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Classical Fluids of Negative Heat Capacity

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It is shown that new parameters X can be defined such that the heat capacity $C_X \equiv T(\partial S/\partial T)_X$ is negative, even when the canonical ensemble [i.e., at fixed $T=(\partial U/\partial S)_Y$ and $Y \neq X$] is stable. This implies an extension of the classical theory of polytropes from ideal gases to general fluids. As examples of negative heat capacity systems we treat blackbody radiation and general gas systems with nonsingular κ_T. For the case of a simple ideal gas we even exhibit an apparatus which enforces a constraint $X(p, V) = \text{const}$ that makes $C_X < 0$. We then show that it is possible to infer the statistical mechanics of canonically *unstable* systems—for which even the traditional heat capacities are negative—by imposing constraints that stabilize the associated noncanonical ensembles. Two explicit models are discussed.

KEY WORDS: Heat capacity; negative fluids; classical blackbody radiation.

1. INTRODUCTION

The idea of negative heat capacities is by now well known for black holes[(1)] and for interacting classical systems like stars[(2)] and certain models of plasma (ref. 3, Fig. 8). The physical realization of many familiar thermodynamic constructions is problematic in the first two cases because of the important role played by gravitation.[(4)] In view of the long-range and universal character of this interaction it is very doubtful that a thermal reservoir which is large enough to enforce a sharply defined temperature would not also completely dominate the gravitational dynamics of any small system to which it was coupled. This is an important practical problem in the thermodynamics of gravitation, but it should not be allowed to obscure the fundamental problem that a system whose heat

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capacity is negative cannot reach thermal equilibrium even with an idealized reservoir.

The physical argument is that a system with negative heat capacity warms up by losing heat and cools down by gaining it. If heat flows from hot to cold, then any temperature difference with respect to the reservoir will engender heat flows which increase the difference. The mathematical argument proceeds by contradiction. Let $\hat{H}$ represent the system's Hamiltonian and let Y stand for one or more of the usual extensive parameters in addition to the energy. [This discussion can be generalized to include the case where any of the extensive parameters Y_i is replaced by its intensive conjugate, $P_i \equiv (\partial U/\partial Y_i)$; see, for example, ref. 5.] If the system is in equilibrium with a reservoir at fixed Y and fixed temperature $T = (\partial U/\partial S)_Y$, then elementary statistical mechanics gives the canonical partition function:

$$Z(T, Y) \equiv \mathrm{Tr}(e^{-\beta \hat{H}})_Y \tag{1.1a}$$

where $\beta \equiv 1/k_B T$ and the trace extends over all states of fixed Y. Taking the logarithm gives $-\beta$ times the Helmholtz free energy, $F(T, Y)$. Using the standard formulas for the entropy and heat capacity, $S = -(\partial F/\partial T)_Y$ and $C_Y \equiv T(\partial S/\partial T)_Y$, we find that the usual heat capacity is proportional to the variance of the energy:

$$C_Y = k_B \beta^2 \left(\frac{\partial^2 \ln(Z)}{\partial \beta^2} \right)_Y = k_B \beta^2 \langle (\hat{H} - \langle \hat{H} \rangle)^2 \rangle_{T,Y} \tag{1.1b}$$

This is a manifestly positive quantity, so the assumption of thermal equilibrium must be erroneous whenever C_Y is negative.

In view of the preceding arguments it is usually assumed that systems with negative heat capacity can be treated statistically only in the microcanonical ensemble. We have just seen the problem when it is a usual heat capacity C_Y, but one might ask how the matter stands for a more general heat capacity $C_X \equiv T(\partial S/\partial T)_X$, where X is not restricted to be a normal extensive parameter of the canonical ensemble. The answer is that quantities X can always be defined such that C_X is less than zero, even when C_Y is positive and the canonical ensemble is completely stable (ref. 6, pp. 42, 45). Examples of functions X will be given below. The physical picture is of a system coupled to a reversible work source that adds or withdraws energy so as to keep some quantity X fixed. The system will have $C_X < 0$ if the constraint $X = \text{const}$ is chosen so that any heat flow from the reservoir is overbalanced by the work drawn off by the reversible work source.

We will prove the existence of such constraints generally in the context of normal thermodynamics where the natural extensive parameters are internal energy and volume. This context entirely avoids systems based upon the sort of long-range and universal forces that would mediate strong interactions with the reservoir. We first give the general solution under the assumption that the isothermal compressibility $[\kappa_T \equiv -(1/v)(\partial v/\partial p)_T]$ is nonsingular; then we give a detailed mechanical realization of such a constraint for the simple ideal gas. To illustrate that singular κ_T need not pose a problem, we show how negative heat capacities can be defined also for blackbody radiation.

