Paths of Discovery
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THE STORY OF NEGATIVE SPECIFIC HEAT

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1. Stable and Unstable Matter

A key property of matter usually encountered in the laboratory is mechanical and thermodynamic stability: an isothermal compression of the system increases the pressure, resulting in a positive isothermal compressibility. Likewise, an extraction of heat at constant volume and particle number leads to a reduction of the temperature T and consequently to a positive specific heat. Formally, stability manifests itself in the extensivity of various thermodynamic quantities such as the internal energy and the entropy. It means that they are proportional to the number of particles N in the system. The Hamiltonian H_N is bounded from below by a constant proportional to N. In statistical mechanics H_N is usually approximated in terms of pairwise-additive two-body potentials $\phi(\mathrm{x}_i, \mathrm{x}_j)$,

$$H_N = \frac{1}{2m}\sum_{i=1}^{N} \mathbf{p}_i^2 + \sum_{i(<j)} \sum_{j} \phi(\mathbf{x}_i - \mathbf{x}_j), \tag{1}$$

where xi and pi denote the position and momentum of particle i, and m is the particle mass. If the pair potential ϕ exhibits a significant repulsive core – as is the case for atoms and molecules under ordinary conditions – the system is thermodynamically stable and shows all the properties predicted from kinetic theory. During the approach to equilibrium, macroscopic density and temperature gradients diffuse away, and the system ends up in an equilibrium state, corresponding to a stationary solution of the Boltzmann equation, characterized by a homogeneous distribution in space and a Maxwell-Boltzmann distribution of the momenta.

This situation is totally different for purely negative pair potentials without a repulsive core such as the gravitational potential. The total poten-

tial energy becomes proportional to the number of interacting particle pairs and, hence, proportional to N^2. The kinetic energy, however, remains extensive and increases proportionally to N. The familiar thermodynamic limit cannot be performed, in which N and the volume V are increased to infinity keeping the density $\rho = N/V$ constant, and the lower bound proportional to N for the Hamiltonian H_N ceases to exist. Such systems are thermodynamically unstable. Even if one starts out with initial conditions for the particles homogeneous in space and Maxwell-Boltzmann distributed in momentum space, one or possibly more clusters are formed in the course of the natural evolution such that a large percentage of the particles are concentrated in a very narrow region in space. The remaining particles form a diluted atmosphere in which the heavy cluster floats. For a certain range of internal energies, the microcanonical heat capacity of such systems may be negative: an extraction of heat from the system results in an *increase* in the temperature. Microcanonically, the temperature is defined by thermal contact with a small thermometer, whereas the canonical temperature is fixed by contact with a big external heat bath.

The theoretical basis for an understanding of such systems was laid by Thirring and coworkers some time ago [1, 2], and was recently reinvestigated [3]. They studied a cell model which is simple enough to be solved exactly, but which nevertheless exhibits all the surprising and unfamiliar properties of thermodynamic instability. In this model the particles interact with each other via a purely-attractive box-type potential but are totally isolated otherwise, forming a microcanonical system. Then one can show analytically that maximum-entropy equilibrium states exhibit thermodynamic instability. For large internal energies E the system behaves like an ideal gas and has a positive specific heat $C_V = dNk_B/2$, where $d = 2$ or 3 is the dimension of space, k_B is the Boltzmann constant, and N the number of particles. If E is reduced below a threshold close (but not exactly equal) to zero, a single cluster is formed in equilibrium and the specific heat becomes negative. Further decrease of E makes the cluster grow and take in more and more particles, simultaneously diluting the atmosphere. Since the potential energy decreases proportional to $N_c(N_c-1)/2$, where N_c is the number of particles in the main cluster, the kinetic energy and consequently the temperature increases accordingly. This temperature increase is discussed in more detail in Section 2 and is also demonstrated in a short film produced some time ago [4]. The process of condensing more and more particles into the cluster with decreasing E continues until almost no particles remain in the atmos-

