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Derivation of Quantum Statistics from Gauss's Principle and the Second Law

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Quantum statistical laws are derived from bona fide stationary probability distributions of physical stochastic processes. These distributions are shown to be the laws of error for which the average occupation numbers are the most probable values. They determine uniquely the statistical entropy functions and the second law gives the quantum statistical distributions.

1. INTRODUCTION

It is well known that classical statistics is concerned with the distribution of n distinguishable particles among m energy levels or "cells." Maxwell-Boltzmann (MB) "statistics" assumes that all of the m^n arrangements have equal probabilities. This is the classical limit of Fermi-Dirac (FD) and Bose-Einstein (BE) statistics, both of which affirm the inherent indistinguishability of the particles. In the case of FD statistics, where the Pauli exclusion principle applies, there cannot be more than one particle in any cell and all distinguishable arrangements are assumed to have equal probabilities. Since there are $\binom{m}{n}$ arrangements, or the number of ways of populating m cells with n $(\leq m)$ particles, the probability of any arrangement is $\binom{m}{n}^{-1}$. In the BE case, there is no occupancy restriction and the number of distinguishable distributions is $\binom{m+n-1}{n}$, each having a probability $\binom{m+n-1}{n}^{-1}$. An intermediate case can also be contemplated (Gentile, 1940a,b) where the occupancy number is restricted to some finite number of particles, but it does not lead to any physical process (Lavenda and Dunning-Davies, submitted) in the sense to be described in this paper.

The negative binomial coefficient is a standard result of combinatorial theory which was derived by Planck (1900) by working backward from his modified expression for the spectral distribution function of blackbody

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radiation which took into consideration the newly discovered fact that the spectral distribution was found to be proportional to the absolute temperature at low frequencies. Essentially, what Planck did was to use the relation between the spectral distribution function and the average energy of an oscillator to obtain the temperature as a function of the energy. Then with the aid of the second law, the temperature was eliminated between the two expressions and the entropy, as a function of energy, was obtained upon integration. Planck had then to justify his expression of the entropy and this he did, reluctantly, using Boltzmann's connection between the entropy and the "number of complexions" or the number of ways the total energy can be shared among m oscillators. Planck had simply referred to it as "the number of combinations with repetitions of m elements of class n" without giving any physical insight into the nature of this peculiar result (Planck, 1906; see also Klein, 1972, p. 255). Not satisfied with Planck's deduction of the combinatorial formula for the number of ways n energy units ε can be distributed over m oscillators, Ehrenfest and Kamerlingh Onnes (1914) showed that the negative binomial coefficient resulted from considering the permutations of the n symbols ε and the $m-1$ divider symbols separating the m cells. In contrast to the classical result m^n, where each particle has m independent choices, the counting done by Planck showed that some of these distributions, obtained by permutating the particles assigned to the different cells corresponded to the same distribution. The negative binomial aspect was emphasized by Moyal (1949), and Feller (1950) referred to the negative binomial distribution as a limiting form of BE statistics.

The principal difficulty in deriving both quantum and classical statistics has always been Boltzmann's principle relating entropy to the logarithm of the complexions or microscopic states compatible with a given macroscopic state. Planck (1900, 1906; see also Fowler, 1936) called this a "thermodynamic" probability, although it is not a probability at all but rather a binomial, negative binomial, or multinomial coefficient in the cases of FD, BE, or MB statistics, respectively. These numbers are then maximized subject to the constraints of constant number of particles and total energy. Dealing with coefficients of probability distributions rather than with the distributions themselves necessitates the assumption of equal *a priori* probabilities if there is to be any connection with probability at all. There are also the questions of quantum indistinguishability, as opposed to classical distinguishability, and how to tell one from another. Recently, interest has been revived in these fundamental questions (Tersoff and Bayer, 1983; Constantini, 1987; Maddox, 1987; Lavenda, 1988).

