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A statistical model for instable thermodynamical systems

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Abstract

A generic model is presented for statistical systems which display thermodynamic features in contrast to our everyday experience, such as infinite and negative heat capacities. Such system are instable in terms of classical equilibrium thermodynamics. Using our statistical model, we are able to investigate states of instable systems which are undefined in the framework of equilibrium thermodynamics. We show that a region of negative heat capacity in the adiabatic environment, leads to a first order like phase transition when the system is coupled to a heat reservoir. This phase transition takes place without a phase coexistence. Nevertheless, all intermediate states are stable due to fluctuations. When two instable system are brought in thermal contact, the temperature of the composed system is lower than the minimum temperature of the individual systems. Generally, the equilibrium states of instable system cannot be simply decomposed into equilibrium states of the individual systems. The properties of instable system depend on the environment, ensemble equivalence is broken.

Keywords: Negative heat capacity; Instable systems; Hierarchy; Phase transitions; Fluctuations; Dynamic phase coexistence

1. Introduction

There is increasing interest in studying small systems with a typical size in the nanometer range. Such systems are still much too big to be understood in terms of pure quantum mechanical states. On the other hand, also thermodynamical concepts reach their limit. As has been shown experimentally for small sodium clusters [1], instable thermodynamic states can appear when coexistence at the transition between two phases is suppressed due to the limited size. One of the most intriguing consequences is the existence of negative heat capacities [1–4], which were already predicted in the context of long-range interactions [5,6]. However, experiments on small metal clusters give only the first, but presumably most direct evidence for a new type of behavior in finely structured matter. The nanometer length scale is dominating for several years in polymer science. For instance, copolymers form regular micro-phase separated states where the extension of the obtained micro-phases can reach down to a few nanometers. In particular asymmetric copolymers, having a long block of species *A* and short block of species *B*, can establish equilibrium super-structures, where the *B*-blocks are located in regular arrays of nanometer size spheres embedded in a matrix of *A*-blocks. As has been shown recently [7], such nanometer sized and well separated polymeric spheres can undergo well defined crystallization and melting processes. However, in contrast to the experiments on small metal clusters, only the ensemble of a huge number of such small systems ordered in a well defined super-structure has been analyzed thermodynamically up to now. Nevertheless, since individual systems can only interact by exchanging heat, the

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observed thermodynamic properties of the array of many such systems can be different from the corresponding behavior of a homogeneous, bulky polymer.

In order to learn more about the *general properties* of instable systems a solvable statistical model is needed. It is the aim of the present work to propose and discuss such a generic model for instable (and as we will see, necessarily non-extensive) systems under different conditions. It will be shown that systems having infinite or even negative heat capacities can obtain well defined states also when coupled to a heat reservoir or among each other. However, these states are now different to the states obtained when such systems are isolated or in contact with a tiny thermometer. This is because fluctuations are determining the states, which leads to different predictions for different ensembles. It will be shown that the equilibrium states cannot be associated with the individual systems, but has to be understood as a property of the composed system and can, therefore, also change with the environment.

The rest of this work is organized as follows. In Section 2, it is shown under which conditions in equilibrium thermodynamics (ETD) negative heat capacities can be defined and which are the consequences of such unusual properties. In Section 3, we introduce the model of a hierarchically organized phase space which allows a statistical analysis of systems having a non-positive heat capacity. We distinguish between two types of models: regular hierarchies, which lead to infinite heat capacities in the micro-canonical treatment, are considered in Section 4. Closed hierarchies lead to negative heat capacities and are analyzed in Section 5. In both cases thermal coupling to a heat reservoir leads to well defined states which, however, differ from those obtained in the adiabatic environment. For closed hierarchies a state of dynamic coexistence is obtained, which reflects a phase transition between a low and a high energy phase without thermodynamic coexistence. Thermal equilibrium between non-extensive systems is considered in Section 6. Here, we show for case of regular hierarchies, that the temperature of the composed system is always lower than the temperatures of the individual systems without thermal coupling, in marked contrast to the behavior of stable systems. In Section 7, my conclusions are presented.

2. Unstable systems, negative heat capacities and non-extensivity

From the fundamentals of thermodynamics it follows that systems in contact to an infinite heat reservoir must have a positive heat capacity. This is closely related to the condition of stability of thermodynamic equilibrium states. The proof for this conclusion is sketched in Fig. 1.

