INSTITUTE OF PHYSICS PUBLISHING EUROPEAN JOURNAL OF PHYSICS

Eur. J. Phys. **26** (2005) N13–N16 doi:10.1088/0143-0807/26/4/N01

NOTE

Entropy maximization in the free expansion process

C Fernández-Pineda[1] **and S Velasco**[2]

[1] Departamento de Física Aplicada I, Facultad de Físicas, Universidad Complutense, 28040 Madrid, Spain
[2] Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Salamanca, 37008 Salamanca, Spain

Received 7 January 2005, in final form 17 March 2005
Published 20 May 2005
Online at stacks.iop.org/EJP/26/N13

Abstract
The entropy maximum principle is applied to obtain the final equilibrium state in the free expansion of a perfect gas. This provides an example where the entropy of an isolated system at equilibrium has an *absolute* maximum which is not a *local* maximum.

The entropy maximum principle is the guide to solving the so-called *basic problem* of thermodynamics [1, 2]: to predict the equilibrium conditions of an isolated composite system when some internal constraints have been removed. For isolated hydrostatic (or PVT) systems, the mathematical formulation of this principle is usually given by the following inequality [3, 4],

$$(\Delta S)_{U,V} = (\delta^1 S + \delta^2 S + \cdots)_{U,V} \leqslant 0, \tag{1}$$

where the symbol Δ denotes an arbitrary virtual (variational) change from equilibrium, while $\delta^1 S$ and $\delta^2 S$ denote, respectively, the first- and second-order virtual changes for the entropy in a Taylor's series expansion of ΔS. In order to apply the entropy maximum principle some thermodynamics textbooks make the two usual mathematical requirements:

$$(\delta^1 S)_{U,V} = 0, \tag{2}$$

$$(\delta^2 S)_{U,V} < 0. \tag{3}$$

Then, equation (2) is used to obtain the equilibrium conditions, while inequality (3) is used to analyse the stability of the equilibrium state. Equation (2) implies that the first derivatives (assumed continuous and bounded) of the entropy with respect to the independent variables in the maximization process must be zero at equilibrium (*local* or *relative* extremum). This can lead to the fact that students may have the impression that the application of the entropy maximum principle to specific systems always involves finding a *local* maximum. However, strictly speaking, condition (1) only requires that the entropy reaches its largest value (*absolute* or *global* maximum) at equilibrium [5]. In other words, for the entropy of an isolated system

0143-0807/05/040013+04$30.00

it is possible, but not necessary, to have a *local* maximum at equilibrium. This misconception comes because the right formulation of the *Gibbs general equilibrium and stability conditions* is ([3, pp 56, 57], [6, 7])

$$(\delta^1 S)_{U,V} \leqslant 0 \qquad \text{(equilibrium)}, \tag{4}$$

$$(\delta^2 S)_{U,V} < 0 \qquad \text{(stability)}. \tag{5}$$

Conditions (4) and (5) must be verified simultaneously: while (4) grants that the equilibrium state has an entropy value equal to or larger than any other value in its vicinity, (5) grants that the equilibrium is stable. The stability condition (5) requires that the entropy surface must lie below the tangent plane at the equilibrium point, independent of the fact that this plane is horizontal or not (i.e., independent that the first-order virtual variation was zero or negative). In other words, condition (5) requires the concavity in the direction of the negative S-axis of the entropy surface in the vicinity of the equilibrium point.

As has been pointed out by several authors ([6–8], [3, p 61]) one may omit the sign of inequality in (4) if all virtual changes are possible in two directions while the inequality sign holds when virtual displacements are possible in only one direction. However, examples where the equilibrium state verifies the inequality sign in (4) are very scarce in the literature. Haase [9] has illustrated one of these cases by means of an example concerning the distribution of a solute (naphtalene) in two immiscible solvents (water and benzene). The goal of this note is to discuss a simpler example related to a process well-known in basic courses in thermodynamics: the free (or Joule) expansion process.

