (2), is given in ref. 15. Point 3 is a direct generalization.[10]

Let us furthermore argue that the knowledge of the canonical equilibria $m_c(\beta)$, for all β, is sufficient to know whether ensemble inequivalence occurs or not. From the knowledge of all $m_c(\beta)$, we can compute all canonical equilibrium energies $\{h\,(m_c(\beta))\}$. If this energy ensemble is the same as the energy range of the system, then the whole curve $S(E)$ can be constructed from $\{(h\,(m_c(\beta))\,,s\,(m_c(\beta)))\}$. This curve is always concave, as a canonical equilibrium (not necessarily unique) may be associated to each point. Thus there is no ensemble inequivalence. Conversely, if the canonical energy range is different from the system energy range, then for these energies, microcanonical equilibria are not canonical ones, and ensembles are inequivalent. This discussion also shows that a microcanonical phase diagram, where the convexity changes and convexification points or surface are represented, contains all information necessary to construct the associated canonical phase diagram (the converse is wrong in general).

The problem of ensemble inequivalence is thus reduced to the study of the concavity of the function $S(E)$. More generally, microcanonical phase transitions then correspond to a lack of analyticity of the entropy $S\,(E)$, whereas ensemble inequivalence or canonical phase transitions are characterized by convexity changes of the entropy $S\,(E)$. We note that in systems with short range interactions, the mechanism of phase separation justifies the Maxwell construction, and explain why entropy functions are generally concave. These considerations are model independent, which leads to the central point of the paper, in Sections 3 and 4: we have the opportunity to classify all the possible phase transitions for these systems (or equivalently, to classify the analyticity breakings, convexification and concavity properties of $S(E)$); we will make use for this purpose of the tools of singularity theory[(4)] (or catastrophe theory[(41)]).

[10]Here is a sketch of a possible proof: a canonical state m_c, with energy $E=h\,(m_c)$, is by definition said to be metastable if it is a local, and not a global minimum of the free energy functional (for an infinite dimensional m, one has to specify explicitly some topology). If the energy is continuous, states close to m_c have an energy close to E. The application of point 2 to a class of states with energy close to E proves 3.

3. CLASSIFICATION OF LONG-RANGE INTERACTING SYSTEMS PHASE-TRANSITIONS AND OF STATISTICAL ENSEMBLE INEQUIVALENCE

In this section, we focus on the case where no symmetry property is assumed for the dependence of the functionals s and h on the coarse-grained variable m. We classify all maximization, convexity and convexification singularities of an entropy–energy curve. For each situation, we are interested in singularities which are not removed by any small perturbation of the functions s and h defining the variational problems (1) and (2). Let us suppose that s and h depend on $N+1$ parameters; heuristically we will say that a singularity is generic with codimension n if it spans an $N-n$ dimensional hypersurface in the $N+1$ dimensional parameter space. Thus, if one explores an $n+1$ dimensional hypersurface in that space, that is if $n+1$ parameters can be varied, a codimension n singularity will be *generically* observed. If we consider the energy E to be one of these parameters (the internal one), n then refers to the number of external parameters which has to be varied to observe *generically* codimension n singularities. Varchenko[42] classified singularities of the convex envelope of a finite set of smooth bounded function, up to codimension 2. Aicardi[1] completed this classification and applied it to the classification of phase transitions for binary mixtures. These works do not, however, consider maximization singularities. Brysgalova[6] classified maximization singularities for variational problems depending on a parameter. We know no mathematical results classifying both singularities and convexification properties of a variational problem. We now first describe "codimension -1" points (see below), and classify all codimension 0 and 1 singularities (that is with none or one external parameter), when only one constraint (the energy) is considered. We then search in the literature which of these transitions have been found in actual physical models of interacting particles.

3.1. Generic Points on a $S(E)$ Curve

We describe here *generic points* of a $S(E)$ curve, that is points accessible without tuning the energy. Formally, these would be "codimension -1" singularities. We thus consider the three sources of singularity we are interested in: maximization singularity, convexity property and convexification. The corresponding generic points are:

- **Maximization singularities and analytic properties**. A generic point with respect to maximization is a point where $S(E)$ is analytic.

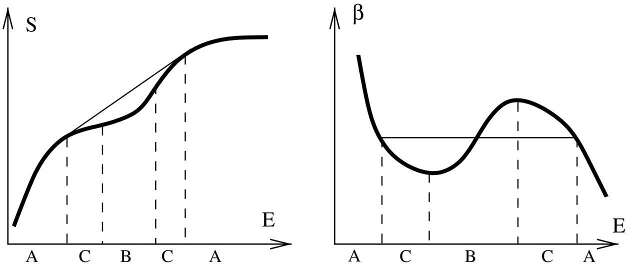

Fig. 1. The three types of generic points on the $S(E)$curve. Points in A zones are concave and belong to the concave envelop: they correspond to a canonical solution; B points are convex, thus canonically unstable; C points are concave but do not belong to the concave envelop: they are canonically metastable. The thin line is the canonical curve in the inequivalence range.

- **Convexity properties**. A generic point with respect to the convexity properties is a point where the second derivative of $S(E)$ is non-zero, so that S has a definite concavity. This defines two types of generic points with respect to the convexity properties, the concave and the convex ones.
- **Properties with respect to convexification**. A generic point of the curve $S(E)$ may or may not belong to the concave envelop of S. Thus, there are two types of generic points with respect to convexification.

We may now combine the different properties to get the different types of generic points:

- A concave point may or may not belong to the concave envelop of S. Consequently, there are two types of concave generic points: those who belong to the concave envelop (points A on Fig. 1), and those who do not belong to the envelop (points C on Fig. 1).
- A convex point cannot belong to the concave envelop, so that there is only one type of such generic points (points B on Fig. 1).

We have now classified the three types of generic points. The microcanonical and canonical ensembles are equivalent at points of the A type, and inequivalent at points of the B or C types (B or C define the *inequivalence range*). The negative specific heat regions correspond to points of the B type. The range of admissible values for E can be decomposed into several intervals, in the interior of which $S(E)$ has the property A, B or C. In codimension 0 (no external parameter), a generic curve $S(E)$ will be characterized by the bounds of these intervals. In the next section, we will follow the same scheme to systematically classify all these bounds, thus all codimension 0 singularities.

3.2. Codimension 0 Singularities

In this section, we construct all *generic entropy curves*, that is curves accessible without tuning an external parameter. We call codimension 0 points the special points met along a generic $S(E)$ curve when varying the energy and no other parameter. They are of codimension 0 with respect to one of the three sources of singularities (the maximization process, the convexity properties of S and the convexification of S), and generic points with respect to the other two: roughly speaking, we can "use" the tuning of the energy to find a special point with respect to just one of the sources. Thus, we first enumerate the codimension 0 singularities arising from each of the three sources, and then combine them with the generic points A, B or C.

3.2.1. The Three Sources of Singularities

- **Maximization singularities and analytic properties.** We want to classify all the singularities for the maximum of a variational problem with a constraint, when the value of the constraint is varied. We do not know any rigorous results dealing with this problem, in the literature. However, we use results from singularity theory,[(6)] proved for variational problems depending on a parameter. Here we have no parameter in the function but its role is played by the energy constraint. This difference might be important in some particular cases; we neglect this possibility in the following. Thus, from, ref. 6 we know that codimension 0 maximization singularities are of only one type. It corresponds to an exchange of stability/metastability between two different branches of solution of the variational problem. At such point E_c, S is continuous, but the derivative $\beta = \partial S/\partial E$ undergoes a *positive* jump. We will refer to these points as *microcanonical first order transitions*.

- **Convexity properties.** There is only one type of codimension 0 singularity arising from the convexity properties of S: the inflexion point, where the second derivative of S vanishes (thus $d\beta/dE = 0$), and the third derivative is non-zero. Since this corresponds to the point where a local minimum of $f(m,\beta) = \beta h(m) - s(m)$ becomes a saddle point, we will refer to it as a *canonical spinodal point*.[11]

[11]We note that due to the long range interactions, the crossing of a spinodal point is not associated to a spinodal decomposition (phase separation and coarsening) as in short range interacting systems. The phenomenology of the dynamics will rather be associated to some global destabilization.