phere, and the equilibrium temperature $T(E)$ reaches a maximum. If E is reduced even more, no further condensation can take place, and the matter starts behaving normally again: the specific heat becomes positive. The equilibrium predictions of the Thirring model for a two-dimensional system ($d=2$) containing a total of $N=400$ particles are depicted by the smooth curve in Fig. 1, where reduced energy and temperature parameters [5, 6] are defined according to

$$e = 1 + \frac{2E}{N(N-1)\varepsilon} \tag{2}$$

and

$$\theta = \frac{2k_B T(\infty)}{N\varepsilon} \tag{3}$$

respectively. Here and in the following, the time argument ∞ refers to thermodynamic equilibrium, and ε denotes the depth of the negative pair potential. From the definition of the specific heat,

$$C_V = 1/(\partial T/\partial E)_V, \tag{4}$$

it follows that regions with negative slope in Fig. 1 correspond to negative C_V.

In spite of its simplicity and artificiality, this cell model explains qualitatively all the salient features of thermodynamically unstable systems. As examples in astrophysics we mention the gravitational collapse of stars after exhaustion of their nuclear fuel, or the formation of stars and galaxies from interstellar matter. Unfortunately, physically realistic pair potentials are much more difficult to handle theoretically. The gravitational $1/r$-potential, for example, exhibits a singularity at the origin which must be weakened by quantum mechanics and defies a purely classical treatment. Furthermore, it is of long range, which complicates numerical treatment. As a first step towards more realistic systems a simple negative Gaussian pair potential may be used:

$$\phi(\mathbf{x}_i, \mathbf{x}_j) = -\varepsilon e^{-|\mathbf{x}_i - \mathbf{x}_j|^2/\sigma^2}. \tag{5}$$

It is of short range, regular at the origin, and well-suited for computer simulation. It has been used by Compagner, Bruin and Roelse [7] to study the equilibrium properties of a class of unstable systems. They have

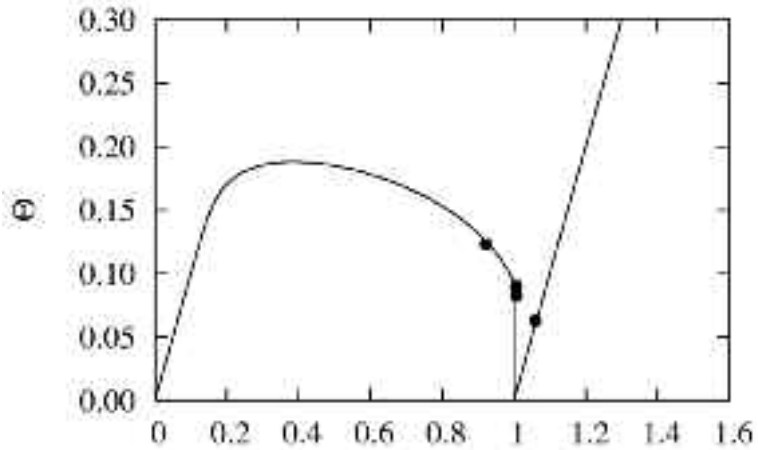

Fig. 1. Plot of the temperature parameter Θ versus the energy parameter e for a 400-particle system in equilibrium. The smooth curve is the prediction of the Thirring model, if the total volume is partitioned into 1600 cells. The points are computer-simulation results for the conditions of the film.

shown that in spite of the differences in potential, the results of the analytical Thirring model above are almost quantitatively confirmed. Using the same pair potential (5), we have performed a series of computer simulations of two-dimensional systems containing $N = 400$ particles [5, 6]. Particular emphasis is placed on the transient behaviour as the natural evolution leads the system from a highly non-equilibrium initial state to final equilibrium.

