

Supercanonical probability distributions

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The canonical probability distribution describes a system in thermal equilibrium with an infinite heat bath. When the bath is finite the distribution is modified. These modifications can be derived by truncating a Taylor-series expansion of the entropy of the heat bath, but their form depends on the expansion parameter chosen. We consider two such expansions, which yield *supercanonical* (i.e., higher-order canonical) distributions of exponential and power-law form. The latter is identical in form to the “Tsallis distribution,” which is therefore a valid asymptotic approximation for an arbitrary finite heat bath, but bears no intrinsic relation to Tsallis entropy.

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The probability that a system in thermal equilibrium with an infinite heat bath occupies microstate i is given by the canonical distribution

$$p_i = Z^{-1} \exp\{-\beta E_i\}, \quad (1)$$

where E_i is the energy of microstate i , $\beta = 1/T_b$, T_b is the temperature of the heat bath in energy units, and $Z(\beta) \equiv \sum_i \exp\{-\beta E_i\}$ is the canonical partition function. Equation (1) is widely regarded as the single most important formula in statistical physics. Our purpose here is to explore the corrections or modifications to it that arise when the heat bath is finite. Such corrections represent an important aspect of the thermodynamics and statistical mechanics of small systems [1–3], which are experiencing a lively renaissance (e.g., [4–8]) stimulated in part by rapid advances in nanotechnology. Much of the literature on finite heat baths has been narrowly focused on the observation that simple ideal heat baths imply power-law probability distributions of the same form as those obtained by extremizing the Tsallis entropy [9–11]. This correspondence has often been interpreted as evidence in support of the Tsallis entropy, but that inference is unjustified [12].

The probability distribution for a system in thermal equilibrium with a finite heat bath is fundamentally given by [13–15]

$$p_i = \frac{W_b(E_0 - E_i)}{\sum_j W_b(E_0 - E_j)}, \quad (2)$$

where E_0 is the total energy of the system and bath together, and $W_b(E)$ is the number of bath states with energies in the interval $(E, E + \Delta E)$, where ΔE is a macroscopically small but finite energy tolerance. Equation (2) is based on the hypothesis of equal *a priori* probabilities, according to which those bath states are presumed to be equally probable, and the further presumption that the heat bath is sufficiently large and complex that $W_b(E) \cong \omega_b(E) \Delta E$, where $\omega_b(E)$ is a differentiable continuous approximation to the true discontinuous density of bath states [15]. If the heat bath were isolated with energy E , its entropy S_b , temperature T_b , and heat capacity C_b would be given by

$$S_b(E) = \log W_b(E), \quad (3)$$

$$\frac{1}{T_b(E)} = \frac{\partial S_b}{\partial E}, \quad (4)$$

and $C_b(E) \equiv (\partial T_b / \partial E)^{-1}$. Note that entropy is dimensionless when temperature is expressed in energy units, which is formally equivalent to replacing Boltzmann’s constant by unity. If the heat bath is a proper thermodynamic system, then as it becomes infinitely large $T_b(E)$ will approach a finite limiting value, while E itself and $C_b(E)$ become infinite. The latter divergence reflects the fact that it requires infinite energy to produce a finite change in the temperature of an infinite system.

The standard derivation of the canonical distribution from Eq. (2) is based on the assumption that the heat bath is much larger than the system, so that $E_i \ll E_0$ and a Taylor series expansion of $S_b(E_0 - E_i) = \log W_b(E_0 - E_i)$ in powers of E_i can reasonably be presumed to converge rapidly [13]. Equation (1) is then an immediate consequence of truncating this expansion at the linear term [13–15]. However, this procedure further implies that Eq. (1) is not exact but is in principle modified by the higher-order terms in the expansion, at least for finite values of E_0 . It is instructive and enlightening to examine the form of those modifications when the quadratic term of order E_i^2 [13–16] is retained. Thus we proceed to explore the implications of the approximation

