SYSTEMS WITH NEGATIVE SPECIFIC HEATW. Thirring^{*)}

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ABSTRACT

Some systems for which the binding energy increases more rapidly than linearly with the number of particles, are shown to exhibit negative specific heat c for some energies. In thermal contact with larger systems, $c < 0$ creates an instability, and in the canonical ensemble one sees only a phase transition. It is argued that supernovae are, in essence, a phase transition of this origin.

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1. A SURPRISING THEOREM THAT IS SIMPLE TO PROVE,
BUT WHICH IS WRONG

It is a fact known to astrophysicists that if radiation energy is extracted from a star whose nuclear fuel is exhausted, the star will contract and heat up. Thus a star acts like a system with negative specific heat^{*)}. There are proofs that under reasonably general assumptions the specific heat of interacting particles is positive. In this paper we shall try to clarify this perplexing situation.

The astrophysical arguments all depend on the virial theorem. Since the latter comes only from the $1/r$ behaviour of the potential and not from its attractiveness, one actually arrives at the more general theorem 1.

Theorem 1

According to classical statistical mechanics, every piece of condensed matter has negative specific heat.

Before proving theorem 1, we have to specify what we mean by condensed matter. Condensed means that the system keeps together without being put in a box, and thus we do not have to include the potential of the box in the Hamiltonian.

By matter we mean a system of N electrons and nuclei with only static Coulomb interactions. Thus the Hamiltonian of our system is

$$H_N = K + V, \quad (1)$$

the kinetic energy K being the usual

$$K = \sum_{i=1}^N \frac{p_i^2}{2m_i} \quad (2)$$

and the potential

$$V = \sum \frac{e_i e_j}{r_{ij}}. \quad (3)$$

Now the proof is trivial. If $\langle \rangle$ denotes the thermal expectation value, the virial theorem tells us

$$\langle -K \rangle = \frac{1}{2} \langle V \rangle = \langle H \rangle \equiv E \quad (4)$$

*) The only reference to this fact that I could find is L.D. Landau and E. Lifchitz, Statistical Physics, 2nd Ed., p. 62, Pergamon Press.

and the equipartition theorem ($k = 1$)

$$\langle K \rangle = \frac{3N}{2} T . \quad (5)$$

For the system to be condensed we have of course, $E < 0$; and in particular from Eqs. (4) and (5) we get

$$-E = \frac{3N}{2} T . \quad (6)$$

Thus, the specific heat

$$c = \frac{dE}{dT} = - \frac{3N}{2} < 0 , \text{ Q.E.D. } . \quad (7)$$

Let us first study this absurd result for the simplest case, namely one particle in a Coulomb potential:

$$H = \frac{p^2}{2m} - \frac{e^2}{r} . \quad (8)$$

Although one particle is not much of a thermodynamic system, the above reasoning should also apply to it. The volume of the phase space under the energy shell ($\theta =$ step function)

$$\bar{\Omega}(E) = \int d^3x \, d^3p \, \theta(E - H) \quad (9)$$

is finite for $E < 0$ and then easily calculated to be $\pi^3 (-E)^{-3/2}$.

This behaviour comes about since in x -space the volume available goes $\sim (E)^{-3}$, and from momentum space we get a factor $(E)^{3/2}$. Actually this also follows immediately in quantum theory where we have $E = -Ry/n^2$, and the number of states $\bar{\Omega}$ below a quantum number n goes as $n^3 \approx |E|^{-3/2}$. Thus for the entropy $S(E)$ we have

$$S(E) = - \frac{3}{2} \ln (-E) , \quad \frac{1}{T} = \frac{dS}{dE} = - \frac{3}{2E} , \quad (10)$$

in agreement with Eq. (6).

