Thermodynamic instability of a confined gas

Harald A. Posch*
Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria

Walter Thirring†
Institut für Theoretische Physik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria

(Received 17 July 2006; published 2 November 2006)

The best possible cooling agent is a system with negative specific heat. If in thermal contact with a second system, any acquisition of energy due to a random fluctuation lowers its temperature, and the energy transfer in this direction is further enhanced. It continues until all the energy is extracted from the second system and their temperatures are at par. We exhibit these microcanonical features with a simple mechanical model of interacting classical gas particles in a specially confined domain and subjected to gravitation. As predicted, most of the gas particles are cooled and collect in the lowest part of the container, where the energy is carried away by a few remaining particles.

DOI: 10.1103/PhysRevE.74.051103 PACS number(s): 05.20.−y, 95.30.Tg, 05.45.Pq, 05.70.−a

I. MOTIVATION

Gravity-dominated systems have a negative specific heat, and in astrophysics this determines the stability and instability of stars [1]. But how could one realize such a system in the lab? Due to its instability, it can exist only in isolation, not in contact with a heat reservoir. Correspondingly, the specific heat in the canonical ensemble is always positive. Negative specific heat can only occur in an isolated system, which is described by the microcanonical ensemble where the density in phase space is concentrated on the energy shell [2,3]. Since it has been shown by Lebowitz and Lieb that for Coulomb systems the microcanonical and canonical ensembles are equivalent [4], there seems to be no hope that one could devise such a gadget on earth. Nevertheless, it turns out to be possible, at least in principle. A negative specific heat, $c \equiv dE/dT < 0$, means that the temperature T is not everywhere increasing with the energy E. As the temperature is related to the entropy S by $1/T = \partial S/\partial E$, a positive specific heat means that $S(E)$ is a concave function. Since S is the logarithm of the volume of the energy shell, and since a concave function never gets above any of its tangents, one can characterize negative specific heat as follows: *The energy shell expands more than exponentially with E*. In gravity-dominated systems this comes about due to the formation of clusters, which causes the systems to heat up tremendously. The lower the energy, the more the particles cluster and the energy shell expands towards high momenta. Since we want cooling, we do something different in this paper and expand the configuration space with energy [1].

Our model is similar to evaporation cooling discussed in connection with Bose-Einstein condensation [5,6]. The conceptual difference lies in the fact that we consider an equilibrium system which, in addition, has a negative heat capacity due to the special shape of the system boundary.

In Ref. [1] we studied a simple two-dimensional billiard consisting of a single particle in a gravitational field, which is elastically reflected from a specially designed "jumping board" at the bottom. Assuming ergodicity, we could show that the system has a negative heat capacity for a particle energy exceeding a certain threshold. The models treated in the present paper are slightly modified extensions of this work, where we consider also N particles, which may exchange energy, but leave the total energy constant.

We consider N particles in two space dimensions confined to the region $-V(y) < x < V(y) > 0$, $y > 0$. They experience a constant force in the negative y direction, so we are working with a Hamiltonian (in suitably chosen units specified below)

$$H = \sum_{i=1}^{N} H_i = \sum_{i=1}^{N} (p_i^2 + y_i). \tag{1}$$

The bottom of this domain is given by the function $V(y)$, which, as shown below and in Ref. [1], is most conveniently given as a function of the vertical coordinate y.

II. CASE OF A SINGLE PARTICLE

To define V, we consider a single particle i, first. If $d\omega_i = dx_i dy_i dp_{x,i} dp_{y,i}$ denotes a volume element in the single-particle phase space, the volume of the energy shell Ω and the one-particle entropy S_i are given by

$$\Omega(E_i) = e^{S_i(E_i)} = \int d\omega_i \delta(H_i - E_i) = \pi \int_0^{E_i} dy V(y). \tag{2}$$