Here, we consider a thermodynamic system S in contact with a heat reservoir S' at temperature T. For the equilibrium states of given internal energy E, entropy functions $S(E)$ and $S'(E)$ can be defined. If S is in stable equilibrium with S', with the freedom to exchange energy in form of heat δQ, the total entropy

$$S_g = S + S', \tag{1}$$

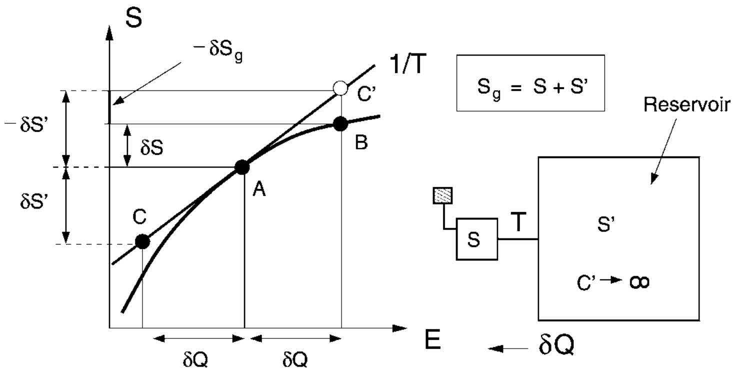

Fig. 1. Illustration of the coupling of a thermodynamic system with a heat reservoir. The heat exchanged with the reservoir δQ decreases the entropy of the (formally infinite) reservoir in a reversible way: $\partial S' = \delta Q/T$.

must display a maximum value, that is, its total change δS_g must be negative, irrespectively of the direction of the exchange of heat. Now, considering a small amount of heat δQ to be transferred from S' to S, this changes the state of S from A to B (see Fig. 1) and increases the entropy $S(E)$ accordingly. At the same time, this heat transfer decreases the entropy of S', given by

$$\delta S' = -\frac{\delta Q}{T}. \tag{2}$$

This can be illustrated by a corresponding change from A to C in the E, S-diagram in Fig. 1 (following the linear slope of $1/T$ along the tangent of $S(E)$ at the state A). The total change in entropy of the composed system, δS_g, is now visualized by the difference δS_g between the state B and C', where C' is mirror-image of C, which accounts for the negative entropy change, $-\delta S'$. Thus, δS_g is negative, if the point B is below the tangent of the curve $S(E)$. The same is true for an exchange of heat in the opposite direction. Therefore, we conclude: the state A corresponds to a stable equilibrium state at the temperature $1/T = \partial S(E)/\partial E|_A$, if the entropy function remains below its own tangent, that is, $S(E)$ is a concave function. This requires

$$\frac{\partial^2 S}{\partial E^2} < 0. \tag{3}$$

On the other hand, the heat capacity is given by

$$\frac{1}{C} = -T^2 \frac{\partial^2 S}{\partial E^2}. \tag{4}$$

Therefore, thermodynamic stability in respect to the exchange of heat is equivalent to a positive heat capacity.

Another argument can be raised from statistical physics. The partition function for a system in equilibrium with a heat reservoir is given by

$$Z = \sum_k e^{-\beta E_k}, \tag{5}$$

where $\beta = 1/T$, and the Boltzmann constant is set to unity in the following. Then we have

$$\bar{C} = \frac{\partial \langle E \rangle}{\partial T} = \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} = \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) \\ = \beta^2 \langle \Delta E^2 \rangle, \tag{6}$$

where the brackets denote the averaging according to the canonical distribution. In anticipation of the case of instable system, we distinguish the values in the canonical ensemble with an over-bar. Now, the heat capacity $\bar{C}$ is directly related to the mean squared fluctuation of the energy, enabled by the heat reservoir. Therefore, the value of $\bar{C}$ has to be positive.

However, our arguments do not exclude the existence of a negative heat capacity when the system is *not coupled* to an infinite heat reservoir. Let us now consider a “thermometrical environment,” where S is coupled to a *small* system S'. The meaning of “small” concerns the value of the heat capacity of the thermometer C', as it becomes clear from the derivations below. The idea is illustrated in Fig. 2.