2. Dynamics Of Cluster Growth

In this section some of the dynamical events are described which may be observed in the film mentioned above [4]. Because of the very long relaxation time for equilibration only three characteristic sections of the whole simulation are distinguished below:

1. *Condensation phase*: This regime far from equilibrium covers the early time from the start of the simulation up to a time $t = 200$ and shows

the onset of cluster formation. Starting with a homogeneous initial distribution (Fig. 2), a few intermediate clusters are formed very early in the run (Fig. 3). These aggregations compete with each other for further growth. When N_c particles condense into a cluster, the potential energy is locally reduced (i.e. increased in absolute value) by an amount proportional to N_c^2. Since the interaction with the surrounding atmosphere is weak, the local kinetic energy of the cluster has to grow by practically the same amount proportional N_c^2. Thus, the cluster temperature in the major clusters grows proportional to the number of particles N_c in the respective cluster [5, 6]. This behaviour is reflected in the average colour of the particles in the film. With growing N_c the two major clusters turn red indicating a high temperature in the cluster, whereas the surrounding gas still remains at a low temperature. This behaviour very closely resembles the creation of a hot star floating in a cold atmosphere. A quantitative analysis of this property may be found in References 5 and 6.

2. *Intermediate phase*: In this time range $400 < t < 500$ of the simulation the system is still very far from equilibrium. The coexistence of various large clusters in a finite volume as depicted in Fig. 3 does not represent a state of maximum entropy and an equilibrium state [5]. Because of the finite volume V of the system it is inevitable for the major clusters to collide with each other, and a single cluster is formed, thereby significantly increasing the entropy of the system. (Fig. 4). Before the collision the main clusters contain about 40 to 80 particles each. Their combined particle number exceeds the equilibrium value, $N_c(\infty) = 140$, of a single cluster surrounded by an atmosphere [6]. The excess particles are simultaneously evaporated off the final cluster during its birth. This process occurs in the film at a time $t \approx 425$. Because of the dramatic increase of N_c, the temperature in the main cluster jumps to 15, whereas the gas temperature still remains at a low level around 6 as verified from the particle colours.
3. *Equilibrium phase*: This section covering the time range $10000 < t < 10050$ shows the dynamics of the system at equilibrium characterized by a single cluster containing $N_c \approx 140$ particles. The weak interaction between cluster and surrounding gas has been sufficient to raise the gas temperature to the same level as in the cluster. The velocities are Maxwell-Boltzmann distributed both in the cluster and the gas, both distributions being identical [5, 6]. All particles are coloured predominantly red in the film.

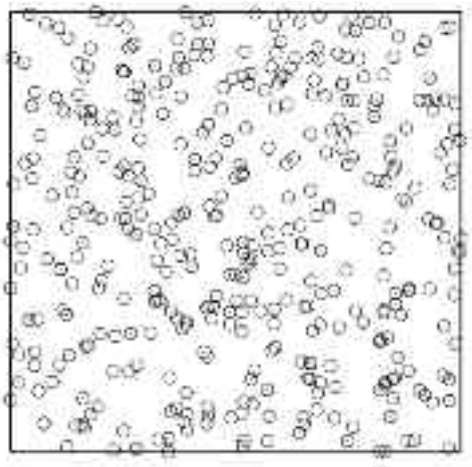

Fig. 2. Random initial configuration. The side length of the central volume is $L = 28.284$.

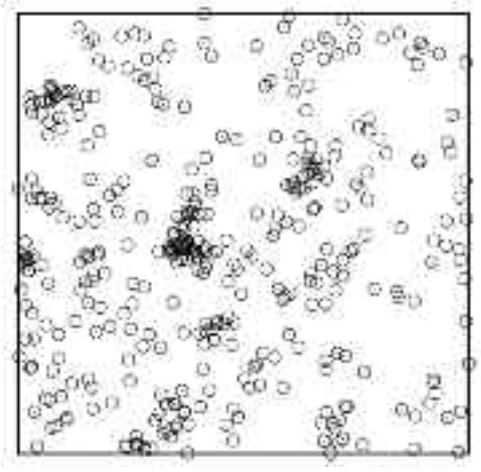

Fig. 3: Instantaneous configuration at a time $t = 20$ corresponding to a state still very far from equilibrium.