Tersoff and Bayer (1983) claim to have shown that distinguishable particles do, in fact, obey BE or FD statistics. They modify the assumption that all distinct configurations have fixed equal probability weighting. That is, they replace the equal *a priori* probability m^{-n} in the multinomial distribution for the occupancy numbers $\{n_i\}$, which satisfy the constraint $\sum_i^m n_i = n$, by a particular form which, when solved recursively, gives the inverse of the negative binomial coefficient for BE statistics. However, it is clear that their particular choice destroys the fact that the modified multinomial distribution is a proper probability distribution; that is, the sum over all $\{n_i\}$ which conserve the particle number should give unity. Their result $\binom{m+n-1}{n}^{-1}$ is in fact independent of the $\{n_i\}$ (Lavenda 1988). The situation is further aggravated by the fact that the probability is $\binom{m+n-1}{n}^{-1}$ while the entropy is logarithm of the inverse of this number; consequently, the greater the probability, the smaller will be the entropy. This contradicts the Boltzmann interpretation of the entropy as the logarithm of the "thermodynamic probability."

Costantini (1987) claims that even classical particles are indistinguishable. He remarks that because of the energy constraint, all cells are not equiprobable [see Lavenda and Scherer (in press) for a similar conclusion]. He reintroduces the *a priori* probabilities $\{p_i\}$ in the multinomial distribution and maximizes subject to the particle and energy constraints. This leads to the MB distribution without the degeneracy factors because the $\{p_i\}$ have been traded for the m^{-n} in the multinomial expression. Appealing to Bernoulli's case, Constantini (1987) sets $n_i = np_i$, for which the multinomial distribution is essentially equal to unity when Stirling's approximation is made. Although this eliminates the problem of the m unknowns $\{p_i\}$, the coincidence between the observed frequencies n_i/n and the expected frequencies p_i means that the fluctuations have disappeared, and this surely can occur only in the limit n, $m \to \infty$ such that their ratio $n/m \to \text{const}$ (Lavenda, 1988).

The crux of the problem lies in treatment of binomial or multinomial coefficients rather than bona fide probability distributions. This introduces the problem of determining the *a priori* probabilities in the expression for the probability distributions. However, I show that these probability distributions are laws of error leading to the average value of the number of particles as the most probable value. The potential which determines the law of error is the entropy and the second law provides thermodynamic expressions for the *a priori* probabilities. This shows that the conventional assumption of *a priori* probabilities is not justifiable.

In order to derive the laws of error for quantum statistics, I turn to an approach that was initiated by Einstein (1917; see also Landsberg, 1986), who derived Planck's radiation law by considering the physical processes of absorption and emission (stimulated + spontaneous) of radiation. This avoided any mention of the Boltzmann connection between entropy and the logarithm of the negative binomial coefficient. Having identified three distinct processes, characterized by three rate parameters, Einstein assumed a dynamical equilibrium between the rates of absorption and emission of radiation. Then, in order to eliminate one of the unknown rate coefficients leaving the other two coefficients in a ratio which could subsequently be identified upon comparison with Planck's law, Einstein took the high-temperature limit. He then substituted these values into the dynamical equilibrium condition which is valid at any temperature.

In this article, I unite the Einstein and Boltzmann approaches by analyzing general classes of stochastic processes that admit stationary probability distributions and derive the relation between the probability distribution and the entropy with the aid of Gauss's principle. This provides for a more direct connection between entropy and probability than that which is contained in Boltzmann's principle. The quantum statistical distributions are then obtained by equating the statistical expressions for the entropy derivative with that obtained from the second law.

2. DERIVATION OF THE PROBABILITY DISTRIBUTIONS

A generic "birth-and-death" or "generation-recombination" process is described by the master equation

$$\dot{f}(n, t) = \vartheta_r(n+1)f(n+1, t) + \vartheta_g(n-1)f(n-1, t) \\ -\{\vartheta_r(n) + \vartheta_g(n)\}f(n, t) \tag{1}$$

where the coefficient $\vartheta_r(n)$ is the probability per unit time that a jump will occur to $n-1$ when the present state is n, while $\vartheta_g(n)$ is the probability per unit time for the jump to $n+1$. Setting $\dot{f}=0$, we solve (1) for stationary probability distribution and find

$$f_n^s(n) = \frac{\vartheta_g(n-1)\vartheta_g(n-2)\cdots\vartheta_g(0)}{\vartheta_r(n)\vartheta_r(n-1)\cdots\vartheta_r(1)} f_\eta^s(0) \tag{2}$$