Now, the non-linear component in the entropy change of the thermometer, $\delta S'(E)$, has to be taken into account too. We consider an entropy function $S(E)$ which is now convex, that is, follows above its tangent at the point A, which still defines the equilibrium

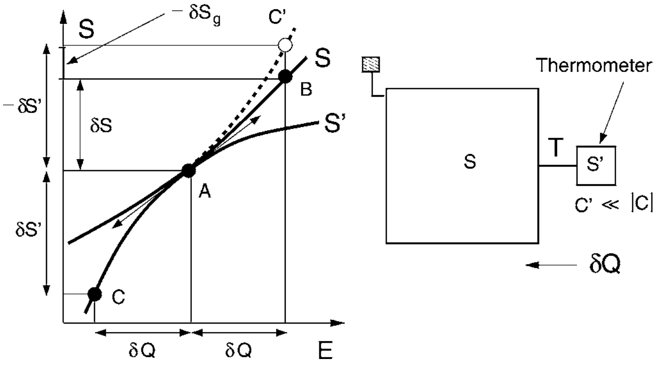

Fig. 2. Illustration of the coupling of a thermodynamic system with a small “thermometric” system. Now, the exchange of heat ∂Q also involves non-linear behavior of the thermometer’s entropy function.

temperature between both systems. A heat uptake, δQ, results again in a change of state indicated by B in Fig. 2. As a consequence the entropy of the thermometer is reduced by $\delta S'$ following the curve $S'(E)$ to the point C. The mirror image (negative entropy change) of the part of the thermometer's curve is denoted by the dashed line and the point C'. Provided, that the absolute value of the second derivative of the thermometer's entropy function is larger than that of $S(E)$ (higher curvature), the total change of entropy is indeed always smaller than zero (B is below C'), irrespectively of the direction of heat exchange. As a consequence, the state A corresponds to an equilibrium between the both systems at the common temperature T, which is indeed thermodynamically stable.

The condition for this stability can be expressed in terms of the total entropy change as follows

$$\delta S_g \simeq -\frac{1}{2T^2}\left(\frac{1}{C'} - \frac{1}{|C|}\right)\delta E^2. \tag{7}$$

Hence, a stable equilibrium is possible, if the condition

$$C' < |C|, \tag{8}$$

is satisfied.

On the other hand, if two systems with $C < 0$ are brought in thermal contact, equilibrium is impossible in terms of ETD. Then, we obtain

$$\delta S_g \simeq \frac{1}{2T^2}\left(\frac{1}{|C_1|} + \frac{1}{|C_2|}\right)\delta E^2, \tag{9}$$

which is always positive. Thus, every change in the state of the two system increases the entropy, which yields to a spontaneous change of state until a region with a positive heat capacity is reached for one or both of the systems.

As a consequence, a system with negative heat capacity cannot be composed of subsystems having the same properties as the overall system—a system with negative heat capacity is necessarily *non-extensive*.

We have to recognize that classical ETD cannot make any further prediction for the behavior of unstable systems either coupled to a heat reservoir or being in thermal contact among each other. In fact, such states would be thermodynamically “impossible” as demonstrated in Eq. (9). As we will see in the following sections, such states are nevertheless statistically well defined. The reason, why thermodynamics cannot be used to analyze such states, is the fact that fluctuations play a predominant role. The concept of fluctuations is not incorporated into the framework of ETD and the preassumptions about thermodynamic equilibrium are made accordingly. To step forward, we need a tractable statistical model which reflects the properties of instable systems and can be analyzed in full detail using statistical methods. Such a model is proposed in the Section 3.

3. Hierarchically organized phase spaces

The aim of the paper is to present a statistical model which is able to reflect the unusual properties of unstable systems only. Such properties are usually only observed for small systems (or long-range interactions) in a certain range of temperature (energy). Also, for the presented model a finite energy range (see Fig. 3) is defined. However, no assumptions about the behavior outside this region of instability is made. This simplifies the mathematical analysis drastically and make it possible to better understand the properties of systems under non-stable thermodynamic conditions. Our model can be visualized geometrically as a hierarchy of states as sketched in Fig. 3. Each level (generation) of the hierarchy g corresponds to a definite energy value $E(g)$. The number of micro-states is then given by

$$\Omega = q^{E(g)/E_0}, \tag{10}$$

where q denote the (constant) branching number of the hierarchically organized phase space. Then we obtain for the Boltzmann entropy according to

$$S = \ln\Omega = \frac{E(g)}{E_0}\ln q. \tag{11}$$

We distinguish two cases concerning the energy steps between to successive generations $\Delta E(g)$:

$$\Delta E(g) = E_0 = \text{constant} \quad \text{regular hierarchy}, \tag{12}$$

$$\Delta E(g) = E_0(1-\delta) \quad \text{closed hierarchy}. \tag{13}$$

Here, δ corresponds to a small dimensionless parameter. For any real system, unstable behavior will only occur in a limited energy range as sketched in the lower part of Fig. 3. We will consider here the minimum energy $E_{\min} = 0$. For closed hierarchies, there