- **Properties with respect to convexification**. The concave envelop of S is made by concave portions joined by straight lines. Thus, the only codimension 0 singularity arising from convexification is the junction of a curved and a straight portion of the concave envelop. Since this corresponds to a jump in the first derivative of the free energy $f(\beta)$, we will refer to it as a *canonical first order transition*. At these points, two canonical equilibrium states correspond to the same β, and only one of those is the microcanonical state; this situation is also called partial equivalence of ensembles.[15]

3.2.2. Construction of the Codimension 0 Singularities

We are now ready to construct all codimension 0 singularities of the $S(E)$ curve, by combining a codimension 0 situation in one of the three sources of singularities with a generic point in the other two.

- Let us first consider the *microcanonical first order transition*, see Fig. 2. At the point where two branches of $S(E)$ meet, the jump in the derivative $\partial S/\partial E$ is necessarily positive, so that the angle is reentrant. The point thus never belongs to the concave envelop of S: it is never visible in the canonical ensemble, it is in the *inequivalence range*. These two branches have a definite concavity, and may both be concave or convex. This determines three types of microcanonical phase transitions, the concave-convex and convex-concave ones being equivalent by change $E \to -E$.
- Let us now turn to the inflexion point, or *canonical spinodal point*: it connects a concave and a convex portion of S, and cannot belong to the concave envelop of S: it is in the *inequivalence range.* There is only one type of such points, represented on Fig. 2.
- The *canonical first order* transition bridges two contact point of the double tangent to the curve $S(E)$. At these two contact points, the $S(E)$ curve is always locally concave and there is only one type of such points, see Fig. 2.

This completes the classification of codimension 0 singularities. To summarize, there exist microcanonical first order transitions (three different types, according to the concavity of the branches), canonical first order transitions (one type), and canonical spinodal points (one type). From these, only the canonical first order transition is visible in the canonical ensemble; the others belong to the inequivalence range. A generic codimension 0 $S(E)$ curve is constructed with A, B or C type segments separated by these singularities.

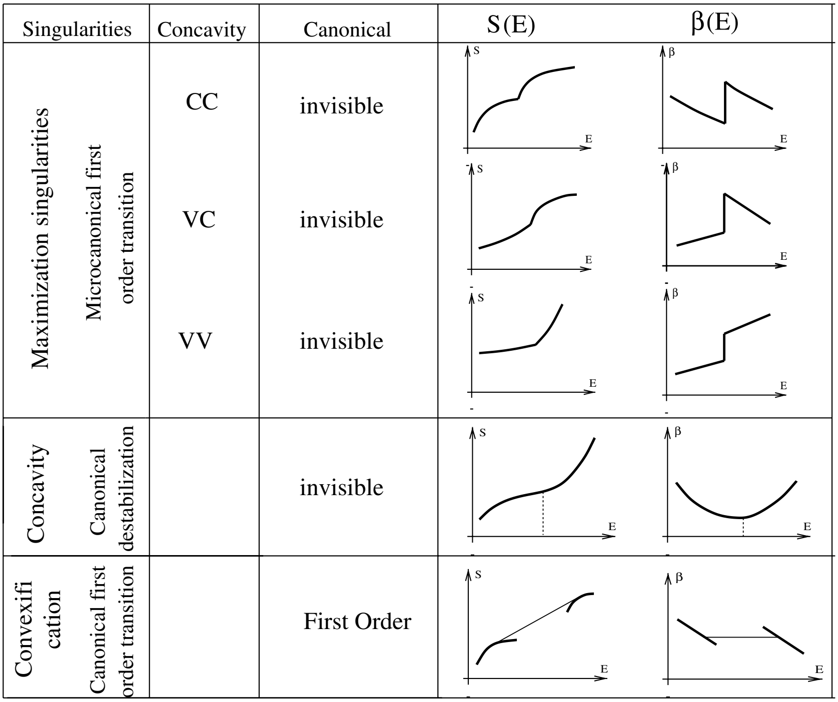

Fig. 2. Codimension 0 singularities. The first three rows are the three types of microcanonical first order transition, the fourth is the canonical spinodal point, and the fifth is the canonical first order transition. C stands for Concave, and V for conVex. The bold line is the microcanonical solution as well as the canonical one when they are equivalent; the thin one is the canonical solution. "Invisible" means that the transition is not visible in the canonical ensemble. The canonical curve in not drawn for invisible situations.

3.2.3. Examples in Physical Systems

Hertel and Thirring[18] introduced in a pioneering paper an exactly solvable model to illustrate the concepts of negative specific heat and inequivalence of ensembles. This simple model already shows the three types of generic points (including the negative specific heat), and all codimension 0 singularities: a *canonical first order transition*, a *canonical spinodal point*, and a *microcanonical first order transition* between a convex and a concave branch. These situations are also found in many different versions of more realistic self-gravitating systems.[9,21,31,39]

Examples can be found in other branches of physics: in ref. 16, Ellis and collaborators show a $\beta(E)$ curve for the quasi-geostrophic model displaying the three types of generic points, a *canonical first order transition*, and a *canonical spinodal point*; in ref. 25 Kiessling and Neukirch find the same phenomenology in a magnetically self-confined plasma torus.

All codimension 0 situations have thus already been found in physical models; we turn now to the the codimension 1 situations.

3.3. Varying an External Parameter: Codimension 1 Singularities

The codimension 1 singularities arise along the $S(E)$ curve when varying the energy and one external parameter: they describe the way a generic $S(E)$ curve can be modified into another one. We follow the same path as in the previous section to classify them: using singularity theory, we first enumerate all codimension 1 situations for any of the three sources of singularities, independently of the two other sources. We then construct all codimension 1 singularities by combinations: either of a codimension 1 situation in one source with a generic point in the other two, or of a codimension 0 situation with respect to two sources with a generic one in the last source.

3.3.1. Codimension 1 Singularities for the Three Sources of Singularities

• **Maximization singularities and analytic properties**. Using results of singularity theory, we know that the codimension 1 maximization singularities are of three types[(6)].

– the first type is the crossing of two microcanonical first order transitions. It happens when three different branches of solutions of the variational problem have the same entropy. We will refer to it as a *microcanonical triple point*.

– the second type is the appearance of a microcanonical first order transition; it corresponds to a point where $d\beta/dE = d^2S/dE^2 = +\infty$. We will call it a *microcanonical critical point*.

– the last type consists in the simultaneous appearance of two microcanonical first order transitions; it happens when a formerly wholly microcanonically metastable branch of $S(E)$ crosses the stable one. Following the terminology used in binary mixture phase transitions, we will call it an *azeotropic point* (see ref. 1, and Fig. 3 for an illustration).

