On the negative specific heat paradox

D. Lynden-Bell *Institute of Astronomy, The Observatories, Madingley Road, Cambridge CB3 0HA*

R. M. Lynden-Bell *University Chemical Laboratory, Lensfield Road, Cambridge*

Summary. All astronomers know that when a star or a star cluster loses energy its temperature will increase in accordance with the virial theorem. Beckenstein & Hawking have demonstrated that black holes display the same phenomenon. Thus astronomical systems display negative specific heat. However, there is a simple proof in statistical mechanics that specific heats are positive. This paradox, first resolved by Thirring, is further explored with a simple model which obeys the virial theorem. The great differences that can arise between Gibbs's canonical ensembles and microcanonical ensembles are thereby further illustrated. If the model is treated canonically it shows a remarkable giant phase transition which replaces a wide zone of negative specific heat found by microcanonical approach.

This behaviour suggested to us that the origin of all normal phase transitions may lie in negative-specific-heat elements that only arise at a *microscopic* level. A simple model of a chemical reaction or ionization demonstrates that this is a correct interpretation of these transitions.

1 Introduction

Negative specific heats are well-known to astronomers [1] but still cause controversy. Following Antonov's demonstration of a system with no entropy maximum [2], Lynden-Bell & Wood [3] showed that bounded self-gravitating gas spheres in thermodynamic equilibrium could show negative specific heats. Thirring [4, 5] realized that this was paradoxical and showed, with Hertel [6—8], that the difficulty was removed once a clear distinction was made between canonical and microcanonical ensembles. They proposed a model system which has a negative specific heat for a range of energy values in the microcanonical ensemble, and a phase transition in the corresponding canonical ensemble. Beckenstein [9] and Hawking [10, 11] have shown that the thermodynamics of black holes involve negative specific heats and many people have first met the idea in that esoteric context. To re-emphasize that self-gravitating systems naturally have negative specific heats [12] we outline the conditions under which they occur and given an exactly calculable self-gravitating model.

1.1 WHEN NEGATIVE SPECIFIC HEAT IS IMPOSSIBLE

In this section we review the reasons why a system in stable thermodynamic equilibrium cannot have a negative specific heat if it is either extensive or in contact with a heat bath.

Consider first a uniform extensive system and divide it into parts by a boundary through which heat may pass. A small quantity of heat dQ flowing through the partition generates a temperature difference and hence a flow of heat from the hotter to the cooler part. The specific heat of each part is the same as that of the whole; if this were negative the flow of heat would enhance the temperature difference, leading to an increased flow of heat. Such a system would not be in thermodynamic equilibrium.

Secondly, consider a system in contact with a heat bath. The relative probabilities of possible states of the system are the same as those of a Gibbs canonical ensemble and the thermodynamics is specified by the partition function

$$Z = \sum_i \exp\left(-\beta E_i\right)$$

where the sum extends over quantum states, i, of the system and $\beta^{-1} = kT$. The mean energy $\langle E \rangle$ and the fluctuations in energy can be determined from Z. The specific heat C_v is related to the mean square fluctuation by [13]

$$C_v = k\beta^2 \langle (E - \langle E \rangle)^2 \rangle.$$

This shows that the specific heat of a system in contact with a heat bath must be positive. This also shows that any system with particles moving independently in a fixed potential must have a positive specific heat as it may be considered as an ensemble of particles. In a r^{-1} potential orbits of greater energy have less kinetic energy, but even such a system of particles will fail to have negative specific heat. A system which can show negative heat capacity can not be divided into equal weakly coupled parts.

Imagine a system of negative heat capacity $C_1 = -|C_1|$ connected to a system of positive heat capacity C_2. If an amount of heat dQ is transferred from system 1 to system 2, then the first will increase its temperature from T_0 to $T_0 + dQ/|C_1|$ and the second will increase to $T_0 + dQ/C_2$. These new temperatures will cause a reversed heat flow if and only if $|C_1|^{-1} < C_2^{-1}$. Thus the system is only stable provided $C_2 < |C_1|$. This result which has often been discussed [3, 4, 11] demonstrates that a system of negative heat capacity can only be in equilibrium with a system of positive heat capacity provided that the sum of the heat capacities remains negative. Thus to measure temperature in this context one must take care to use a *small* thermometer.

1.2 ATTRACTIVE FORCES GENERATE NEGATIVE SPECIFIC HEATS

An isolated self-gravitating system such as a star obeys the virial theorem $2\mathcal{T} + \mathcal{V} = 0$ where $\mathcal{T}$ is the kinetic and $\mathcal{V}$ the potential energy. For a perfect gas the kinetic energy is proportional to temperature and $\mathcal{T} = \frac{3}{2}NkT$. From the virial theorem we therefore find $E = \mathcal{T} + \mathcal{V} = -\mathcal{T} = -\frac{3}{2}NkT$. Thus the heat capacity is $-\frac{3}{2}Nk$. The argument is over-simplified since isothermal spheres cannot be confined by their own gravity and therefore a confining spherical box is required. When such a box is present the virial theorem is modified by surface terms to read $2\mathcal{T} + \mathcal{V} = 3pV$ where p is the surface pressure and V is its volume. Lynden-Bell & Wood showed that this modification does not remove the negative heat capacity, however they only considered the self-consistent mean field, they did not allow for the entropy of fluctuations and they only briefly dismissed the singularities that occur in the gravitational potential energy when two particles are at the same point.

In Thirring's model [4, 5] the particles interact with each other via a square well potential which is only present when both particles are within a particular region of space. Hertel & Thirring [6] extended this model to allow the possibility of several condensation regions. These models are exactly soluble but are not dominated by gravity. Here we propose a simple self-gravitating model which although somewhat contrived is exactly calculable in both ensembles and in both classical and quantum mechanics (Sections 2 and 3). Having seen that large-scale attractive forces cause negative specific heats in the microcanonical ensemble and a giant phase transition in the canonical one, we ask whether all normal phase transitions may not be generated by negative specific heat elements at a microscopic level. To investigate this we consider in Section 4 a simple model of a chemical dissociation. We isolate microscopic negative specific heat elements which cause the transition.