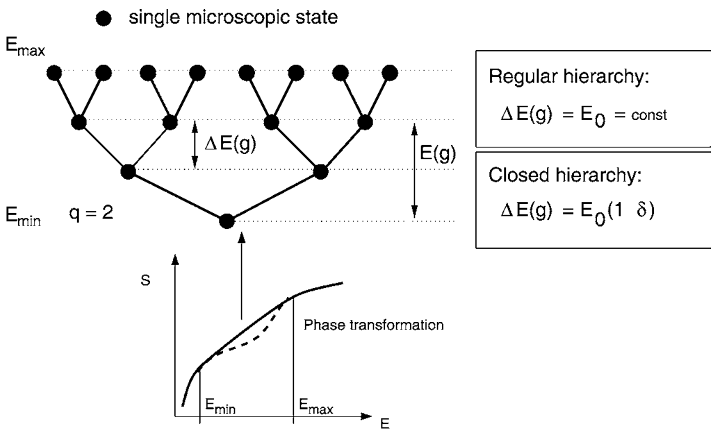

Fig. 3. Sketch of an hierarchically organized phase space. The micro-states are represented by bullets and form a regularly branched tree. Each level, g, of the tree represents a definite energy state. The energy difference between two successive levels in the hierarchy is given by $\Delta E(g)$. If these energy steps are constant, we call it a regular hierarchy. If $\Delta E(g)$ decreases with the level, we call it a closed hierarchy.

exist an upper limit for the energy, due to the contraction of levels, given by

$$E_{\max} = \frac{E_0}{\delta}. \tag{14}$$

4. Regular hierarchies

We start with the simplest case where the steps between successive levels of the hierarchy are constant, see Eq. (12). This leads to a linear relation between Boltzmann's entropy and the energy

$$S = \frac{E}{E_0}\ln q = \frac{E}{T_B}, \tag{15}$$

with

$$T_B = \frac{E_0}{\ln q}. \tag{16}$$

Hence, the temperature is constant and independent of the energy E contained in the system. We call T_B the *Boltzmann temperature*. Because of $\partial^2 S/\partial E^2 = -1/(T^2 C)$, the heat capacity C is infinite.

We consider now S in contact with an infinite heat reservoir S' at a given temperature T. In the following we count all energies in units of E_0 for the sake of simplicity. Then, the energy variable E (as well as the temperature) is dimensionless. To recover the original units, these quantities have to be multiplied by E_0 at the end. The partition function is given by

$$Z = \sum_k \exp\left\{-\frac{E_k}{T}\right\} = \int_0^{E_{\max}} \mathrm{d}E\, \Omega(E) \exp\left\{-\frac{E}{T}\right\}, \tag{17}$$

where k denote all microscopically accessible states of the system. This sum can be replaced by an energy integration (or summation) where all micro-states which correspond to a certain energy level E are represented again by $\Omega(E)$. Using Eqs. (11) and (15) one obtains

$$Z = \int_0^{E_{\max}} \mathrm{d}E \exp\left\{-\frac{E}{T} + \frac{E}{T_B}\right\} = \frac{1}{a}(1 - \mathrm{e}^{-aE_{\max}}), \tag{18}$$

with

$$a = \frac{1}{T}\left(1 - \frac{T}{T_B}\right) = \beta\tau, \tag{19}$$

and

$$\tau = 1 - \frac{T}{T_B}, \tag{20}$$

$$\beta = \frac{1}{T}. \tag{21}$$

The maximum energy, $E_{\max}$, becomes important when T is higher than T_B. Note that the canonical distribution $\exp\{-aE\}$ is monotonous. For $\tau > 0$, that is,

$T < T_B$, the distribution is simply decaying, the most probable value of the internal energy is the smallest value (lower bound), which is equal to zero. For $T > T_B$, the distribution is simply ascending, the upper bound of the internal energy, $E_{\max}$, is realized with maximum probability. On the other hand, the canonical value $\bar{E}$ of the internal energy is given by

$$\frac{\bar{E}}{T} = \frac{\langle E\rangle}{T} = \frac{1}{\tau}\left(1 - \frac{\tau E_{\max}\mathrm{e}^{-\tau E_{\max}}}{1 - \mathrm{e}^{-\tau E_{\max}}}\right), \tag{22}$$

where the brackets denote the averaging over the canonical distribution. For $T < T_B$, we can consider the limit $E_{\max} \to \infty$. Then we get

$$\bar{E} = \frac{T}{\tau} \quad \text{for} \quad E_{\max} \to \infty. \tag{23}$$