(Note that the definition of the entropy in Ref. [1] is based on the volume *under* the energy shell, whereas here the volume of the energy shell is used. For *large N*, both definitions are known to give equivalent results.) To obtain a negative specific heat, we require $\Omega(E_i)$ to grow more than exponentially with E_i. With the ansatz

$$e^{S_i(E_i)} = E_i^{\alpha} \exp(E_i^{\gamma}), \quad \alpha \geq 1, \gamma > 1,$$

one obtains for $S_i(E_i)$

$$S_i(E_i) = \alpha \ln E_i + E_i^{\gamma}, \tag{3}$$

and the confining $V(y)$ becomes

*Electronic address: Harald.Posch@univie.ac.at
†Electronic address: Walter.Thirring@univie.ac.at

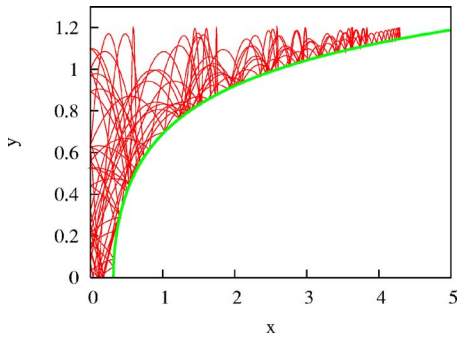

FIG. 1. (Color online) Jumping board according to Eq. (6) and short trajectory for a particle with energy $E_i=1.2$. The gravitational force points into the negative y direction. At the bottom, the particle is elastically reflected from the x axis for $0<x\leq 2/\pi$, and from the jumping board V for $x>2/\pi$. To avoid negative x, the y axis acts as an elastic mirror.

$$V(y) \equiv \frac{1}{\pi}\left(\frac{d}{dE_i}e^{S_i(E_i)}\right)_{E_i=y} = \frac{1}{\pi}\left(\alpha y^{\alpha-1} + \gamma y^{\alpha+\gamma-1}\right)e^{y^\gamma}.$$

$V(y)$ is positive, as required, and acts as a nonlinear jumping board on which the particle is elastically reflected. The thermodynamic temperature is given by

$$T \equiv [dS_i(E_i)/dE_i]^{-1} = E_i(\alpha + \gamma E_i^\gamma)^{-1}, \tag{4}$$

and for the specific heat we find

$$c \equiv (dT/dE_i)^{-1} = \frac{(\alpha + \gamma E_i^\gamma)^2}{\alpha - \gamma(\gamma-1)E_i^\gamma}. \tag{5}$$

The two parameters α and γ offer a wide choice of possible jumping boards and, hence, realizations of thermodynamic systems.

Let us consider a simple special case, $\alpha=1$ and $\gamma=2$, for which

$$V(y) = \pi^{-1}(1+2y^2)\exp(y^2). \tag{6}$$

A short trajectory is shown in Fig. 1, where negative x are avoided by an elastic reflection at the y axis. The thermodynamic temperature in this case is

$$T = E_i(1+2E_i^2)^{-1}, \tag{7}$$

and the specific heat becomes

$$c \equiv dE_i/dT = (1+2E_i^2)^2(1-2E_i^2)^{-1}, \tag{8}$$

which is negative for $E_i>1/\sqrt{2}$, as desired. However, due to our definition of the entropy, the kinetic temperature, which is defined as the microcanonical average of the kinetic energy, $T_{\text{kin}}\equiv\langle p_i^2\rangle$, differs from the thermodynamic temperature T,

$$\begin{aligned}\langle p_i^2\rangle &= e^{-S_i(E_i)}\int d\omega_i p_i^2 \delta(p_i^2 + y_i - E_i)\\ &= \pi e^{-S_i(E_i)}\int_0^{E_i} dy(E_i - y)V(y)\\ &= [1-\exp(-E_i^2)]/2E_i.\end{aligned} \tag{9}$$

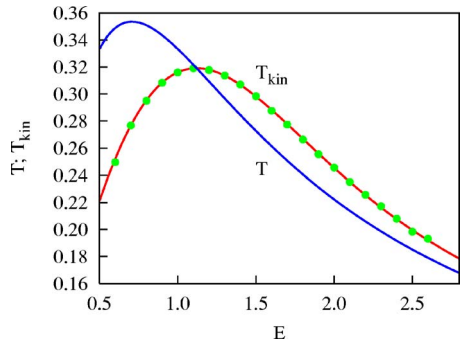

FIG. 2. (Color online) Energy dependence of the kinetic temperature (microcanonically averaged kinetic energy), $T_{\text{kin}}\equiv\langle p^2\rangle$, and of the thermodynamic temperature T for a single particle, $N=1$. The points for $\langle p^2\rangle$ are computer simulation results and the smooth curves are the respective theoretical expressions.