$$S_b(E_0 - E_i) = S_b(E_0) - \beta_1 E_i - \beta_2 E_i^2, \quad (5)$$

where

$$\beta_1 \equiv \left(\frac{\partial S_b}{\partial E} \right)_0 = \frac{1}{T_b^0}, \quad (6)$$

$$\beta_2 \equiv -\frac{1}{2} \left(\frac{\partial^2 S_b}{\partial E^2} \right)_0 = \frac{\beta_1}{2C_b^0 T_b^0}, \quad (7)$$

subscript zero denotes evaluation at $E = E_0$, $T_b^0 \equiv T_b(E_0)$, and $C_b^0 \equiv C_b(E_0)$. Combining Eqs. (2), (3), and (5), we obtain

$$p_i = Z_2^{-1} \exp\{-\beta_1 E_i - \beta_2 E_i^2\}, \quad (8)$$

where

$$Z_2(\beta_1, \beta_2) \equiv \sum_i \exp\{-\beta_1 E_i - \beta_2 E_i^2\}. \quad (9)$$

It follows from Eq. (7) that β_2 vanishes for an infinite heat bath, whereupon $Z_2(\beta_1, \beta_2)$ reduces to $Z(\beta)$ and Eq. (8) reduces to Eq. (1). If higher-order terms had been retained in Eq. (5),

they too would clearly vanish in the same limit. The canonical distribution therefore becomes exact when the heat bath is infinite, but not otherwise. Its universality derives from the fact that the only bath parameter it depends upon is the temperature.

According to Eq. (8), the probabilities p_i are unequal, so the entropy S of the system must be evaluated as the Boltzmann-Gibbs-Shannon (BGS) entropy

$$S = - \sum_i p_i \log p_i, \quad (10)$$

which contrary to a common misconception is not uniquely or inherently associated with a canonical (or any other) probability distribution [15]. Combining Eqs. (8) and (10), we obtain

$$S = \beta_1 \bar{E} + \beta_2 \bar{E}^2 + \log Z_2, \quad (11)$$

where $\bar{Q} \equiv \langle Q_i \rangle \equiv \sum_i p_i Q_i$. When $\beta_2 = 0$, Eq. (11) reduces to the standard canonical expression for the entropy S . The quadratic term in Eq. (5) therefore introduces an additional term $\beta_2 \bar{E}^2$ into the entropy of the system. It follows from Eq. (9) that

$$\frac{\partial \log Z_2}{\partial \beta_1} = - \bar{E}, \quad (12)$$

$$\frac{\partial \log Z_2}{\partial \beta_2} = - \bar{E}^2, \quad (13)$$

which combine with Eq. (11) to imply that

$$dS = \beta_1 d\bar{E} + \beta_2 d\bar{E}^2. \quad (14)$$

Note, however, that \bar{E}^2 is not an independent variable, because \bar{E} and \bar{E}^2 are both functions of E_0 , so $d\bar{E}$ and $d\bar{E}^2$ are both simply proportional to dE_0 and therefore to each other. Thus dS is simply proportional to $d\bar{E}$, so that the second law of thermodynamics remains valid in the form $d\bar{E} = T dS$, which defines and determines the temperature T of the system. Thus

$$\frac{1}{T} = \frac{dS}{d\bar{E}} = \beta_1 + R\beta_2 = \frac{1}{T_b^0} \left(1 + \frac{R}{2C_b^0 T_b^0} \right), \quad (15)$$

where

$$R \equiv \frac{d\bar{E}^2}{d\bar{E}} = \frac{d\bar{E}^2/dE_0}{d\bar{E}/dE_0}. \quad (16)$$

The parameters β_1 and β_2 are functions of E_0 via Eqs. (6) and (7), so T can be evaluated by substituting Eq. (9) into Eqs. (12) and (13), differentiating the results with respect to E_0 using the chain rule, substituting the resulting expressions for $d\bar{E}/dE_0$ and $d\bar{E}^2/dE_0$ into Eq. (16) to obtain R , and combining the result with Eq. (15). Unfortunately, the resulting expression for T is so complicated that it does not seem useful or enlightening. Note, however, that Eq. (15) implies that $T \neq T_b^0$ unless the heat bath is infinite, in which case $\beta_2 \rightarrow 0$ and $C_b^0 \rightarrow \infty$ as discussed above.