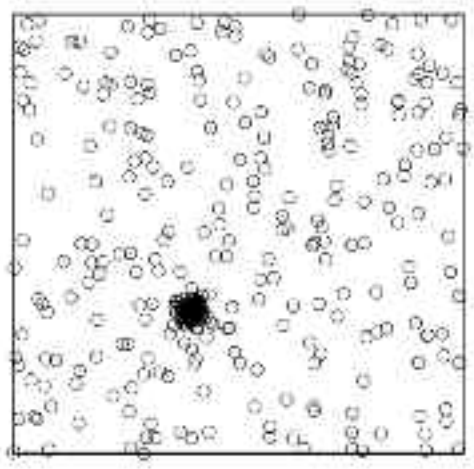

Fig. 4. Instantaneous configuration for the simulation at time $t = 8000$ already close to equilibrium.

It is remarkable that the cluster diameter is practically independent of the number of particles it contains. This fact has been investigated further in Refs. 5 and 6.

In the simulation shown in the film [4], all particles are distributed randomly over the accessible volume V at time $t = 0$. An alternative initial condition would be a state of minimum potential energy $-\varepsilon N(N-1)/2$ for which all N particles are in a perfect cluster and on top of each other. To obtain the same total energy as in the simulation shown in the present film the initial kinetic energy would have to be extremely large. Such a simulation has been carried out independently and reported in Ref. 6. There it is also shown that the initial perfect cluster disintegrates quickly by boiling off particles into the atmosphere. It eventually approaches equilibrium states macroscopically identical to the states shown in the third section of the present film and with the same number of particles $N_c(\infty)$ in a single big cluster.

The most unusual feature of unstable systems is that the microcanonical specific heat may become negative for low enough internal energy E. To understand this phenomenon let us consider for a moment a thermodynamically stable system. Increasing the temperature at constant pressure of the condensed phase, a first order phase transition takes place at a

transition temperature T_b. By adding energy, particles are boiled off into the gas at T_b until the condensed phase has disappeared altogether. Similarly, keeping not the pressure but the volume constant any addition of energy leads to an evaporation of particles from the condensed phase to the coexisting gas until the condensed phase has disappeared at a critical temperature T_c. In both cases the field which a condensed particle experiences – and hence its potential energy – is practically independent of the number of particles still remaining in the condensed phase (apart from surface effects). Any increase of the total internal energy E necessarily results in an increase of the kinetic energy of the particles and therefore of the temperature. The specific heat is always positive and the entropy a concave function of E. Since the total energy of stable systems is extensive, the entropy in non-concave regions may always be increased by separating the system into two or more phases, subdividing the total energy accordingly. In such a case the Second Law of thermodynamics tells us to take the concave envelope of the entropies of the individual parts.

For thermodynamically unstable systems, however, any evaporation of cluster particles reduces the field experienced by a particle still in the cluster and increases its potential energy. In such a case the kinetic energy and hence the temperature may become smaller in spite of an increase of the total internal energy E. To understand the phase diagram in Fig. 1, let us first consider the case of an almost totally condensed system for which $e \approx 0$. An increase of e frees only very few particles from the cluster and has only a minor effect on the potential energy of the cluster particles. The temperature also increases and the specific heat is positive as is obvious from Fig. 1. Only after an appreciable amount of cluster particles – say 30% – have been evaporated, any further increase of E results in such a large relative reduction $\Delta N_c/N_c$ of cluster particles that the effect mentioned above is initiated: the temperature is reduced and the specific heat becomes negative. In Fig. 1 this occurs for $e \approx 0.4$. The effect becomes the more pronounced the larger $\Delta N_c/N_c$, and continues to grow until the cluster disappears. This happens for $E \approx 0$ or $e \approx 1$, respectively. However, we cannot speak of a critical temperature in this case because the thermodynamic state of the system is determined by the total internal energy E and not by the temperature. As a consequence, the entropy for thermodynamically unstable systems is not an everywhere concave function of E. This does not contradict the Second Law of thermodynamics because E is not an extensive property for such systems and cannot be subdivided into separate phases. The construction of a concave envelope is of no physical significance.

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