In Fig. 2 we compare the prediction of Eq. (9) (smooth line) with computer simulation results (points), which were obtained from time averages of the kinetic energy of the particle. The excellent agreement supports our tacit assumption that the system may be considered ergodic, at least in principle. Also shown is the thermodynamic temperature T.

III. N ENERGETICALLY COUPLED PARTICLES

Next, we investigate whether also for N particles, the Hamiltonian (1) leads to a region with negative heat capacity. It turns out to be the case, since $S_i\sim E_i^2$ for a single particle is a sufficiently strong volume expansion of the energy shell with energy E_i.

For the proof we use the following equivalences:

$$\begin{aligned}\text{Positive heat capacity } &\Leftrightarrow E\mapsto S(E) \text{ is concave} \Leftrightarrow S(E)\\ &\leq S(E_0) + S'(E_0)(E-E_0),\end{aligned} \tag{10}$$

for every E_0. The last inequality means that the graph of such a concave function $S(E)$ is below any of its tangents. We have

$$\begin{aligned}e^{S(E)} &= \int \prod_{i=1}^N d\omega_i \delta\left(\sum_{j=1}^N H_j - E\right)\\ &= \int \prod_{k=1}^N dE_k \delta\left(\sum_{j=1}^N E_j - E\right)\prod_{i=1}^N \int d\omega_i \delta(H_i - E_i)\\ &= \int_0^\infty \prod_{k=1}^N dE_k \delta\left(\sum_{j=1}^N E_j - E\right)\exp\left(\sum_{i=1}^N S_i(E_i)\right).\end{aligned} \tag{11}$$

Now we use $S_i(E_i)=\ln E_i + E_i^2$, and introduce the integration variables $\lambda_i=E_i/E$, to arrive at

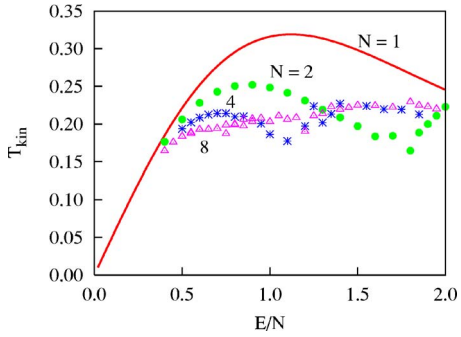

FIG. 3. (Color online) Caloric curves for $N=1$ (smooth line), $N=2$ (full green dots), $N=4$ (blue stars), and $N=8$ (pink triangles) particles. The respective *kinetic* temperature, $T_{\mathrm{kin}} \equiv \langle \Sigma_{i=1}^{N} p_i^2 / N \rangle$, is plotted as a function of the energy per particle, E/N.

$$e^{S(E)} = \int_0^1 \prod_{k=1}^{N} d\lambda_k \delta\left(\sum_{j=1}^{N} \lambda_j - 1 \right) \times \exp\left(E^2 \sum_{i=1}^{N} \lambda_i^2 + (2N-1)\ln E + \sum_{i=1}^{N} \ln \lambda_i \right) \geq e^{E^2/N + (2N-1)\ln E} g_N, \tag{12}$$

where

$$g_N = \int_0^1 \prod_{k=1}^{N} d\lambda_k \lambda_k \delta\left(\sum_{j=1}^{N} \lambda_j - 1 \right)$$

is a constant depending only on N. The inequality follows, because $\Sigma_{i=1}^{N} \lambda_i^2 \geq 1/N$. If $S(E)$ were concave, there should be a bound according to Eq. (10), $e^{S(E)} \leq A e^{BE}$ for all $E \geq 0$, where $A, B \in R^+$. This contradicts the previous inequality (12). Thus, there should be a range of energies, for which the specific heat remains negative even for large N.