Although our parameters X can be extensive, for canonically stable systems they necessarily exhibit the following properties in contrast to the usual parameter Y ($= V$, for example):

$$C_X = T\left(\frac{\partial S}{\partial T}\right)_X \neq \left(\frac{\partial U}{\partial T}\right)_X \tag{1.2a}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \neq \left(\frac{\partial U}{\partial S}\right)_X \equiv T' \tag{1.2b}$$

The final inequality means that the statistical ensemble at constant T and X is not weighted by the Boltzmann factor of (1.1a), as is the ensemble at constant Y. In fact the ensemble at constant X fails even to exist; the instability of any such system can be seen from the previously cited physical argument. Our results are nonetheless derived using the fundamental relation obtained from the canonical ensemble at fixed T and V. This suggests that by choosing different extensive parameters one might be able to explore the statistical mechanics of a system with negative C_V—in which case it would be the noncanonical ensemble at fixed T' and X which would exist rather than the canonical ensemble at fixed T and V—without recourse to the microcanonical ensemble. After completing our discussion of how to constrain instabilities into a canonically stable system we shall discuss two canonically *un*stable systems for which we can define stable ensembles by means of very simple constraints.

2. THERMODYNAMICS

Let $X(p, V)$ be some function of pressure and volume. Then one can write for the incremental heat input into the system (ref. 6, problem 13.1, pp. 11, 22)

$$T\,dS = C_V\,dT + l_V\,dV = \left[C_V + l_V\left(\frac{\partial V}{\partial T}\right)_X\right] dT + l_V\left(\frac{\partial V}{\partial X}\right)_T dX \tag{2.1a}$$

$$= C_p\,dT + l_p\,dp = \left[C_p + l_p\left(\frac{\partial p}{\partial T}\right)_X\right]dT + l_p\left(\frac{\partial p}{\partial X}\right)_T dX \qquad (2.1\text{b})$$

$$= C_X\,dT + l_X\,dX \qquad (2.1\text{c})$$

where l_X is the appropriate "latent heat." The two expressions which result for l_X are

$$l_X = l_V\left(\frac{\partial V}{\partial X}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial X}\right)_T \qquad (2.2\text{a})$$

$$l_X = l_p\left(\frac{\partial p}{\partial X}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial X}\right)_T \qquad (2.2\text{b})$$

Their consistency is a simple consequence of the reciprocity theorem:

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial V}{\partial p}\right)_T = -1 \qquad (2.3)$$

Note that $l_X\,dX$ is not generally the work done on the system, although $l_V\,dV = p\,dV$ for the special case of the simple ideal gas. From (2.1) we can infer two expressions for C_X:

$$C_X = C_V + l_V\left(\frac{\partial V}{\partial T}\right)_X \qquad (2.4\text{a})$$

$$= C_p + l_p\left(\frac{\partial p}{\partial T}\right)_X \qquad (2.4\text{b})$$

Subtracting C_V from (2.4a) and taking the ratio with (2.4b)–(2.4a) gives

$$\frac{C_X - C_V}{C_p - C_V} = \frac{1}{1-\theta}, \qquad \text{i.e.,} \quad \frac{C_X}{C_V} = -\frac{\gamma-\theta}{\theta-1} \qquad (2.5)$$

where

$$\theta \equiv \frac{l_p}{l_V}\left(\frac{\partial p}{\partial V}\right)_X = \left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial V}\right)_X \qquad (2.6)$$

Note that θ depends only upon the definition of X and an equation of state relating V, p, and T.

The generalized heat capacity C_X was introduced long ago (ref. 6, problems 9.11 and 9.22, pp. 42, 45). It has also been studied recently in the context of enforced adiabats, i.e., processes in which differential heat flow can occur along a path provided the initial and final entropies are equal.[7] If X is a function of p alone, then $\theta = 0$ and $C_X = \gamma C_V = C_p$. Also one sees from (2.6) that if X is a function of V only, then $\theta \to \infty$, and Fig. 1 confirms

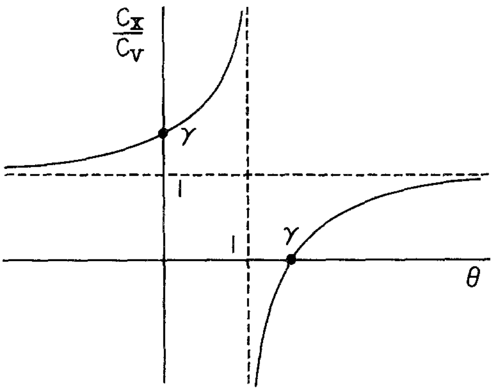

Fig. 1. Plot of the generalized heat capacity C_X (in units of C_V) versus the quantity θ defined in Eq. (2.6). Note that each value of θ corresponds to a different choice of the quantity $X(p, V)$ which is held fixed.

$C_X \to C_V$. Thus C_X covers a range of heat capacities which include C_V (at $\theta \to \infty$) and C_p (at $\theta = 0$).

If one assumes with Emden a special fluid with internal energy proportional to the absolute temperature and $pV = HT$ (H a constant), which are his assumptions A and B (ref. 8, pp. 6, 7), one finds of course again Fig. 1. The results here represent a generalization. Our notation C_X, θ, γ is γ, k, κ respectively in Emden. His Fig. 1 (ref. 8, p. 16) is equivalent to our Fig. 1, but holds only for his special case. Further, whereas we do not restrict C_X, Emden's interest is in polytropes, and so he states his γ to be a constant. For this reason his interest in negative heat capacities is also only incidental. Emden's Fig. 1 is not well known, as it does not appear either in Emden's or Chandrasekhar's review,[9] and we are indebted to a referee for drawing attention to it.