The truncated series expansion in Eq. (5) could readily be extended to higher order if desired, but the resulting formalism rapidly becomes so cumbersome that it seems unlikely to be useful. It is more fruitful to observe that E_i is not the only possible variable in powers of which $S_b(E_0 - E_i)$ might usefully be approximated by a truncated Taylor series. As is well known,

$W_b(E)$ in finite ideal systems, such as ideal gases or harmonic solids, is typically proportional to E^α , where the exponent α is on the order of the number of particles or degrees of freedom of the system [9,13–15]. This suggests that faster convergence might be obtained by regarding $S_b(E) = \log W_b(E)$ as a function of $\log E$ rather than E itself. We therefore proceed to approximate $S_b(E) - S_b(E_0)$ by a truncated Taylor series expansion in powers of $\log E - \log E_0$. Since E_0 will remain large but finite, the lowest-order correction to the canonical distribution is obtained by truncating the expansion at the linear term. Thus we write

$$\begin{aligned} S_b(E) &= S_b(E_0) + \alpha(\log E - \log E_0) \\ &= S_b(E_0) + \log \left(\frac{E}{E_0} \right)^\alpha, \end{aligned} \quad (17)$$

where

$$\alpha \equiv \left(\frac{\partial S_b}{\partial \log E} \right)_0 = E_0 \left(\frac{\partial S_b}{\partial E} \right)_0 = E_0 \beta_1 = \frac{E_0}{T_b^0} \quad (18)$$

and use has been made of Eq. (6). Combining Eqs. (2), (3), (17), and (18), we obtain

$$p_i = \widehat{Z}^{-1} \left(1 - \frac{\beta_1 E_i}{\alpha} \right)^\alpha, \quad (19)$$

where

$$\widehat{Z}(\alpha, \beta_1) \equiv \sum_j \left(1 - \frac{\beta_1 E_j}{\alpha} \right)^\alpha. \quad (20)$$

Aside from minor notational differences, Eq. (19) is of precisely the same form as the so-called Tsallis distribution previously obtained by extremizing the Tsallis entropy [17], and subsequently legitimized by the observation that it describes a system in equilibrium with an ideal finite heat bath for which $W_b(E)$ has the same power-law form [9]. The present derivation shows that this distribution is actually much more general: it is not restricted to ideal heat baths but rather represents a first-order asymptotic approximation to $S_b(E)$ for an arbitrary finite heat bath with an arbitrary quasicontinuous density of states. This derivation also provides exact expressions for the parameters α and β_1 in terms of the caloric equation of state $T_b(E)$ of the heat bath and the total energy E_0 . Moreover, the systematic expansion procedure on which this approximation is based could in principle be extended to higher order to generate a sequence of increasingly accurate controlled approximations.

The general validity of Eq. (19) as an asymptotic approximation to p_i for an arbitrary finite heat bath, together with the associated exact expressions for the parameters α and β_1 therein, constitute the principal result of this Rapid Communication. This result implies that the power-law probability distribution of Eq. (19) is no less general, and indeed is quite likely more accurate for finite E_0 , than the usual canonical distribution of Eq. (1), to which Eq. (19) clearly reduces in the limit $\alpha \rightarrow \infty$ or $E_0 \rightarrow \infty$. Thus, in spite of their quite different mathematical character, Eqs. (1) and (19) are birds of a feather; they are both based on truncating a Taylor series expansion of $S_b(E)$ about the point $E = E_0$ at the linear term, but with respect to different variables.