A free expansion is the one in which a gas confined in an adiabatic vessel expands into vacuum. Therefore, we consider the following system: an adiabatic cylinder contains an internal adiabatic piston which divides the volume into two chambers. The left chamber contains n moles of a gas (g) while the right one is *occupied* by vacuum (v). The gas-vacuum system can be considered as an isolated composite system described by only three parameters, the temperature of the gas, T_{g}, the volume occupied by the gas, V_{g}, and the volume of vacuum, V_{v}. Initially, the piston is fixed by a pin so that the gas occupies a volume, $V_{\mathrm{g},i}$, at a temperature, $T_{\mathrm{g},i}$, and the vacuum occupies a volume, $V_{\mathrm{v},i}$. Once the pin is removed, the piston becomes a movable, frictionless piston, and the system evolves from the initial state $(V_{\mathrm{g},i}; T_{\mathrm{g},i}; V_{\mathrm{v},i})$ towards a stable equilibrium state $(V; T_{\mathrm{g,eq}}; 0)$, where V is the total volume of the cylinder. Our aim is to analyse this final equilibrium state from the viewpoint of the entropy maximum principle.

For simplicity, we consider the free expansion of a perfect gas (an ideal gas with constant molar heat capacities $\bar{C}_V$ and $\bar{C}_P$). Then, the entropy of the total system is given by

$$S = S_{\mathrm{g}} + S_{\mathrm{v}} = ns_0 + n\bar{C}_V \ln T_{\mathrm{g}} + nR \ln V_{\mathrm{g}}, \tag{6}$$

where s_0 is a constant, R is the molar gas constant and $S_{\mathrm{v}} = 0$. Furthermore, since the internal energy and the volume of the total system remain constant one has

$$U = U_{\mathrm{g}} + U_{\mathrm{v}} = n\bar{C}_V T_{\mathrm{g}} = \text{constant}, \tag{7}$$

where $U_{\mathrm{v}} = 0$, and

$$V = V_{\mathrm{g}} + V_{\mathrm{v}} = \text{constant}. \tag{8}$$

From equation (7) one has $T_{\mathrm{g}} = \text{constant}$, i.e., as is well known, a free expansion of a perfect gas causes no change in its temperature. Therefore, $T_{\mathrm{g,eq}} = T_{\mathrm{g},i}$. On the other hand, since the volume V_{g} cannot decrease from its initial value, equation (8) implies $V_{\mathrm{g},i} \leqslant V_{\mathrm{g}} \leqslant V$. Therefore, under the external constraints (7) and (8), equation (6) can be written as

$$S_{U,V} \equiv S(V_{\mathrm{g}}) = ns_0^* + nR \ln V_{\mathrm{g}} \qquad (V_{\mathrm{g},i} \leqslant V_{\mathrm{g}} \leqslant V), \tag{9}$$

where $s_0^* = s_0 + \bar{C}_V \ln T_{\mathrm{g},i}$ is a constant.

Equation (9) shows that, for a free expansion of a perfect gas, the maximization process for the total entropy (6) can be described by only one independent variable, the volume, V_{g}, of the gas. So, condition (2) for the entropy to have a *local* maximum at equilibrium requires that the first derivative of function (9) vanishes

$$\left(\frac{\mathrm{d}S}{\mathrm{d}V_{\mathrm{g}}}\right)_{\mathrm{eq}} = \frac{nR}{V_{\mathrm{g,eq}}} = 0. \tag{10}$$

But the latter equality cannot be verified by any of the allowed values of V_{g}. In other words, entropy (9) does not present any *local* maximum for $V_{\mathrm{g},i} \leqslant V_{\mathrm{g}} \leqslant V$. However, since $\mathrm{d}S/\mathrm{d}V_{\mathrm{g}} = nR/V_{\mathrm{g}} > 0$, function (9) increases monotonically with V_{g}, so that one verifies that

$$S(V_{\mathrm{g}}) \leqslant S(V) \qquad \forall\ V_{\mathrm{g}} \in [V_{\mathrm{g},i}, V]. \tag{11}$$

Thus, the total entropy reaches its absolute maximum value at $V_{\mathrm{g}} = V$ and, therefore, $V_{\mathrm{g,eq}} = V$. In this case, only virtual displacements from equilibrium with $\delta V_{\mathrm{g}} \equiv V_{\mathrm{g}} - V < 0$ are possible and one has

$$(\delta^1 S)_{U,V} = \left(\frac{\mathrm{d}S}{\mathrm{d}V_{\mathrm{g}}}\right)_{\mathrm{eq}} \delta V_{\mathrm{g}} = \frac{nR}{V}\delta V_{\mathrm{g}} < 0, \tag{12}$$

in agreement with the inequality sign in (4).