Thus we have formally

$$c = \frac{dE}{dT} = - \frac{3}{2} . \quad (11)$$

However, for a real thermodynamic system we need many particles, and then one soon realizes where the proof of theorem 1 goes wrong. First of all we shall need a box, otherwise $\bar{\Omega}$ will be infinite since we can always send one particle to infinity and lower the energy of the rest. Even in box

$$\bar{\Omega}_N = \int_{\text{box}} d^{3N}r \int d^{3N}p \delta(E - H_N) (N!)^{-1} \quad (12)$$

diverges if we have several particles. Carrying out the p integration we have

$$\bar{\Omega}_N \sim \int d^{3N}r \left(E - \sum \frac{e_i e_j}{r_{ij}} \right)^{3N/2}, \quad (13)$$

where the integral goes over the region where $E > \sum e_i e_j / r_{ij}$. To have $\bar{\Omega}_N \neq 0$ for $E < 0$ we need an attractive pair (i,j) , but then the integral diverges for small r_{ij} since the integrand then goes as $r_{ij}^{-3N/2}$. Thus we have also to modify the potential at small distances to get a meaningful expression for $\bar{\Omega}_N$ for which the formal arguments of the proof apply. Therefore we have to take into account an external virial due to the box, and an internal virial due to a small distance repulsion. In the next section we shall try to estimate the effect of the former for the gravitational case ($e_i e_j \rightarrow -km_i m_j$) where we have only attractions, and therefore the best chance for a small effect of the box. In Section 3 the question of the internal virial will be settled for a very truncated form of the potential for which $\bar{\Omega}_N$ can be calculated exactly.

To conclude this section we shall comment on the quantum theoretic problem. There $\bar{\Omega}_N(E)$ = Number of states below E exists even without cut-off at small distances. The non-relativistic Hamiltonian (1) has for arbitrary N a lower eigenvalue E_0 , in contradistinction to the relativistic case where we get a collapse for $e_i e_j \rightarrow -km_i m_j$ and N sufficiently large. A recent analysis of Dyson¹⁾ and collaborators has shown that $|E_0| \sim N$ is a rather exceptional situation for particular combinations of statistics and signs of e . In many cases $|E_0|$ increases faster with N . We shall see later that this leads to interesting thermal consequences. Regarding theorem 1, one might think that it applies rather to the quantum theoretic case, since there the problem of the internal virial disappears. However, the equipartition theorem holds only in the classical limit, the virial theorem being generally true. Thus there seems to be no system for which the proof of theorem 1 holds. Nevertheless we shall see that theorem 1 reflects an essential feature of statistical mechanics for gravitationally interacting systems.

2. A NON-RIGOROUS TREATMENT OF THE GRAVITATIONAL CASE

In this section we shall estimate $\bar{\Omega}_N$ for $e_i e_j \rightarrow -\kappa$ by a method which has some intuitive appeal and may be appropriate for (unshielded) long-range forces. The idea is that the main part of the gravitational potential that a particle feels comes mainly from the bulk of the particles at large distances rather than from its immediate neighbours. Thus we shall divide the volume V of the box in $M \ll N$ cells of equal size, large enough to contain many particles but small enough so that the potential can be treated as constant inside a cell. Instead of integrating over all particle coordinates $d^{3N} r$, we shall sum over the number of particles n_α in the cell around the point x_α ($\alpha = 1 \dots M$). This is exact if the integrand is constant for all particle configuration leading to the same occupation numbers. It is a standard combinational problem to transform $d^{3N} r (N!)^{-1}$ into

$$\sum_{n_1=0}^{\infty} \frac{1}{(n_1)!} \sum_{n_2=0}^{\infty} \frac{1}{(n_2)!} \dots \sum_{n_M=0}^{\infty} \frac{1}{(n_M)!} \delta_{N, \sum_{\alpha=1}^M n_\alpha} \left(\frac{V}{M}\right)^N.$$