Note that because of Eq. (15), we have $\langle S\rangle = \langle E\rangle/T_B$. On the other hand we have

$$\bar{F} = \bar{E} - T\bar{S}. \tag{24}$$

Using Eq. (18), we obtain

$$\frac{\bar{F}}{T} = \ln a - \ln(1 - \mathrm{e}^{-aE_{\max}}). \tag{25}$$

In the limit of $E_{\max} \to \infty$ ($T < T_B$), we can use Eq. (23), which yields $T = \bar{E}/(1 + \bar{E}/T_B)$. Using further Eqs. (24) and (25), one gets

$$\bar{S} = \frac{\bar{E}}{T_B} + \left(1 + \ln\frac{\bar{E}}{\Delta E}\right) = \langle S\rangle + \Delta S. \tag{26}$$

The additional term ΔS provides the stability property (negative curvature) for the entropy in the isothermal environment. For consistency, one can check that $1/T = \partial\bar{S}/\partial\bar{E}$ is obeyed.

The entropy of a regular hierarchy, coupled to a heat reservoir, is not given by the average (expectation) value (due to the fluctuation of the energy state) but contains a part which is related to the coupling itself, thus $\langle S\rangle \neq \bar{S}$.

The heat capacity in the isothermal environment is given by

$$\bar{C} = \frac{\partial}{\partial T}(\bar{E}) = \frac{1}{\tau^2}\left\{1 - \frac{(\tau E_{\max})^2}{4\,\mathrm{sh}^2(\tau E_{\max}/2)}\right\}. \tag{27}$$

For the limit $E_{\max} \to \infty$, this yields

$$\bar{C} = k\frac{1}{\tau^2} \quad \text{for} \quad E_{\max} \to \infty. \tag{28}$$

On the other hand, $\bar{C}$ is finite at $T = T_B$, for a finite value of $E_{\max}$

$$\bar{C} = \frac{1}{12}E_{\max}^2 \quad \text{for} \quad T = T_B. \tag{29}$$

Hence, the isothermal environment leads to a thermodynamic behavior which is different from that in the isolated state. The unusual properties of the isolated system are reflected by a *critical point like divergency* of the heat capacity when approaching the Boltzmann temperature in the ETD limit.

5. Closed hierarchies and dynamical coexistence

The relation between the internal energy and the number of generation in the hierarchy is now given by

$$g = -\frac{1}{\delta}\ln\left(1 - \frac{E\delta}{E_0}\right), \tag{30}$$

where we have assumed $\delta \ll 1$, that is, $\ln(1-\delta) \simeq -\delta$. Using the simple relation between the entropy and the g, see Eq. (11), one obtains

$$S = -\ln q\frac{1}{\delta}\ln\left(1 - \frac{E\delta}{E_0}\right). \tag{31}$$

According to Eq. (14), we have $E_{\max} = 1/\delta$. The temperature of a closed hierarchy is thus given by

$$T_0 = T_B - \frac{E\delta}{E_0\ln q} = T_B\left(1 - \frac{E}{E_{\max}}\right), \tag{32}$$

where the Boltzmann temperature of the regular hierarchy, see Eq. (16), has been used. Note that the temperature of a closed hierarchy can not be larger than T_B. For the heat capacity we obtain

$$C = -\frac{1}{T_B}\frac{1}{\delta} = -\frac{E_{\max}}{T_B}, \tag{33}$$

which displays negative values in the whole range of the internal energy.

The first non-trivial approximation of $S(E, \delta)$, see Eq. (31), is given by

$$S \simeq \frac{E}{T_B}\left(1 + \frac{1}{2}\frac{E}{E_{\max}}\right). \tag{34}$$

If E is much smaller than $E_{\max}$, the first term is sufficient which corresponds to the case of the regular hierarchy. Since Eq. (34) is analytically better tractable,