• **Convexity properties**

– Varying the energy and an additional parameter allows one to pick up on the $S(E)$ curve points where the second and third derivatives

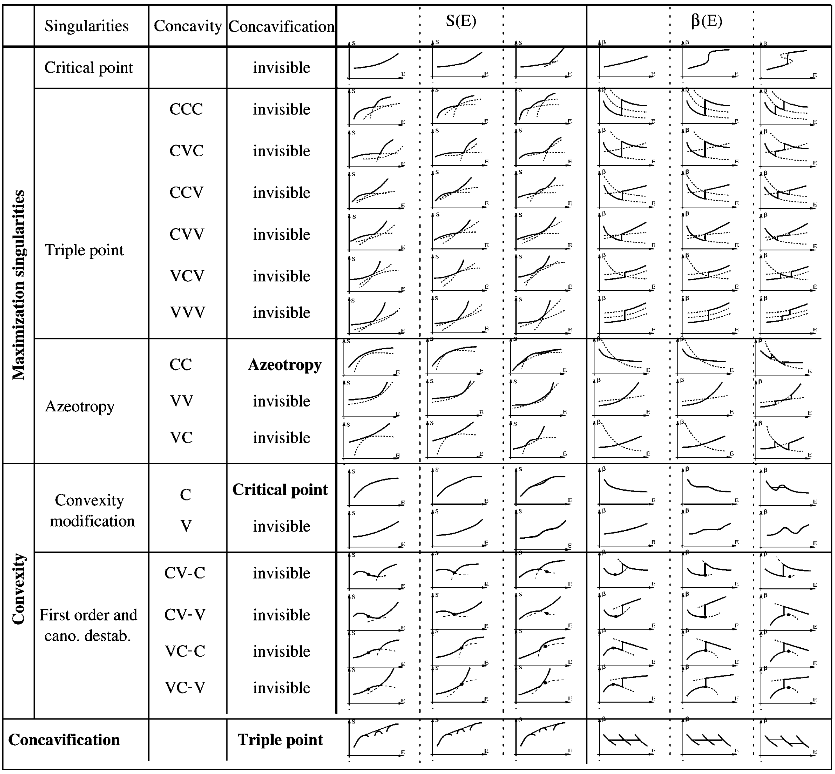

Fig. 3. Codimension 1 singularities. The three curves $S(E)$ and $\beta(E)$ for each singularity correspond to the situation just before the singularity is crossed, right at the singularity, and just after it. See the text for comments; the meaning of the curves is as in Fig. 2, and dotted lines represent metastable or unstable microcanonical branches.

of $S(E)$ vanish. They show up as inflexion points with a horizontal tangent in the $\beta(E)$ curve. This situation will be called a *convexity change*.

• **Properties with respect to convexification.** When varying an external parameter, the structure of the concave envelop, as a succession of concave regions and straight lines, changes. The codimension 1 singularities arising from convexification are precisely the points where this structure changes; they are of two types:

– The first one is the appearance of a straight portion in the concave envelope in a formerly concave region. This requires that d^2S/dE^2 and d^3S/dE^3 vanish together. It is actually a convexity change as described above, but with the additional request to be in the concave envelop. This type of convexity change is the *canonical critical point*.

– The second one is the breaking of a straight portion in two straight portions separated by a concave zone. This happens when there is a triple tangent to the $S(E)$ graph; this will be called a *canonical triple point*.

3.3.2. Construction of the Codimension 1 Singularities

The codimension 1 singularities are constructed by combining a codimension 1 situation from one of the three sources of singularity, with a generic point for the other two, or by combining two codimension 0 singularities.

- The *microcanonical triple point* involves three different branches of solution, that may all be either convex or concave. We refer them by three letters, for instance CVC (C for concave and V for convex). The first letter refers to the convexity of the low energy branch, the second one to the convexity of the appearing branch, and the third one to the convexity of high energy branch (see Fig. 3). There are eight types of such points, however, the CCV and VCC or the CVV and VVC cases, respectively, are equivalent (by a change $E \to -E$). The six remaining cases are illustrated on Fig. 3. All these situations are always invisible in the concave envelop, thus always canonically invisible.

- The *microcanonical critical point* necessarily arises, in codimension 1, inside a convex region of the $S(E)$ curve, invisible in the concave envelop. Thus, there is only one type of such points, see Fig. 3.

- The *azeotropy* phenomenon involves two branches, but it is not possible to have the lower branch convex and the upper one concave. This leaves three cases, from which only the concave-concave (CC) one is visible in the canonical ensemble; see Fig. 3. We refer to these situations by two letters, for instance CV, where the second letter refers to the appearing branch.

- There are two types of *convexity change*: one corresponds to the appearance of a convex zone inside a concave one (referred by C), and the other of a concave zone in a convex one (referred by V). The first case may be visible after convexification. When such it is the *canonical critical point*. See Fig. 3.

- The *canonical triple point*, or triple tangent case, always connects three concave parts of the $S(E)$ curve, so that there is only one type of such points, see Fig. 3.

- We turn now to a combination of two codimension 0 singularities: the *encounter of* a *canonical spinodal point with a microcanonical first order transition*. Let us suppose that the branch with the inflexion point is the low energy one (other cases are recovered by the change $E \to -E$). The four cases CV-C, CV-V, VC-C and VC-V exist, where the two first letters refer to the concavity of the branch with the inflexion point, and the last one, to the concavity of the other branch, see Fig. 3. The canonical first order transition always happens alone, so that there is no other possible combination of codimension 0 situations.

The codimension 1 singularities allow us to discuss the onset of ensemble inequivalence, i.e. how the concavity of the $S(E)$ curve is destroyed when varying an external parameter. The inspection of the above classification tells us that this can happen in only two ways: at a canonical critical point and at an azeotropic point.

Let us also summarize the links between microcanonical and canonical codimension 1 singularities. The canonical critical point corresponds to the appearance of a convex intruder in the entropy, the canonical triple point is linked to a convexification singularity, whereas the canonical azeotropy occurs together with a CC microcanonical azeotropy.

We give now examples of physical models displaying some of these codimension 1 situations.

3.3.3. Examples in Physical Systems

A cut-off is often imposed to regularize the short-range singularity of self gravitating systems; the tuning of this new parameter allows to observe codimension 1 singularities. The first rigorous study of the free energy of self gravitating fermions has been performed by Hertel and Thirring,[19] and the illustration of ensemble inequivalence associated to a first order canonical phase transition is presented in ref. 40. A comprehensive description of the phenomenology of the phase diagram may be found in[9]: in addition to all types of codimension 0 singularities, the phase diagram exhibits a microcanonical critical point, a canonical critical point, and a crossing point between a microcanonical first order transition and a canonical spinodal point. In Section 2.2, we argued that the knowledge of the entropy–energy curve, in particular of its concavity and convexification properties, is sufficient to characterize both the microcanonical and canonical phase transitions. In order to illustrate this point we draw a schematic $(-E, r)$ phase diagram for self-gravitating fermions (r is the short range cut-off) on Fig. 4. On this diagram, both microcanonical and canonical phase transitions are represented.

A similar phenomenology has been found in the study of many different versions of self gravitating systems, the external parameter being always the short distance cut-off imposed on the gravitational interaction in various ways.[9,39]. We refer to the article[8] for a more complete bibliography and a more comprehensive description of phase transitions in self-gravitating systems.

To summarize, if all codimension 0 singularities have been found in various models of interacting particles, just a few codimension 1 situations have already been observed. The classification thus allows to point out new possible phenomenologies: *microcanonical* and *canonical triple points*, *azeotropy*, and *convexity change* V (that is appearance of a concave zone inside a convex one) have to our knowledge never been described in the literature on long range interacting systems. Inspection of these transitions shows that not only negative specific heat may occur in systems with long range interaction, but also a wide zoology of uncommon behaviors.

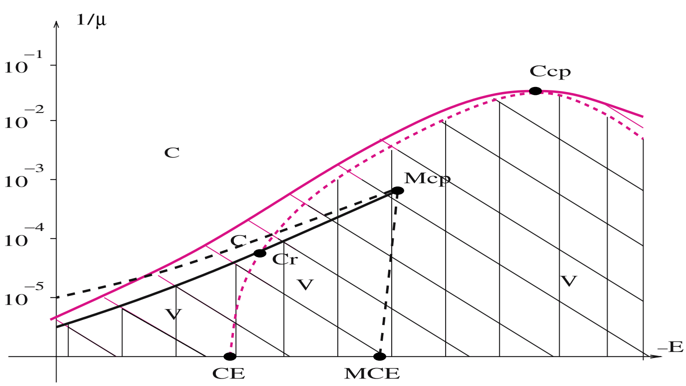

Fig. 4. Schematic phase diagram for self-gravitating fermions. Horizontal and vertical axis are respectively minus the energy and a small length scale cut-off. This illustrates that a microcanonical diagram including microcanonical phase transitions as well as entropy concavity and convexification properties is sufficient to summarize the canonical phase transitions. The bold line is a first order microcanonical phase transition line (between gaseous and core-halo phases), ending at a **microcanonical critical point (Mcp)**. The grey line is a canonical first order transition line (convexification singularity), with a **canonical critical point (Ccp)**. The dashed grey line is a line of canonical spinodal point. It crosses the microcanonical first order phase transition at Cr. The hashed zone is the inequivalence area, absent in the canonical ensemble; the doubly hashed is the negative specific region. The bold dashed line is a line of microcanonical stability change, marking the limits of stability of the gaseous and core-halo phases (such microcanonical stability changes are not described in our classification). For $1/\mu = 0$, we recover the self-gravitating isothermal collapse (CE) and gravitational phase transition (MCE) points. A similar phase diagram has been done independently in ref. 10.

