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Thermoequilibrium statistics for a finite system with energy nonextensivity

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A first-principles derivation is presented of canonical distributions for a finite thermostat taking into account nonextensive energy. Parameterizing this energy by λ, we derive an explicit form for the distribution functions by regulating λ, and then explore the nontrivial relationship between these functions and energy nonextensivity, as well other system parameters such as system size. A variational entropy function is also derived from these distribution functions..

finite system, energy nonextensivity, first-principles method, canonical distribution function

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Studies into the family of small or finite-size systems reveal that these systems show complex statistical characteristics very different from large systems, and expose failings in our understanding of thermostatistics for finite systems and their nonequilibrium dynamics [1–4]. One of these characteristics is nonextensivity (refer to [2] and references therein for examples), which means that macroscopic quantities of such systems may not be proportional to system size. A thermodynamic quantity of a nonextensive system is called nonadditive if this quantity is not the sum of that of its subsystems. Nonextensivity might arise from surface effects or interactions between subsystems. Thus, extensive energy and entropy may become inappropriate in treating finite systems.

There has already been much discussion on the properties of finite systems that has raised many questions and controversies [5–7]. To describe the behaviors of these systems, one point worth noting is that the Boltzmann-Gibbs statistical mechanics, which is based on the concept of extensive entropy, is not applicable [1,8,9]. Consequently, it is questionable to assume an exponential distribution for finite systems. Therefore, one of the first things to work out for a statistical description of finite systems is to find the appropriate probability distribution. Some published results obtained by first principles (see [8] for example) have shown that a small system, in equilibrium with a finite reservoir, may follow a q-exponential distribution of nonextensive statistical mechanics (NSM), as proposed by Tsallis [9]. This NSM has been used widely in many areas, and considered effective in solving many physical problems [10–13]. Results from mathematical proofs are able to demonstrate a connection between the system's finiteness and nonextensivity of the theory. However, most proofs have relied on the additivity of energy. Clearly, for large systems, this assumption is acceptable and provides a helpful approximation in obtaining the statistics in the thermodynamic limit. The assumption is, however, questionable when establishing statistics for finite systems. Related problems arising from this additive energy assumption can be found in [14–17].

Work in [18] represents a first attempt to build statistics for finite systems based on energy nonadditivity. A result proved in this work was that additive energy is unnecessary in the development of a NSM for small systems by mean field theory. In our present work, we follow on from [18], and provide results that have greater generality. We have introduced the high-temperature approximation for the sake of simplicity. In the following sections, the possible canoni-

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cal distribution and thermodynamic entropy are derived. Based on the results from these calculations, a summary and some interesting inferences are given.

1 Probability distribution for the model

We present here introductory material and brief outlines of proofs required in later sections. As in [19], let us begin with an adiabatically and mechanically isolated system Σ, with finite N particles and energy E. The probability distribution function can be given by

$$p(X)=\frac{1}{\Omega(E)}\delta[E-H(X)]. \tag{1}$$

Next, divide this system into two interacting subsystems Σ_1 and Σ_2 with Hamiltonians $H_1(X_1)$ and $H_2(X_2)$. Assuming the nonadditive rule of energy suggested in [20,21], we can write the energy of the system as

$$\begin{aligned}H(X)&=H(X_1,X_2)\\&=H_1(X_1)+H_2(X_2)+\lambda H_1(X_1)H_2(X_2),\end{aligned} \tag{2}$$

where λ is a coupling constant, which denotes the nonextensivity of the system. Here is the generalized form of the additive energy; $\lambda H_1(X_1)H_2(X_2)$ is the interaction energy between Σ_1 and its thermostat system Σ_2. Obviously, we still have the assumption $H_1(X_1)\ll E$, even if the thermodynamic limit $N\to\infty$ is invalid. If we substitute eq. (2) into eq. (1), the probability distribution of Σ_1 is given by

$$\begin{aligned}p(X_1)&=\frac{1}{\Omega(E)}\int_{(X_2)}\delta[E-H_1(X_1)-H_2(X_2)\\&\quad-\lambda H_1(X_1)H_2(X_2)]\mathrm{d}X_2\\&=\frac{1}{\Omega(E)}\int_{(X_2)}\delta\{E-H_1(X_1)\\&\quad-[1+\lambda H_1(X_1)][K(P_2)+V(R_2)]\}\mathrm{d}X_2\\&=\frac{1}{\Omega(E)}\int_{(R_2)}\Omega_k\{E-H_1(X_1)\\&\quad-[1+\lambda H_1(X_1)]V(R_2)\}\mathrm{d}R_2,\end{aligned} \tag{3}$$