In this way we obtain (all $m_i = \frac{1}{2}$)

$$\begin{aligned} \bar{\Omega}(E) &= (N!)^{-1} \int d^{3N} p d^{3N} r \theta \left[E - \sum_{j=1}^N p_j^2 - \sum_{i>j}^N v(r_i, r_j) \right] = (N!)^{-1} \int d^{3N} r \\ &\quad \exp \left\{ \frac{3N}{2} \ln \left[E - \sum_{i>j}^N v(r_i, r_j) \right] 2\pi e / 3N \right\} \\ &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_M=0}^{\infty} \delta_{N, \sum_{\alpha=1}^M n_\alpha} \exp \left\{ \frac{3N}{2} \ln \left[E - \sum_{\alpha>\beta}^M n_\alpha v(x_\alpha, x_\beta) n_\beta \right] 2\pi e / 3N - \right. \\ &\quad \left. - \sum_{\alpha=1}^M n_\alpha \ln n_\alpha M / eV \right\}. \end{aligned} \quad (14)$$

Here we have used Stirling's formula to the accuracy $N! = (N/e)^N$. So far our manipulations rest on the assumption that the potential is constant in each cell and $n_i \gg 1$, which can be achieved by making N and M sufficiently large. Next we make an approximation that is popular in statistical mechanics, namely represent $\sum_{\alpha} n_\alpha$ by a single term for which the summand reaches a maximum as function of the n_α subject to the condition $\sum_{\alpha=1}^M n_\alpha = N$:

$$\bar{\Omega}(E) = \sum_{n_\alpha} e^{S[n_\alpha]} \delta_{N, \sum_\alpha n_\alpha} \approx e^{S[n_\alpha^0]} -$$

$$-\frac{\partial S}{\partial n_j^0} = \frac{3N}{2} \frac{2}{3NT} \sum_{\beta=1}^M v(x_\alpha, x_\beta) n_\beta^0 + \ln \frac{n^0 M}{v} = \mu/T = \text{const} . \quad (15)$$

Here we have identified temperature as

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3N}{2} \frac{1}{E - \sum_{\alpha>\beta}^M n_\alpha v(x_\alpha, x_\beta) n_\beta} . \quad (16)$$

Here the E-dependence of n_α the n_i^0 does not matter since

$$\sum_{\beta=1}^M \frac{\partial S}{\partial n_\beta^0} \frac{\partial n_\beta^0}{\partial E} = -\alpha \sum_{\beta=1}^M \frac{\partial n_\beta^0}{\partial E} = -\alpha \frac{\partial}{\partial E} N = 0 . \quad (17)$$

The maximum condition (15) is, of course, the barometric formula $n_\alpha \sim e^{-V(x_\alpha)/T}$, $V(x)$ being the potential due to all particles. This procedure can be justified rigorously in the limit $N \rightarrow \infty$ if the n_α^0 correspond to an absolute maximum of S . We shall not attempt to find conditions on v , which assures a maximum, since in our case it is not true anyway. However, one might note that not only in the trivial case $v = 0$ but also for $v(x,y) = (\kappa/N) (x - y)^2$ for which the many-body problem can be solved (15) leads to the exact result. The case of interest for us is $v(x,y) = -\kappa/|x - y|$. We know already that then the expression for $\bar{\Omega}$ diverges and we shall keep a cut-off at small distances in mind for the case of trouble. Furthermore we shall pass to the continuum limit

$$n_\alpha \frac{M}{V} = \rho(x_\alpha) , \quad \sum_{\alpha=1}^M \rightarrow \frac{M}{V} \int d^3x$$

$$N = \sum_{\alpha=1}^M n_\alpha = \int d^3x \rho(x) , \quad S = - \int d^3x \rho_0(x) \ln \frac{\rho_0(x)}{(\pi T)^{3/2} e^{5/2}} \quad (18)$$

for which Eqs. (15) assume the familiar form of the equations of static equilibrium of a star consisting of an isothermal ideal gas

$$\rho_0(x) = e^{(\kappa/T) \int d^3x' [\rho_0(x')/|x-x'|]} \text{const} . \quad (19)$$