4. CLASSIFICATION OF PHASE TRANSITIONS AND ENSEMBLE INEQUIVALENCE SITUATIONS IN SYSTEMS WITH SYMMETRY

The classification of the previous section succeeded in reproducing the phenomenology of many different systems, but not all of them. In particular, the various situations associated with second order phase transitions do not appear. The reason is that the notion of codimension 0, codimension 1 singularities and so on were introduced under the only hypothesis that the functional $s(m)$ is infinitely differentiable, without any reference to the physical system considered. However, the symmetries of the physical situation, if present, will reflect in the functional $s(m)$, which then has to verify *a priori* some additional hypothesis. This will lower the codimension of some singularities, creating a much richer phenomenology already at the level of codimension 0 and 1 singularities. Thus, we have to complete our classification to apply it to physical systems with symmetries, like the parity symmetry of an Ising spin system, the rotational symmetry of a self gravitating system in a spherical box...

4.1. Relation Between Symmetry and Codimension on a Simple Example

To make clearer the point raised in the previous paragraph, let us consider the mean field Ising model. Without external field, it displays a second order phase transition in the canonical ensemble, not described in the classification so far: this is directly related to the parity symmetry of the model. With an external field, this symmetry is destroyed, as well as the second order phase transition; a first order phase transition, codimension 0 singularity even in the absence of symmetry, may however remain.

To be more precise, we consider a functional $s(m, E)$ with $m \in \mathcal{R}$, with a parity symmetry: $s(-m, E) = s(m, E)$. As a consequence, all derivatives of odd order vanish in $m = 0$: $\partial_m^{(2n+1)} s|_{(0,E)} = 0$. Let us consider now a microcanonical critical point, defined as a point (m_c, E_c) where $\partial_m^{(n)} s|_{(m_c,E_c)} = 0$, for $n = 1, 2, 3$. Without any hypothesis on the function s, this requires *a priori* to satisfy three equations. Thus, a generic critical point can only be found by adding another degree of freedom, besides m and E, and is of codimension 1. For instance a normal form for a critical point is given by $s(E, \lambda) = \max_m \left\{-m^4 + bm^2 + am\right\}$, where a and b are linear combination of E and λ, and λ is a tunable external parameter. The critical point is given by $a = b = 0$ and the line of microcanonical first order transition is given by $a = 0$ and $b > 0$. However, if s is symmetric under parity, all odd derivatives automatically vanish at $m = 0$, so that finding a critical point breaking this symmetry requires only to satisfy one equation, varying E.

Moreover as the first derivative identically vanishes, the transition is continuous: a microcanonical second order phase transition is in that case a codimension 0 phenomenon. For instance, a normal form is given by $s(E) = \max_m \left\{ -m^4 + (E - E_c)\, m^2 \right\}$.

In the following, we make the hypothesis that for a more general symmetry, at least one variable m_2 may be found such that all odd derivatives with respect to m_2 of $s(m_1, m_2, E, \lambda)$ identically vanish: $\partial_{m_2}^{(2n+1)} s|_{m_2=0} = 0$. This is actually the case for a rotational symmetry, where the radius r plays the role of m_2. A case by case study should be done for any other symmetry.

We are not aware of any mathematical result we could use to enumerate the new singularities, such as ref. 6 for the non-symmetric case. We will thus use in the following the heuristic, but systematic, criterion based on the "number of equations to be solved", as explained in this paragraph.

4.2. Codimension 0 Singularities

The singularities associated to the convexity properties, as well as those concerning the convexification, are not modified when a symmetry is assumed. As seen above, however, there is now an additional singularity due to the maximization process: the second order phase transition, associated with a symmetry breaking. At these points, a microcanonically stable branch obeying the symmetry loses stability, and a non-symmetric stable branch appears. By convention, we will suppose that the symmetric branch is stable at energies larger than E_c, and the broken symmetry branch is stable for energy smaller than E_c, although it is not necessary. $S(E)$ and dS/dE are continuous at $E = E_c$, but d^2S/dE^2 experiences a *negative jump* (a positive jump if the opposite convention were adopted).

A priori, the high and low energy branches may be concave or convex, but because of this negative jump condition, the association of a concave low energy branch with a convex high energy branch is impossible. We are thus left with three types of second order phase transitions denoted CC, VC and VV where the first letter refers to the low energy branch convexity, see Fig. 5. Only the CC microcanonical second order phase transition is visible in the canonical ensemble: it is the canonical second order phase transition. This completes the classification of codimension 0 singularities.

4.3. Codimension 1 Singularities

The new codimension 1 singularities arise on one hand from the new codimension 1 singularities due to the maximization, and on the other

Singularities		Concavity	Convexification	S(E)	β(E)
Maximization singularities	Microcanonical second order transition	CC	Second Order		
		VC	invisible		
		VV	invisible		

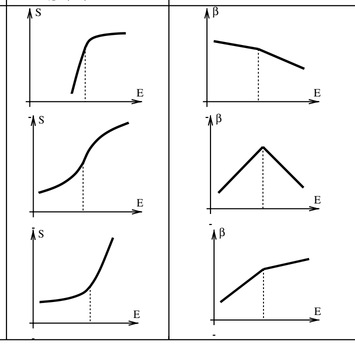

Fig. 5. New codimension 0 singularities for systems with symmetry.

hand from the combination of the second order phase transition (of codimension 0) with other codimension 0 singularities. We first identify the new codimension 1 singularities, due to symmetry.

4.3.1. Codimension 1 Singularities for the Three Sources of Singularities

- **Maximization singularities and analytic properties**

The microcanonical critical point, microcanonical triple point and azeotropic point are unchanged. Five new singularities are added.

– the first one appears when the first five derivatives of s vanish together along a certain direction. A normal form is given by $S(E,\lambda) = \max_m \left\{-m^6 - 3bm^4/2 - 3am^2\right\}$, where a and b are linear combinations of E and λ, and λ is the tunable external parameter which gives access to codimension 1 singularities. In the (E,λ) plane, it connects a line of microcanonical first order transitions with a line of second order phase transitions; following the usual canonical terminology we will refer to it as a **microcanonical tricritical point**.[14] Figure 6 shows the transition lines in the (E,λ) plane in the vicinity of a microcanonical tricritical point. The qualitative features of this diagram are universal: they do not depend on the polynomial form chosen for S.