To test this result on the computer, the particles are energetically coupled such that their total energy is strictly conserved and the system is microcanonical. The coupling is achieved by selecting, with period τ, $N/2$ particle pairs and adding random velocities to the particle velocities of each pair. Subsequently, the new velocities are renormalized such that the pair energy is unchanged, which also conserves the total energy. Typically, $\tau = 100$ time units. In Fig. 3 we compare the energy dependence of the kinetic temperature $T_{\mathrm{kin}} \equiv \langle \Sigma_{i=1}^{N} p_i^2 / N \rangle$ for two, four, and eight particles to the exact single-particle result (smooth line), which is taken from Fig. 2. From there we also infer that, whenever $T_{\mathrm{kin}}(E)$ has a negative slope, also the heat capacity $c = [dT(E)/dE]^{-1}$ is expected to be negative. In Fig. 3, energy intervals with a negative slope may still be observed for two and four particles, although the energy regions where this happens are significantly reduced. Numerically, regions with a negative slope cease to exist for $N \geq 8$. Most likely, this is due to a lack of ergodicity for our simulation, since the particles do not have enough time to explore the region very far out to the right on top of the board.

In spite of this failure to numerically locate the region with negative specific heat for more than four particles, we still may deduce the gross behavior of the system. To evaluate the integral Eq. (11) we have to look for the maximum of the exponent $\Sigma_i S_i(E_i) = \Sigma_i (E_i^2 + \ln E_i)$ in the region $0 < E_i$, $\Sigma_i E_i = E$. Were it not for the logarithm, the maximum would be on the boundary: one E_i equal to E, and all the others zero. The logarithm moves the location of the maximum inside this region to a point where all the derivatives vanish. Taking care of $\Sigma_i E_i = E$ with a Lagrange multiplier λ, we get the condition $2E_i + 1/E_i = \lambda$. This equation has the solutions

$$E_i = \lambda [1 \pm (1 - 8/\lambda^2)^{1/2}]/4.$$

The solution for the absolute maximum will have one big member, say $E_1 = \lambda[1 + (1 - 8/\lambda^2)^{1/2}]/4$, and the others, $E_2, \ldots, E_N = \lambda[1 - (1 - 8/\lambda^2)^{1/2}]/4$, are small. λ is determined by $E = N\lambda[1 - (1 - 8/\lambda^2)^{1/2}]$. Thus, two "phases" emerge: An "atmosphere" (particle 1) and a "condensate" (all the other particles). Both have the same temperature, Eq. (7). Most interesting is the case of a single high-energetic particle, say particle 1, and the remaining particles in a dense phase around the origin. Since the temperature goes as $E_i/(1 + 2E_i^2)$, the temperature in both phases decreases with increasing E. The emergence of two phases nicely illustrates the instability connected with the negative specific heat. The particles 2 to N give most of their energy to particle 1, which carries it away.

A thermodynamic interpretation of this equilibrium runs as follows: There are N particles with a negative heat capacity for $E_i > 1/\sqrt{2}$, and a positive heat capacity for $E_i < 1/\sqrt{2}$. At the beginning, the particle with the highest energy is actually the coldest, with most of its energy spent to get on the jumping board. Therefore, it will tend to extract energy from the other particles. By this mechanism, all the other particles with $E_i > 1$ lose energy and become hotter. This process continues until all the other particles have lost most of their energy, such that $E_i < 1/\sqrt{2}$, and their heat capacity becomes normal and positive again. By giving off energy to the hottest particle, which on average has the tendency to get as far away from the origin as possible, the remaining $N-1$ particles cool off again. They gather (condense) in the potential minimum near the origin, where they assume the same low temperature.

To test these ideas by computer simulation, we consider a planar system of $N = 1000$ point particles, which move in a constant gravitational force field of unit strength, pointing into the direction of the negative y axis (see Fig. 4). At the bottom the particles are elastically reflected from the x axis, for $0 < x \leq V(0)$, and from the jumping board V, for $x > V(0)$, where $V(0) = 1/\pi$ is the intersection of V with the x axis. For simplicity, the particles are also elastically reflected from the positive y axis to ensure positive x for all time.