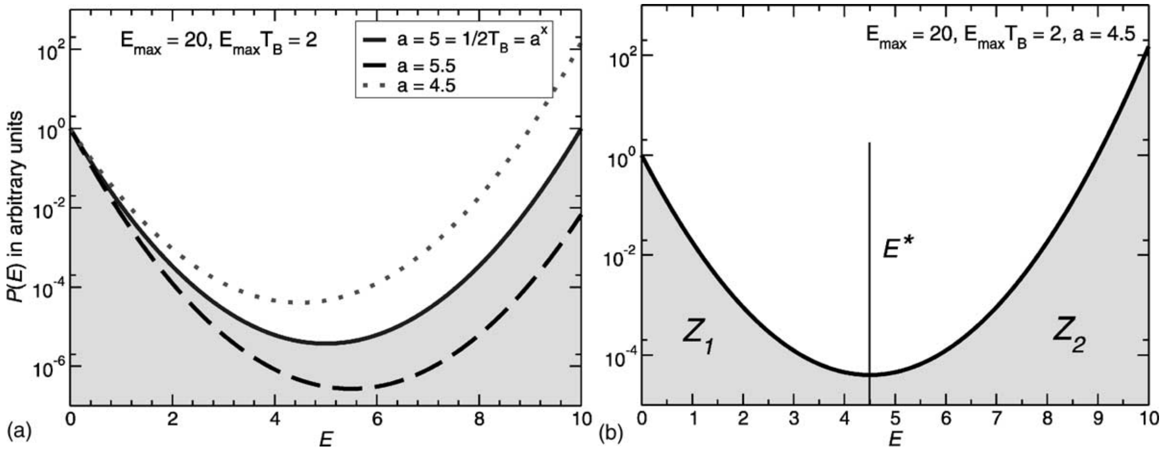

Fig. 4. (a) Canonical distribution of the internal energy $P(E)$ for different values of the temperature function $a = \beta\tau$. The distribution is symmetric around the minimum value E^*, for $a^\times = 1/2T_B$. (b) The integration of the partition function can be separated in two parts with respect to E^*.

and it contains all relevant properties of the closed hierarchy, we will use Eq. (34) exclusively in the following.

The canonical partition function is given by

$$Z = \int_0^{E_{\max}} \mathrm{d}E\, \mathrm{e}^{S-E/T} = \int_0^{E_{\max}} \mathrm{d}E\, \mathrm{e}^{-\mathcal{F}}. \tag{35}$$

Using Eqs. (34) and (19) we obtain

$$\mathcal{F} = E\beta\tau - \frac{1}{2}\frac{E^2}{E_{\max}T_B}. \tag{36}$$

The canonical distribution function $P(E) = \exp(-\mathcal{F})$ is plotted for different values of $a = \beta\tau$ in the left part of Fig. 4.

In marked contrast to stable distributions, $P(E)$ exhibit a minimum value (instead of a maximum) at

$$E^* = T_B\beta\tau E_{\max}. \tag{37}$$

For large values of $E_{\max}/T_B$ the both peaks at $E = 0$ and $E = E_{\max}$ dominate the partition function. In order to evaluate the partition function, we subdivide the integration in two parts with respect to E^* as indicated in the right part of Fig. 4.

$$Z = Z_1 + Z_2 = \int_0^{E^*} \mathrm{d}E\, \mathrm{e}^{-\mathcal{F}} + \int_{E^*}^{E_{\max}} \mathrm{d}E\, \mathrm{e}^{-\mathcal{F}}. \tag{38}$$

We denote Z_1 as the *low energy phase* and Z_2 as the *high energy phase*, respectively. Both parts have the same functional form which is given by

$$Z_{1,2} = \exp(-\mathcal{F}(E^*)) \int_0^{c_{1,2}} \mathrm{d}x \exp\left\{-\frac{1}{2}\frac{x^2}{T_B E_{\max}}\right\}, \tag{39}$$

with $c_1 = E^*$ and $c_2 = E_{\max} - E^*$. Evidently, both parts equally contribute for $E^* = E_{\max}/2$. Therefore, we introduce a cross-over temperature $T^\times$, using Eq. (37), according to

$$T_B\beta\tau = \frac{1}{2} \to T^\times = \frac{2}{3}T_B. \tag{40}$$

Note that $T^\times$ does not depend on δ. It is useful to define the deviation from the cross-over temperature, Δ, according to

$$\Delta = 1 - \frac{T^\times}{T}, \tag{41}$$

as well as the scaling variable η as

$$\eta = \frac{E_{\max}}{T_B}. \tag{42}$$

In the following we always assume $\eta \gg 1$, which means that many levels of the closed hierarchy are involved, see Eq. (16).

As shown in the Appendix A, the following approximation for the integral in Eq. (39) can be used

$$\int_0^c \mathrm{d}x \exp(b^2x^2) \simeq \frac{1}{cb^2}\exp(b^2c^2) \quad \text{for} \quad bc \gg 1, \tag{43}$$

Then, we obtain from Eqs. (36)–(42) the following result

$$Z \simeq \frac{2}{\sqrt{\eta}}\left[\frac{1}{1-3\Delta} + \frac{1}{1+3\Delta}\exp\left(\frac{3}{2}\eta\Delta\right)\right] \quad \text{for} \quad \eta \gg 1. \tag{44}$$

Now, in the vicinity of the cross-over temperature, that is, $\Delta \ll 1$, the internal energy can approximated by

$$\bar{E} = \langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} \simeq \frac{E_{\max}}{1+\mathrm{e}^{-3/2\eta\Delta}}. \tag{45}$$

Hence, the internal energy in contact with a heat reservoir displays a smooth step at $\Delta = 0$, which develops into a sharp jump for $\eta \to \infty$.

