Thoughts on Negative Heat Capacities.

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Abstract.

By referring to well-established deductions from the Second Law of Thermodynamics and to the fact that concavity is the essence of this law, it is shown that the existence of negative heat capacities for closed systems is incompatible with the Second Law. However, it is seen that the heat capacity of an open system could be negative.

1. Introduction.

With a forthcoming special issue of the American Journal of Modern Physics due to be devoted to the topic of Negative Heat Capacities, it seems appropriate to reconsider the general theoretical position within thermodynamics of these negative heat capacities. This seems all the more important since this general situation, although discussed in detail in the later years of the last century, appears to be missing from much modern thermodynamic literature.

The possibility of a star possessing a negative heat capacity has been accepted for some time (Eddington, 1926). This phenomenon has been attributed to the lack of homogeneity due to gravitational interaction so that, even if the heat capacity of each small element of the system is positive, the overall heat capacity could be negative since the total energy in this case is not the sum of the energies of the individual parts – the energy of the gravitational interactions of these parts must be taken into account also (Landau & Lifshitz, 1958). Subsequently, self-gravitating gas spheres in a bounded region of space and in thermodynamic equilibrium were shown to be possible possessors of negative heat capacities (Lynden-Bell & Wood, 1967). In fact, the virial theorem for an ideal gas with $1/r$ potential has been used to demonstrate the existence of a negative heat capacity (Thirring, 1970, 1972). This somewhat paradoxical result was attributed to lack of a clear distinction between the canonical and micro-canonical ensembles. It was claimed that, when such a distinction was attempted, negative heat capacities occurred over a range of energy values in the micro-canonical ensemble, while a phase transition occurred in the canonical ensemble (Hertel & Thirring, 1971, 1972). This notion was examined further using simple models which obey the virial theorem. However, since the various ensembles are simply mathematical constructs, the fact that different physical effects appear to occur for one and the same system in these two ensembles must raise questions which surely deserve serious investigation followed by answers?

The fact that each of the above demonstrations of the existence of negative heat capacities is flawed, either by a logical error or by a situation in which thermodynamic reasoning may not be applied has been discussed elsewhere already (Lavenda & Dunning-Davies, 1990). However, it seems to be the case that, when negative heat capacities are discussed, there often seems to be an unwritten assumption that their actual existence is allowable and does not violate any well-established laws; invariably attention is confined to making deductions based on this underlying assumption (Landsberg & Pecaric, 1987). In what follows it is intended to examine the validity of this unwritten assumption.

In the first section following it is shown by using established, published results that the very existence of negative heat capacities for *closed* systems is incompatible with the Second Law of Thermodynamics. Further, it has been shown (Lavenda & Dunning-Davies, 1990) that the actual essence of the Second Law is concavity and, as has been demonstrated quite clearly (Dunning-Davies, 1993) this lends added support to this assertion that, *in closed systems,* negative heat capacities are incompatible with the Second Law. This is followed by an examination of an interesting example proposed by Lorentz which adds further credence to the arguments presented here.

Consideration then turns to the specific case of two systems in thermal contact with special attention being devoted to the interpretation of the results when one, or both, systems possess negative heat capacities. (For the content of this section the invaluable help of Dr. d. Pollard must be acknowledged.) This is followed by a consideration of the case of an ideal classical gas undergoing a polytropic change. This is of relevance since it has been claimed (Landsberg & Leff, 1989) that, although not generally realised, negative heat capacities are possible along certain types of path in this example. Whether or not this is true, is certainly of both importance and relevance as far as these considerations are concerned.

The question of the virial theorem and negative heat capacities – a subject mentioned already – is then addressed before the extension to *open* systems is discussed and it is noted that, in open systems, it is not prohibited for the heat capacity to assume a negative value.