– the second one occurs when s has two equal maxima, and one of these is quartic along one direction. A normal form is given by $S_1(E,\lambda) = \max_{m_1} \left\{-m_1^4 - 2am_1^2;\ -m_1^2 + b\right\}$, where a and b are linear combinations of

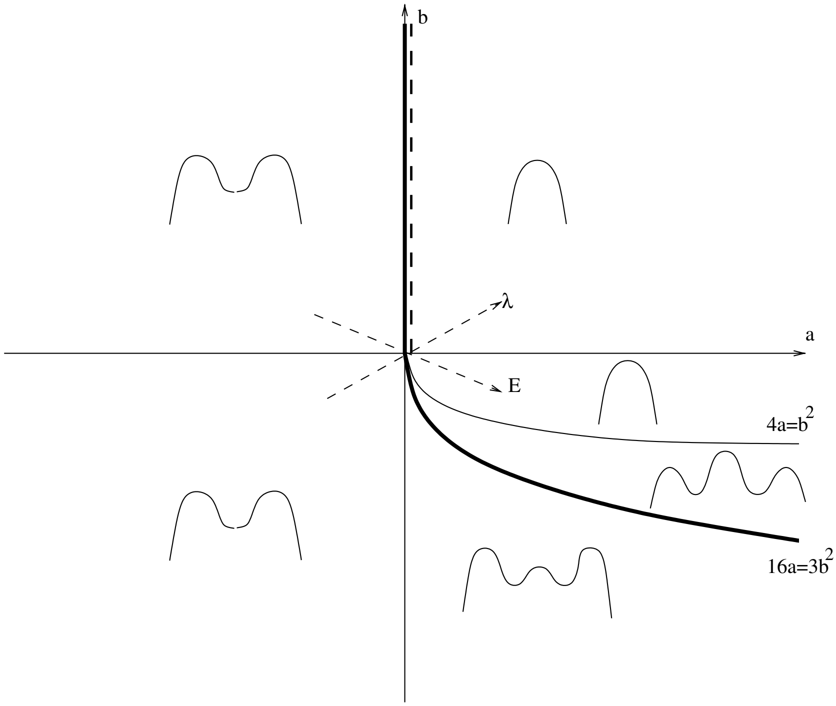

Fig. 6. Transition lines in the vicinity of a **microcanonical tricritical point**, from the normal form $S(E,\lambda) = \max_m \{-m^6 - 3bm^4/2 - 3am^2\}$. The tricritical point is reached for $a = b = 0$. Small insets show the typical behavior of $s_{a,b}(m)$in the various areas. The curve $4a = b^2$corresponds to the appearance of three local maxima. The bold curve ($16a = 3b^2$, $b < 0$) is a first order transition line. The bold-dashed curve is a second order transition line, with negative concavity jump when going on the dashed side of the curve. a and b are linear combinations of E and λ. Some possible directions for E and λ are represented by the dashed arrows; with these orientations, the transition is first order for $\lambda < 0$ and second order for $\lambda > 0$.

E and λ. In the (E,λ) plane, it connects a line of microcanonical first order transitions with a line of second order phase transitions. It is a **microcanonical critical end point**.[14] Transition lines in the vicinity of a microcanonical critical end point are shown on Fig. 7.

– the third and fourth happen at a crossing of two second order transition lines, when the maximum of s is quartic along two directions having the symmetry property. A normal form is given by $S(E,\lambda) = \max_{m_1,m_2} \{-m_1^4 - 2am_1^2 - m_2^4 - 2bm_2^2 - cm_1^2m_2^2\}$, where $a \to 0$ and $b \to 0$ are linear combinations of E and λ, and c is a finite constant with $c > -1$. Two cases have to be considered (see Fig. 8).

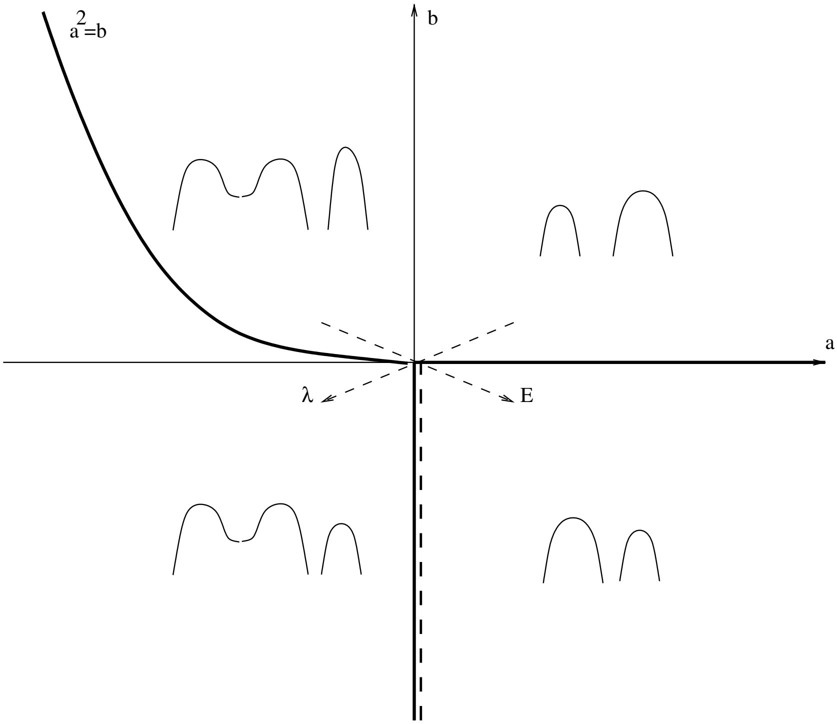

Fig. 7. Transition lines in the vicinity of a **microcanonical critical end point**, from the normal form $S(E,\lambda)=\max_m\left\{-m^4-2am^2;\ -m^2+b\right\}$. Small insets show the typical behavior of $s_{a,b}(m)$in the various areas, the lhs figure referring to the quartic part. Meaning of curves and arrows are as in Fig. 6.

When $c<1$, varying the external parameter λ, two second order transitions come closer and closer; once the critical value of the parameter is reached, they cross each other and remain unaffected. We are not aware of any standard denomination for this singularity; as it involves four phases ($m_1=m_2=0$, $m_1=0$ and $m_2\neq 0$, $m_1\neq 0$ and $m_2=0$, and $m_1\neq 0$ and $m_2\neq 0$), we call it a **second order quadruple point**. When $c>1$, the doubly asymmetric phase $m_1\neq 0$ and $m_2\neq 0$ is unstable (see Fig. 8). For $a<0$ and $b<0$, the two phases $m_1=0$ and $m_2\neq 0$, $m_1\neq 0$ and $m_2=0$ may have the same entropy, and a first order transition between them occurs when $a=b$. It is a **microcanonical bicritical point**.(14) Transition lines for all these situations are shown in Fig. 8.

– the last new singularity is the simultaneous appearance of two second order phase transitions. It happens when the coefficient of the quartic term around the maximum of s, along a certain direction, has a