Within the same approximation, the heat capacity is given by

$$\bar{C} \simeq \frac{\eta^2}{4\cosh^2((3/4)\eta\Delta)}. \tag{46}$$

Thus, the heat capacity is positive, as expected, and displays a *major singularity* for $\eta \to \infty$. On the other hand, Eqs. (45) and (46) can be taken as a *signature of a first order phase transition*, taking place in between the low energy phase and the high energy phase of the hierarchy. Directly at $T^{\times}$, the system fluctuates between both phases. These large fluctuations (in contact with a heat reservoir) are responsible for the stable behavior of the free energy $\bar{F} = -T\ln Z$. Therefore, we can call such a behavior as *dynamical phase coexistence*, being an alternative, thermodynamically stabilizing, scenario to the usual static phase coexistence.

6. Non-extensive systems in thermal equilibrium

In the last two sections we have shown that the behavior of unstable systems is well defined under isothermal conditions. However, these results could not have been obtained using thermodynamical arguments, since the stabilization of the states are given by fluctuations. We now turn to another question which cannot be answered in the framework of classical ETD, namely the behavior of unstable systems in thermal contact among each other. In this work we will restrict ourselves to regular hierarchies in thermal equilibrium.

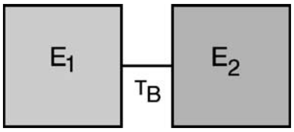

Fig. 5. Two instable systems, having the energies E_1 and E_2 and the same temperature T_B, are brought in thermal contact.

Let us bring two regular hierarchies of the same type, having the energies E_1 and E_2, respectively, in thermal contact, see Fig. 5. The two parameters which define a regular hierarchy are T_B and $E_{\max}$. After the thermal coupling is established, we can no more identify the energy content of both systems. The number of micro-states, Ω, of the composed system is therefore given by taking into account all possible distributions of the total energy, $E = E_1 + E_2$, over both subsystems. For simplicity we assume $E_{1,2} \ll E_{\max}$. Then, we can write

$$\Omega = \int_{-E_1}^{E_2} \Omega_1(E_1+\Delta E)\Omega_2(E_2-\Delta E)\mathrm{d}\Delta E = \int_{-E_1}^{E_2} \exp\left(\frac{E_1+\Delta E}{T_B}\right)\exp\left(\frac{E_2-\Delta E}{T_B}\right)\mathrm{d}\Delta E. \tag{47}$$

Therefore, the entropy of the overall system is given by

$$S = \ln \Omega = \frac{E}{T_B} + \ln E. \tag{48}$$

Coupling the overall system to a thermometer, we can measured a temperature T given by

$$\frac{1}{T} = \frac{1}{T_B} + \frac{1}{E} > \frac{1}{T_B}. \tag{49}$$

Hence, the *temperature* of the coupled system *has changed* and depends from the total energy content. The temperature of two instable system in thermal contact at the same individual temperatures is smaller than the individual temperatures of both parts. This is also valid for the more general case of different individual temperatures T_1 and T_2 (dropping

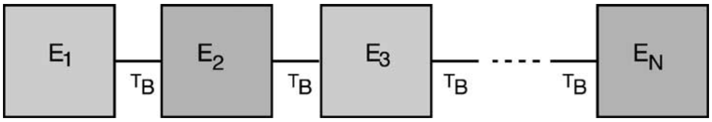

Fig. 6. Many instable systems having the same temperature T_B are brought in thermal contact.

the index "B"). Here, the following equation can be derived

$$\frac{1}{T}=\frac{1}{T_1}\left(1+\frac{\tau}{\exp((E/T_1)\tau)-1}\right), \tag{50}$$

with $\tau = 1 - T_1/T_2$ and with $T_1 < T_2$ without loss of generality. This proves the general inequality for the thermodynamic equilibrium of two instable systems of the type of regular hierarchies

$$T < \min(T_1, T_2). \tag{51}$$

The temperature of the overall system is smaller than the minimum temperature of both parts, in marked contrast to the usual "mixing rule" for stable systems.