Guided by intuition we shall look for spherically symmetric solutions and hence use for V the unit sphere. Their Eq. (19) reads ($r = |x|$)

$$\begin{aligned} \rho_0(r) &= \rho_0(1) \exp \left\{ \frac{4\pi\kappa}{T} \left[\int_0^r dr' r'^2 \rho(r') (1/r - 1) + \int_r^1 dr' r' \rho(r') (1 - r') \right] \right\} \\ &= \rho(1) \exp \left\{ -\frac{1}{T} [V(r) - V(1)] \right\}. \end{aligned} \quad (20)$$

The differential version of Eq. (20)

$$T \frac{d\rho_0}{dr} = -\frac{4\pi\kappa}{r^2} \rho_0(r) \int_0^r dr' r'^2 \rho_0(r') \quad (21)$$

allows us to express the quantities of interest by the asymptotic form of ρ :

$$N = -\frac{T}{\kappa} \frac{\rho_0'(1)}{\rho_0(1)}, \quad V(1) = -N\kappa$$

$$\begin{aligned} 4\pi T \rho_0(1) - 3NT &= 4\pi T \int_0^1 dr r^3 \frac{d\rho_0}{dr} = -\kappa \int_0^1 dr' r'^2 4\pi \rho_0(r') \frac{1}{r'} \int_0^{r'} dr r^2 4\pi \rho_0(r) = V \\ S &= - \int d^3x \rho_0(x) \ln \frac{\rho_0(x)}{(\pi T)^{3/2} e^{5/2}} = \frac{3N}{2} \ln \pi T - \frac{7}{2} N - N \ln \rho(1) + \frac{N^2 \kappa}{T} + 8\pi \rho(1). \end{aligned} \quad (22)$$

We are now prepared to approach the central issue, namely whether the effect of the external virial will upset our conclusion that the system as a whole has negative c . From Eq. (22) we note

$$E = \frac{3N}{2} T + V = -\frac{3N}{2} T + 4\pi T \rho_0(1). \quad (23)$$

Here the last term represents the contribution of the external virial, and the question is whether its temperature derivate will overcome the $-3N/2$ we had obtained at the beginning. We shall see that this is not the case; on the contrary, it also contributes negatively. This comes from the property of a star to heat up when it shrinks, and hence $\rho(1)$ decreases with increasing temperature. To see this one has to use the well-known solution of Eq. (21) corresponding to a ρ strongly concentrated at the origin. One finds that $\rho \sim 1/r^2$ is a solution for $T_0 = N\kappa/2$,

$E_0 = - N^2\kappa/4$, and for small deviations from these values the solution is

$$\rho(r) = \frac{N}{4\pi r^2} \left\{ 1 + \frac{T - T_0}{T_0} \left[1 - 2(r^{(-1+i\sqrt{7})/2} + r^{(-1-i\sqrt{7}/2)}) \right] \right\}. \quad (24)$$

With Eq. (22) we then obtain [for $|(T - T_0)/T_0| \ll 1$]

$$\begin{aligned} E &= - \frac{N^2\kappa}{4} - \frac{7}{2} N(T - T_0) \\ S &= N \left[\frac{3}{2} \ln \frac{\pi N \kappa}{2} - \ln \frac{N}{4\pi} + \frac{1}{2} - \frac{7}{2} \frac{T - T_0}{T} \right]. \end{aligned} \quad (25)$$