2 Definition of our model

2.1 INTRODUCTION

Consider a set of particles confined to the surface of a sphere of variable radius. We shall give the sphere a gravitational mass part or all of which we may consider to be made up of the sum of the masses of the particles on its surface. The individual particles move freely around the sphere and interact weakly with each other, so weakly that the interaction energy is negligible at any one time but nevertheless strongly enough to set up an equilibrium distribution. We shall leave out the gravitational interactions of the particles as individuals and instead transfer their gravity to the symmetrical sphere. Under these approximations the Lagrangian for the system is

$$\mathscr{L} = \tfrac{1}{2}M\dot{r}^2 + \tfrac{1}{2}GM^2 r^{-1} + \sum_{i=1}^{N} \tfrac{1}{2}mr^2(\dot{\theta}_i^2 + \sin^2\theta_i \dot{\phi}_i^2)$$

where r is the sphere's radius and (r, θ_i, ϕ_i) is the position of the ith particle. Although this is only an approximate Lagrangian for real gravitating particles on a sphere, nevertheless it is an exact Lagrangian function. Thus as far as the mathematics is concerned the system is well defined by this Lagrangian and the ranges of the variables. We shall allow the sphere to range freely in radius between r_0 and r_e these being rigid spherical boundaries near the centre and at the edge.

2.2 STATISTICAL MECHANICS OF A MICROCANONICAL ENSEMBLE OF FIXED ENERGY

The model has $2N + 1$ coordinates θ_i, ϕ_i, r and corresponding to these the $2N + 1$ momenta

$$p_{\theta_i} = mr^2\dot{\theta}_i, \quad p_{\phi_i} = mr^2\sin^2\theta_i\dot{\phi}_i \quad p_r = M\dot{r}.$$

The condition of fixed total energy is

$$\tfrac{1}{2}p_r^2 M^{-1} + \sum_{i=1}^{N} \tfrac{1}{2}m^{-1}r^{-2}[p_{\theta_i}^2 + p_{\phi_i}^2 (\sin\theta_i)^{-2}] = E + \tfrac{1}{2}GM^2 r^{-1}. \qquad (2.1)$$

The volume of phase space for which r lies in a range dr while the p run over all values for which the total energy is less than E is

$$\frac{d\tau(E, r)}{dr}dr = dr \int\int_{<E} \cdots \int dp_r \prod_{i=1}^{N} dp_{\theta_i} dp_{\phi_i} d\theta_i d\phi_i. \qquad (2.2)$$

Let

$$x_1^2 = \tfrac{1}{2}p_r^2 M^{-1}, \quad x_2^2 = \tfrac{1}{2}p_{\theta_1}^2 m^{-1}r^{-2}, \quad x_3^2 = \tfrac{1}{2}p_{\phi_1}^2 (mr^2 \sin^2 \theta_1)^{-1}, \quad x_4^2 = \tfrac{1}{2}p_{\theta_2}^2 m^{-1}r^{-2},$$

$$x_5^2 = \tfrac{1}{2}p_{\phi_2}^2 (mr^2 \sin^2 \theta_2)^{-1} \quad \text{etc.}$$

then the condition that the energy should be less than E becomes

$$\sum_{j=1}^{2N+1} x_j^2 < E + \tfrac{1}{2}GM^2 r^{-1} = E - \mathscr{V}. \tag{2.3}$$

Notice that the x_j^2 are the kinetic energies associated with the different components of momentum in the system. With this notation our expression becomes

$$\frac{d\tau}{dr} = \underset{<E-\mathscr{V}}{\iint \cdots \int} \left(\prod_{j=1}^{2N+1} dx_j \right) (2M)^{1/2} \prod_{i=1}^{N} 2mr^2 \sin \theta_i \, d\theta_i \, d\phi_i$$

$$= (2M)^{1/2} (8\pi m r^2)^N \underset{<E-\mathscr{V}}{\iint \quad \int} \prod_{j=1}^{2N+1} dx_j$$

where the final integration is to be carried out over the interior of the $2N+1$ dimensional hypersphere of radius $(E - \mathscr{V})^{1/2}$. Now this hypervolume is well known to be

$$\pi^{N+\frac{1}{2}} [(N + \tfrac{1}{2})!]^{-1} (E - \mathscr{V})^{N+\frac{1}{2}}.$$

Differentiating our final expression for $d\tau/dr$ with respect to E we obtain the hypervolume of phase space with energy between E and $E + dE$ and sphere radius between r and $r + dr$

$$\frac{d^2\tau}{dE\,dr}\, dE\, dr = \frac{\pi^{N+\frac{1}{2}}}{(N - \tfrac{1}{2})!} (2M)^{1/2} (8\pi m)^N r^{2N} (E - \mathscr{V})^{N - \frac{1}{2}}\, dE\, dr. \tag{2.4}$$

We now consider a microcanonical ensemble of systems distributed uniformly within this shell of energy. For such an ensemble the distribution of r is given by the above expression suitably normalized. Thus the probability of finding the radius of a system in the range $[r, r + dr]$ is

$$P(r)\, dr = \frac{r^{N+\frac{1}{2}} [2a - r]^{N - \frac{1}{2}}\, dr}{\displaystyle\int_{r_0}^{r_e} r^{N+\frac{1}{2}} [2a - r]^{N - \frac{1}{2}}\, dr}, \quad \text{for} \quad r_0 \le r \le \begin{cases} r_e \\ \text{and } 2a \end{cases} \tag{2.5}$$

where $a = \tfrac{1}{4}GM^2 (-E)^{-1} = \tfrac{1}{2}r\,\mathscr{V}/E$ is very close to the most probable value of r. We have inserted the value of $\mathscr{V} = -\tfrac{1}{2}GM^2 r^{-1}$ and the restriction $r < 2a$ is implied by expression (2.3).