Finally, we consider the thermal equilibrium of N regular hierarchies of the same type as sketched in Fig. 6. We obtain

$$\Omega = \frac{E^{N-1}}{(N-1)!}\exp\left(\frac{E}{T_B}\right). \tag{52}$$

Using the limit of large N, we can assume $N - 1 \simeq N$. This yields to the following expression for the inverse temperature of the overall system

$$\frac{1}{T}=\frac{N}{E}+\frac{1}{T_B}=\frac{1}{T_0}+\frac{1}{T_B}. \tag{53}$$

Here, we have introduced an "energetic" temperature

$$T_0 = [E] = \frac{E}{N}, \tag{54}$$

where the brackets $[\dots]$ denote the averaged value per subsystem. Using Eq. (53), we obtain for the heat capacity

$$C=\frac{E^2}{N}\left(\frac{1}{T_0}+\frac{1}{T_B}\right)^2. \tag{55}$$

Assuming that the overall energy is proportional to the number of subsystems, N, the heat capacity is *extensive*. In the limit $T_0 \ll T_B$, we get for the specific heat $c = C/N$

$$c=\frac{C}{N}\simeq 1 \quad \text{for} \quad T_0 \ll T_B. \tag{56}$$

This limit corresponds to a sparse load of the individual hierarchies with energy. In the opposite case we get

$$c=\frac{C}{N}\simeq\left(\frac{T_0}{T_B}\right)^2 \quad \text{for} \quad T_0 \gg T_B. \tag{57}$$

Here, in average many levels of the individual hierarchies are energetically loaded. The non-trivial feature is the strong dependency of the specific heat $c = C/N$ from the energy content, that is, from the energetic temperature.

7. Conclusions

An analytically tractable model for instable statistical system has been proposed. Using this model, we were able to analyze the behavior of such systems which are unstable in the sense of classical ETD (having non-positive heat capacities) in situations which are not accessible by ETD. It can be shown, that energy fluctuations can establish a thermodynamic equilibrium. For stable thermodynamic systems, energy fluctuations are usually much smaller compared to the observed energy of the system. This is of course no more true for the model discussed here. In the instability region the whole energy contents takes part in fluctuations. The properties of such equilibrium states are somewhat different to those of stable systems. In particular, the state of the composed system has a new quality, which cannot be reduced to the "product of states of individual systems." One should denote such states as *fluctuation induced thermodynamical equilibrium*, to distinguish them from equilibrium states in the framework of classical ETD, where fluctuation effects are not considered. Therefore, the role of temperature (as defined in the usual sense as $1/T = \partial S/\partial E$) is reduced, which leads to unusual results, such as the possibility of an equilibrium between systems of different temperature and the reduction of the temperature for instable systems in equilibrium, see Eqs. (49)–(51) and (53).

Instable statistical systems can be driven through phase transitions when being in contact to a heat reservoir. For the model of a regular hierarchy (marginally instable) a power-like singularity of the heat capacity is shown when the temperature of the heat reservoir approaches the intrinsic temperature T_B of the system. This resembles a continuous phase transition scenario. Most interesting is the behavior of true instable systems having a negative heat capacity. Here, a phase transition between a low energy phase and high energy phase takes place at a temperature $T^{\times}$ without static coexistence. However, at $T^{\times}$, fluctuations between both states occur which, on the other hand, stabilize the equilibrium with the heat reservoir at this temperature. Such a *fluctuation induced phase equilibrium* can be called a *dynamical phase coexistence*.

Appendix A

We consider the integral

$$I = \int_0^c \mathrm{d}x \exp\left(\frac{1}{2}b^2x^2\right). \tag{58}$$

First, we perform a Gaussian transformation

$$I = \frac{1}{\sqrt{2\pi}} \int_0^c \int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{d}y \exp\left(-\frac{y^2}{2} + bxy\right). \tag{59}$$

After carrying out the x-integration, we obtain

$$I = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}y\, \mathrm{e}^{-y^2/2} \frac{1}{by}(\mathrm{e}^{bcy} - 1). \tag{60}$$

In the limit of $bc \gg 1$, the integral is dominated by a Gaussian peak at

$$\bar{y} = bc. \tag{61}$$

Then, we can approximate the integral by

$$\begin{aligned} I &\simeq \frac{1}{\sqrt{2\pi}} \frac{1}{b\bar{y}} \exp\left(\frac{1}{2}b^2c^2\right) \int_{-\infty}^{\infty} \mathrm{d}y \exp\left(\frac{1}{2}(y-\bar{y})^2\right) \\ &= \frac{1}{b^2c} \exp\left(\frac{1}{2}b^2c^2\right), \end{aligned} \tag{62}$$

which is given in Eq. (43). The first correction to $\bar{y}$ is of the order $1/bc$.

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