Initially, all particles are at the origin and have randomly oriented momenta, such that all their energies are unity, $E_i(0) = p_{x,i}^2(0) + p_{y,i}^2(0) = 1$; $i = 1, \ldots, N$. Then, for the first 4000 time units, the system is evolved in time as an ideal gas *without any interaction between particles*. This time is sufficient by far to reach a stationary state, for which Fig. 4 is a

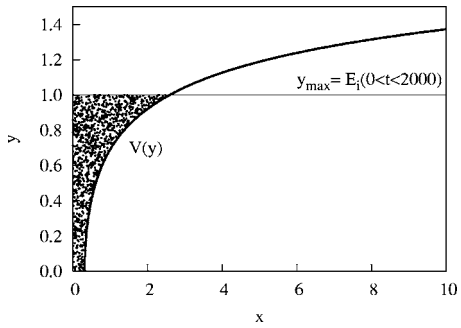

FIG. 4. Geometry of the jumping-board model. The points indicate the location of 1000 ideal gas particles, all with unit energy, which were evolved for a sufficiently long time to reach a stationary state.

typical snapshot. As is apparent from this figure, the maximum height the particles may reach is determined by their energy, $y \leq y_{max}=E_i$, which is still the same for all particles.

Next, for times $t>4000$, interactions between particles are switched on in such a way that the total energy is constant and the system remains microcanonical. Periodically, after every two time units, ten particle pairs are randomly selected and the kinetic energies within each pair are interchanged, but keeping the original directions of their momenta unchanged. With this modification, the system is evolved for another 8000 time units. A snapshot of the particles at $t=12\,000$ is shown in Fig. 5. For clarity, the same spatial region as in Fig. 4 has been selected, although some particles are much further to the right and/or higher up in potential energy (respective y) to appear in this figure. For example, the particle furthest to the right and on top of the jumping board for this particular snapshot is located at $(5916, 2.9)$.

The qualitative behavior of the system with activated particle interactions may be inferred from this figure. The particles tend to "condense" near the center and are simultaneously cooled off as predicted, where the excess energy is carried to the right by a small fraction of the particles. To make this statement more explicit, we show in Fig. 6, how

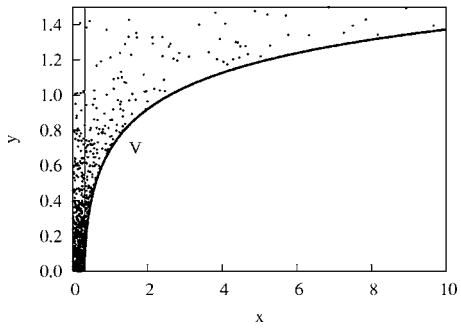

FIG. 5. Snapshot of the particle locations at a time $t=12\,000$, after the system has been evolved for 8000 time units by permitting periodic kinetic-energy exchange for randomly selected particle pairs as explained in the main text. Only a tiny part of the accessible space is shown. The total energy is still a constant of the motion. The vertical line, $x=V(y=0)=0.319$, marks the upper boundary of the central region discussed in the main text.

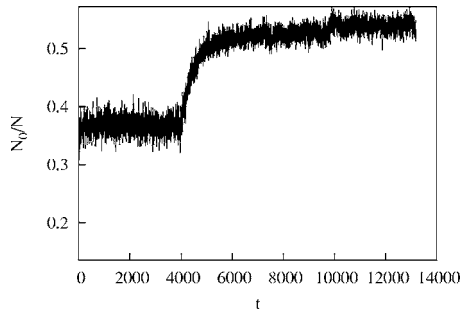

FIG. 6. Time evolution of the ratio of particles, $N_0(t)/N$, in the central region $0 \leq x \leq V(y=0)=1/\pi=0.319$ to the left of the vertical line of Fig. 5, for a system containing $N=1000$ particles. The particle interactions are switched on at $t=4000$.

the fraction $N_0(t)/N$ of particles in the central region $0 \leq x \leq V(0)$ to the left of the vertical line in Fig. 5, changes with time in our computer experiment. Furthermore, Fig. 7 depicts the time evolution of the instantaneous kinetic energy per particle, $K_0(t)/N_0(t)$, for the particles in the central region $0 \leq x \leq V(0)$. Once the particle interactions are activated at $t=4000$, one observes a sharp increase of the number of particles $N_0(t)$ near the origin, and a simultaneous drop of the kinetic energy per particle, $K_0(t)/N_0(t)$ and, hence, the temperature for the condensed particles. Incidentally, a plot of the potential energy per particle as a function of time (not shown) looks very similar to Fig. 7, which is a consequence of equipartition.