2. The Second Law and Negative Heat Capacities.

It is well-known in thermodynamics that conclusions based on Carathéodory’s principle are frequently characterised by a multiplicity of possibilities. In particular, unless supplemented by additional assumptions, this principle leads to four possible types of thermodynamics – all similar in logical structure but distinct in detail. These four types of thermodynamics, together with their main properties, have been derived rigorously by Landsberg (1961). The properties directly relevant to the present discussion are reproduced in Table 1.

Table 1.

Types of Thermodynamics.

Type	I	II	III	IV
Direction of heat flow in terms of empirical temperature	high → low	high → low	low → high	low → high
Sign of the absolute temperature	positive	negative	Positive	negative
Direction of heat flow in terms of absolute temperature	high → low	low → high	low → high	high → low
Quasistatic heat capacity	positive	negative	negative	Positive

When viewing these various properties, it should be remembered that the idea of an empirical temperature is deduced from the Zeroth Law of Thermodynamics and there is no reason at that stage to suppose that heat flow is from high to low, rather than from low to high, empirical temperatures. It actually follows that Carathéodory's principle leads to the conclusion that either

(i) heat flows from places of high absolute temperature to those of low absolute temperature

or

(ii) heat flows from places of low absolute temperature to those of high absolute temperature.

As is seen from the table, conclusion (i) holds for thermodynamics of types I and IV, while (ii) holds for thermodynamics of types II and III. However, Carathéodory's principle is essentially a mathematical statement concerning the adiabatic accessibility of states. When physics, in the form of the Clausius statement of the second Law is introduced, it is seen that conclusion (ii) must be excluded and, from this, it follows immediately that thermodynamics of types II and III are unacceptable on physical grounds. Referring to the table once again, it is seen that thermodynamics of types II and III are those for which the heat capacity is negative; for types I and IV, the heat capacity is seen to be strictly positive. Hence, in order to ensure the continued validity of the Second Law of Thermodynamics, negative heat capacities cannot occur. However, it should be noted that, if reference is made to Landsberg's book (1961), all the discussion up to this point has been concerned purely with closed systems; the notion of an open system has yet to be introduced and so, the possibility of negative heat capacities in open systems remains an open question at this stage.

It might be noted also that the Second Law of Thermodynamics has been stated in various ways although the basis of the subject is firmly rooted in the two formulations due to Clausius and Kelvin. The connections between these two forms and that due to Carathéodory have been examined fairly extensively (Landsberg, 196; Dunning-Davies, 196, 1969). However, there is another apparent form of the Second Law which appears in the literature although, in the traditional development of the subject, it is really a deduction from the fundamental forms due to Clausius and Kelvin. This other form is

"For and adiabatically enclosed system
the entropy can never decrease."

This form attains greater prominence in those approaches to thermodynamics in which the existence of an entropy function is a basic assumption. In the traditional approach, the existence of an entropy function is deduced. It is worth enquiring as to the position of this alternative statement in the present context. Once again, though, the position has been examined in detail by Landsberg (1961) who has shown that this statement concerning entropy increase holds only for thermodynamics of types I and IV; it simply does not hold for those types of thermodynamics which admit negative heat capacities.

Hence, conclusions concerning negative heat capacities based on this alternative statement of the Second Law agree with those deduced earlier – negative heat capacities cannot occur in closed systems if the second Law is to remain inviolate. Again, all the results mentioned here are supported by later work (Lavenda & Dunning-Davies, 1990; Dunning-Davies, 1993) emphasising that the essence of the Second Law is concavity. Indeed, if concavity is indeed the essence of the Second Law, it follows immediately that the heat capacity must be positive in a closed system.