To show that negative values are possible, note that $C_X < 0$ if and only if $1 < \theta < \gamma$. Now let θ_0 be a constant in this range and consider the relation $\theta = \theta_0$. Identification of the isothermal compressibility κ_T and simple applications of the reciprocity and inverse theorems give

$$\kappa_T(p, V)\, V \left(\frac{\partial X}{\partial V}\right)_p = \theta_0 \left(\frac{\partial X}{\partial p}\right)_V \tag{2.7}$$

This is a linear partial differential equation with possibly nonconstant but certainly nonzero coefficients. We can of course freely specify $X(p_0, V)$ for some fixed pressure p_0 and the general solution follows by exponentiation:

$$X(p, V) = P\left(\exp\left[\frac{1}{\theta_0}\int_{p_0}^{p} dz\, \kappa_T(z, V)\, V \frac{\partial}{\partial V}\right]\right) X(p_0, V) \tag{2.8a}$$

The symbol “P” stands for “path-ordering.” It means that the various noncommuting factors of $\kappa_T(z, V)\, V\,\partial/\partial V$ are to be ordered according to the z integration with those nearer $z = p$ to the left of those nearer $z = p_0$. Generally if $\mathcal{O}(z)$ is an operator or matrix-valued function of z, then one makes the following definition:

$$P\left(\exp\left[\int_a^b dz\, \mathcal{O}(z)\right]\right) \equiv \sum_{n=0}^{\infty} \int_a^b dz_1 \int_{z_1}^b dz_2 \cdots \int_{z_{n-1}}^b dz_n\, \mathcal{O}(z_n)\, \mathcal{O}(z_{n-1}) \cdots \mathcal{O}(z_1) \quad (2.8b)$$

To make the preceding discussion more concrete, suppose that the entropy has the form appropriate to a simple ideal gas:

$$S(U, V, N) = k_B N \ln\left[\left(a\frac{U}{N}\right)^{1/(\gamma-1)} \frac{V}{N}\right] \quad (2.9)$$

where N is the number of particles and a is related to the chemical constant i. In fact, if $\gamma = 5/3$, then $a = 2/3(k_B)^{-5/3}\exp(2i/3)$. A simple exercise reveals that $\kappa_T = 1/p$. Substituting this into expression (2.8a) gives

$$X(p, V) = X\left(p_0, V\left[\frac{p}{p_0}\right]^{1/\theta_0}\right) \quad (2.10)$$

In other words, $X(p, V)$ can be any function of Vp^{1/θ_0}. Since keeping X fixed is the same as keeping Vp^{1/θ_0} fixed, we can make X extensive by taking $X(p, V) = Vp^{1/\theta_0}$. In fact, the negative nature of C_X can be obtained directly and very simply from this expression for $X(p, V)$.

3. A DEVICE DEMONSTRATING HOW X CAN BE KEPT CONSTANT

A primitive apparatus is depicted in Fig. 2. A thermal reservoir of temperature T_{res} surrounds a large, diathermal cylinder of cross-sectional

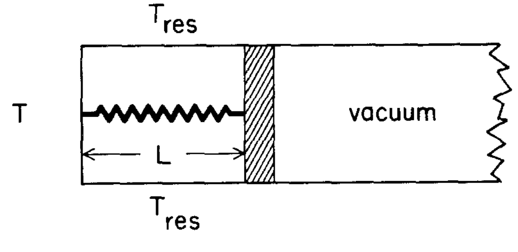

Fig. 2. Sketch of a system which realizes negative heat capacity using a simple ideal gas.

area A. The cylinder contains a movable piston which is attached to a spring whose force constant k can be stiffened or loosened by winding or unwinding the coils of the spring. The piston seals a fixed quantity of the gas into one end of the cylinder while the other end is vacuum. Transducers measure the length L of the gas-filled section and the pressure, $p = kL/A$. These transducers control the winding mechanism which adjusts the spring's force constant according to the rule

$$k(L) = \frac{k_0}{L^{\theta_0 + 1}} \tag{3.1}$$

where k_0 is a constant. It is easy to see that this serves to maintain the constraint $Vp^{1/\theta_0} = \text{const.}$

To determine the state of the system, we allow energy to flow so as to maximize the total entropy of the three components: the gas, the spring, and the reservoir. The energy of the spring is simple to compute from Hooke's law:

$$U_{\text{spring}} = \int_{L_0}^{L} dx\, k(x)\, x = \text{const} - \frac{1}{\theta_0 - 1}\, pV \tag{3.2}$$

Since

$$U_{\text{gas}} = \frac{1}{\gamma - 1}\, pV$$

it follows that

$$U_{\text{spring}} = \text{const} - \left(\frac{\gamma - 1}{\theta_0 - 1}\right) U_{\text{gas}}$$

Now suppose that the internal energy of the gas increases by an amount ΔU_{gas}. The preceding relation and energy conservation imply that the corresponding increases in the spring and reservoir energies are

$$\Delta U_{\text{spring}} = -\left(\frac{\gamma - 1}{\theta_0 - 1}\right) \Delta U_{\text{gas}} \tag{3.3a}$$

$$\Delta U_{\text{res}} = \left(\frac{\gamma - \theta_0}{\theta_0 - 1}\right) \Delta U_{\text{gas}} \tag{3.3b}$$