Thus we have actually

$$c \Big|_{T=T_0} = - \frac{7}{2} N, \quad (26)$$

being even more negative than according to theorem 1. Now clearly this result cannot be exact because we have not used the cut-off without which there is no S . The fact is that $S[\rho_0]$ is not a maximum. Looking at the second derivative $\rho^2 S / \delta \rho_0(x) \delta \rho_0(x)$ one finds by expansion in spherical harmonics that for $\ell \neq 0$ it is actually a negative definite kernel but not for $\ell = 0$. This can be seen directly by inserting $\rho(r) = (N/4\pi) (3 - \gamma) r^{-\gamma}$, $\gamma < 3$, into S for $E = - N^2\kappa/4$. One calculates

$$S(\gamma) = N \left\{ \frac{3}{2} \ln \frac{\pi N \kappa}{6} - \ln \frac{N}{4\pi} + \frac{3}{2} \ln \frac{7 - 2\gamma}{5 - 2\gamma} - \ln (3 - \gamma) - \frac{\gamma}{3 - \gamma} \right\}. \quad (27)$$

S_γ is actually zero for $\gamma = 2$, as it has to be since $\rho \sim r^{-2}$ is a solution of Eq. (21). But $S_{\gamma\gamma}|_{\gamma=2} = N/3$. Thus we do not have an absolute maximum but a relative minimum. What happens is that S is unbounded and goes to ∞ for $\gamma = 2.5$ (Fig. 1). This shows that entropy favours a strong concentration at the origin, and we shall encounter this collapse on further occasions. Our findings are parallel to the classical results of the instability of an isothermal ideal star. The origin is clearly the need for a cut-off to get a bounded S . There seem to be ways of modifying the $1/r$ potential in order to get stability without introducing too much internal virial to make c positive. We shall not discuss this here, since in the next section we shall construct a system with negative c in a much simpler fashion such that the evaluation of S involves no problems.

3. AN EXACT SOLUTION FOR A SOMEWHAT ARTIFICIAL VERSION OF A STAR

In this section we shall analyse a system that incorporates the essential features of the previous one, which lead to $c < 0$. We shall be guided by the two conditions²⁾ which guarantee that for the microcanonical $S(E)$ one has

$$\frac{\partial^2 S}{\partial E^2} < 0 \text{ and therefore } c = - \left(T^2 \frac{\partial^2 S}{\partial E^2} \right)^{-1} > 0 .$$

They are roughly that at large distances the forces are not repulsive and that $E \sim N$. The former condition is satisfied for the gravitational case, and thus the failure of the second must be responsible for $c < 0$. This leads us to the following model for a star. Inside an interaction volume V_0 , each particle has an attractive interaction with the other particles inside the volume and outside V_0 the particles are free. With the step-function

$$\theta_{V_0}(x) = \begin{cases} 1 & \text{if } x \in V_0 \\ 0 & \text{if } x \notin V_0 \end{cases} \quad (28)$$

a non-local potential having this feature is ($v > 0$ is constant)

$$v(x_k, x_j) = - 2v \theta_{V_0}(x_k) \theta_{V_0}(x_j) . \quad (29)$$

In this way the total potential energy is $-v N_0^2$, where N_0 is the number of particles in V_0 . The evaluation of $\bar{\Omega}$ is now a simple combinatorial problem, and we find (if the volume outside V_0 is $e^F \cdot V_0$)

$$\begin{aligned} \bar{\Omega}(E) &= \frac{1}{N!} \int d^{3N}p \, d^{3N}x \, \theta \left[E - \sum_i p_i^2 - \sum_{i>j} v(x_i, x_j) \right] = \frac{\pi^{3N/2}}{N! (3N/2)!} \int d^{3N}x \\ &\quad \theta \left(E + v \sum_{i>j} \theta_{V_0}(x_i) \theta_{V_0}(x_j) \right)^{3N/2} \\ &= \frac{v^N \pi^{3N/2}}{(3N/2)!} \sum_{N_0=0}^N \frac{(E + N_0^2 v)^{3N/2} e^{F(N-N_0)}}{N_0! (N - N_0)!} = \sum_{N_0=0}^N e^{S(E, N, N_0)} . \quad (30) \end{aligned}$$