Expression (2.5) is worthy of study. $P(r)$ has a very strong maximum at $r = a(N + \tfrac{1}{2})/N \simeq a$ provided that a is in the range (r_0, r_e) and very few exceptions occur with $|r - a| > 3(2N)^{-1/2}a$. For N large we have a very strong tight maximum. However, if a is less than r_0 then $P(r)$ is strongly concentrated towards r_0 while if a is greater than r_e then $P(r)$ is strongly concentrated towards r_e. The latter is also true if E is positive. When a is between r_0 and r_e and away from either end of that range then the average value of r^{-1} is a^{-1} and thus $\langle \mathscr{V} \rangle = 2E$ in exact agreement with the virial theorem.

It is instructive to calculate the distribution of one of the x_j (they each have the same distribution). To do this we calculate $[d^2\tau(E, r, x_j)/dr\, dx_j]\, dr\, dx_j$; the volume of phase space in which r and x_j are allowed small ranges and the energy is $< E$. This calculation is especially simple when one realizes that it may be made following the derivation of equation (2.4) by replacing E by $E - x_j^2$ and integrating over a $2N$ dimensional hypersphere rather than a $2N + 1$ dimensional one. Thus in place of (2.4) one obtains

$$\frac{d^3\tau}{dE\, dr\, dx_j} dE\, dr\, dx_j = \frac{\pi^{N-\frac{1}{2}}}{(N-\frac{3}{2})!} (2M)^{1/2}(8\pi m)^N r^{2N}(E - x_j^2 - \mathscr{V})^{N-3/2} dE\, dr\, dx_j.$$

The probability distribution for r and x_j follows from this

$$P(r, x_j)\, dr\, dx_j = \frac{r^{2N}[E - \mathscr{V} - x_j^2]^{N-3/2}\, dr\, dx_j}{\iint r^{2N}[E - \mathscr{V} - x_j^2]^{N-3/2}\, dr\, dx_j} \tag{2.6}$$

from this it follows that the mean x_j^2 at fixed r is given by

$$x_j^2 = \frac{E - \mathscr{V}}{2N + 1} \tag{2.7}$$

since each x_j has the same distribution the average energies associated with each of the $2N + 1$ components of momentum are all equal. If further we average over r we have $\langle \mathscr{V} \rangle = 2E$

$$\langle x_j^2 \rangle = -E/(2N + 1) \quad \text{provided} \quad r_0 < a < r_e. \tag{2.8}$$

If we take this average energy per quadratic degree of freedom in the Hamiltonian to be our measure for $\frac{1}{2}kT$ then

$$E = -(2N + 1)\, \frac{1}{2}kT \quad \text{provided} \quad r_0 < a < r_e. \tag{2.9}$$

Thus for a wide range of negative energies we have a negative specific heat. The greatest achievable binding energy is when everything is at rest on the inner sphere thus

$$-E = \frac{1}{2}GM^2 r_0^{-1}.$$

When the binding energy is between this value and half of it, r is confined to a region very close to r_0. The kinetic energy per momentum component is still given by the equipartition theorem (2–7) but now $\mathscr{V}$ takes the value $-\frac{1}{2}GM^2 r_0^{-1} = \chi_0$. Thus $E = (2N + 1)\, \frac{1}{2}kT - \chi_0$ and over this range of energy the specific heat is positive and equal in modulus to its former negative value.

When $a > r_e$ a similar argument holds

$$E = (2N + 1)\, \frac{1}{2}kT - \chi_e \tag{2.10}$$

where

$$\chi_e = -\frac{1}{2}GM^2 r_e^{-1}$$

and we again have a positive specific heat. Thus the graph of T as a function of E is as shown in Fig. 1 which also shows $a(E)$ and the multivalued $E(\beta)$.

The definition of temperature used above may not be universally agreed for such strange systems. However, use of the temperature $T = (dS/dE)^{-1}$, defined through the entropy, $S = k \log (d\tau/dE)$ of a microcanonical ensemble only differs to order $1/N$ of the leading terms. It gives $E = -(2N + 3)\, \frac{1}{2}kT$ in place of (2.9) and approximately

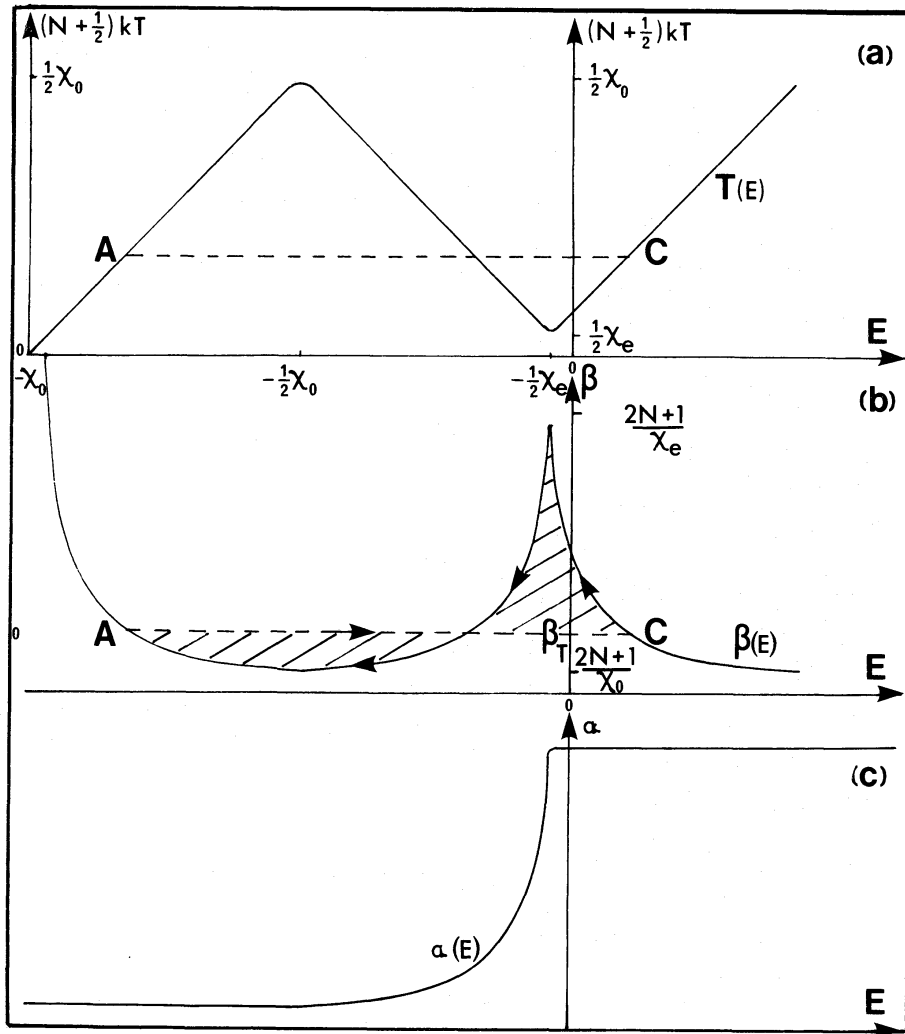$$E \simeq (2N - 1)\, \frac{1}{2}kT - \chi_e$$