To compute the change in entropy note that with $X = Vp^{1/\theta_0}$ we can express the volume in terms of X and U:

$$V = X^{\theta_0/(\theta_0 - 1)}[(\gamma - 1)\, U_{\text{gas}}]^{-1/(\theta_0 - 1)} \tag{3.4a}$$

Substitution into (2.9) gives the entropy of the gas as

$$S_{\text{gas}} = -\frac{k_B N}{\gamma - 1}\left(\frac{\gamma - \theta_0}{\theta_0 - 1}\right)\ln(U_{\text{gas}}) + f(X, N) \tag{3.4b}$$

where $f(X, N)$ is a simple function whose precise form is irrelevant to our discussion. If T_{gas} is the gas temperature before the addition of the increment ΔU_{gas}, then the gas entropy increases by

$$\Delta S_{\text{gas}} = -\frac{1}{T_{\text{gas}}}\left(\frac{\gamma - \theta_0}{\theta_0 - 1}\right) U_{\text{gas}} \ln\left(1 + \frac{\Delta U_{\text{gas}}}{U_{\text{gas}}}\right) \tag{3.5a}$$

The reservoir is a reversible heat source at constant temperature, so its entropy increases by

$$\Delta S_{\text{res}} = \frac{1}{T_{\text{res}}}\left(\frac{\gamma - \theta_0}{\theta_0 - 1}\right) \Delta U_{\text{gas}} \tag{3.5b}$$

The spring and its winding mechanism are assumed to constitute a reversible work source, so their entropies are unchanged. For $1 < \theta_0 < \gamma$ we see that the total entropy can be made to increase without bound by having ΔU_{gas} approach $-U_{\text{gas}}$. Hence heat flows from the reservoir even as the gas expands and cools down; the excess energy goes into unwinding the spring. This is precisely the sort of instability that one expects from a system with negative heat capacity.

4. BLACK BODY RADIATION WITH NEGATIVE HEAT CAPACITY

So much for our mechanical contraption. Provided that the isothermal compressibility κ_T is nonsingular, expression (2.8) gives the general solution for a constrant $X(p, V)$ such that

$$C_X = -\left(\frac{\gamma - \theta_0}{\theta_0 - 1}\right) C_V$$

In fact negative heat capacities can be defined even for systems where both κ_T and $C_p = \gamma C_V$ are singular. To illustrate this fact, we consider blackbody radiation. A fundamental relation for this system is

$$S(U, V) = \frac{4}{3} a^{1/4} V^{1/4} U^{3/4} \tag{4.1}$$

where a is the Stefan–Boltzmann constant. Some differentiations and rearrangements suffice to give the standard results:

$$U = aVT^4 \tag{4.2a}$$

$$p = \tfrac{1}{3}aT^4 \tag{4.2b}$$

The latter implies that κ_T and C_p are infinite for this system.

To obtain a negative heat capacity, let us again consider extensive constraints of the form

$$X(p, V) = Vp^{1/\theta} \tag{4.3}$$

By using (4.2b) to solve for $T(V, X)$ and then substituting into (4.2a), we obtain the following expressions for V:

$$V = \left(\frac{1}{3}U\right)^{1/(1-\theta)} X^{-\theta/(1-\theta)} = \left(\frac{a}{3}T^4\right)^{-1/\theta} X \tag{4.4}$$

These relations allow us to write the entropy in terms of either U and X or T and X:

$$\frac{1}{4}S = 3^{(-5+4\theta)/(4-4\theta)} a^{1/4} X^{-\theta/(4-4\theta)} U^{(4-3\theta)/(4-4\theta)} = \left(\frac{a}{3}\right)^{(\theta-1)/\theta} XT^{(3\theta-4)/\theta} \tag{4.5}$$

To see that θ can be chosen to make the system at fixed U and X unstable, we merely differentiate the first of these expressions twice:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_X = \frac{4\theta - 3\theta^2}{(4-4\theta)^2}\frac{S}{U^2} \tag{4.6}$$

Concavity obviously fails for $0 < \theta < 4/3$. That this range of values also corresponds to a negative heat capacity follows from differentiation of the second incarnation of the entropy in (4.5):

$$C_X \equiv T\left(\frac{\partial S}{\partial T}\right)_X = \left(1 - \frac{4}{3\theta}\right) C_V \tag{4.7}$$

Of course the limit $\theta \to \infty$ just recovers C_V.

5. STATISTICAL MECHANICS MODELS: GENERALITIES

We stress that all of the preceding analysis was carried out using conventional thermodynamics, and, for special purposes, specific equations for the entropy—typically (2.9) and (4.1)—which follow from the canonical ensemble. We are therefore led to suggest that the whole process might be profitably inverted when it is desired to study a system for which the *conventional* heat capacity C_Y is negative. In this case the entropy $S(U, Y)$ cannot be everywhere concave, and the canonical partition function cannot exist for all values of T and Y. One could always infer a fundamental relation for such a system by computing the number of states at fixed U and Y, but we feel it might be very much simpler to instead search for a new parameter X for which the noncanonical partition at fixed $T' = (\partial S/\partial U)_X$ and X exists. After a brief notational digression we shall discuss two explicit models which illustrate our suggestion.