Unfortunately, the thermodynamic relations implied by the power-law distribution of Eq. (19) are more complicated than those for the exponential distribution of Eq. (8). Combining Eqs. (10) and (19), we obtain

$$S = -\alpha \left\langle \log \left(1 - \frac{\beta_1 E_i}{\alpha} \right) \right\rangle + \log \widehat{Z}. \quad (21)$$

It follows from Eqs. (19) and (20) that

$$\frac{\partial \log \widehat{Z}}{\partial \alpha} = \left\langle \log \left(1 - \frac{\beta_1 E_i}{\alpha} \right) \right\rangle + \frac{\beta_1}{\alpha} \left\langle \frac{E_i}{1 - \beta_1 E_i / \alpha} \right\rangle, \quad (22)$$

$$\frac{\partial \log \widehat{Z}}{\partial \beta_1} = - \left\langle \frac{E_i}{1 - \beta_1 E_i / \alpha} \right\rangle. \quad (23)$$

Combining Eqs. (21)–(23), we obtain

$$S = -\alpha \frac{\partial \log \widehat{Z}}{\partial \alpha} - \beta_1 \frac{\partial \log \widehat{Z}}{\partial \beta_1} + \log \widehat{Z}. \quad (24)$$

As before, the temperature T of the system could in principle be evaluated as $T = (dS/d\overline{E})^{-1}$, where S is given by Eq. (24), but the result is again so complicated that it seems of dubious utility or interest. Of course, there is no need to evaluate T in order to make use of the probability distribution of Eq. (19); it must simply be remembered that according to Eq. (6) the parameter β_1 is fundamentally related to the temperature $T_b^0 = T_b(E_0)$ of the heat bath evaluated at the total energy E_0 , and not to the temperature T of the system itself.

As is well known, the canonical distribution of Eq. (1) satisfies and can be derived from a principle of maximum entropy [15,18,19], so the question naturally arises as to whether the supercanonical distributions of Eqs. (8) and (19) can likewise be derived from such a principle. The answer is a qualified “yes,” but it must be kept in mind that the probability distribution p_i is fundamentally determined by Eq. (2), the validity of which is neither derived from nor contingent on a maximum entropy principle. On the contrary, maximum entropy principles derive their validity from the probability

distribution, not vice versa [20], and they obviously depend critically on both the form of the entropy and the constraints imposed upon its maximization. The present development is based on the BGS entropy S of Eq. (10), which we regard as sacrosanct, but the probability distribution obtained by maximizing it still depends upon the constraints. When the only constraint (apart from normalization) is on the value of the mean energy $\overline{E} = \langle E_i \rangle$, the canonical distribution of Eq. (1) results. It is easy to verify that the exponential supercanonical distribution of Eq. (8) results when an additional constraint is imposed on the mean-square energy $\overline{E^2} = \langle E_i^2 \rangle$. This is simply the second-order special case of the maximum entropy method of moments [21]. It is also easy to verify that the power-law supercanonical distribution of Eq. (19) results when S is maximized subject to a constraint on the value of $\langle \log(E_0 - E_i) \rangle$, but the physical significance of that unusual constraint is not immediately obvious (cf. [22]). Of course, it is well known that Eq. (19) can also be obtained by maximizing the Tsallis entropy subject to a conventional constraint on \overline{E} [17]. However, the fundamental significance of that result seems dubious, because it is straightforward to determine a function $\sigma(p)$ such that the extremization of $\sum_i \sigma(p_i)$ subject to a constraint on \overline{E} will reproduce an arbitrary probability distribution of the form $p_i = p(E_i)$. Any monotonic function of $\sum_i \sigma(p_i)$ then defines an “entropy” with the same extremum property. It is straightforward to confirm that the Tsallis and Rényi entropies can be constructed from Eq. (19) in precisely this way, but this is a mere mathematical exercise with no physical content.

Finally, we emphasize that the deviations from the canonical distribution that occur when the heat bath is finite do not in any sense invalidate or necessitate modifications to or “generalizations” of the BGS entropy of Eq. (10), as has often been suggested by the advocates of Tsallis entropy. The terminology “Tsallis distribution” therefore seems unfortunate and inappropriate, since the power-law distribution of Eq. (19) does not depend in any way on the Tsallis entropy for its general validity or significance.

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