3. Digression on Concavity and the Second Law.

Support for the above mentioned assertion that the essence of the Second Law is concavity and that, when the entropy is not a first-order homogeneous function of the extensive variables, there is no reason to suppose that the entropy will be additive or superadditive is proved by an interesting example provided by Lorentz (Lorentz, 1927):

A pencil of rays of a particular colour is split, by means of a thin plate, into two parts – a reflected part and a transmitted one. If the energy density of the incident pencil is u and those of the reflected and transmitted ones are u_1 and u_2, then

$$u = u_1 + u_2.$$

It may be shown that, if the entropy is a concave function of the internal energy and is zero when the internal energy is zero, then, if the entropies of the incident, reflected and transmitted waves are s, s_1, s_2, respectively,

$$s < s_1 + s_2;$$

that is, the effect of splitting the pencil of rays is to produce an increase in total entropy.

Consider three values of the internal energy u_1, u_2 and $(u_1 + u_2)$. Between the values u = 0 and $u = u_1 + u_2$, the entropy

$$s = s(u)$$

is concave if

$$s[(1-\lambda)(u_1+u_2)] \geq (1-\lambda)s(u_1+u_2),$$

where $0 \leq \lambda \leq 1$; that is, any point on the curve lies above the chord joining the two given points.

In particular, if

$$(1-\lambda)(u_1+u_2) = u_1$$

then

$$\lambda = u_2/(u_1+u_2), \text{ say.}$$

Similarly, if

$$(1-\lambda)(u_1+u_2) = u_2,$$

then

$$\lambda = u_1/(u_1+u_2), \text{ say.}$$

Using these latter two results separately in the equation expressing concavity of the entropy leads to

$$s(u_1) \geq (1-\lambda)s(u_1+u_2) = u_1 s(u_1+u_2)/(u_1+u_2)$$

and

$$s(u_2) \geq (1-\lambda)s(u_1+u_2) = u_2 s(u_1+u_2)/(u_1+u_2).$$

Addition of the latter two equations gives

$$s(u_1) + s(u_2) \geq s(u_1 + u_2).$$

Hence,it has been shown that, if the entropy $s(u)$ is a concave function of the internal energy u for which

$$s(0) = 0,$$

the entropy is subadditive *not* superadditive.

This simple example would appear to support the earlier assertion (Lavenda & Dunning-Davies, 1990) that, when homogeneity no longer holds, it is concavity which contains the essence of the Second Law of Thermodynamics, not superadditivity; the Second Law is assumed valid universally but the above example shows that that is not so for the property of superadditivity.

4. Two Systems in Thermal Contact.

Now consider two *closed*, isolated systems – one with heat capacity C_1 and at temperature T_1, the other with heat capacity C_2 and at temperature T_2, where $T_2 < T_1$. Suppose these systems are put into thermal contact with one another and achieve thermal equilibrium at temperature T. Then, by conservation of energy

$$C_1(T - T_1) + C_2(T - T_2) = 0 \qquad \text{(i)}$$

or

$$T = \frac{C_1T_1 + C_2T_2}{C_1 + C_2},$$

this result holding for both positive and negative heat capacities.

If

$$\alpha = \frac{C_1}{C_1+C_2} \quad \text{and} \quad \beta = \frac{C_2}{C_1+C_2}$$

the above equation (i) may be written

$$T = \alpha T_1 + \beta T_2 \qquad \text{(ii)}$$

where

$$\alpha + \beta = 1.$$

Now it remains to examine various separate cases:-

Case 1.

If both heat capacities are positive

$$\alpha > 0, \ \beta > 0$$

and (ii) gives

$$\begin{aligned} T &= \alpha T_1 + (1 - \alpha)T_2 \\ &= T_2 + \alpha(T_1 - T_2) \\ &> T_2 \end{aligned}$$

and

$$\begin{aligned} T &= (1 - \beta)T_1 + \beta T_2 \\ &= T_1 - \beta(T_1 - T_2) \\ &< T_1 \end{aligned}$$

Hence, in this case

$$T_1 > T > T_2$$

and

$$C_1(T - T_1) < 0, \quad C_2(T - T_2) > 0$$

which means that the system at the higher temperature has lost heat while that at the lower temperature has gained heat or, in other words, heat has flowed from the higher to the lower temperature.

Case 2.

