Statistical Distribution of a Completely Open System Based on Incomplete Shannon Entropy

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Abstract. Micro canonical, canonical and grand canonical systems are special cases of completely open systems. Within the framework of non-extensive and incomplete statistics, we derive the statistical distribution for a completely open system on the basis of incomplete Shannon entropy, using the maximum entropy principle. We calculate the physical properties of a linear filament using this distribution. The results are the same as those calculated using the incomplete E-V distribution, except that average values of the thermodynamic variables replace the corresponding constant values. However, the relative fluctuations in thermodynamic variables are completely different. In the canonical and grand canonical distributions, relative fluctuations are proportional to $1/N$. In the incomplete statistical distribution for a completely open system, the relative fluctuations are proportional to 1. This result can explain some phenomenon that traditional and current statistical mechanics cannot explain, such as the large fluctuations of critical, super-cooled and overheated states.

1. Introduction
We deduced the statistical distribution of a completely open system and a few thermodynamic formulas by applying Tsallis entropy [1] and the maximum entropy principle in our previous paper [2]. However, even with these tools it is still complicated to study the thermodynamic properties of a completely open system with the Tsallis statistical distribution. In this paper, we will use another approach. In 2001 French physicist Q.A. Wang proposed a modification to Tsallis statistics called incomplete statistics [3]. Wang also discussed some physical systems on the basis of incomplete entropy [3-5] and incomplete Shannon entropy [6,7]. Others made a contribution to the field [8-10].

It is well known that multi-particle systems with complex interactions can have fractal or chaotic phase spaces. The macroscopic behavior of such systems might be influenced by the edge effect and other factors related to the structure of the phase space. In such cases, we cannot accurately calculate the Hamilton canonical equation (for classical systems) or the Schrödinger equation (for quantum systems). Therefore, we cannot characterize all the microstates of the system and their corresponding probabilities. This problem is referred to information imperfection.

We denote the total number of possible microstates for a system as $v$. Owing to information imperfection, the number of microstates that we can record is $w$ ($w$ can be greater or less than $v$). Let $\{p_i\}$ denote the probability distribution for microstates of the system ($p_i$ is the probability of microstate $i$, $i=1,2,3,...,w$). If $w=v$, the distribution is complete; if $w\neq v$, the distribution is incomplete. Since the normalizing condition $\sum p_i = 1$ holds for a complete distribution, the statistical average of a physical quantity $O$ is simply $\bar{O} = \sum_i O_i p_i$, where $O_i$ is the value of $O$ in state $i$. 
For an incomplete distribution, $\sum p_i = Q = 1$. To normalize the incomplete distribution, we assume that $\sum \frac{p_i}{Q} = \sum p_i^\prime$, and that $\sum p_i^\prime = 1$. Since each $p_i \in [0,1]$, we have $q \in [0,\infty)$. The statistical average of a physical quantity $O$ is given by $\bar{O} = \sum O_i p_i^\prime$. \hfill (1) 

The statistical physics based on Eq. (1) is called incomplete statistics.

2. Theory

2.1. The probability distribution and the partition function

The Shannon entropy is defined as the statistical average of $-k \ln p_i$ (where $k$ is the Boltzmann constant). Within the framework of complete statistical physics, its formula is $S = -k \sum p_i \ln p_i - S_0$. We usually express the Shannon entropy as an absolute entropy with constant $S_0=0$. The arbitrary entropy constant can be nonzero, and derives from the Clausius entropy. We should emphasize that selecting a non-zero entropy constant does not violate the first, second, or third laws of thermodynamics. BG statistical mechanics assumes that entropy is extensive, so in that framework $S_0$ should also be extensive.

In non-extensive systems with long-range interactions, we take $S_0$ as a non-extensive, nonzero constant. Within the framework of incomplete and non-extensive statistical physics, the statistical average is based on Eq. (1), so the Shannon entropy can be written in the following form [6-7]:

$$S_q = -k \sum p_i^\prime \ln p_i - S_0.$$ \hfill (2)

We call this quantity as incomplete Shannon entropy.

Here we consider a single-component system which only does expansion work (systems that do work in other forms can be analyzed analogously) and is surrounded by a heat-particle source. The system can do work by changing volume, and it can exchange both heat and particles with the source. This system is completely open. The source is so enormous that these interactions do not influence its macroscopic states, and each microscopic state of the system can have a different particle number $N_i$, mechanical energy $E_i$ and volume $V_i$, in which the volume $V_i$ is a microscopic quantity, and represents a new concept, and it is different from purely mechanical quantities such as coordinates and momentum, while having some common ground with the mechanical energy number. For example, a determined value of the volume $V_i$ may correspond more microscopic states such as the mechanical energy $E_i$ and particle number $N_i$. The volume is alterable in a completely open system, when the volume change the coordinates of particles can also change (i.e., the microscopic states change). So, different microscopic states may correspond with different volume, the energy and particle number.