where $K(P_2)$ is the kinetic energy and $V(R_2)$ is the potential energy of the particles in the thermostat system, with the set of momenta and coordinates denoted by P_2 and R_2, respectively. For simplicity, we let H_1, H_2 and H represent $H_1(X_1)$, $H_2(X_2)$, and $H(X)$ in the following work. Hence $\Omega_k\{\bullet\}$ can be given in the form

$$\Omega_k\{y\}=\int_{(P_2)}\delta[y-u(\lambda,H_1,P_2)]\mathrm{d}P_2, \tag{4}$$

in which we have set $y=E-H_1-(1+\lambda H_1)V(R_2)$ and $u(\lambda,H_1,P_2)=[1+\lambda H_1(X_1)]K(P_2)$. Here $\Omega_k\{y\}$ can be regarded as the hyper-surface corresponding to u=y. Naturally, it is equal to the derivation of the hyper-volume of the momentum space associated with P_2 by the quantity $u(\lambda,H_1,P_2)$, i.e. $\Omega_k\{y\}=\partial\Gamma_k/\partial y$ with

$$\Gamma_k(y)=\int_{u\leqslant y}\mathrm{d}P_2. \tag{5}$$

After introducing new variables,

$$D_k=\sqrt{\frac{1+\lambda H_1}{2m_n}}(\overrightarrow{P_\alpha})_n, \tag{6}$$

with k=3(n−1)+α and the mass of n-th particle m_n, the equation u=y can be written as $\sum_{k=1}^{3N_2}D_k^2=y$. The integration (4) finally gives

$$\Omega_k\{y\}=b\left(\frac{2m}{1+\lambda H_1}\right)^{\frac{3N_2}{2}}y^{\frac{3N_2}{2}-1}. \tag{7}$$

Here b depends only on N_2. Thus, we can get the following distribution:

$$\begin{aligned}p(X_1)&=\frac{b}{\Omega}(1+\lambda H_1)^{-\frac{3N_2}{2}}\\&\quad\times\int\{E-H_1-[1+\lambda H_1]V(R_2)\}^{\frac{3N_2}{2}-1}\mathrm{d}R_2\\&=\frac{b}{\Omega}(1+\lambda H_1)^{-\frac{3N_2}{2}}(E-H_1)^{\frac{3N_2}{2}-1}\\&\quad\times\int\left[1-\frac{1+\lambda H_1}{E-H_1}V(R_2)\right]^{\frac{3N_2}{2}-1}\mathrm{d}R_2,\end{aligned} \tag{8}$$

where b/Ω is the normalization constant if the mass of the particle is fixed. This equation is exact, because we have not made any approximation so far. For an adiabatically system, it is easy to see the following relationship:

$$\frac{1+\lambda H_1}{E-H_1}V(R_2)=\frac{1+\lambda H_1}{H-H_1}V=\frac{V}{H_2}. \tag{9}$$

If the high-temperature approximation is introduced, we immediately get H_2>>$V(R_2)$, which indicates that the kinetic energy is much greater than the potential energy. Next, the integral in eq. (8) can be expanded as follows:

$$\begin{aligned}&\int\left[1-\frac{1+\lambda H_1}{E-H_1}V(R_2)\right]^{\frac{3}{2}N_2-1}\mathrm{d}R_2\\&=\int\left[1-\left(\frac{3}{2}N_2-1\right)\frac{1+\lambda H_1}{E-H_1}V(R_2)\right]\mathrm{d}R_2\\&=V^{N_2}-\left(\frac{3}{2}N_2-1\right)\frac{1+\lambda H_1}{E-H_1}\int V(R_2)\mathrm{d}R_2,\end{aligned} \tag{10}$$

where V represents the volume of the system. Considering the result above, the energy distribution function for finite systems can be written as

$$p(\epsilon) \propto (1+\lambda\epsilon)^{-\frac{3N_2}{2}}(E-\epsilon)^{\frac{3N_2}{2}-1}\left[1-\left(\frac{3N_2}{2}-1\right)\frac{1+\lambda\epsilon}{E-\epsilon}k\right]. \quad (11)$$

Here, we have replaced H_1 by ε and $k=\int V(R_2)\mathrm{d}R_2/V^{N_2}$ which include potential energy contributions. Moreover, we will find that $\frac{1+\lambda\epsilon}{E-\epsilon}k \ll 1$ obtained in the high-temperature approximation. By employing the same trick as eq. (10), eq. (11) can be replaced by

$$p(\epsilon) \propto (1+\lambda\epsilon)^{-\frac{3N_2}{2}}(E-\epsilon)^{\frac{3N_2}{2}-1}\left(1-\frac{1+\lambda\epsilon}{E-\epsilon}k\right)^{\frac{3N_2}{2}-1}. \quad (12)$$