Thus the expression for $\bar{\Omega}$ is again a sum but in this case over a single variable. Now it is easy to see when S as a function of N_0 has a maximum. Indeed (with stirling)

$$\frac{\partial S(E, N, N_0)}{\partial N_0} = \frac{3N N_0 v}{E + N_0^2 v} - \ln \frac{N_0}{N - N_0} - F = 0 \quad (31)$$

has for $E < 0$ only one solution since

$$\frac{\partial^2 S}{\partial N_0^2} = \frac{3N \nu E - 3N N_0^2 \nu}{(E + N_0^2 \nu)^2} - \frac{N}{N_0(N - N_0)} < 0 \quad 0 < N_0 < N, E < 0. \quad (32)$$

To discuss Eq. (31) we shall introduce "intensive" quantities $\alpha, \varepsilon, \theta$ where, however, the scaling law is different than usual:

$$E = N^2 \nu(\varepsilon - 1), \quad T = \frac{2}{3} N \nu \theta, \quad N_0 = N(1 - \alpha). \quad (33)$$

From Eqs. (30) and (31) we get a parameter representation for θ as function of ε :

$$\theta = \varepsilon - 2\alpha + \alpha^2 \quad (34)$$

$$\varepsilon = 2\alpha - \alpha^2 + \frac{3(1 - \alpha)}{F + \ln(1 - \alpha)/\alpha} \quad (35)$$

If we take a large F ("atmosphere much larger than star") there will be a sizeable region with $|\ln(1 - \alpha)/\alpha| \ll F$. Then we get

$$\theta = \frac{3}{F} (1 - \varepsilon/2), \quad \theta_{,\varepsilon} = -\frac{3}{2F} < 0 \quad (36)$$

and thus again a negative specific heat. On the other hand, near the minimum of the energy, $\varepsilon \rightarrow 0, \alpha \rightarrow 0$, we have

$$\theta = \varepsilon - 2e^{-3/\varepsilon}, \quad \theta_{,\varepsilon} \rightarrow 1 \quad (37)$$

and a normal behaviour. This is expected since in this limit all particles are in V_0 and the interaction is just a constant. For $E > 0, \varepsilon > 1$ nothing guarantees that Eq. (35) determines α uniquely, and actually it is not true for larger F . This is shown by the graph of $\theta(E)$, which has an over-hang for $\varepsilon > 1$. Of course, in this case one has to choose the α that gives the larger S , and thus bridge the overhang by a vertical line (Fig. 2). This means that at this point we have a peculiar phase transition where for constant E the temperature and N_0 changes suddenly. Figure 2 can be described as follows. For large E most particles are outside V_0 and the system behaves normally. On extracting energy, the system first cools down until suddenly a finite fraction of the particles fall into V_0 . At this moment T jumps up and keeps increasing with decreasing E . Finally, when most particles are in V_0 , c again becomes positive.

One will have noticed that Eq. (31) is just the usual equilibrium condition of an ideal gas and a similar system with our additional energy $-\nu N^\gamma$. One can generalize this for systems with energy $-\nu N^\gamma$. If we minimize the sum of the entropies of such a system and a normal ideal gas

$$S = S_1(E_1, N_1) + S_2(E_2, N_2) =$$

$$= N_1 \left[\frac{3}{2} \ln (E_1 + N_1^\gamma \nu) - \frac{5}{2} \ln N_1 + \ln V_1 \right] + N_2 \left[\frac{3}{2} \ln E_2 - \frac{5}{2} \ln N_2 + \ln V_2 \right], \quad (38)$$

subject to $N_1 + N_2 = N$, $E_1 + E_2 = E$, we obtain for the corresponding "intensive" quantities

$$E = \nu N^\gamma (\varepsilon - 1), \quad N_2 = \alpha N, \quad \theta = \frac{3T}{2N^{\gamma-1} \nu}, \quad F = \ln \frac{V_2}{V_1} \quad (39)$$

the relations:

$$\frac{\gamma(1-\alpha)^{\gamma-1}}{\varepsilon - 1 + (1-\alpha)^\gamma} = \frac{2}{3} \ln \frac{1-\alpha}{\alpha} + \frac{2F}{3}$$

$$\theta = \varepsilon - 1 + (1-\alpha)^\gamma. \quad (40)$$

For $\gamma = 2$ this reduces to Eqs. (34) and (35). For $\gamma = 1$ we have the problem of particles that can fall into an external potential well, a system which has positive c . However, for larger γ 's we get at certain energies $c < 0$ (Fig. 3). This shows that systems whose energy increases more than linearly with N in particle exchange with normal systems will lead to negative c .

4. HOW THESE STRANGE SYSTEMS BEHAVE IN THERMAL CONTACT

So far we have studied the systems with $c < 0$ using the microcanonical ensemble assuming that the usual ergodicity arguments that go along with it also apply. Since $\partial^2 S / \partial E^2 \neq 0$, the transition to the canonical ensemble requires detailed study. Let us first put our system 1 with $c < 0$ in thermal contact (exchange of E , not of N) with another system, System 2. The usual expression for the variation of the total entropy S with

$$\left(\frac{1}{T_i} = \frac{\partial S_i}{\partial E_i}, \quad \frac{1}{C_i} = -T_i^2 \frac{\partial^2 S_i}{\partial E_i^2} \right)$$

$$S(E) = S_1(E_1) + S_2(E - E_1)$$

$$\delta S = \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \frac{(\delta E_1)^2}{2} \left(\frac{1}{C_1 T_1^2} + \frac{1}{C_2 T_2^2} \right). \quad (41)$$

tells us the following. Since our T_1 are positive, we gain entropy for $T_1 \neq T_2$ by transferring energy from the hotter to the colder system. For $T_1 = T_2$ we have a stable situation if $(1/c_1) + (1/c_2) > 0$. Thus if both c 's are < 0 we never get a stable equilibrium, and for $c_2 > 0$ only if $|c_1| > c_2$. This can be understood as follows. If $c_1 < 0$, $c_2 < 0$ and one system is slightly hotter it will transfer energy to the other. In doing so it will heat up even more, and more energy will be transferred. In this way one gets further and further away from $T_1 = T_2$ and equilibrium can only be reached if one of the c 's again becomes > 0 . This also explains the instability we found in Section 2 for the pure gravitational case. For $c_2 > -c_1 > 0$ and, say, $T_1 > T_2$, energy goes from 1 to 2. Now both temperatures increase, but T_1 faster than T_2 since $|c_1| < c_2$. Thus again no equilibrium is reached. Only for $c_2 < |c_1|$, T_2 will change faster than T_1 , and then an equilibrium is established. For the canonical ensemble, System 2 would be the heat bath and therefore $c_2 > |c_1|$. Thus there will never be an equilibrium as long as $c_1 < 0$ and the systems will exchange energy until E_1 is such that $c_1 > 0$. This means that in Figs. 2 and 3 the part with $c < 0$ will be bridged by horizontal lines. This means that given T by System 2, the system will jump from the lowest energy where $T_1 = T$ to the highest energy where $T_1 = T$. The jump occurs when the free energy on the lower side equals the free energy F on the upper side. This is evident by plotting $S(E)$ (Fig. 4) where the part with the wrong convexity is bridged by a straight line since then the upper branch gives the lower F . This explains why in the canonical ensemble there are no negative c 's;

$$F = -T \ln \left[\int_0^{\infty} dE S(E) e^{-E/T} \right] \quad (42)$$

always has the right convexity such that

$$c = -T \frac{\partial^2 F}{\partial T^2} > 0 . \quad (43)$$

What happens in the canonical ensemble is that the region of $c < 0$ jumped over by a phase transition of the first kind. This situation can be illustrated by a system where at a certain E there is a positive jump in dS/dE :

$$S = \begin{aligned} & N \ln \frac{E}{NE_0\gamma} && \text{for } \gamma N E_0 \leq E \leq E_0 \\ & 2N \ln \frac{E}{NE_0\gamma^{1/2}} && \text{for } N E_0 \leq E < \infty \end{aligned} \quad 0 < \gamma \ll 1. \quad (44)$$