in place of (2.10).

Figure 1. (a) The relationship between temperature and energy in the classical model. The full line is for the isolated system. The inverse of the gradient gives the specific heat. Note the negative C_v portion of the curve, this would be still broader but to get convenient dimensions for the figure we have taken r_e only 12½ times r_0 instead of $r_e \gg r_0$. For the canonical ensemble the negative specific heat region is absent and the average over the ensemble undergoes the dotted phase transition from A to C. (b) Gives β against E. The entropy change is the same whether a subset of systems makes the phase transition by traversing the curve for an individual system or by behaving like an ensemble. Thus $\Delta S = \int k\beta \, dE$ is zero taken around the curve that sets out along the phase transition path AC or returns via the individual $\beta(E)$ curve to A. Thus the two shaded areas are equal. (c) $a(E)$ the harmonic mean radius of the sphere as a function of energy. For large N the radius has a very strong probability of being very close to this. Notice that when the sphere is not touching a wall the graph of $a(E)$ is the same $\beta(E)$.

2.3 WHAT HAPPENS WHEN THIS SYSTEM IS PUT IN A HEAT BATH?

It is of interest to consider more precisely what will happen when our negative heat capacity system is placed in contact with a heat bath. Fluctuations will lead it to become momentarily hotter or colder than the bath and it will then evolve in whatever direction it started off. If that were a fluctuation to lower energy then the system will give out more and more heat getting hotter and hotter meanwhile, until it reaches the maximum in the $T(E)$ curve of Fig. 1. It will then be much hotter than the bath so it will continue to give out heat and will evolve down the positive C_v branch of the curve giving out still more heat but now getting cooler. Eventually it will reach a stable equilibrium on the positive specific heat

branch of the $T(E)$ curve. A similar evolution towards higher energy would occur if the fluctuation were to higher energy initially. Thus a system of negative specific heat will evolve out of that state before achieving equilibrium with a heat bath. This reflects the behaviour that we find in the canonical ensemble.

2.4 STATISTICAL MECHANICS OF A CLASSICAL CANONICAL ENSEMBLE

The Hamiltonian of the system is

$$H = \frac{p_r^2}{2M} - \frac{GM^2}{2r} + \sum_{i=1}^{N} \left(\frac{p_{\theta_i}^2}{2mr^2} + \frac{p_{\phi_i}^2}{2mr^2 \sin^2 \theta_i} \right) = E. \tag{2.11}$$

The Zustandsumme is classically

$$Z = \int \ldots \int \exp(-\beta E) \, dp_r \, dr \prod_{i=1}^{N} dp_{\theta_i} \, d\theta_i \, dp_{\phi_i} \, d\phi_i$$

$$= \iint \exp(-\beta) \left(\frac{p_r^2}{2M} - \frac{GM^2}{2r} \right) \prod_{i=1}^{N} Z_i(r) \, dp_r \, dr \tag{2.12}$$

where

$$Z_i(r) = \iiint \exp\left(-\tfrac{1}{2}\beta m^{-1} r^{-2}\right) [p_{\theta_i}^2 + p_{\phi_i}^2 (\sin \theta_i)^{-2}] \, d\phi_i \, dp_{\phi_i} \, d\theta_i \, dp_{\theta_i}$$

$$= 4\pi (2\pi m \beta^{-1})^{1/2} r \int_0^\infty \exp\left(-\tfrac{1}{2}\beta^2 p_{\theta_i}^2 m^{-1} r^{-2}\right) dp_{\theta_i} = 8\pi^2 mr^2/\beta. \tag{2.13}$$

Inserting this into our expression for Z and performing the integration over p_r we find

$$Z = (2\pi M/\beta)^{1/2} (8\pi^2 m/\beta)^N \int_{r_0}^{r_e} r^{2N} \exp(\tfrac{1}{2}\beta GM^2/r) \, dr. \tag{2.14}$$

We notice that the integrand is large when r is large and is also large when r is small. Thus almost all the systems in the ensemble are close to either radius r_0 or radius r_e. Contrast this with our microcanonical ensemble at fixed energy in which these extremes are only reached when E is either small or large. The contributions from the two regions where the integral is large may be evaluated roughly as follows. Since most of the contribution comes close to the end point we logarithmically differentiate the integrand $f(r)$ there and replace the integrand by $f(r_0) \exp[-\alpha(r-r_0)]$ where $-\alpha$ is the derivative of $\log f$ at $r = r_0$. We then add the contributions from the two end points. The integral is approximately $I_1 + I_2$ where

$$I_1 = r_0^{2N} [\exp(\beta\chi_0)] \alpha_0^{-1} \{1 - \exp - [\alpha_0(r_e - r_0)]\}$$

and $\alpha_0 = r_0^{-1}(\beta\chi_0 - 2N)$ and

$$I_2 = r_e^{2N} [\exp(\beta\chi_e)] \alpha_e^{-1} \{1 - \exp - [\alpha_e(r_e - r_0)]\}$$

and $\alpha_e = r_e^{-1}(2N - \beta\chi_e)$.