We now make the *general* substitution $\vartheta_r = \alpha n$ and $\vartheta_g = \beta(m - \eta n)$, where rate parameters α and β are independent of n. For the case $\eta = 1$ (FD statistics), we may imagine an adsorption isotherm where the rate of evaporation of molecules n from a surface consisting of m sites is αn while the rate of condensation is proportional to the surface not already covered $(m-n)$ with β as the constant of proportionality, whereas for $\eta = -1$ (BE statistics), we may think of Einstein's mechanism (1917) of absorption and emission of radiation where α, β, and γ $(=\beta m)$ are the coefficients of absorption and induced and spontaneous emission, respectively. With this general substitution, the stationary distribution (2) can be written as

$$f_\eta^s(n)=\frac{(m+\eta-\eta n)\cdots m}{n!}\left(\frac{\beta}{\alpha}\right)^n f_\eta^s(0) \tag{3}$$

where

$$\frac{(m+\eta-\eta n)\cdots m}{n!}=\begin{cases}\binom{m}{n} & \eta=1\\ \binom{m+n-1}{n}, & \eta=-1\end{cases} \tag{4}$$

In the generally accepted interpretation of the negative binomial coefficient, which Planck (1900) obtained with the aid of Boltzmann's principle working backward from his proposed radiation law, m represents the number of oscillators, which must be a positive integer. It appears here as the ratio of the coefficients of spontaneous and stimulated emission, which need not be an integer; in fact, the conservation of probability $\sum_{n=0}^{\infty} f_{-1}^s(n)=1$ holds for *any positive* value of m.

The average equation of motion corresponding to the master equation (1) is

$$\dot{\bar{n}}=-\alpha\bar{n}+\beta(m-\eta\bar{n}) \tag{5}$$

In the case of FD statistics, the existence of the stationary solution $\bar{n}^s=\gamma/(\alpha+\beta)$ does not impose any condition on the relative magnitudes of the rate parameters, while in the case of BE statistics, the existence of the stationary solution $\bar{n}=\gamma/(\alpha-\beta)$ requires that $\alpha>\beta$. We shall see that this condition, which interpreted in terms of the absorption and emission of radiation means that the rate of absorption of radiation must be greater than the rate of stimulated emission, is guaranteed by the second law [see equation (16) below].

In the limit as $m\to\infty$ and $\beta/\alpha\to 0$ such that their product $m\beta/\alpha\to$ const, the transition probabilities per unit time become $\vartheta_g=\alpha\bar{n}^s$ and $\vartheta_r=\alpha n$. The stationary solution to the master equation (1) then is

$$f_0^s(n)=\frac{(\bar{n}^s)^n}{n!}\exp(-\bar{n}^s) \tag{6}$$

which is the Poisson distribution.

Einstein (1917) postulated the existence of a dynamical equilibrium between the average rates of emission and absorption of radiation. This can be compared with a more formal approach of employing the second law to establish such a dynamical equilibrium. In order to do so, it is necessary to define the statistical entropies associated with each of the three stationary distributions. This will now be accomplished through an extension of Gauss's principle (Gauss, 1963).

3. GAUSS'S PRINCIPLE AND THE SECOND LAW

A common statistical problem is to determine the *most probable* value of a quantity based on a series of observations. The problem is not determinate unless we have some basis for determining the probability of making an error. Corresponding to each law of error there is some quantity which represents the most probable value of the quantity. In his derivation of the normal law of error, Gauss (1963) assumed that the arithmetic mean of the observations was the most probable value of the quantity observed. Instead of assuming that the arithmetic mean of the observations is equal to the most probable value, we shall assume that the arithmetic mean is equal to the mean of the distribution (McBride, 1968; Campbell, 1970). This will enable us to establish the fact that each of the stationary probability distributions (3) and (6) is a law of error for which the mean value is the most probable value and determine uniquely each of the statistical entropy functions.