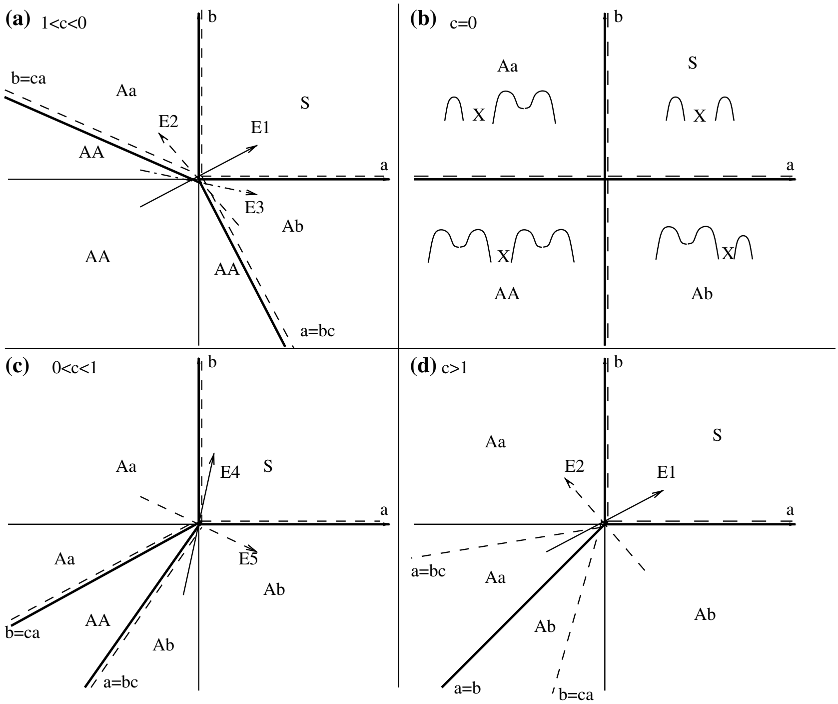

Fig. 8. Transition lines in the vicinity of a crossing of two microcanonical second order transitions, from the normal form $S(E,\lambda)=\max_{m_1,m_2}\left\{-m_1^4-2am_1^2-\ m_2^4-2bm_2^2-2cm_1^2m_2^2\right\}$ (see text). Letters S, Aa, Ab and AA refer to the four phases involved: Symmetric S $m_1 = m_2 = 0$, Antisymmetric Ab: $m_1 = 0$ and $m_2 \neq 0$, Antisymmetric Aa: $m_1 \neq 0$ and $m_2 = 0$, and Antisymmetric AA: $m_1 \neq 0$ and $m_2 \neq 0$. Their entropy is respectively $S_S = 0$, $S_{Aa} = a^2$, $S_{Ab} = b^2$ and $S_{AA} = \left(b^2+a^2-2cab\right)/\left(1-c^2\right)$. Panels (a), (b) and (c) represent respectively $-1<c<0$, $c=0$, $0<c<1$ and all correspond to a **second order quadruple point** (this is not a standard term). Panel d is for $c>1$ and corresponds to a **microcanonical bicritical point**. For $c=0$, small insets show the typical behavior of $s_{a,b}(m_1, m_2)$ in the various areas, the rhs (resp. lhs) figure referring to the dependence on m_1(resp m_2). The second order lines are represented by bold-dashed curve, with negative concavity jump when going on the dashed side of the curve. Possible directions for E are represented by the arrows in panels (a), (c) and (d).

double root for e. We will refer to it as a **second order azeotropic point**. If we call λ the free parameter, the locus of a second order phase transition is represented by a curve in the (λ, E) plane; a second order azeotropy occurs when a line of constant λ is tangent to this curve. A normal form is given by $S(E,\lambda)=\max_m\left\{-m^4+2\left(E^2-\lambda\right)m^2\right\}$ (see Fig. 9).

- **Convexity properties**. No new singularity arises from the inspection of the convexity properties.

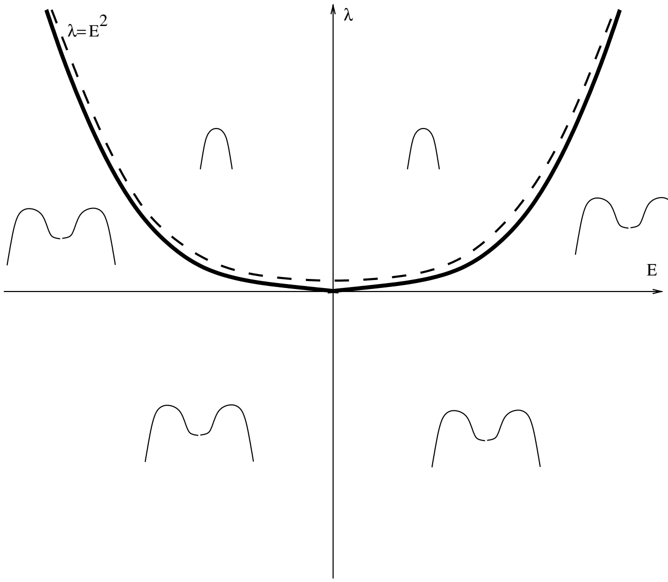

Fig. 9. Transition lines in the vicinity of a **second order azeotropy**, from the normal form $S(E,\lambda)=\max_m\left\{-m^4+2\left(E^2-\lambda\right)m^2\right\}$. The bold-dashed curve is a second order transition line, with negative concavity jump when going on the dashed side of the curve.

- **Properties with respect to convexification**. No new singularity arises from the convexification of $S(E)$.

4.3.2. Construction of the Codimension 1 Singularities

We now have to construct the new codimension 1 singularities by combining a new codimension 1 situation for the maximization process with a generic point for the other two sources of singularities, or by combining a second order phase transition with another codimension 0 situation. Although the procedure is straightforward, discussing all cases is tedious. We have chosen to give a detailed discussion for the **tricritical** and **bicritical points** only, in both ensembles. Table I summarizes all the results.

Tricritical points: Inspection of the entropy development around $m=0$ for the **microcanonical tricritical point** shows that at the tricritical point $\lambda=\lambda_c$, $E\to E_c^-$, the temperature is given by $\beta(E)\simeq-C(E_c-E)^{1/2}$, where C is a positive constant. This proves that the low energy branch (less symmetric phase with our convention) is necessarily convex. According to the concavity of the high energy branch, there are thus two types of such points, which we denote VV and VC. Because of the convexity of at least one of the branch, both types are invisible in the canonical ensemble. See Fig. 10.

Table I. This Table Summarizes the New Codimension 1 Singularities, when some Symmetry of the System is Considered

Singularity type	Microcanonical singularity	Nbr	Canonical (Nbr)	Ineq.
Maximization	Tricritical	1/2	None	None
	Critical end point	1/6	None	None
	2nd order quadruple	4/20	2nd order quadruple (4) Bicritical (2)	None
	Bicritical	2/8	Bicritical(2)	2
	2nd order azeotropy	1/2	2nd order azeotropy (1)	None
Convexity	2nd order +inflexion	1/2	Tricritical (1)	1
Convexification	2nd order +convexification	1	Critical end point (1)	None

The third column is the number of singularities of a given type (the second number when convexity properties are taken into account, the first one when not). The fourth column is the number of singularities visible in the canonical ensemble together with their type. The last column gives the number of singularities associated with the appearance/disappearance of an energy range of ensemble inequivalence. For instance, they are 4 types of microcanonical second order quadruple points, 20 when convexity is taken into account, 6 of which are canonically visible, giving respectively 4 canonical second order quadruple points and 2 canonical bicritical points. This last one is associated to the onset of ensemble inequivalence.

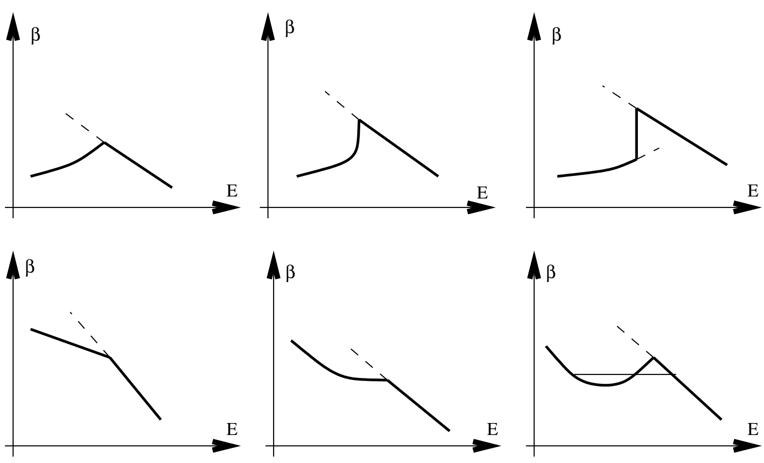

Fig. 10. Schematic caloric curves around a microcanonical VC (upper row) and a canonical (lower row) tricritical point, respectively before (left), at (center), and after (right) the singularity. The bold lines is the microcanonical solution as well as the canonical one when they are equivalent; the thin line is the canonical solution in the inequivalence range (not drawn on the top row); the dashed line represents microcanonically metastable or unstable branches. Note the ensemble inequivalence onset around a canonical tricritical point.

We can construct a codimension 1 situation by superposing a second order transition (codimension 0) with a canonical spinodal point in one of the two branches (codimension 0). If the inflexion point is in the low energy branch, the second order transition evolves from a CC situation to a VC one. This is visible in the canonical ensemble. As it corresponds to the appearance of a first order transition from a second order one, it is a **canonical tricritical point**. As a first order canonical transition appears at this point, this singularity is associated to the onset of ensemble inequivalence, see Fig. 10. If the inflexion point is in the high energy branch, the situation evolves from VV to VC; it is not visible in the canonical ensemble.