Thus, the final distribution can be given as

$$p(\epsilon) \propto (1+\lambda\epsilon)^{-\frac{3N_2}{2}+1}\left(1-\frac{1+k\lambda}{E-k}\epsilon\right)^{\frac{3N_2}{2}-1}. \quad (13)$$

In the above derivation, we have taken $\frac{3N_2}{2} \simeq \frac{3N_2}{2}-1$. From eq. (13), we conclude that the distribution of a finite system with nonadditive energy is dependent on the size of the system and the nonextensive parameter. Having assumed that $\epsilon \ll E$, we can expand $\left(1+\lambda E\frac{\epsilon}{E}\right)^{-1}$ to the first order, as long as the factor λE is not much larger than 1, implying that the nonextensive energy $\lambda H_1 H_2$ is relatively small compared with H_2. Thus, we obtain

$$p(\epsilon) \propto \left[1-\frac{\lambda E+1}{E-k}\epsilon\right]^{\frac{3N_2}{2}-1}. \quad (14)$$

In seeking to explicitly reveal the influence of nonextensivity, we neglect the potential energy to reduce the complexity of the equation; i.e. we are considering the distribution for an ideal non-interacting classical system. Hence the final distribution eq. (13) reduces to

$$p(\epsilon) = C\left[1-\frac{\lambda E+1}{E}\epsilon\right]^{\frac{3N_2}{2}-1}, \quad (15)$$

where C is a normalization constant. Moreover, because interactions are ignored, it is reasonable to assume that $E=\frac{3N_2}{2}\theta$, where $\theta/2$ represents the mean kinetic energy per degree of freedom in the reservoir. By employing the normalization condition

$$\int_0^E p(\epsilon)\mathrm{d}\epsilon = 1, \quad (16)$$

one can easily get the expression for C. Figure 1 shows curves of the probability distribution in eq. (15).

These curves suggest that probabilities associated with for high-energy states increases as nonextensive energy declines. If λ=0, curves reduce to exponential decays as $N_2 \to \infty$. However, if $\lambda \neq 0$, no trend to a Boltzmann distribution will occur because of nonextensive energy considerations.

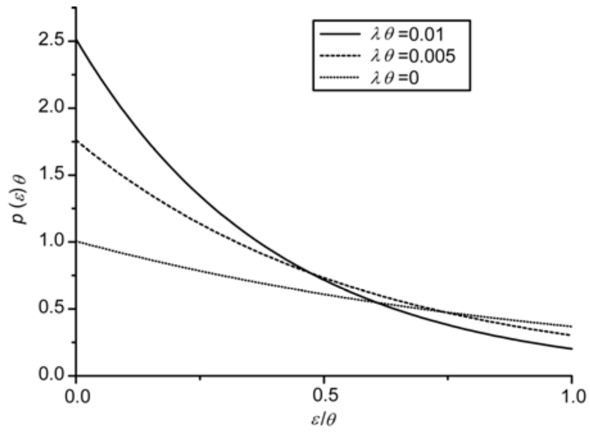

Figure 1 Probability distribution versus energy for fixed particle number N_2=100 and different values of $\lambda\theta$.

Notably, for weak potential energy, we can derive this energy distribution in an alternative way. Adopting the conclusion of [16], we get

$$p(X_1) = C\left[1-\frac{H_1(X_1)}{E}\right]^{\frac{3N_2}{2}-1}. \quad (17)$$

As is discussed above, both H_1 and $\lambda H_1 H_2$ are much smaller than H_2, and hence we obtain the conclusion that $E \simeq H_2$. Imposing this constraint, we can rewrite the Hamiltonian in eq. (2) as

$$H(X) = H(X_1, X_2) = H_1'(X_1) + H_2(X_2), \quad (18)$$

where $H_1'(X_1) = (1+\lambda E)H_1(X_1)$. If we substitute $H_1'(X_1)$ for the $H_1(X_1)$ in eq. (17), the original distribution transforms exactly into the form of eq. (15), which justifies eq. (15) from another standpoint. The above calculations suggest that NSM distributions for small systems based on nonadditive energy exist. Additionally, as we have not taken account of specific forms of interactions, this distribution might be applicable for various specific forms of the potential energy.