After the system and the source reach equilibrium, the mean values of $N$, $E=U$ and $V$ will be definite. They are given by the formulas $\sum p_i^\prime E_i = U$, $\sum p_i^\prime V_i = V$, $\sum p_i^\prime = 1$. \hfill (3)

We can introduce a Lagrangian function

$$F = \sum p_i^\prime \ln p_i + \alpha \sum p_i^\prime N_i + \beta \sum p_i^\prime E_i + \kappa \sum p_i^\prime V_i + \gamma \sum p_i^\prime S_0/k$$

Where $\alpha$, $\beta$, $\kappa$ and $\gamma$ are Lagrangian multipliers. From this we can calculate the conditional extrema, the probability distribution of microstates $p_i$ (called the N-E-V distribution, because the particle number $N$, energy $E$ and volume $V$ are all alterable), and the partition function $Z_q$:  

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\[ p_i = \exp(-\alpha N_i - \beta E_i - \kappa V_i - \gamma - 1/q) = \exp(-\alpha N_i - \beta E_i - \kappa V_i) / Z_q(\alpha, \beta, \kappa) \]

\[ Z_q(\alpha, \beta, \kappa) = \exp(\gamma + 1/q) = \left[ \sum_i \exp(-\alpha q N_i - \beta q E_i - \kappa q V_i) \right]^{1/q} \]

Inserting Eq. (4) into the incomplete Shannon entropy (2) with \( S_q = 0 \), we obtain \( S_q = k \left( \gamma + 1/q + \alpha N + \beta U + \kappa V \right) \). The constraint that \( E=0, V=0 \) and \( S_q=0 \) should hold when \( N=0 \) leads to the rule \( \gamma + 1/q = 0 \), so \( Z(\alpha, \beta, \kappa) \) is not always equal to 1, and becomes a practical partition function.

2.2. The thermodynamic formulas

Substituting (4) and (5) into (3), we obtain

\[ N = -\frac{\partial \ln Z_q(\alpha, \beta, \kappa)}{\partial \alpha}, \quad U = -\frac{\partial \ln Z_q(\alpha, \beta, \kappa)}{\partial \beta}, \quad V = -\frac{\partial \ln Z_q(\alpha, \beta, \kappa)}{\partial \kappa}. \]

And substituting (4) and (5) into (2), we have

\[ S_q = k \left( \alpha \beta \kappa \right) \]

Notice (6), we have now

\[ \alpha = \frac{\partial S_q}{\partial N} \bigg|_{U,V}, \quad \beta = \frac{\partial S_q}{\partial U} \bigg|_{N,V}, \quad \kappa = \frac{\partial S_q}{\partial V} \bigg|_{N,U}. \]

Contrast Eq. (8) with the fundamental thermodynamic equation for open systems, T\( S_d = U + P d V - \mu d N \). By analogy, we can select the constants

\[ \alpha = -\mu / k T, \quad \beta = 1 / k T, \quad \kappa = P / k T. \]

More, the fluctuations in the thermodynamic variables are

\[ \frac{\overline{N^2} - N^2}{N^2} = -\frac{1}{q^2 Z_q^2} \left[ \frac{1}{q^2} \frac{\partial^2 Z_q}{\partial \alpha^2} - \left( \frac{\partial Z_q}{\partial \alpha} \right)^2 \right] + \frac{1}{q^2 Z_q^2} \left[ \frac{1}{q^2} \frac{\partial^2 Z_q}{\partial \beta^2} - \left( \frac{\partial Z_q}{\partial \beta} \right)^2 \right] \]

3. Applications

Consider a linear filament composed of independent units, each of which has two (or more, for example DNA) possible states: short (length \( a \) and energy \( ea \)) or long (length \( b \) and energy \( eb \)). \( T \) is the temperature of the system, and \( J \) is the tension in the filament. The partition function for the N-E-V distribution for this system is

\[ Z_q(\alpha, \beta, \kappa) = \left( \sum_j e^{-\alpha q N_j - \beta q E_j - \kappa q V_j} \right)^{1/q} = \left( \sum_j e^{-\alpha q N_j} \sum_{\ell \in \Omega} e^{-\beta q E_j(\ell) - \kappa q V_j} \right)^{1/q}, \]

Where \( \alpha = -\mu / k T, \beta = 1 / k T, \kappa = J / k T \), and \( \Omega \) is the degeneracy of the system with energy level \( E_j \) and length \( L \). If there are \( N_a \) units in state a and \( N_b \) units in state b, then the energy and length of the system are

\[ E(\ell) = N_a \epsilon_a + N_B \epsilon_b, \quad L = N_a a + N_b b, \quad (N = N_a + N_b). \]

The degeneracy \( \Omega = N_a! / (N_a! N_b!) \) is the combinatorial number for selecting \( N_a \) from \( N \) units.