Bicritical points: We base our discussion of the **microcanonical bicritical point** on Fig. 8d. Depending on the orientation of the E and λ axis in the (a, b) plane, there are two ways to cross the singularity. Along the first one (E_1, solid line on Fig. 8d), the first order phase transition disappears at the singularity point, and the succession of phases is Aa-Ab-S→Aa-S; we still adopt the convention that the symmetric phase is the one of highest energy). Taking into account the two negative concavity jumps associated with the second order transitions, as well as the direction of E in the (a, b) plane, we are left with four possible concavity configurations for this Aa-Ab-S→Aa-S singularity: VVV→VV, VVC→VC, VCC→VC, and CCC→CC (the CVC→CC case is eliminated by the choice of the direction for E: indeed, $S_{Aa} = a^2$, $S_{Ab} = b^2$, and the choice of the E direction is such that Ab is more concave than Aa). Only the last one (CCC→CC) is visible in the canonical ensemble. As it involves a canonically invisible range near the first order transition, it is associated with the ensemble inequivalence onset. In the canonical ensemble, this situation involves a first order and a second order phase transitions before the singularity and a second order one after it. From the explicit computation of $F(\beta)$ from the normal form, we conclude that the second order transition before the transition is visible in the canonical ensemble. This singularity is thus a **canonical bicritical point**; see Fig. 11 for schematic entropic and caloric curves in that case. Along the E_2 direction (dashed line on Fig. 8d), the first order phase transition disappears and two second order phase transitions take place: Aa-Ab→Aa-S-Ab. Taking into account the two concavity jumps associated with the second order transitions, we have four possible concavity configurations for this Aa-Ab→Aa-S-Ab type: VV→VVV, VV→VCV, VC→VCC, CC→CCC (the case CV→CCV is also possible, but equivalent, by symmetry, to the VC→VCC one). Only the CC→CCC case is canonically visible, and it is associated with ensemble inequivalence onset. It is also a **canonical bicritical point**.

The same discussion is carried out for all other singularities in appendix. This allows to enumerate all possible microcanonical and canonical

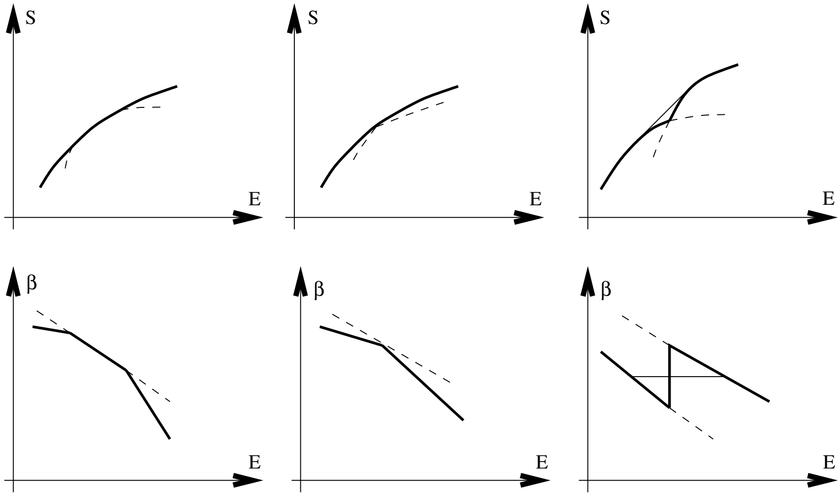

Fig. 11. Schematic entropic and caloric curves around a bicritical point, of CCC→CC type, before, at and after the singularity. Lines have the same signification as in Fig. 10. Note the other type of inequivalence onset.

transitions and their mutual relationship. The results are summarized in Table I. Most of the new singularities take place in the inequivalence range, and thus are canonically invisible, but two new types of inequivalence onset are found, associated with the canonical tricritical and bicritical points.

Let us comment further on the links between canonical and microcanonical ensembles. As the canonical optimization problem and the microcanonical one are formally equivalent (once the energy constraint is considered as a parameter in the microcanonical problem, which is what we have done), we should find exactly the same singularities in the two ensembles, even though we have constructed the canonical solution by convexification of the microcanonical one and not directly from the optimization problem. This is indeed what we find, proving the consistency of our results. All microcanonical singularities have thus a canonical equivalent, but the microcanonical phenomenology is much richer, as it allows many more concavity configurations. We review in the following paragraph the different situations already observed in the literature, and point out the ones which have not been found yet.

4.4. Examples

One of our main goals is to study the onset of ensemble inequivalence, or equivalently the failure of the concavity of $S(E)$ varying an external parameter. For non-symmetric systems, the canonical critical point and the azeotropic point have been shown to be the only two types of inequivalence onset. Two new types are identified for systems with symmetry. One is the canonical tricritical point, across which a CC microcanonical second order transition becomes a VC one. Onset of inequivalence through a **canonical tricritical point** has been observed at least twice, in a toy model of self gravitating system[2] and in a spin system.[5] This situation has also been studied in a general setting.[27] Onset of inequivalence around a **canonical bicritical point** has to our knowledge never been found.

Concerning the other codimension 1 singularities listed in this section, we are aware of just a few references. A **microcanonical tricritical point** with a concave high energy branch has been found in a spin system;[5] a **microcanonical critical end point** has been observed in ref. 2. All the other classified situations, some of which are rather exotic, have apparently never been found. As for the non-symmetric case, we expect some of these new situations to be found when more complex models are studied. Let us note that some of these singularities have of course been found in a purely canonical setting: see for instance ref. 26.

5. CONCLUSION

We have proposed in this article a classification of phase transitions in non additive systems. It relies on the fact that these systems are "mean field like", which enables one to find the microcanonical and canonical equilibrium states as solutions of variational problems. Taking advantage of this structure, and making use of existing results from singularity theory when available, or of heuristic arguments when not, we have classified all phase transitions for these systems up to codimension 1, that is we have enumerated all the elementary pieces building the phase diagrams of systems with one constraint (usually the energy) and one free parameter. All these results are summarized by Figs. 2, 3, 5 and Table I.

This classification gives a unique framework to understand the unusual thermodynamic phenomena arising in the many fields of physics concerned by this non-additivity problem: astrophysics, two dimensional and geophysical turbulence, some models of plasma physics. All phase diagrams obtained so far in these fields (analytically or numerically), are reproduced by the classification. In addition, we have exhibited some phenomenologies likely to appear in the non-additive context, but not yet found in any specific model. Among them, we can mention azeotropy and canonical bicritical points, which are new types of ensemble inequivalence onset. Moreover, lots of singularities associated with precise convexity and convexification properties have also not been observed. We have not emphasized in the paper the critical exponents of the various transitions; however, it is clear that since the mean field approach is valid, they are totally universal for the systems considered, and may be calculated easily.

We have restricted in this article the classification to codimension 1 situations (corresponding to systems with one free parameter), and one conserved quantity (the energy in the whole article). It is thus possible to generalize this work, either by classifying situations of codimension greater than 2, or, maybe more interestingly, by considering systems with two or more conserved quantities (angular momentum, total circulation for fluids models). Taking into account more conserved quantities is likely to give a much richer phenomenology, as shown for instance in the work,[43] for the self gravitating gas with short range cut off, and conserved angular momentum, in addition to the energy. Another problem not analyzed in this work is the possibility of singularities at the border of the accessible energy range for the system.

APPENDIX

In this appendix we give a detailed discussion of the construction of all codimension 1 singularities in a system with symmetry (see Section 4.3.2), corresponding to the microcanonical critical end point, to the second order quadruple point, and to the second order azeotropic point.