The likelihood of a given number of independent observations of n is

$$\prod_{\text{observations}} f^s(n; \bar{n}^s) \tag{7}$$

and since $\bar{n}^s$ makes it a maximum, (7) must satisfy the likelihood equations

$$\sum_{\text{observations}} \frac{1}{f^s}\frac{\partial f^s}{\partial \bar{n}^s} = 0 \tag{8}$$

Gauss's principle may now be used to determine the functional form of $f^s(n; \bar{n}^s)$ by requiring the likelihood equations (8) to be equivalent to

$$\sum_{\text{observations}} (n - \bar{n}^s) = 0 \tag{9}$$

The condition can be met if there is a φ such that (Keynes, 1921)

$$\frac{1}{f^s}\frac{\partial f^s}{\partial \bar{n}^s} = \varphi(n - \bar{n}^s) \tag{10}$$

for all observations n. The function φ can depend upon $\bar{n}^s$ but not upon n; that is, since the left-hand side of equation (10) contains only one value of n, φ cannot involve any other value of n. But if it depended on the value of n, it would be invalidated by any other equation where the left-hand side depended on a different value of n.

Integrating (10) gives

$$\ln f^s(n) = -(n - \bar{n}^s)\frac{\partial S}{\partial \bar{n}^s}(\bar{n}) - S(\bar{n}^s) + \Sigma(n) \tag{11}$$

where we have set $\varphi = -\partial^2 S/\partial \bar{n}^{s2}$ and $\Sigma(n)$ is a constant of integration. The partial derivative in equation (11) is used to denote the fact that S can depend on additional variables which are held constant. Any law of error of this type leads to the mean value as the most probable value of the quantity observed.

All three stationary distributions—the binomial, negative binomial, and Poisson distributions—can be cast in the form of the law of error given by (11). For the probability distributions f_η^s in equation (3) we find

$$S_\eta(\bar{n}^s) = \frac{m}{\eta} \ln m - \bar{n}^s \ln \bar{n}^s - \frac{1}{\eta}(m - \eta \bar{n}^s) \ln(m - \eta \bar{n}^s) \tag{12}$$

which, for $\eta = 1$, is the entropy of an ideal FD gas, while for $\eta = -1$, it is the entropy of an ideal BE gas in units where Boltzmann's constant is equal to unity. The integration constant in equation (11) is

$$\Sigma_\eta(n) = \frac{m}{\eta} \ln m - n \ln n - \frac{1}{\eta}(m - \eta n) \ln(m - \eta n) \tag{13}$$

provided m and n are sufficiently large to warrant Stirling's approximation. The "stochastic" entropy (13) has the same functional dependence on n that the entropy (12) has upon $\bar{n}^s$. The symmetry between expressions in equations (12) and (13) maximizes the probability distributions f_η^s, when n coincides with $\bar{n}^s$, the average value, which is also the most probable value. This is fundamental to statistical mechanics, since it is responsible for there being a single thermodynamics rather than a separate thermodynamics for the microcanonical and canonical ensembles (Greene and Callen, 1951). Therefore, the binomial and negative binomial distributions are the *laws of error* giving the probabilities for deviations from the FD and BE statistics, respectively. We now want to determine these statistical distributions by making appeal to the second law.

In addition to the average number of particles, the thermodynamic entropy will be a function of the volume V and average energy $\bar{\mathscr{E}}$ which, if the particle energy is ε, will be given by $\bar{\mathscr{E}} = \bar{n}^s \varepsilon$. At constant volume, we have

$$\left(\frac{\partial S}{\partial \bar{n}^s}\right)_V = \left(\frac{\partial S}{\partial \bar{n}^s}\right)_{\bar{\mathscr{E}},V} + \left(\frac{\partial S}{\partial \bar{\mathscr{E}}}\right)_{\bar{n}^s,V} \frac{d\bar{\mathscr{E}}}{d\bar{n}^s} = \frac{-\mu + \varepsilon}{T} \tag{14}$$