In order to deal with many different ensembles, we shall introduce a general notation based on that of Callen.[10] Suppose that the natural extensive parameters of the entropic representation are the energy U and $Y_1,..., Y_r$. For each extensive parameter we define an intensive conjugate as follows:

$$F_0 \equiv \left(\frac{\partial S}{\partial U}\right)_{Y_1,..., Y_r} \tag{5.1a}$$

$$F_i \equiv \left(\frac{\partial S}{\partial Y_i}\right)_{U, Y_1,..., Y_{i-1}, Y_{i+1},..., Y_r} \tag{5.1b}$$

Of course $F_0 = 1/T$, and the F_i associated with familiar parameters such as V and N have similar expressions in terms of the intensive parameters of the energetic representation. Just as one can Legendre transform the energy to obtain the various thermodynamic potentials, so one can Legendre transform the entropy to obtain the various Massieu functions. We shall denote them by the symbol S with the list of their natural intensive parameters appended in square brackets:

$$S[F_0, F_1,..., F_q] \equiv S - F_0 U - \sum_{i=1}^{q} F_i Y_i, \qquad q \leqslant r \tag{5.2}$$

Note that one need not transform in order. For example, with $r = 5$ it would be perfectly valid to consider the Massieu function, $S[F_3, F_5] \equiv S - F_3 Y_3 - F_5 Y_5$.

The Massieu function $S[F_0, F_1,..., F_q]$ is associated with the ensemble at fixed $F_0, F_1,..., F_q, Y_{q+1},..., Y_r$. Suppose that the system's quantum states are labeled by a generic quantum number α and that each such state has energy $u(\alpha)$ and $Y_i = y_i(\alpha)$. The partition function associated with the ensemble at fixed $F_0, F_1,..., F_q, Y_{q+1},..., Y_r$ is

$$\begin{aligned} &Z[F_0, F_1,..., F_q](Y_{q+1},..., Y_r) \\ &\quad \equiv \sum_{\alpha} \exp\left\{-k_B^{-1}\left[F_0 u(\alpha) + \sum_{i=1}^{q} F_i y_i(\alpha)\right]\right\} \\ &\quad \quad \times \delta[Y_{q+1} - y_{q+1}(\alpha)] \cdots \delta[Y_r - y_r(\alpha)] \end{aligned} \tag{5.3}$$

With this notation $Z(U, Y_1,..., Y_r)$ is just the degeneracy function of the microcanonical ensemble; $Z[F_0](Y_1,..., Y_r)$ is the usual partition function of the canonical ensemble. The ensemble average of the expectation value of an operator $\hat{\mathcal{O}}$ is

$$\langle\langle \hat{\mathcal{O}} \rangle\rangle_{F_0,..., F_q, Y_{q+1},..., Y_r} \equiv \sum_{\alpha} \langle\alpha|\, \hat{\mathcal{O}}\, |\alpha\rangle \frac{\exp\{-k_B^{-1}[F_0 u(\alpha) + \sum_{i=1}^{q} F_i y_i(\alpha)]\}}{Z[F_0, F_1,..., F_q](Y_{q+1},..., Y_r)} \times \delta[Y_{q+1} - y_{q+1}(\alpha)] \cdots \delta[Y_r - y_r(\alpha)] \tag{5.4}$$

The connection to thermodynamics derives from the relation

$$S[F_0, F_1,..., F_q](Y_{q+1},..., Y_r) = k_B \ln\{Z[F_0, F_1,..., F_q](Y_{q+1},..., Y_r)\} + (\text{subdominant terms}) \tag{5.5}$$

The "subdominant terms" of the right-hand side are corrections to the leading-order approximation for the partition function in the method of steepest descent.[11] When the thermodynamic limit exists and is nonzero, these corrections typically scale as the logarithm of an extensive parameter divided by an extensive parameter and are negligible for large systems away from phase transitions.

6. SPECIFIC STATISTICAL MECHANICS MODELS

Our first model consists of a system of N distinguishable interacting particles where the condition of the ith particle is represented by two nonnegative integers, m_i and n_i. A state of this system is accordingly described by an $2N$-plet of nonnegative integers. Suppose that there are two extensive parameters U and Y in addition to N. Suppose further that for the state $|\mathbf{m}, \mathbf{n}\rangle$ these parameters are

$$u(\mathbf{m}, \mathbf{n}) = (n_1 + \cdots + n_N)\, \varepsilon_0 \tag{6.1a}$$

$$y(\mathbf{m}, \mathbf{n}) = (m_1 + \cdots + m_N)\, y_0 - N \cosh\left(\frac{u}{N\varepsilon_0} - n_0\right) y_0 \tag{6.1b}$$

where ε_0, y_0, and n_0 are positive constants. The second term of the relation for y constitutes the interaction. It means that we cannot consider the total amount of y to result from independent contributions from each particle. In general the energy would also have this property, although it does not in this simple model.