- **The microcanonical critical end point** is schematically represented in Fig. 7. With axis (E, λ) as drawn, there is one first order transition for $\lambda < 0$, and a first order then a second order transitions for $\lambda > 0$. Combining the three types of second order transitions with the two possible concavities of the additional branch yields six different situations, denoted C-CC, V-CC, C-VC, V-VC, C-VV and V-VV, where the first letter refers to the first order transition concavity and the two last ones refer to the second order transition. Other directions for E and λ on Fig. 7 are recovered by symmetry.

- the **second order quadruple point** involves four phases, visible on Fig. 8, denoted AA, Aa, Ab, and S (A refers to asymmetric and S to symmetric, see Fig. 8a, b and c). Let us analyze the convexity of the entropy $d^2S(E)/dE^2$, where the energy E is along a fixed direction in the (a, b) plane. Each of the four second order transitions AA-Aa, AA-Ab, Aa-S and Ab-S involves a negative concavity jump, independently of the way the transitions are crossed in the (a, b) plane. Taking into account the signs of these jumps, the 6 following cases are possible, for the concavity of the branches AA, Aa, Ab and S, respectively: VVVV, VVVC, VVCC, VCVC, VCCC, CCCC. *A priori*, we do not have any information about which branch between Aa or Ab is more convex than the other; however, fixing the direction of E in the (a, b) plane may force the concavity jump between Aa and Ab to have a definite sign, as we will see.

When crossing the singularity, the type of transition (succession of phase on the E line) depends on the E direction (see for instance E_1, E_2 and E_3 on Fig. 8). Along the E_1 direction, one goes from a succession of phases AA-Ab-S to AA-Aa-S; along the E_2 direction, the succession is Ab-S-Aa $\rightarrow$Ab-AA-Aa; along E_3, the succession is AA-Ab $\rightarrow$AA-Aa-S-Ab (this is possible only if the parameter c in the normal form is such that $-1 < c < 0$): three transitions appear from a single one; along E_4, the succession is Ab-S $\rightarrow$Ab-AA-Aa-S (this is possible only if the parameter c in the normal form is such that $0 < c < 1$): also in this case, three transitions appear from a single one. All other possible directions for E and λ can be recast into one of the four previous situations, using the changes of variables $E \rightarrow -E$, $\lambda \rightarrow -\lambda$, and the symmetric role played by the branches Aa and Ab. For instance, the E_5 direction on Fig. 8c leads to Aa-AA-Ab $\rightarrow$ Aa-S-Ab, which is actually the same as E_2, once the changes $E \rightarrow -E$, $\lambda \rightarrow -\lambda$ are made.

Taking into account the previously studied concavity configurations, 5 possible AA-Ab-S $\rightarrow$AA-Aa-S transitions are found: VVV$\rightarrow$VVV, VVC$\rightarrow$VVC, VCC$\rightarrow$VVC, VCC$\rightarrow$VCC, CCC$\rightarrow$CCC (the VVC$\rightarrow$VCC case is also possible, but equivalent, by symmetry, to VCC$\rightarrow$VVC). Only the CCC$\rightarrow$CCC type transitions are visible in the canonical ensemble; it is not associated with the onset of ensemble inequivalence. Moreover, the continuity of $\beta(E)$and of $S(E, \lambda)$ insures the continuity of $F(\beta, \lambda)$ and of $\partial_\beta F(\beta, \lambda) = -E(\beta)$. Therefore, the microcanonical AA-Ab-S $\rightarrow$ AA-Aa-S, CCC$\rightarrow$CCC second order quadruple point is associated to a AA-Ab-S$\rightarrow$AA-Aa-S **canonical second order quadruple point.**

Taking into account the concavity configurations, 5 possible Ab-AA-Aa $\rightarrow$Ab-S-Aa transitions are found: VVV$\rightarrow$VVV, VVV$\rightarrow$VCV, CVV$\rightarrow$ CCV, CVC$\rightarrow$CCC, CCC$\rightarrow$CCC (the VVC$\rightarrow$VCC case is also possible, but equivalent, by symmetry, to CVV$\rightarrow$CCV). Only the CCC$\rightarrow$CCC and the CVC$\rightarrow$CCC types are canonically visible, and the latter is associated with the onset (disappearance when crossed that way) of an energy range where ensembles are not equivalent: the convex AA branch is replaced by a first order transition in the canonical one. The same reasoning as above for the continuity of $F(\beta, \lambda)$ and of $\partial_\beta F(\beta, \lambda) = -E(\beta)$ insures that the CC microcanonical second order transitions remain second order transitions in the canonical ensemble. We conclude that the microcanonical

Ab-AA-Aa→Ab-S-Aa, CCC→CCC second order quadruple point is associated to a Ab-AA-Aa→Ab-S-Aa **canonical second order quadruple point**, and the microcanonical Ab-AA-Aa →Ab-S-Aa, CVC→CCC second order quadruple point is associated to a Ab-Aa→Ab-S-Aa **canonical bicritical point**.

Taking into account the concavity configurations, 5 possible AA-Ab→AA-Aa-S-Ab singularities are found: VV→VVVV, VV→VVCV, VC→VVCC, VC→VCCC, CC→CCCC. The direction of E in the vicinity of the singularity (for instance E_3 on Fig. 8a) implies that the Aa branch is more convex than the Ab one; that's why the VV→VCCV case has to be eliminated. Only the CC→CCCC type is canonically visible; it is not associated with ensemble inequivalence onset. We conclude that the microcanonical AA-Ab→AA-Aa-S-Ab, CC→CCCC second order quadruple point is associated with a AA-Ab→AA-Aa-S-Ab **canonical second order quadruple point**.

Finally, taking into account the concavity configurations, 5 possible Ab-S →Ab-AA-Aa-S singularities are found: VV→VVV, VC→ VVVC, VC→VVCC, CC→CVCC, CC→CCCC. The direction of E implies that the Ab branch is more convex than the Aa one, so that we have eliminated the CC→CVVC case. The CC→CCCC case is canonically visible, not associated with ensemble inequivalence onset, and corresponds to a Ab-S →Ab-AA-Aa-S **canonical second order quadruple point**. The CC→CVCC case is also canonically visible, and is associated to ensemble inequivalence onset. Before the singularity, the system shows canonically a second order phase transition, and, after the singularity, a first and a second order one. Thus, it is a Ab-S→Ab-Aa-S **canonical bicritical point** (this is the canonical equivalent-upon symmetry- of the microcanonical Aa-Ab-S→Aa-S bicritical point).

- a **second order azeotropy** involves the appearance of two second order transitions. If we use the convention that the low energy state is an asymmetric one (as on Fig. 9), then just after the crossing of the singularity, one observes, varying the energy, two second order transitions, with the configuration asymmetric-symmetric-asymmetric. The jumps in d^2S/dE^2 are thus exactly opposite. Moreover, the jump is exactly zero at the transition point (the entropy change is there quartic). Thus, the concavity is not changed at the transition point. This yields two types of such points, depending on the concavity of S, denoted as VV and CC, with the usual convention.

Only the CC case is visible in the canonical ensemble. In the canonical ensemble, the second derivative of the free energy with respect to β is singular, and we observe the appearance of two jumps at the singularity point. It is thus a **canonical second order azeotropy**.

- a **second order transition may superpose with an inflexion point in one of the two branches**. If the inflexion point is in the low energy branch, the second order transition evolves from a CC situation to a VC one. This is visible in the canonical ensemble. As it corresponds to the appearance of a first order transition from a second order one's, it is a **canonical tricritical point.** As a first order canonical transition appears at this point, this singularity is associated to the birth of an interval of energy for which microcanonical and canonical ensembles are inequivalent.

If the inflexion point is in the high energy branch, the situation evolves from VV to VC; it is not visible in the canonical ensemble.

- finally, a **concave-concave second order transition may coincide with the boundary of a straight segment of the concave envelop** of $S(E)$. There is only one type of such point. It is canonically visible. In the canonical ensemble, it gives a crossing between a first order and a second order canonical phase transitions. It is thus a **canonical critical endpoint.** It appears at the boundary of an ensemble inequivalence range, but it is not associated with ensemble inequivalence appearance.

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