in accordance with the second law, where μ is the chemical potential and T is the absolute temperature, measured in energy units. The notation used in equation (14) merits a word of comment. On the left-hand side, S is actually expressed in terms of $\bar{n}^s$ and V with $\bar{\mathscr{E}}$ being replaced by $\bar{n}^s\varepsilon$, while, on the right-hand side, S is expressed in its original form, as a function of n, $\bar{\mathscr{E}}$, and V. The first term is due to the explicit variation of $\bar{n}^s$

with the other variables $\bar{\mathscr{E}}$ and V held constant: The second term adds the contribution of the intermediate variable $\bar{\mathscr{E}}$.

The condition that the derivative of the *statistical* entropy (12) with respect to $\bar{n}^s$ coincide with that of the *thermodynamic* entropy given by (14) is

$$\bar{n}^s = \frac{m}{e^{(\varepsilon-\mu)/T} + \eta} \tag{15}$$

which, for $\eta = 1$, is the FD distribution, while for $\eta = -1$, it is the BE distribution. Both FD and BE statistics give

$$\beta/\alpha = e^{-(\varepsilon-\mu)/T} \tag{16}$$

Introducing (15) into (11) and comparing it with the logarithm of the stationary distribution (3), we get

$$S - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V \bar{n}^s = \frac{m}{\eta}\ln(1 + \eta e^{-(\varepsilon-\mu)/T}) = -\ln f_\eta^s(0) \tag{17}$$

in view of (16). Using the thermodynamic relation $TS = \bar{\mathscr{E}} - \eta\bar{n}^s + PV$, this expression can be written as

$$PV = T\frac{m}{\eta}\ln[1 + \eta e^{-(\varepsilon-\mu)/T}] \equiv T \ln \Xi_\eta \tag{18}$$

where, for $\eta = 1$, Ξ_η is the grand partition function for FD statistics, while for $\eta = -1$, it is the grand partition function for BE statistics.

For FD statistics, the stationary probability distribution (3) is the binomial distribution $f_1^s(n) = \binom{m}{n} p^n q^{m-n}$ with *a priori* probabilities p and q such that $p + q = 1$. In view of equations (3) and (16), we observe that the *a priori* probabilities are equal when $\varepsilon = \mu$, implying from (15) that $m = 2\bar{n}^s$. The entropy attains its maximum value $S_1 = m \ln 2$, which means that FD particles, such as electrons, are near the Fermi level and are equally as likely to be found above and below this level. The novelty here is in showing that this state corresponds to that of maximum entropy. No such state of maximum entropy can occur for BE statistics because $\mu < 0$ in equation (15), for otherwise the average number of particles would be negative in the lowest energy level $\varepsilon = 0$.

In the case of photons, we must set $\mu = 0$ in equation (15), which is commonly attributed to the fact that the photon number is not conserved, and $\varepsilon = h\nu$. However, since photons do not interact with each other, they cannot arrive at equilibrium by themselves (Würfel, 1982). For blackbody radiation, the photon chemical potential, equal to the difference of the electrochemical potentials of the two energy levels, vanishes because there is a uniform electrochemical potential of the electron system. Therefore, for blackbody radiation, expression (16) reduces to $\beta/\alpha = e^{-h\nu/T}$, which is in disaccord with Einstein's condition (1917) $\alpha = \beta$ for any two levels with the same statistical weights.