Inserting Eqs. (13) into Eq. (12), we have:

\[ Z_q(\alpha, \beta, \kappa) = \left( \sum_j e^{-\alpha q N_j} \left( e^{\epsilon_a - \beta q E_j - \kappa q V_j} + e^{\epsilon_b - \beta q E_j - \kappa q V_j} \right)^{1/q} \right) \]

We define \( \gamma = e^{-\alpha q} \left( e^{\epsilon_a - \beta q E_j} + e^{\epsilon_b - \beta q E_j} \right) \). When \( \gamma < 1 \), the series becomes

\[ Z_q(\alpha, \beta, \kappa) = (1 - \gamma)^{-1/q}. \]

The average unit number is

\[ \bar{N} = -\frac{\partial \ln Z(\alpha, \beta, \kappa)}{\partial \alpha} \]

The average length is

\[ \bar{L} = -\frac{\partial \ln Z(\alpha, \beta, \kappa)}{\partial \kappa} \]
\[ i = \frac{ae^{(\lambda - \varepsilon_1)/kT} + be^{(\lambda - \varepsilon)/kT}}{e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}} \] is the average length of a single unit in the filament.

The internal energy is
\[ U = -\frac{\partial \ln Z(\alpha, \beta, \kappa)}{\partial \beta} = \frac{N}{e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}} = \frac{N}{e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}}. \] (16)

Where \( \bar{\varepsilon} = (e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT})/(e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}) \) is the average energy of a unit.

The results have an extra parameter \( q \) compared to the BGS theory, since \( k/q \) replaces the Boltzmann constant \( k \). The average unit number also replaces the constant unit number. The solution in BGS theory (i.e., \( q=1 \)) is compared to two solutions for values of the deformed parameter \( q>1 \) and \( q<1 \) in Figures 1. The entropy is
\[ S_q = \frac{\bar{\varepsilon} - \mu}{T}. \] (17)

The effect of the incompleteness can be estimated using the energy difference:
\[ \Delta U = U - U_0 = \frac{e^{(\lambda - \varepsilon_1)/kT}e^{(\lambda - \varepsilon)/kT}(e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}) + (e^{(\lambda - \varepsilon_1)/kT}e^{(\lambda - \varepsilon)/kT})(e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT})}{e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}} \] where \( U_0 \) is the internal energy of the linear filament when \( q=1 \).

The squared relative fluctuations are
\[ \frac{\bar{e}^2 - U^2}{U^2} = 1 + \frac{\bar{e}^2}{\bar{e}^2} \frac{1}{\bar{e}^2} \frac{T^2}{L^2} = 1 + \frac{T^2}{L^2} \frac{1}{\bar{e}^2} \frac{\bar{e}^2}{\bar{e}^2} = 1 + \frac{T^2}{L^2} \] (19)

where \( \bar{e}^2 = e^{(\lambda - \varepsilon_1)/kT}e^{(\lambda - \varepsilon)/kT}(e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}) \) is the mean squared energy of an individual unit,
\[ \bar{l}^2 = \frac{e^{(\lambda - \varepsilon_1)/kT}e^{(\lambda - \varepsilon)/kT}}{e^{(\lambda - \varepsilon_1)/kT} + e^{(\lambda - \varepsilon)/kT}} \] is the mean squared length of an individual unit.

Figure 1. The deviation (\( U \) or \( L \)) from \( q=1 \) for values of the deformed parameter \( q>1 \) and \( q<1 \).

4. Conclusions
By introducing the concepts of non-extensive entropy constant and microscopic volume in incomplete statistics, we deduce the statistical distribution of a completely open system using the maximum entropy principle in Eqs.(4-5) and the corresponding thermodynamic formulas in Eqs.(6-11). When the deformation parameter \( q \) 1, both results reduce to the statistical distribution deduced by T. L. Hill by the method of ensemble transformation in small systems [11]. However, our approach belongs to the family of non-extensive statistical mechanics, and is suitable for systems with any size.

The case of a linear filament system (comparable to biomacromolecules such as DNA) has never before been discussed in incomplete statistics. In this paper, we derive analytical results for the internal energy, average length, and entropy of the linear filament in Eqs. (15-17).

The order of magnitude of the relative fluctuations in thermodynamic quantities is 1. T. L. Hill found the same result for classical systems with very small numbers of particles (10^{12}-10^{15}), but our results can apply to the systems of any size. This result can account for the large fluctuations and instability observed in critical phenomena, supercooled states, and overheated states that are not explained by traditional or current statistical mechanics.
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