Essence of the Third Law: The Delineation of Two Forms of Thermodynamics (*)&(**).

B. H. LAVENDA (1) and J. DUNNING-DAVIES (2)

(1) Università di Camerino - 62032 Camerino (MC), Italy
(2) Department of Applied Mathematics, University of Hull - Hull HU6 7RX, UK

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Summary. — The third law is generalized to the effect that for systems in internal thermodynamic equilibrium, either the entropy tends to zero with the temperature, implying a state of complete order, or the entropy tends to its maximum value as the temperature increases without limit, indicating a state of complete disorder.

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1. – The third law for conventional thermodynamics.

The third law, or Nernst's postulate, is stated conventionally as "the contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at absolute zero" [1]. It is usually contended that the appreciation of the Nernst postulate had to await the discovery of quantum statistics, since classical statistics did not obey the postulate [2].

We shall state the third law in such a way that it incorporates the classical ideal gas. The entropy density of quantum statistics is, in energy units where Boltzmann's constant is unity,

\[ s(x) = x \ln \left( \frac{y + x}{x} \right) \pm y \ln \left( \frac{y + x}{y} \right), \]

where " + " and " - " signs refer to Bose-Einstein (BE) and Fermi-Dirac (FD) statistics, respectively. The number of quanta or particles in a given frequency interval is denoted by \( x \). For BE statistics, \( y \) represents the number of oscillators in a

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given frequency interval per unit volume, while for FD statistics it represents the
total number of states available. In the small-x limit, (1) reduces to

\[ s(x) = -x \ln \left( \frac{x}{y} \right). \]

The entropy density, (2), satisfies the inequality

\[ s((1 - \lambda)x_1 + \lambda x_2) \geq (1 - \lambda)s(x_1) + \lambda s(x_2), \]

where the parameter \( \lambda \in [0, 1] \). The inequality in (3) asserts that every point of the
chord connecting the end points \( x_1 \) and \( x_2 \) lies below the curve. Such a function is said
to be concave [3]. Moreover, since \( s(0) = 0 \), we can choose one of the end points of the
interval at the origin, say \( x_1 = 0 \). Then the criterion of concavity reduces to [4]

\[ s(\lambda x) \geq \lambda s(x). \]

Then, setting \( \lambda x = x_a \) and \( (1 - \lambda)x = x_b \) such that \( x_a + x_b = x \), the sum of (4) and
\( s((1 - \lambda)x) = (1 - \lambda)s(x) \) gives

\[ s(x_a) + s(x_b) \geq s(x_a + x_b), \]

showing that the quantum statistical entropy is subadditive.

The same conclusion can be reached by the concavity criterion

\[ s''(x) < 0, \]

where the prime denotes differentiation, and the third law

\[ s(0) = 0 \quad \text{for} \quad T = 0. \]

The temperature is given by the second law

\[ s'(x) = \frac{\chi}{T}, \]

where \( \chi \) is the intensive variable conjugate to \( x \). Taken together (6) and (7) imply that
\( s(x)/x \) is a decreasing function (theorem 127, p. 99 of ref. [3]). This means that

\[ x^2 \frac{d}{dx} \left( \frac{s(x)}{x} \right) = xs'(x) - s(x) \leq 0, \]

or

\[ s(x)/x \geq s'(x). \]

This is a sufficient condition that the entropy density satisfy (5) (theorem 103, p. 83 of
ref. [3]). Hence,

\[ \text{Concavity (6) + Third law (7) } \Rightarrow \text{Subadditivity (5)} \]

We can even do away with the third law, in the form (7), and show that
subadditivity follows directly from the concavity of the entropy. The concavity of the