Most of the cooling is achieved within about 1000 time units. To convert to regular units, we note that our unit of length L is given by $L=\pi x_0$, where x_0 is the distance, where the jumping board crosses the x axis. The unit of mass is twice the mass of a particle, and the unit of time is $\sqrt{L/g}=\sqrt{\pi x_0/g}$, where g is the gravitational acceleration. Assuming $L=1$ μm and $g \approx 10$ m s^{-2}, the time unit is about 0.3 ms. Within 3 s, particles with a mass of 1.2×10^{-24} kg (corresponding to C_{60} molecules) are cooled from 0.43 μK to about 0.17 μK. The state reached, however, is not yet stationary, but the process of condensation and cooling still continues but with a progressively lower and lower rate. This is also observed in Figs. 6 and 7.

At this stage a few remarks are in order:

(i) Thermodynamic instability means that the system cannot coexist with a large heat bath. As a consequence, the

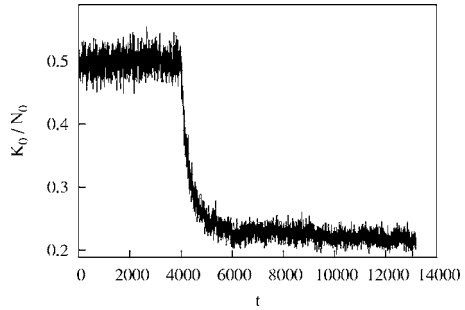

FIG. 7. Time evolution of the kinetic energy per particle for all particles in the central region $0 \leq x \leq V(y=0)=1/\pi=0.319$, which is bounded by the vertical line in Fig. 5. The total number of particles $N=1000$.

canonical distribution $\exp(-\beta H)$ is not normalizable. The reason is that $\int_0^{V(y)} dx \cdots \sim \exp(y^2)$, and $\exp(-\beta H) \sim \exp(-y)$ is powerless to render this integrable.

(ii) Inserting a mass, $H=p^2/m+my$, we note that the trajectories satisfy the equivalence principle and are independent of m, which only affects the time scale. In quantum theory this does not hold any longer.

(iii) The thermal behavior can be looked at as a very effective form of evaporation cooling, which has been most extensively studied to generate ultracold gases in connection with Bose-Einstein condensation [5].

IV. COUPLED SYSTEMS WITH POSITIVE AND NEGATIVE HEAT CAPACITIES

Next we consider two systems:

(1) A particle on a jumping board with a less-than-exponential phase-space growth with energy, for which the specific heat is *positive* (index p),

$$e^{S_p(E_p)} = E_p^{10},$$

$$V_p(y) = \frac{10}{\pi} y^9,$$

$$c_p = 10,$$

$$T_p = \frac{E_p}{10},$$

$$T_{\mathrm{kin},p} = \frac{E_p}{11}, \tag{13}$$

(To avoid the singular slope at the origin, the board is regularized by a horizontal bottom for $0 \le x \le (10/\pi)(0.2)^9$. This does not affect the thermodynamic properties.)

(2) A particle on a board with a *negative* specific heat (index n) for a large-enough energy, for which the equivalent quantities are chosen as follows:

$$e^{S_n(E_n)} = E_n e^{(9E_n^2/2)},$$

$$V_n(y) = \frac{1}{\pi}(1-9y^2)e^{9y^2/2},$$

$$c_n = \frac{(9E_n^2+1)^2}{(1-9E_n^2)} < 0 \quad \text{for } E_n > 1/3,$$

$$T_n = E_n/(9E_n^2+1),$$

$$T_{\mathrm{kin},n} = \frac{[1-\exp(-9E_n^2/2)]}{9E_n}. \tag{14}$$

For the same reasons as before, the thermodynamic temperatures T_n and T_p differ slightly from the respective kinetic temperatures $T_{\mathrm{kin},n}$ and $T_{\mathrm{kin},p}$. For both models, these temperatures are shown in Fig. 8 as a function of the respective energies, where the points refer to computer simulation results. The scatter of points for the n system at large energies E_n indicates the difficulties of achieving ergodicity, when the particle is very far to the right on top of the board.