Of great interest is the ratio I_2/I_1 as this gives the ratio of the numbers of systems in the excited states near r_e to the numbers of systems in the states close to the ground state r_0.

$$\frac{I_2}{I_1} = \left(\frac{r_e}{r_0}\right)^{2N+1} \exp\left[\beta(\chi_e - \chi_0)\right] \left\{\frac{1 - \exp\left[-(2N - \beta\chi_e)(1 - r_0/r_e)\right]}{2N - \beta\chi_e}\right\}$$

$$\times \left\{\frac{\beta\chi_0 - 2N}{1 - \exp\left[-(\beta\chi_0 - 2N)(r_e/r_0 - 1)\right]}\right\}.$$

When $\beta\chi_0 \gg 2N \geqslant \beta\chi_e$ we may approximate to the much simpler form which holds near the phase transition

$$\frac{I_2}{I_1} = \left(\frac{r_e}{r_0}\right)^{2N+1} \left\{\exp\left[\beta(\chi_e - \chi_0)\right]\right\} \cdot \frac{\beta\chi_0}{2N}.$$

At the phase transition $I_2 = I_1$ and $\beta_T(\chi_0 - \chi_e) \simeq (2N + 1) \log r_e/r_0 + \log(\log r_e/r_0)$. Near that temperature of transition which we call β_T a change in β given by $\Delta\beta/\beta = (2N + 1)^{-1}$ suffices to change the phase almost completely. Thus the phase transition is extremely sharp. At temperatures below the phase transition we need only consider I_1 while above it we need only consider I_2. Thus away from the phase transition the average energy of a system $\langle E \rangle$ is given by

$$\langle E \rangle = -d \log Z/d\beta = \begin{cases} (N + \frac{1}{2})\beta^{-1} - \chi_0 & \text{for} \quad \beta > \beta_T + \Delta\beta \\ (N + \frac{1}{2})\beta^{-1} - \chi_e & \text{for} \quad \beta < \beta_T - \Delta\beta. \end{cases}$$

Putting $\beta^{-1} = kT$ we see that away from the phase transition the ensemble has the positive specific heat $(N + \frac{1}{2})k$. In the phase transition itself the specific heat is very large. It reaches values as high as $\frac{1}{4}k\beta_T^2(\chi_e - \chi_0)^2$ at maximum. Thus at the phase transition the fluctuation in energy is of the same order of size as the energy itself. In accordance with the theorem the specific heat of the ensemble never becomes negative. Perdang has previously demonstrated these giant energy fluctuations [15].

3 Quantized system

3.1 INTRODUCTION

The quantum mechanics of our system is quite interesting, as its energy levels are related to those of the hydrogen atom and its statistical mechanics has interesting analogies to the properties of white dwarf stars provided that the particles are taken to be fermions. A further bonus of non-relativistic quantum systems is that the zero point vibrations are sufficiently strong to prevent collapse to $r = 0$; thus the artificial inner sphere of radius r_0 may be dispensed with. The outer sphere is still necessary to restrain the system at large energies. We show in this section that fermion systems show a region of negative specific heat in the microcanonical ensemble and a phase transition for the canonical system in a heat bath.

The Quantum Mechanical Hamiltonian of the system is

$$H = -\frac{\hbar^2}{2M}\left(\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}\right) - \frac{\hbar^2}{2mr^2}\left\{\sum_{i=1}^{N}\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\sin\theta_i\frac{\partial}{\partial\theta_i} + \frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2}\right\} - \frac{GM^2}{2r} \tag{3.1}$$

where M is the total mass of the shell, m is the mass of one of the N particles and r, θ_i, ϕ_i are the coordinates of the ith particle.

r^2H is separable: the solution of the angular part for each particle is a spherical harmonic with eigenvalue $\frac{1}{2}m^{-1}\hbar^2 l_i(l_i + 1)$ where l_i is an integer. If the particles are fermions of spin $\frac{1}{2}$

not more than $2(2l_i + 1)$ of them may have the same l_i value; there is no restriction for bosons.

The equation for the radial part $R(r)$ is

$$\left\{ -\frac{\hbar^2}{2M}\left(\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}\right) + \frac{\hbar^2}{2mr^2}\sum_i l_i(l_i + 1) - \frac{GM^2}{2r}\right\} R = ER \qquad (3.2)$$

which is similar to the hydrogen atom radial equation.

Using standard methods [16], solutions can be found of the form

$$R(r) = \exp(-\zeta r)\, r^s P_n(r) \qquad (3.3)$$

where P_n is an nth order polynomial in r; s (which is not necessarily an integer) is given by

$$s(s + 1) = \frac{M}{m}\sum_i l_i(l_i + 1) = \frac{M}{m} N\langle l(l + 1)\rangle. \qquad (3.4)$$

The constant ζ is

$$\zeta = \tfrac{1}{2}GM^3\hbar^{-2}(s + 1 + n)^{-1} \qquad (3.5)$$

and the energies of the bound states are

$$E = -G^2M^5[8\hbar^2(s + n + 1)^2]^{-1}. \qquad (3.6)$$

The lowest states of the system are those in which no particle has angular momentum ($s = 0$). These hydrogenic states have energies

$$E = -\chi_B, \quad -\tfrac{1}{4}\chi_B, \quad -\tfrac{1}{9}\chi_B \qquad (3.7)$$

where

$$\chi_B = -G^2M^5(8\hbar^2)^{-1}$$

but are inaccessible if the particles are spin ½ fermions. The lowest fermion state has the minimum value of s consistent with double occupancy of (l, m_l) states. For large N we find

$$l_{\max} = (\tfrac{1}{2}N)^{1/2} \qquad (3.8)$$

and

$$\Sigma l(l + 1) = \tfrac{1}{4}N^2. \qquad (3.9)$$

This gives a minimum value for s of $\tfrac{1}{2}N(M/m)^{1/2}$ and the ground state of the fermion system has energy $-\chi_F$

$$\chi_F = G^2M^4 m(2N^2\hbar^2)^{-1} \qquad (3.10)$$

and radius

$$r_F = \langle r^{-1}\rangle^{-1} = 2N^2\hbar^2(GM^2m)^{-1}. \qquad (3.11)$$

3.2 STATISTICAL MECHANICS OF A MICROCANONICAL ENSEMBLE OF QUANTIZED SYSTEMS

In order to calculate the entropy associated with a given energy in the microcanonical ensemble we need $W(E)$, the number of ways in which a given value of E may be obtained.