If both heat capacities are negative

$$\alpha > 0, \ \ \beta > 0$$

and, using the same argument as in Case 1, it again follows that

$$T_1 > T > T_2.$$

However, in this case, it is seen that

$$C_1(T - T_1) > 0, \quad C_2(T - T_2) < 0;$$

that is, the system at the higher temperature gains heat while that at the lower temperature loses heat or, in other words, heat flows from the lower to the higher temperature in violation of the Second Law of Thermodynamics.

Case 3.

It remains to consider the case when one heat capacity is positive and the other negative. In this case, either

$$\alpha > 0, \qquad \beta < 0$$

or

$$\alpha < 0, \qquad \beta > 0.$$

If $\alpha > 0, \beta < 0$, (ii) gives

$$T = T_2 + \alpha(T_1 - T_2) > T_2$$

0,

$$T = T_1 - \beta(T_1 - T_2) > T_1$$

so that

$$T > T_1 > T_2.$$

An analogous argument shows that, if $\alpha < 0, \beta > 0$, then

$$T_1 > T_2 > T.$$

However, the situation covered by the case $\alpha > 0, \beta < 0$ may be achieved if either

$$C_1 < 0, \ C_2 > 0, \ C_1 + C_2 < 0$$

or

$$C_1 > 0, \ C_2 < 0, \ C_1 + C_2 > 0.$$

In the first of these

$$C_1(T - T_1) < 0, \ \ C_2(T - T_2) > 0$$

so that heat flows from the higher to the lower temperature in accordance with the Second Law.

However, in the second

$$C_1(T - T_1) > 0, \;\; C_2(T - T_2) < 0$$

so that heat flows from the lower to the higher temperature in violation of the Second Law.

Again, the case $\alpha < 0, \beta > 0$ may be achieved if either

$$C_1 > 0, C_2 < 0, C_1 + C_2 < 0$$

or

$$C_1 < 0, C_2 > 0, C_1 + C_2 > 0.$$

A similar argument shows that, in the first of these, heat flows from the higher to the lower temperature but, in the second, it flows from the lower to the higher temperature in violation of the Second Law.

It might be noted also that, if

$$C_1 = -C_2,$$

the equation representing conservation of energy is satisfied only if

$$T_1 = T_2.$$

If T_1 and T_2 are unequal, the said equation leads to the conclusion that the equilibrium temperature is infinite.

All the above results are well-known (Landsberg & Pecaric, 1987), as is the interpretation. Since the Second Law of Thermodynamics precludes the flow of heat from a system at one temperature to a system at a higher temperature in the absence of other effects, it must be concluded that, when negative heat capacities are involved, the *only* allowable case is when the two heat capacities are of different sign and their sum is negative. However, while this conclusion may seem reasonable theoretically, in practice, if a closed system has a negative heat capacity, it cannot be ensured that it comes into contact only with other closed systems possessing positive heat capacities and such that the sum of the two heat capacities is negative. Hence, the only realistic conclusion which may be drawn from these considerations is that closed systems must have positive heat capacities; the existence of closed systems with negative heat capacities would lead to violations of the Second Law.

5. An Ideal Gas undergoing a Polytropic Change.

For an ideal classical gas

$$pV = RT,$$

where all the symbols have their usual meanings, and Joule's Law

$$\left(\partial U/\partial V\right)_T = 0$$

hold.

Also, for such a gas,

$$C_p - C_V = p\left(\partial V/\partial T\right)_p = R.$$

Now consider an ideal classical gas of constant heat capacities C_p, C_V undergoing a quasistatic change for which $d'Q = CdT$, where C is a constant. In this case

$$d'Q = dU + pdV = \left(\partial U/\partial T\right)_V dT + \left[\left(\partial U/\partial V\right)_T + p\right] dV$$

that is

$$CdT = C_V dT + pdV = C_V dT + (RT/V)dV$$

or

$$(C_V - C)\frac{dT}{T} = \left(C_p - C_V\right)\frac{dV}{V},$$

which may be integrated to give

$$TV^{n-1} = \text{constant},$$

$n = \left(C_p - C\right)/(C_V - C)$.