Let us first observe that this system can have negative C_Y. If we fix the values of U and Y at

$$U = n\varepsilon_0 \tag{6.2a}$$

$$Y = my_0 - N\cosh\left(\frac{n}{N} - n_0\right) y_0 \tag{6.2b}$$

where m and n are nonnegative integers, then the microcanonical ensemble gives

$$Z(U, Y, N) = \frac{(N+n-1)!}{n!\,(N-1)!}\,\frac{(N+m-1)!}{m!\,(N-1)!} \tag{6.3}$$

Using Stirling's approximation to neglect the subdominant terms results in the following expression for the entropy:

$$S = k_B N\left\{\left(1+\frac{m}{N}\right)\ln\left(1+\frac{m}{N}\right) - \frac{m}{N}\ln\left(\frac{m}{N}\right) + \left(1+\frac{n}{N}\right)\ln\left(1+\frac{n}{N}\right) - \frac{n}{N}\ln\left(\frac{n}{N}\right)\right\} \tag{6.4}$$

[We shall henceforth consider n and m to be continuous parameters whose relation to U and Y is given by (6.2).] The identity

$$\left(\frac{\partial}{\partial U}\right)_{Y,N} = \frac{1}{\varepsilon_0}\left(\frac{\partial}{\partial n}\right)_{m,N} + \frac{1}{\varepsilon_0}\sinh\left(\frac{n}{N} - n_0\right)\left(\frac{\partial}{\partial m}\right)_{n,N} \tag{6.5}$$

facilitates differentiating with respect to U at constant Y. The potential for instability emerges from two applications of this identity:

$$\left(\frac{\partial S}{\partial U}\right)_{Y,N} = \frac{k_B}{\varepsilon_0}\ln\left(\frac{n+N}{n}\right) + \frac{k_B}{\varepsilon_0}\sinh\left(\frac{n}{N} - n_0\right)\ln\left(\frac{m+N}{m}\right) \tag{6.6a}$$

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{Y,N} = -\frac{k_B}{\varepsilon_0^2}\frac{N}{n(n+N)} - \frac{k_B}{\varepsilon_0^2}\sinh^2\left(\frac{n}{N} - n_0\right)\frac{N}{m(m+N)} + \frac{k_B}{N\varepsilon_0^2}\cosh\left(\frac{n}{N} - n_0\right)\ln\left(\frac{m+N}{m}\right) \tag{6.6b}$$

At $n = n_0 N$ the second term of (6.6b) vanishes, and the third term can be made to dominate the first by choosing

$$m < N\left[\exp\left(\frac{1}{n_0(n_0+1)}\right) - 1\right]^{-1}$$

Of course a violation of concavity with respect to U at fixed Y and N implies that C_Y can become negative:

$$C_Y = Nk_B \left\{ \ln\left(\frac{n+N}{n}\right) + \sinh\left(\frac{n}{N} - n_0\right) \ln\left(\frac{m+N}{m}\right) \right\}^2$$
$$\times \left\{ \frac{N^2}{n(n+N)} + \sinh^2\left(\frac{n}{N} - n_0\right) \frac{N^2}{m(m+N)} \right.$$
$$\left. - \cosh\left(\frac{n}{N} - n_0\right) \ln\left(\frac{m+N}{m}\right) \right\}^{-1} \tag{6.7a}$$

$$\xrightarrow[n = n_0 N]{} Nk_B \frac{\ln^2((n_0+1)/n_0)}{1/n_0(n_0+1) - \ln((m+N)/m)} \tag{6.7b}$$

A corollary is that the canonical partition function cannot exist for all T, since otherwise C_Y would be positive semidefinite by Eq. (1.1b). From direct examination of the putative partition function

$$Z\left[\frac{1}{T}\right](Y, N) = \sum_{n=0}^{\infty} \frac{(N+n-1)!}{n!\,(N-1)!}$$
$$\times \frac{\Gamma[Y/y_0 + N\cosh(n/N - n_0) + N]}{\Gamma[Y/y_0 + N\cosh(n/N - n_0) + 1](N-1)!} \exp(-\beta\varepsilon_0 n) \tag{6.8}$$

we find that the sum fails to converge for $k_B T \geqslant [N/(N-1)]\,\varepsilon_0$.

Although it was possible to treat this system using the microcanonical ensemble, an equally valid approach is suggested by the fact that the entropy (6.4) is a concave function of U, X, and N, where we define

$$X \equiv Y + N\cosh\left(\frac{U}{N\varepsilon_0} - n_0\right) y_0 \tag{6.9}$$

One consequence of this is the existence of the noncanonical ensemble at fixed $F'_u = (\partial S/\partial U)_{X,N}$ and $F'_x = (\partial S/\partial X)_{U,N}$:

$$Z[F'_u, F'_x](N)$$
$$= \sum_{m_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \exp[-k_B^{-1}(n_1 + \cdots)\,\varepsilon_0 F'_u - k_B^{-1}(m_1 + \cdots)\,y_0 F'_x] \tag{6.10a}$$

$$= [1 - \exp(-k_B^{-1} F'_u \varepsilon_0)]^{-N}\,[1 - \exp(-k_B^{-1} F'_x y_0)]^{-N} \tag{6.10b}$$

Of course this gives us the natural Massieu function of the ensemble:

$$S[F'_u, F'_x](N) = -Nk_B\{\ln[1-\exp(-k_B^{-1}F'_u\varepsilon_0)] + \ln[1-\exp(-k_B^{-1}F'_x y_0)]\} \tag{6.11}$$

A straightforward application of thermodynamics allows us to recover the ensemble averages of the extensive variables:

$$U = -\left(\frac{\partial S[F'_u, F'_x]}{\partial F'_u}\right)_{F'_x, N} = \frac{N\varepsilon_0}{\exp(k_B^{-1}F'_u\varepsilon_0)-1} \tag{6.12a}$$

$$X = -\left(\frac{\partial S[F'_u, F'_x]}{\partial F'_x}\right)_{F'_u, N} = \frac{Ny_0}{\exp(k_B^{-1}F'_x y_0)-1} \tag{6.12b}$$