To do this we use the formula for the occupation numbers of the states with $l = l_i$

$$n_l = g(2l + 1)\{\exp [\gamma l(l + 1) - \alpha] + 1\}$$

where g is the degeneracy due to spin and α and γ are Lagrange multipliers which are fixed by

$$\Sigma\, n_l = N$$

$$\Sigma\, n_l l(l + 1) = L. \tag{3.12}$$

3.2.1 The non-degenerate case

Consider first values of L which are considerably greater than the limiting value of $L_0 = N^2/4$ for Fermi–Dirac particles, when the occupation numbers are small and

$$n_l = 2(2l + 1) \exp [\alpha - \gamma l(l + 1)] \tag{3.13}$$

$$\left.\begin{array}{l} N = \gamma^{-1} e^{\alpha} \\ L = \gamma^{-1} N. \end{array}\right\} \tag{3.14}$$

This gives

$$W(L) = \frac{(2L)^N}{N!}. \tag{3.15}$$

Thus a bound state with energy $E \gg -\chi_F$ and radial quantum number n has degeneracy

$$W(E, n) = \left(\frac{2e^2}{N^3}\right) \left[\left(\frac{\chi_B}{-E}\right)^{1/2} - (n + 1)\right]^{2N}. \tag{3.16}$$

To obtain the degeneracy associated with a particular value of E one must sum $W(E, n)$ over all values of n. As these levels are close the sum may be replaced by integration giving

$$W(E) = \frac{1}{2}\left(\frac{e^2}{2}\right)^N \left(\frac{\chi_F}{-E}\right)^{N + \frac{1}{2}} (2N + 1)^{-1}\, N^{3/2}. \tag{3.17}$$

The entropy associated with the system at energy E is $k \log W$ which gives for $N \gg 1$

$$S \simeq Nk(2 - \log 2) - (N + \tfrac{1}{2})\, k \log\left(\frac{-E}{\chi_F}\right) \quad \text{for} \quad -\chi_F \ll E \leqslant 0. \tag{3.18}$$

If the energy is changed by a small amount a temperature, T, can be defined

$$T = (dE/dS)_v = -E[(N + \tfrac{1}{2})\, k]^{-1}. \tag{3.19}$$

This is positive, but decreases as the energy increases so that the specific heat, C_v is negative

$$C_v = (dE/dT)_v = -(N + \tfrac{1}{2})\, k. \tag{3.20}$$

Two such systems in contact have a *minimum* entropy if their energies are equal ($\partial^2 S/\partial E^2$ is positive); they will exchange energy until one reaches degeneracy.

These results agree with those obtained from classical arguments in the previous section with an infinite volume. The imposition of a spherical box radius r_e, raises the energies of

those states with a significant amplitude at or above r_e. Provided r_e is much larger than the Fermi radius (at least by a factor N) this only affects states where classical behaviour occurs and the expressions of the previous section may be used. The qualitative effect of imposing a box is to decrease the entropy at energies comparable to and greater than χ_e. This leads to a point of inflexion on the $[S(E)]$ curve, Fig. 2(a), and a minimum temperature at the corresponding value of E, Fig. 2(b).
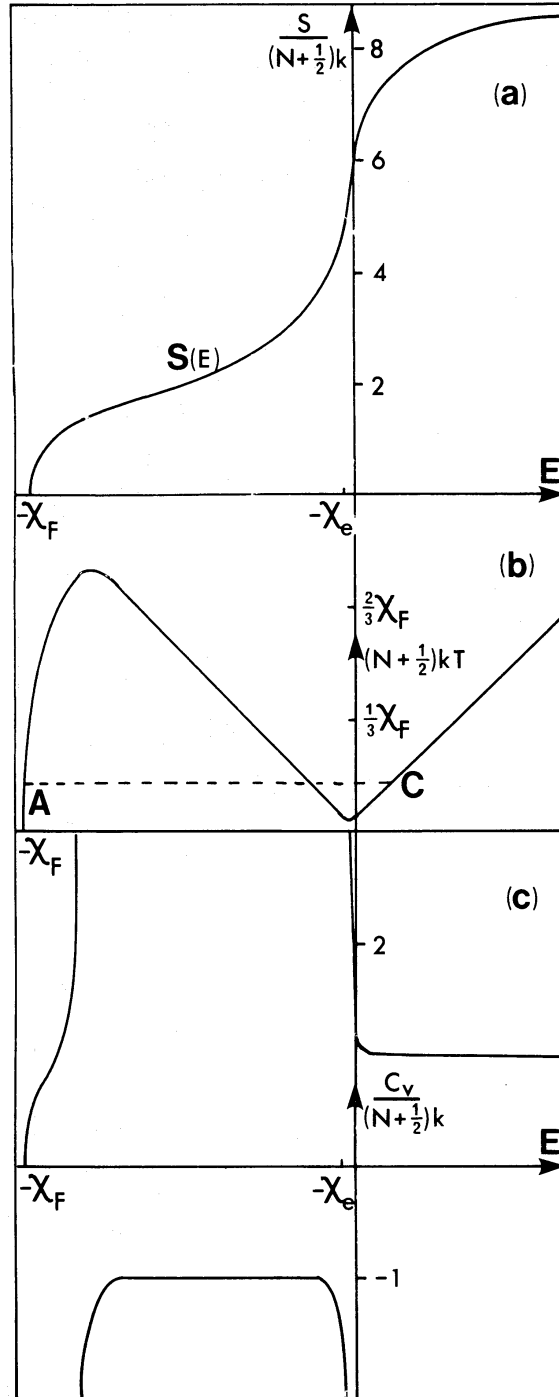
Figure 2. (a) The entropy of a system of Fermions on a gravitating sphere as a function of energy. (b) The temperature as a function of energy. (c) Specific heat (heat capacity) as a function of energy for the microcanonical system. The canonical ensemble has a very large positive C_v at the phase transition just as the classical system does.