Multiplying both sides of $\bar{n}^s = \gamma/(\alpha - \beta)$ by $h\nu$ and rearranging gives

$$\alpha\bar{\mathscr{E}} = \beta\{\bar{\mathscr{E}} + mh\nu\} \tag{19}$$

where $m = 8\pi\nu^2/c^3$ is the number of oscillators per unit volume and c is the velocity of light. Rather, Einstein's (1917) condition of dynamical equilibrium is

$$\alpha\bar{\mathscr{E}} = e^{-h\nu/T}\beta\{\bar{\mathscr{E}} + mh\nu\} \tag{20}$$

for states with equal statistical weights. In order to eliminate one of the coefficients so that the other two appear only in a ratio, which could then be compared with the corresponding term in Planck's formula, Einstein (1917) assumed that $\bar{\mathscr{E}} \to \infty$ with T and obtained $\alpha = \beta$. He then substituted this back into equation (20) and compared it with Planck's law to determine the value of γ/α. However, there is no justification for introducing the asymptotic relation $\beta/\alpha = 1$, derived from (20) in the limit as $T \to \infty$, back into the same relation, which is valid for *any* T.

4. LIMITING DISTRIBUTION AND CLASSICAL DISTINGUISHABILITY

Casting the Poisson distribution in the form of the law of error equation (11) yields a statistical entropy function $S(\bar{n}^s) = \bar{n}^s - \bar{n}^s \ln \bar{n}^s$. However, such an entropy function is not *extensive*. The extensive property requires the entropy per "cell" (or oscillator) S/m to be a function of the average occupation index $\bar{n}^s/m$ only. In order to render the entropy extensive, the term $\bar{n}^s \ln m$ must be added to the entropy expression. But this is precisely the contribution to the entropy that would come from the permutation of $\bar{n}^s$ *distinguishable* particles among m cells for which there are $m^{\bar{n}^s}$ distinct arrangements. Hence, the statistical entropy is

$$S_0(\bar{n}^s) = \bar{n}^s - \bar{n}^s \ln \bar{n}^s + \bar{n}^s \ln m + \text{const.} \tag{21}$$

and equating its derivative with (14) gives

$$\bar{n}^s = e^{-(\varepsilon-\mu)/T} m \tag{22}$$

which is the MB distribution.

Equating the logarithm of (6) with (11), where the entropy is given by (21), and solving for the stochastic entropy yields

$$\Sigma_0(n) = n - n \ln\left(\frac{n}{m}\right) = \ln\left(\frac{m^n}{n!}\right) \tag{23}$$

where the second equality follows from Stirling's approximation for n sufficiently large. The statistical entropy (21) is the same function of $\bar{n}^s$ that the stochastic entropy (23) is of n. Thus, when n coincides with its average value $\bar{n}^s$, the stationary probability distribution $f^s(n)$ is maximized, making $\bar{n}^s$ the most probable value of n. Consequently, the Poisson distribution is the limiting form of the law of error leading to the average value as the most probable value.

It will now be appreciated that our approach is diametrically opposite to that of Gibbs, who found it necessary to divide the number m^n of possible arrangements by $n!$, which is the number of permutations of n *identical* particles. The stochastic entropy (23) is essentially the logarithm of the statistical weight $\Delta\Gamma = m^n/n!$. The factor $(n!)^{-1}$ is necessary to make the stochastic entropy an extensive quantity or, equivalently, $(\bar{n}^s!)^{-1}$ makes the statistical entropy extensive in the Gibbs formulation. It is rather surprising that for the same pragmatic reason, we have found it necessary to introduce the term $\bar{n}^s \ln m$ into the entropy expression which was obtained from the probability distribution (6) as the limit of the distributions (3) for *indistinguishable* particles.

For sufficiently large n, the logarithm of the Poisson distribution (6) can be written as

$$\ln f_0^s(n) = n \ln\left(\frac{\bar{n}^s}{n}\right) + (n - \bar{n}^s) \tag{24}$$

As a first approximation to $\ln(\bar{n}^s/n)$ we may use the mean of its upper and lower bounds; that is,

$$\ln\left(\frac{\bar{n}^s}{n}\right) \approx \tfrac{1}{2}[(\bar{n}^s - n)/\bar{n}^s + (\bar{n}^s - n)/n]$$

The approximation is better the closer $\bar{n}^s/n$ is to one. In this approximation,

$$f_0^s(n) \approx \exp[-(n - \bar{n}^s)^2/2\bar{n}^s] \tag{25}$$

which is the normal approximation to the Poisson distribution having the same mean and variance, $\bar{n}^s$.

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