2 Entropy function in ideal case

With entropy as defined in [22] as a measure of disorder or randomness in a thermodynamic system, we can give the thermodynamic entropy by a variational relation:

$$\mathrm{d}S = \beta(\mathrm{d}\overline{\epsilon} - \overline{\mathrm{d}\epsilon}), \quad (19)$$

where β is the inverse temperature. This expression for the variation in entropy can be viewed as a generic entropy definition of an uncertainty measure, and the specific form can be derived from this entropy expression if the probability distribution is given. Let $\{p_i\}$ be the set of probabilities corresponding to the spectrum $\{\varepsilon_i\}$. In the ideal case, we can write the probability distribution for a finite system with nonadditive energy as

$$p_i = p(\epsilon_i) = \frac{1}{Z}\left(1 - \frac{1+\lambda E}{E}\epsilon_i\right)^{\frac{3N_2}{2}-1}, \quad (20)$$

where Z is given in the form

$$Z = \sum_i \left(1 - \frac{1+\lambda E}{E}\epsilon_i\right)^{\frac{3N_2}{2}-1}. \quad (21)$$

From the definition eq. (19)

$$\mathrm{d}S = \beta(\mathrm{d}\overline{\epsilon} - \overline{\mathrm{d}\epsilon}) = \beta \sum_i \epsilon_i \mathrm{d}p_i, \quad (22)$$

where ε_i (p_i) can be solved from the energy probability distribution eq. (20)

$$\epsilon_i(p_i) = \frac{E}{1+\lambda E}\left[1 - (p_i Z)^{\frac{2}{3N_2-2}}\right], \quad (23)$$

we have a very specific form for the entropy, namely

$$\mathrm{d}S = \beta \frac{E}{\lambda E+1}\sum_i \mathrm{d}p_i - \beta \frac{E}{\lambda E+1}\sum_i (p_i Z)^{\frac{2}{3N_2-2}}\mathrm{d}p_i. \quad (24)$$

Considering the variational condition $\sum_i \mathrm{d}p_i = 0$, obtained from $\sum_i p_i = 1$, one can get

$$\mathrm{d}S = -\beta \frac{E}{\lambda E+1} Z^{\frac{2}{3N_2-2}} \sum_i p_i^{\frac{2}{3N_2-2}} \mathrm{d}p_i. \quad (25)$$

After integration, the expression for entropy is

$$S = -\beta \frac{E}{\lambda E+1} Z^{\frac{2}{3N_2-2}} \sum_i \frac{3N_2-2}{3N_2} p_i^{\frac{3N_2}{3N_2-2}} + \text{const}, \quad (26)$$

in which the const ensures that S vanishes in the absence of uncertainty.

The dependence of S for a two-state system on a single-state probability for different values of λE is given in Figure 2, from which S is seen to be maximal for states of equal probability. Moreover, the value of entropy decreases as λ increases; the explanation is that an increasing interaction energy reduces the residual uncertainty for the system of interest.

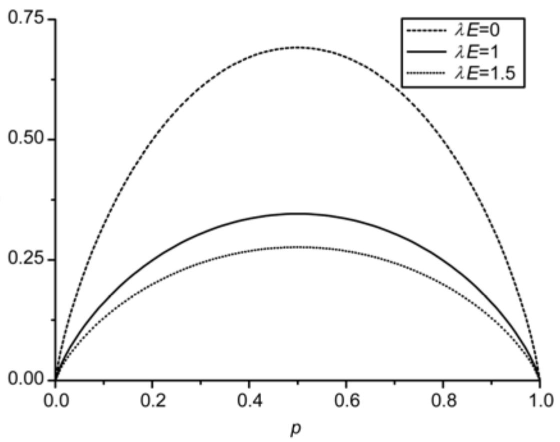

Figure 2 Entropy S for two-state system versus probability for fixed particle number N_2=100 and different values of λE.

If λ=0, we find that entropy reduces to the same form as the Tsallis entropy

$$S = Z^{q-1}\frac{1}{q-1}\left(1 - \sum_i p_i^{\ q}\right), \quad (27)$$

where $q = \frac{3N_2}{3N_2-2}$. This nonextensive index coincides with that of [23], the index deduced on the basis of additive energy.

3 Discussion and conclusion

In summary, under the assumption of nonadditive energy, we have derived the energy probability distribution for finite size systems from first-principles. The Boltzmann distribution can be obtained by taking λ=0 and the thermodynamic limit, $N_2 \to \infty$. From eq. (13), the nonextensive energy precludes the distribution from reducing to Boltzmann form even if $N_2 \to \infty$. These calculations have been made without considering explicit expressions for the potential energy. Thus, the validity of the conclusions might be general and independent of differences in the potential energy. The result is valid to describe the general thermostatistics of finite systems. The Boltzmann distribution appears as a special case within the framework. However, some questions with the procedure still remain. For example, the basic assumption that the energy nonextensivity of finite systems can be parameterized by a fixed constant λ, unrelated to the properties of the system, is not a sound hypothesis. This nonextensive parameter depends on the characteristics, such as size and interactions of the system. Some adjustment of this model can be brought by introducing a λ related to size, but calls for further research. These investigations can be applied to the analysis of various systems [24–27]. By deepening our understanding of distribution functions and their statistics, we would have a very powerful tool for the study of complex systems.

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