To assure that the equilibrium state is stable one must require the fulfilment of condition (5). In the present example, one has

$$(\delta^2 S)_{U,V} = \left(\frac{\mathrm{d}^2 S}{\mathrm{d}V_{\mathrm{g}}^2}\right)_{\mathrm{eq}} (\delta V_{\mathrm{g}})^2 = -\frac{nR}{V^2}(\delta V_{\mathrm{g}})^2 < 0, \tag{13}$$

which grants the stability of the final equilibrium state $V_{\mathrm{g,eq}} = V$. We note that for a perfect gas $nR = PV/T$ and the isothermal compressibility is $k_T = 1/P$, so that inequality (13) can be written as

$$(\delta^2 S)_{U,V} = -\frac{1}{T_{\mathrm{g},i} V k_T}(\delta V_{\mathrm{g}})^2 < 0, \tag{14}$$

which can be related with the mechanical stability condition $k_T > 0$.

Finally, following the lines reported in [8, 9], we suggest analysing the final equilibrium state obtained in the free expansion from the viewpoint of the internal energy minimum principle. In this case, the entropy of the gas during the virtual process remains constant and equals the entropy at the final equilibrium state. One can check that the internal energy reaches its *absolute* minimum value at $V_{\mathrm{g,eq}} = V$, but this is not a *local* minimum, and that this equilibrium state is stable. Both extremum principles predict the same final equilibrium state.

To conclude, we have applied the entropy maximum principle to obtain the final equilibrium state and its stability in a free expansion of a perfect gas. This provides a simple and pedagogical example in which the entropy reaches its *absolute* maximum value at equilibrium, but this is not a *local* maximum. Standard thermodynamics textbooks usually do not provide information about this question.

Acknowledgments

SV thanks financial support by Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain under grants BFM 2002-01225 FEDER and BFM 2003-07106 FEDER, and by Junta de CyL-FSE of Spain under grants SA080/04 and SA092/04.

References

[1] Kestin J 1979 *A Course in Thermodynamics* vol II (New York: Hemisphere) p 2

[2] Callen H B 1985 *Thermodynamics and an Introduction to Thermostatistics* 2nd edn (New York: Wiley) pp 25–6

[3] Gibbs J W 1961 *The Scientific Papers of J W Gibbs. Thermodynamics* vol I (New York: Dover) p 57

[4] Tisza L 1966 *Generalized Thermodynamics* (Cambridge, MA: MIT Press) p 43

[5] For a general mathematical study of these topics see, for example, Marsden J E and Tromba A J 1988 *Vector Calculus* 3rd edn (New York: Freeman) chapter 4

[6] Haase R 1969 *Thermodynamics of Irreversible Processes* (Reading, MA: Addison-Wesley) p 50

[7] Münster A 1970 *Classical Thermodynamics* (London: Wiley-Interscience) pp 56–8

[8] Sanfeld A 1971 Equilibrium, stability and displacements *Physical Chemistry. An Advanced Treatise. Vol. I. Thermodynamics* ed W Jost (New York: Academic) chapter 2A (see section X, Stability of Chemical Systems)

[9] Haase R 1956 *Thermodynamik der Mischphasen* (Berlin: Springer) p 105 (See, also, [7])

[10] Fernández-Pineda C and Velasco S 2001 Application of thermodynamic extremum principles *Am. J. Phys.* **69** 1160–5

[11] Velasco S and Fernández-Pineda C 2002 A simple example illustrating the application of thermodynamic extremum principles *Eur. J. Phys.* **23** 501–11