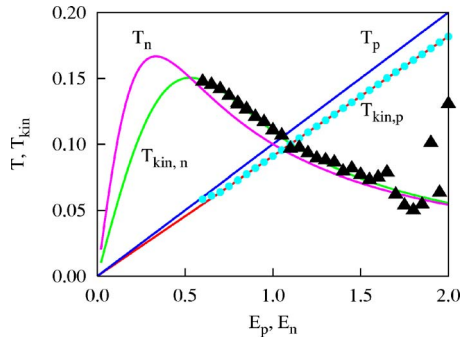

FIG. 8. (Color online) Dependence of the thermodynamic temperatures T and the kinetic temperatures T_{kin} on the particle energy E for the jumping-board models with positive (index p) and negative (index n) heat capacity. The smooth curves are theoretical predictions and the points are computer simulation results.

What happens when these systems are microcanonically coupled such that the total energy is constant, $E=E_p+E_n=\text{const}$ [7]? Denoting the energy deviation from the mean, $E/2$, by q,

$$E_p \equiv (E/2)+q, \quad E_n \equiv (E/2)-q,$$

we study the total entropy as a function of q,

$$S(q) = S_p[(E/2)+q] + S_n[(E/2)-q]$$
$$= 10\ln(1+q) + \tfrac{9}{2}(1-q)^2 + \ln(1-q).$$

In the middle panel of Fig. 9, we show this function for three values of the average energy, $E/2=1$ (smooth red line), $E/2=1.03$ (dashed green line), and $E/2=0.97$ (dotted violet line). The respective density of states $\Omega(q) \equiv e^{S(q)}$ is shown in the top panel, and the derivative $dS(q)/dq$ in the bottom panel of the same figure. Since $dS(q)/dq$ is proportional to $(1/T_p)-(1/T_n)$, its zeroes indicate equilibrium states for which the temperatures of the two subsystems coincide.

For the most interesting case, $E/2=1$, there exist three zeroes for $dS(q)/dq$: a metastable state for $q=0$ with a (weak) local maximum of $S(q)$, an unstable equilibrium for $q=1/3$, and a globally stable state with the highest entropy maximum for $q=2/3$. The possibility of three zeroes was our original motivation for the particular choice of jumping boards for the n and p subsystems in Eqs. (13) and (14). The stability properties are most easily understood in connection with Fig. 8: Depending on the fluctuation of the unstable state $q=1/3$ (respectively, $E_n=2/3$, $E_p=4/3$), the coupled system may evolve to either of two equilibrium states:

(i) towards the (locally) stable state $q=0$ (respectively, $E_n=E_p=1$), whereby the p subsystem loses energy to the n subsystem with an overall reduction of the temperature;

(ii) towards the (globally) stable state $q=2/3$ (respective $E_n=1/3$, for which the specific heat of the n system *diverges*, and $E_p=5/3$). In this case, energy is transferred from the n subsystem to the p subsystem, until the highest possible ther-

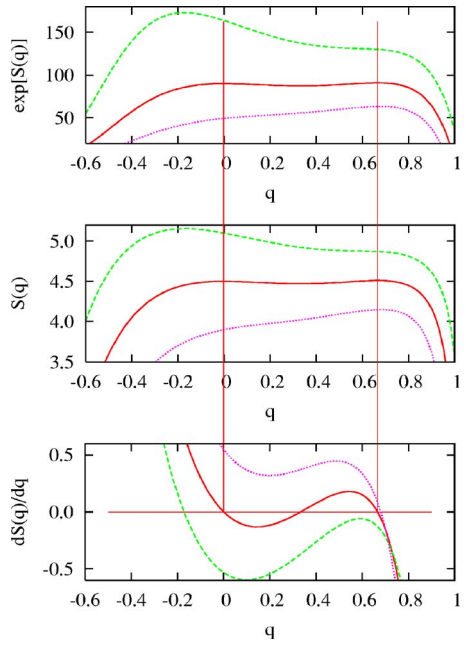

FIG. 9. (Color online) Theoretical predictions for the energetically coupled jumping-board models, one with a positive (p) and the other with a negative (n) heat capacity. Each subsystem contains a single particle. Top: density of states, $e^{S(q)}$; middle: $S(q)$; bottom: $dS(q)/dq$. Here, $q=(E_p-E_n)/2$ denotes the fluctuating particle energies with respect to the constant mean energy $E/2$. $E/2=1.03$: dashed green lines; $E/2=1.00$ smooth red lines; $E/2=0.97$ dotted pink lines.

modynamic equilibrium temperature is reached by the two subsystems.