14

A second point of inflexion in the $S(E)$ curve is introduced at low energies as the number of states available to the system is reduced by degeneracy effect. The entropy decreases to zero as the energy approaches $-\chi_F$. This point of inflexion gives a maximum temperature. The specific heat, Fig. 2(c), is negative between these points. Below the lower energy both canonical and micro-canonical ensembles have identical positive specific heats.

3.3 THE QUANTIZED CANONICAL ENSEMBLE

The thermodynamic behaviour of a canonical ensemble depends on the partition function Z. As in the classical case there are two principal contributions to Z, Z_1 from low lying states and Z_2 from states with energy near zero, a phase transition occurring when these are equal. As the states near $E = 0$ do not show any degeneracy effects Z_2 is identical with that for the classical system

$$Z_2 = \frac{1}{N!} \left(\frac{2m}{\hbar^2 \beta} \right)^{N+\frac{1}{2}} \left(\frac{1}{4\pi} \frac{M}{m} \right)^{1/2} I_2$$

where I_2 is the classical integral defined in equation (2.15).

Under the conditions of Section 2

$$I_2 \simeq r_e^{2N+1} (2N)^{-1} \exp(\beta\chi_e)$$

giving an expression for Z_2

$$Z_2 = \frac{1}{4} \left(\frac{4er_e^2 N}{r_F^2 \chi_F \beta} \right)^{N+\frac{1}{2}} \left(\frac{M}{\pi em} \right)^{1/2} \exp(\beta\chi_e).$$

The expressions for Z_1 can be obtained by considering the values of the Lagrange multipliers (equation 3.14) when few particles are above the minimum energy. For spin $\frac{1}{2}$ Fermions the Lagrange multipliers α and γ (equation 3.12) can be expressed in terms of the Fermi−Dirac integrals [14] $F_n(x)$

$$F_n(x) = \int_0^\infty \frac{z^n \, dz}{\exp(z - x) + 1} \tag{3.21}$$

as

$$N = 2\gamma F_0(-\alpha)$$

$$L = 2\gamma^{-2} F_1(-\alpha). \tag{3.22}$$

For large positive values of x degeneracy effects appear. At sufficiently low temperatures (large γ) F can be expanded

$$F_n(x) = \frac{x^{n+1}}{n+1} + \frac{\pi^2 n}{6} x^{n-1} + O(x^{n-3}) \tag{3.23}$$

giving

$$\alpha = -\frac{1}{2}\gamma N$$

$$\gamma = \pi[6(L - L_0)]^{-1/2} \tag{3.24}$$

where L_0 is the minimum value of L for the system. Substituting these quantities into the

Fermi–Dirac expression for $W(L)$, the number of ways in which a given value of L may be achieved we obtain

$$W(L) = \exp \left[\frac{2\pi}{\sqrt{6}}(L - L_0)^{1/2} \right]. \tag{3.25}$$

The partition function may now be calculated from

$$Z = \sum_{n, L} \exp \left[\beta \chi_B (n + 1 + \sqrt{NL})^{-2} \right] W(L). \tag{3.26}$$

At low temperatures only the states near the ground state will be populated. In the temperature range $N^{-1}\chi_F \gg kT \gg N^{-3/2}\chi_F$ it is possible to replace the summations in equation (3.26) by integrations and to use equation (3.25) for $W(L)$. In this range the energy can be expanded about the minimum Fermi energy $-\chi_F$ to give

$$Z = \int_0^\infty \int_0^\infty \exp \left[\beta \chi_F (1 - 2n(NL_0)^{-1/2} - (L - L_0)/L_0 \right] \exp \frac{2\pi}{\sqrt{6}}(L - L_0)^{1/2} \, dn \, d(L - L_0)$$

$$= (\pi N^3)^{3/2} (\beta \chi_F)^{-5/2} \frac{1}{8\sqrt{6}} \exp \left\{ \frac{\pi^2 N^2}{24 \chi_F \beta} + \beta \chi_F \right\}. \tag{3.27}$$

From this

$$E + \chi_F = \frac{5}{2} kT + \left(\frac{\pi^2 N^2}{24 \chi_F} \right) k^2 T^2. \tag{3.28}$$

In the temperature range where this treatment is valid within the term in T^2 is always greater than the linear term

$$C_v = \frac{kN^2\pi^2}{12\chi_F\beta} = k\pi N \left(\frac{\Delta}{\chi_F} \right)^{1/2} 6^{-1/2} \tag{3.29}$$

where $\Delta = E + \chi_F$ is the energy difference of the system from its ground state. The specific heat of the microcanonical ensemble is given by this formula at low energies as shown in Fig. 2(c).

The phase transition in the canonical ensemble occurs when Z_1 is equal to Z_2. If N is large the temperature of the transition is given by $\beta = \beta_F$ where

$$\beta_F(\chi_F - \chi_e) = 2N \log (r_e/r_f).$$

This result is very similar to the classical result.

4 A simple model of ionization (or chemical) equilibrium

We consider two types of particles, A and B, which are in the ground state tied together in pairs A·B. We take the forces between them to be saturated when such a pair exists and we shall take the interaction potential to be a δ function. This will of course lead to a single bound state and we shall take its binding energy to be χ. Let n_{AB} be the number density of pairs in some initial ground state. We shall model this system by a microcanonical ensemble of boxes each of volume n_{AB}^{-1} and each containing one particle of type A and one of type B.

We shall show that each of these microsystems shows negative specific heat when the energy of each box above its ground state is just greater than χ so that dissociation has begun but the energy per free particle is small compared with χ. When many such systems are combined into a canonical ensemble we get the usual transition and the associated latent heat χ per AB pair.