Inverting to solve for the intensive variables and Legendre transforming should give the microcanonical entropy:

$$S = S[F'_u, F'_x] + F'_u U + F'_x X \tag{6.13a}$$

$$= k_B N\left\{\left(1+\frac{X}{Ny_0}\right)\ln\left(1+\frac{X}{Ny_0}\right) - \frac{X}{Ny_0}\ln\left(\frac{X}{Ny_0}\right) + \left(1+\frac{U}{N\varepsilon_0}\right)\ln\left(1+\frac{U}{N\varepsilon_0}\right) - \frac{U}{N\varepsilon_0}\ln\left(\frac{U}{N\varepsilon_0}\right)\right\} \tag{6.13b}$$

Inserting relation (6.9) and comparing with (6.4) and (6.2) shows that we have indeed recovered the correct entropy.

Note that although we first used the microcanonical partition function (6.3) to find the entropy (6.4), this was not necessary. We did it only for the pedagogical purpose of demonstrating the system's instability at fixed U, Y, and N using a conventional technique whose validity was not subject to question. Once the validity of noncanonical ensembles is accepted, such an appeal to the microcanonical ensemble is neither necessary nor desirable. Indeed, by varying the model only slightly, we can eliminate even the possibility of an exact microcanonical solution. Suppose, for example, that the extensive parameters have the following expressions in terms of the system's quantum numbers:

$$u(\mathbf{m}, \mathbf{n}) = (n_1 + \cdots + n_N)\,\varepsilon_0 \tag{6.14a}$$

$$y(\mathbf{m}, \mathbf{n}) = (m_1 + \cdots + m_N)\,y_0 - Ny_0\cosh\left[\frac{1}{N}\sum_{i=1}^{N}(n_i n_{i+1})^{1/2} - n_0\right] \tag{6.14b}$$

where $n_{N+1} \equiv n_1$. Note that in this case we can still define

$$x(\mathbf{m}, \mathbf{n}) \equiv (m_1 + \cdots + m_N)\,y_0 \tag{6.15}$$

and compute the partition function $Z[F'_u, F'_x](N)$. In fact the result is identical to expression (6.11) above. Of course the parameter X will no longer relate to Y precisely as in (6.9), *but the corrections will be subdominant in the thermodynamic limit.* Therefore, we obtain the same final expression for the entropy in the thermodynamic limit.

Aside from its contrived nature, one might criticize the model we have just considered on the grounds that X, not Y, is the "natural" extensive parameter for this system. Since the system is stable at fixed U, X, and N, it could be argued that we have done nothing beyond implementing at the level of statistical mechanics the purely thermodynamic considerations of Section 2. We do not agree. The correct identification of extensive parameters depend upon symmetries of the weak interactions which are typically neglected in statistical mechanics. It is entirely possible that consideration of the equilibration mechanism would reveal Y, not X, as the more natural extensive parameter. However, we prefer to shift the focus of the debate. The origin of instabilities which lead to negative heat capacity is an anomalously rapid growth in the density of states. We achieved this in the previous model by means of a second set of quantum numbers, the m_i, such that at fixed Y the number of m_i configurations grows exponentially with the energy. The same sort of instability can be attained by building interactions into the energy without involving a second extensive parameter. In this incarnation the utility of alternate ensembles is beyond dispute because no one can question the presence of U among the system's extensive parameters.

The model we have in mind consists, as before, of N distinguishable, interacting particles. The states of this system are labeled by N independent quantum numbers n_i, each of which runs over the nonnegative integers. The energy eigenvalues are

$$u(\mathbf{n}) = N\left\{\ln\left[1+\frac{1}{N}\sum_{i=1}^{N} n_i\right]\right\}^{2/3} \varepsilon_0 \tag{6.16}$$

where ε_0 is a positive constant. By fixing the value of U at

$$U = N\left\{\ln\left[1+\frac{n}{N}\right]\right\}^{2/3} \varepsilon_0 \tag{6.17}$$

where n is a nonnegative integer, we see that the degeneracy function is

$$Z(U, N) = \frac{(N+n-1)!}{n!\,(N-1)!} \tag{6.18}$$

Using Stirling's approximation to neglect the subdominant terms results in the following expression for the entropy:

$$S = k_B N\left(\left(\frac{U}{N\varepsilon_0}\right)^{3/2} - \left\{\exp\left[\left(\frac{U}{N\varepsilon_0}\right)^{3/2}\right] - 1\right\}\right.$$
$$\left.\times \ln\left\{1 - \exp\left[-\left(\frac{U}{N\varepsilon_0}\right)^{3/2}\right]\right\}\right) \tag{6.19}$$

At large U and fixed N the first term dominates and one can see that although the temperature is positive, the heat capacity is not:

$$-\frac{1}{T^2 C} \equiv \left(\frac{\partial^2 S}{\partial U^2}\right)_N \xrightarrow[U \gg N\varepsilon_0]{} \frac{3}{4}\frac{k_B}{N\varepsilon_0^2}\left(\frac{N\varepsilon_0}{U}\right)^{1/2} \tag{6.20}$$

It follows that the canonical partition function:

$$Z\left[\frac{1}{T}\right](N) = \sum_{n=0}^{\infty} \frac{(N+n-1)!}{n!\,(N-1)!} \exp\left\{-\beta\varepsilon_0 N\left[\ln\left(1+\frac{n}{N}\right)\right]^{2/3}\right\} \tag{6.21}$$

cannot exist since otherwise C_Y would have to be positive by relation (1.1b). Though it is not obvious, the sum in fact fails to converge for any temperature.