We have numerically verified the density of states for $E/2=1$ in Fig. 10, where $e^{S(q)}$ (smooth line) is compared to a histogram of $q=E_n-1$ constructed from the simulation. The coupling between the n and p particles is achieved by periodically (every 20 time units) adding random vectors sampled from a Boltzmann distribution to the particle velocities, and normalizing the total energy to $E=2$. The agreement in Fig. 10 is very satisfactory. However, for $q<-0.6$, that is, for $E_n>1.6$, it becomes progressively difficult to achieve ergodicity, and systematic deviations are observed (not shown in Fig. 10).

V. CONCLUDING REMARKS

Generally, negative specific heat is related to other properties of a system by the following theorem [8]:

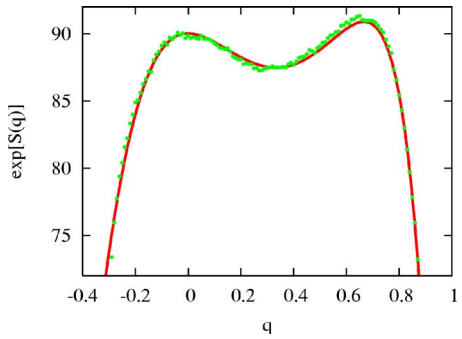

FIG. 10. (Color online) Comparison of the theoretical density of states $e^{S(q)}$ with the histogram of $q=E_n-1$ of the energetically coupled jumping-board models with positive and negative heat capacities. Each subsystem consists of a single particle, and $E/2=1$. A single fit parameter is used for the height of the histogram.

Let $F:R^n\rightarrow R$, with $F(0)=0$. Then, the three stability conditions

(i) Extensivity (stability against implosion):

$$F(\lambda z)=\lambda F(z), \quad \lambda \in R^+,$$

(ii) Subadditivity (stability against explosion):

$$F(z_1+z_2)\leq F(z_1)+F(z_2),$$

(iii) Convexity (thermodynamic stability):

$$F[\lambda z_1+(1-\lambda)z_2]\leq F(z_1)+(1-\lambda)F(z_2),$$

are related such that each pair of conditions implies the third.

In terms of physics, F should be thought of the energy as a function of entropy, particle number, and volume. By this theorem, if one of the stability notions fails, another has to fail too. In the model treated in this paper, (iii) fails, and it is obvious that (i) fails too.

Usually, stability properties are discussed in the thermodynamic limit. But since all of the quantities are well defined for a few particles, it is permitted to apply thermodynamic considerations to the system with a finite number of particles.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Foundation (FWF), Grant No. P18798, and by the European Science Foundation within the framework of its STOCHDYN program.

[1] H. A. Posch and W. Thirring, Phys. Rev. Lett. **95**, 251101 (2005).
[2] W. Thirring, Z. Phys. **235**, 339 (1970).
[3] D. H. E. Gross, *Microcanonical Thermodynamics: Phase Transitions in "Small" Systems* Lecture Notes in Physics Vol. 66 (World Scientific, Singapore, 2001).
[4] J. L. Lebowitz and E. H. Lieb, Phys. Rev. Lett. **22**, 631 (1969).
[5] O. J. Luiten, M. W. Reynolds, and J. T. M. Walraven, Phys. Rev. A **53**, 381 (1996).
[6] C. N. Cohen-Tannoudji, Nobel Lecture, December 8, 1997.
[7] D. Lynden-Bell, Physica A **263**, 293 (1999).
[8] W. Thirring, *Quantum Mathematical Physics*, 2nd ed., (Springer Verlag, Berlin, 2001).