Let the box be a cube of side L. For an impenetrable box the energy levels of the bound states AB are given by

$$E_b = \frac{\hbar^2 K^2}{2(m_A + m_B)} - \chi$$

where

$$K^2 = \pi^2 L^{-2}(n_x^2 + n_y^2 + n_z^2)$$

and n_x, n_y, n_z are positive integers. The number of bound states with energies less than E is

$$\tau_b(E) = \frac{1}{8} \cdot \frac{4}{3} \pi \left[(E + \chi) \frac{2(m_A + m_B) L^2}{\pi^2 \hbar^2} \right]^{3/2}$$

where we have assumed that n_x, n_y and n_z are large enough that the continuum approximation holds for the counting of the energy levels. For this we need the square bracket above to be much greater than one. In a very similar way we may obtain the free state energy levels

$$E_f = \frac{\hbar^2 K_A^2}{2m_A} + \frac{\hbar^2 K_B^2}{2m_B}$$

and these lead to a number of energy levels $\tau_f(<E)$ given by

$$\tau_f(<E) = \begin{cases} \dfrac{1}{64} \dfrac{\pi^3}{3!} \left[2 \dfrac{(m_A m_B)^{1/2} E L^2}{\pi^2 \hbar^2} \right]^3 & E > 0 \\[3mm] 0 & E < 0. \end{cases}$$

The total number of energy levels with energy less than E is

$$\tau(E) = \tau_b + \tau_f.$$

The entropy of a microcanonical ensemble of systems with energy E is given by

$$S = -k \log (d\tau/dE)$$

and the temperature by $T = (\partial S/\partial E)^{-1}$. Thus we find

$$kT = \frac{\tau'(E)}{\tau''(E)} = \begin{cases} \dfrac{\tfrac{3}{2}(E+\chi)^{1/2} + 3AE^2}{\tfrac{3}{4}(E+\chi)^{-1/2} + 6AE} & E > 0 \\[3mm] 2(E+\chi) & E < 0 \end{cases}$$

where $A = (\pi^2/64)(2m^* L^2/\pi^2\hbar^2)^{3/2}$ and $m^* = m_A m_B/(m_A + m_B)$

$$\frac{k}{C_v} = \frac{dkT}{dE} = \begin{cases} \dfrac{18A^2 E^2 (E+\chi)^{3/2} - 9A\chi(E+\chi) - \tfrac{9}{8}AE^2 + \tfrac{9}{8}(E+\chi)^{1/2}}{(E+\chi)^{1/2}[\tfrac{3}{4} + 6AE(E+\chi)^{1/2}]^2} ; & E > 0 \\[4mm] 2 ; & E < 0. \end{cases}$$

The complicated expression increases from $-16A\chi^{3/2} + 2$ at $E = 0+$ to $\frac{1}{2}$ for large E. Thus just above $E = 0$ where there is just enough energy for dissociation the specific heat is negative provided that $8A\chi^{3/2} > 1$ that is provided $(\pi^2/8)(2m^*\chi L^2/\pi^2\hbar^2)^{3/2} > 1$. This will always be so if the volume of the box $L^3 = n_{AB}^{-1}$ is sufficiently large compared with $h^3(8m^*\chi)^{-3/2}$.

There is an inevitable doubt about applying statistical mechanics to systems with such small numbers of particles, and on the definition of entropy usually employed for a microcanonical ensemble the energy of one free particle alone is $\frac{1}{2}kT$ while for two it is $2kT$ by contrast to the canonical results of $\frac{3}{2}kT$ and $3kT$ respectively. Gibbs pointed out that use of $k \log \tau$ as the entropy removed these anomalies *but*, whether we use a definition of temperature based on $\frac{3}{2}kT$ being the mean energy of the motion of the centre of mass or on

$$T = [\partial(k \log \tau)/\partial E]^{-1}$$

or on $T = k^{-1}(\tau'/\tau'')$ which we have used above, *the negative specific heat at $E = 0+$ remains with us*.

5 Conclusions

Negative heat capacities can only occur in isolated or nearly isolated systems. They are impossible in truly extensive systems in canonical ensembles or for that matter in grand canonical ensembles. However, far from being a strange phenomenon only found in the thermodynamics of black holes they occur widely on a macroscopic scale in astrophysics and with less precision on a microscopic scale throughout physics and chemistry. They are the origin of the large fluctuations that occur at phase transitions and we speculate that they cause those transitions. Indeed, the super-heated liquid and super-cooled gas must be joined by a curve of the abnormal slope corresponding to negative specific heat.

Acknowledgments

References

[1] Eddington, A. S., 1926. *The internal constitution of the stars*, Cambridge University Press.
[2] Antonov, V. A., 1972. *Vestn Leningrad Gos. Univ.*, 7, 135.
[3] Lynden-Bell, D. & Wood, R., 1967. *Mon. Not. R. astr. Soc.*, 136, 101.
[4] Thirring, W., 1970. *Z. Phys.*, 235, 339.
[5] Thirring, W., 1972. *Essays in Physics*, 4, 125.
[6] Hertel, P. & Thirring, W., 1971. *Ann. Phys.*, 63, 520.
[7] Hertel, P. & Thirring, W., 1971. *Comm. Math. Phys.*, 24, 22.
[8] Hertel, P. & Thirring, W., 1972. *Comm. Math. Phys.*, 28, 159.
[9] Beckenstein, J. D., 1974. *Phys. Rev. D*, 9, 3292.
[10] Hawking, S. W., 1974. *Nature*, 248, 30.
[11] Hawking, S. W., 1976. *Phys. Rev. D*, 13, 191.
[12] Aronson, E. B. & Hanson, C. J., 1972. *Astrophys. J.*, 177, 145.
[13] Schrödinger, E., 1952. *Statistical thermodynamics*, p. 25, Cambridge University Press.
[14] Morse, P. M., 1964. *Thermal physics*, pp. 257, 266. Benjamin, N.Y.
[15] Perdang, J., 1976. *Comp. Rend. 94th Congress A.F.A.S.*
[16] Pauling, L. & Wilson, A. B., 1935. *Introduction to quantum mechanics*, Chapter 5, McGraw-Hill.
[17] Gibbs, J. W., 1902. *Elementary principles of statistical mechanics*, Dover.