The free energy is worked out to be for $N \rightarrow \infty$

$$F/N = \theta(T_0 - T) \left(T - T \ln \frac{T}{E_0\gamma} \right) + \theta(T - T_0) \left(2T - 2T \ln \frac{2T}{E_0\gamma^{1/2}} \right) \quad (45)$$

with $T_0 = E_0 e/4$. The specific heat

$$\frac{c}{N} = -T \frac{\partial^2 F}{\partial T^2} = \theta(T_0 - T) + \delta(T - T_0) + 2\theta(T - T_0) \quad (46)$$

shows a phase transition of the first kind at $T = T_0$.

5. WHAT HAS THIS GOT TO DO WITH REALITY

We have noted in the beginning that stars as a whole act like systems with $c < 0$. Of course, our considerations cannot be directly applied to them since they are not isothermal, and have inhomogenous chemical composition, internal energy sources, etc. This complicated situation can only be handled by a computer. Nevertheless our considerations may supply a simplified model for the dramatic events occurring in the history of a star. For instance, at a stage where no more nuclear fuel is available which would burn at this temperature, the core contracts and becomes hotter, giving its energy to the outer part which expands and becomes colder. This corresponds just to the heat exchange between two systems with $c < 0$, described in the last section. The hotter system is now the core and the cooler the outer part of the star. This process seems to occur several times in the lifetime of a star in the formation of red giants or supernovae. These events may therefore be looked at as phase transitions due to the instability of systems with negative specific heat. Another system that should reflect these features is a galaxy. Here the stars are the particles and the dense centre may represent the collapsing phase. However, our considerations shed no light on the time scale^{3,4)} governing these phase transitions. For supernovae where the energy is carried quickly by neutrinos they are fast, but for galaxies where mainly the Newton potential transfers the energy they will be very slow.

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APPENDIX

For free particles one sees immediately from Eq. (15) that $\rho(x) = \text{const.}$ and therefore N/V . This gives the classical

$$S = N \left(\frac{3}{2} \ln \pi T + \frac{5}{2} + \ln \frac{V}{N} \right) . \quad (\text{A.1})$$

For

$$V = \frac{\kappa}{2N} \sum_{i,j}^N (x_i - x_j)^2$$

we first note that this is for $N \rightarrow \infty$ equivalent to

$$V = \kappa \sum_{i=1}^N x_i^2 .$$

The latter is the former plus an harmonic force on the centre of mass, but one degree of freedom out of N does not matter. Thus we anticipate the entropy of a $3N$ dimensional harmonic oscillator

$$S = \frac{3N}{2} \ln \left(\frac{\pi E}{3N} \right)^2 \frac{1}{\kappa} - N \ln N + 4N . \quad (\text{A.2})$$

The barometric formula (14) is now solved by

$$\rho_0(x) = e^{-\kappa x^2/T} \cdot N \left(\frac{\kappa}{T\pi} \right)^{3/2} ,$$

which gives for the entropy

$$S(E,N) = \int d^3x \rho_0(x) \left[\frac{3}{2} \ln \pi T + \frac{5}{2} + \frac{\kappa}{T} x^2 - \ln N + \frac{3}{2} \ln \frac{T\pi}{\kappa} \right] = (\text{A.2}).$$

$$-2 \leq \gamma \leq 2.4$$

$$F = \frac{3}{2} \ln \frac{7-2\gamma}{5-2\gamma} - \ln(3-\gamma) - \frac{\gamma}{3-\gamma}$$

Fig. 1

Fig. 2

$F = 1.5$

Fig. 3

Fig. 4