Our alternate ensemble is based upon the extensive parameter X whose eigenvalues are

$$x(\mathbf{n}) \equiv \sum_{i=1}^{N} n_i \tag{6.22}$$

The natural intensive variable conjugate to X is

$$F'_x \equiv \left(\frac{\partial S}{\partial X}\right)_N \tag{6.23}$$

The simple ensemble to work with is at fixed F'_x and N. Its partition function is

$$Z[F'_x](N) \equiv \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \exp[-k_B^{-1} F'_x x(\mathbf{n})] \tag{6.24a}$$

$$= [1 - \exp(-k_B^{-1} F'_x)]^{-N} \tag{6.24b}$$

The natural logarithm of this partition function gives k_B^{-1} times the Massieu function at fixed F'_x and N:

$$S[F'_x](N) = -N k_B \ln[1 - \exp(-k_B^{-1} F'_x)] \tag{6.25}$$

Standard thermodynamics instructs us to solve for X from the relation

$$X=-\left(\frac{\partial S[F'_x](N)}{\partial F'_x}\right)_N=\frac{N}{\exp(k_B^{-1}F'_x)-1} \tag{6.26}$$

Legendre transformation gives the entropy:

$$S\equiv S[F'_x](N)+F'_xX \tag{6.27a}$$

$$=Nk_B\ln\left[\frac{N+X}{N}\right]+Xk_B\ln\left[\frac{N+X}{X}\right] \tag{6.27b}$$

Substitution of the relation

$$X=N\exp\left[\left(\frac{U}{N\varepsilon_0}\right)^{3/2}\right]-N \tag{6.28}$$

shows that we indeed recover (6.19).

Since an exact microcanonical treatment of this model was possible, it is a matter of taste as to whether or not the alternate ensemble gives a simpler derivation. By the following slight variation of the energy eigenvalues we can eliminate the possibility of an exact microcanonical solution:

$$u(\mathbf{n})=N\left\{\ln\left[1+\frac{1}{N}\sum_{i=1}^{N}(n_in_{i+1})^{1/2}\right]\right\}^{2/3}\varepsilon_0 \tag{6.29}$$

where again $n_{N+1}\equiv n_1$. In this case finding the number of states at fixed U and N is no longer a simple combinatoric problem, if it can be done at all. However, we still have relation (6.28) in the thermodynamic limit of the ensemble at fixed F'_x and N. We have therefore exhibited a system which is unstable when expressed in terms of the usual variables (U and N), and whose statistical mechanics is quite impenetrable with any of the usual ensembles. By choosing a different set of variables (X and N), we obtained a stable system whose statistical mechanics is trivial in terms of one of the natural ensembles of these variables. Although this model is rather simple, it does capture the same anomalously rapid growth in the density of states which is responsible for the instabilities of gravitational thermodynamics. (On a closed spatial manifold it is provably true that *all* the states of any theory with dynamical gravity are degenerate with zero energy!) Given the limitless possibilities for defining alternate ensembles, it is not without reason to hope that this technique will find some application for realistic systems.

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REFERENCES

1. P. C. W. Davies, *Rep. Prog. Phys.* **41**:1314 (1978); R. M. Wald, *General Relativity* (Chicago University Press, Chicago, 1984); D. Pavón and P. T. Landsberg, *Gen. Rel. Grav.* **20**:457 (1988).
2. D. Lynden-Bell and R. M. Lynden-Bell, *Mon. Not. Astron. Soc.* **181**:405 (1977); P. Hertel and W. Thirring, *Ann. Phys.* (N.Y.) **63**:520 (1971).
3. R. A. Smith and T. M. O'Neil, *Phys. Fluids B* **2**:2961 (1990).
4. P. T. Landsberg, *J. Stat. Phys.* **35**:159 (1984); D. C. Wright, *Phys. Rev. D* **21**:884 (1980).
5. F. Schlögl, *Z. Phys.* **267**:77 (1974).
6. P. T. Landsberg, *Thermodynamics and Quantum Statistical Illustrations* (Interscience, New York, 1961).
7. V. J. Menon and D. C. Agrawal, *Phys. Lett.* **139A**:130 (1989).
8. R. Emden, *Gaskugeln* (Teubner, Leipzig, 1907).
9. R. Emden, *Encycl. d. Math. Wiss.*, Vol. VI, 2.B (Teubner, Leipzig, 1922–1934), pp. 373–532; S. Chandrasekhar, *An Introduction to the Study of Stellar Structure* (Chicago University Press, Chicago, 1939).
10. H. B. Callen, *Thermodynamics and An Introduction to Thermostatistics*, 2nd ed. (Wiley, New York, 1987).
11. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics I* (McGraw-Hill, New York, 1953), pp. 434–443.