With n defined in this way, it follows that

$$C = \frac{(n-\gamma)}{(n-1)} C_V$$

where $\gamma = C_p/C_V$.

It follows immediately that C may be negative if $1 < n < \gamma$. Hence, it might appear, at first sight, that an ideal classical gas of constant heat capacities may have a negative heat capacity along so-called polytropic paths described by TV^{n-1} = constant if $1 < n < \gamma$. However, *all* the discussion thus far has been independent of the Second Law and, as has been shown already, introduction of the Second Law results in the exclusion of negative heat capacities for closed systems. Hence, in the above, both C and C_V must be positive and so either

$$n > 1 \quad \text{and} \quad n > \gamma$$

or

$$n < 1 \quad \text{and} \quad n < \gamma.$$

In a sense, this final result is not surprising since, as Chandrasekhar (1957) points out, the above situation is only an ordinary ideal classical gas undergoing a particular type of change.

6. The Virial Theorem and Negative Heat Capacities.

Astrophysical arguments leading to negative heat capacities are all based on the virial theorem (Thirring, 1970, 1972).The error in these arguments is to be found in a confusion between total energy and internal energy and is all the more surprising since the correct application of the virial theorem is laid out clearly in the book by Chandrasekhar (1957). As is shown there, if E is the total energy, U the internal energy, Ω the potential energy and τ the kinetic energy

$$E = U + \Omega$$

and

$$\tau = \frac{3}{2}(\gamma - 1)U$$

so that

$$\tau = U \text{ if and only if } \gamma = 5/3$$

where γ is, as usual, the ratio of the constant pressure and constant volume heat capacities.

Again, it is shown that, by the virial theorem

$$2\tau + \Omega = 3(\gamma - 1)U + \Omega = 0$$

which, together with the above equation for E gives

$$E = -(3\gamma - 4)U.$$

Since a stable configuration for gas spheres is possible only if $\gamma > 4/3$, it follows that the rate of change of *total* energy with temperature T will be opposite that of the *internal* energy. Hence, since the rate of change of total energy with temperature has been found to be negative (Thirring, 1970, 1972) it is follows that the heat capacity of the system, which is the rate of change of the internal energy with temperature, is positive. Hence there is no negative heat capacity and no paradox.

7. Extension to Open Systems.

Although not mentioned repeatedly in each section, attention thus far has been confined explicitly to closed systems. For such systems, the equation representing the combination of the First and Second Laws assumes the form

$$TdS = d'Q = dU + pdV$$

and the heat capacity at constant volume is

$$C_V = T(\partial S/\partial T)_V = (\partial U/\partial T)_V.$$

However, when open systems are considered, the form of the equation representing the combined First and Second Laws becomes

$$TdS = d'Q = dU + pdV - \mu dN,$$

where μ and N represent chemical potential and number of particles respectively, and so, in this case, the heat capacity at constant volume is given by

$$C_V = T(\partial S/\partial T)_V = (\partial U/\partial T)_V - \mu(\partial N/\partial T)_V.$$

Since the second term on the right-hand side of this latter equation may be either positive or negative, the sign of the heat capacity in this case remains indeterminate. Hence, it follows that the heat capacity of an open system could be negative. However, this in no way contradicts the earlier discussion. An open system cannot be isolated and, if an open system and its surroundings are in equilibrium and are considered together as a composite system, that composite system will be a closed system possessing a positive total heat capacity.

8. Conclusions.

In much of what appears in the literature concerning negative heat capacities, there is a tacit assumption that systems possessing such heat capacities are allowable and attention is confined to drawing conclusions based on this assumption. However, here it has been shown quite clearly that a *closed* system of negative heat capacity would violate the Second Law of Thermodynamics; only *open* systems may have negative heat capacities.

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