The Boltzmann Distribution is the Only Distribution That Gibbs-Shannon Entropy is the Thermodynamic Entropy

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It is well know that the Boltzmann distribution can be derived from the maximum entropy principle. In this paper, we demonstrate that we don’t actually need to “maximize” the entropy, requiring the thermodynamic entropy to equal to Gibbs-Shannon entropy does the job.

I. INTRODUCTION

There are two well known ways to derive the Boltzmann distribution: one from micro-canonical ensemble, the other from the maximum entropy principle.

The micro-canonical derivation[4] constructs a micro-canonical ensemble with total energy $E_r$ composed of the system of interest and a reservoir. The fundamental postulates of statistical mechanics states that the probability distribution of micro-states $\omega$ is uniform, that is

$$
\Pr (\omega) = \begin{cases} 
\frac{1}{\Omega_r} & E(\omega) = E_r \\
0 & \text{otherwise} 
\end{cases}
$$

where $E(\omega)$ is the energy of micro-state $\omega$, $\Omega_r$ is the number of micro-states that satisfies $E(\omega) = E_r$. The interaction between the system and reservoir is assumed to be weak, in the sense that no matter what micro-state the system of interest has, the possibility and probability of micro-states of the reservoir is only constrained by the total energy (that is, for fixed $\omega_s$ that has energy $E_s$, the reservoir is a micro-canonical ensemble with energy $E_r = E_T - E_s$). The probability distribution of micro-state of system of interest, $\omega_s$, is therefore obtained by marginalizing out the reservoir’s part, i.e.

$$
\Pr (\omega_s) = \sum_{\omega_r} \frac{1}{\Omega_r} = \frac{\Omega_s}{\Omega_T} \propto \Omega_s
$$

where $\Omega_r$ is the number of different $\omega_r$ that satisfies $E_r = E_T - E_s$, which can be written as $\Omega_r = \exp [S_r/k_B]$ using the entropy formula of micro-canonical ensemble. Since the micro-canonical ensemble is constructed in a way that $E_T \gg E_s$, we then have

$$
S_r = S_r (E_T) - \left( \frac{\partial S_r}{\partial E_r} \right) E_s = S_r (E_T) - \frac{E_s}{T}
$$

that is, $\Omega_r (\omega_s) \propto \exp \left( \frac{-E_s}{k_BT} \right)$, or equivalently, $\Pr (\omega_s) \propto \exp \left( \frac{-E_s}{k_BT} \right)$.

Maximum entropy principle[2,3] derives the Boltzmann distribution by maximizing the Gibbs-Shannon entropy

$$
H = -\sum_i p_i \log p_i \quad \text{under the constraint of} \quad \langle E \rangle = \sum_i p_i E_i = B
$$

and

$$
\sum_i p_i = 1.
$$

This optimization process has been shown to be equivalent to the micro-canonical derivation by applying the maximum entropy principle to the isolated system of the system of interest and reservoir in a two step fashion[4].

After obtaining the equation for Boltzmann distribution, the logic usually continues as first equating the thermodynamic energy $U$ with the ensemble average of the random variable $E$ of system energy, i.e.

$$
U = \langle E \rangle = \sum_i p_i E_i = \sum_i \frac{E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial \log Z}{\partial \beta}
$$

where $Z = \sum_i e^{-\beta E_i}$ is the partition function and $\beta = \frac{1}{k_BT}$. Comparing equation (1) with the thermodynamic equation $E = \frac{\partial (\beta F)}{\partial \beta}$ immediately gives the equation for Helmholtz free energy $F = -k_BT \log Z$. Thermodynamic entropy can then be computed as

$$
S = \frac{E - F}{T} = k_B \sum_i p_i \log p_i = k_B H
$$

where $H = -\sum_i p_i \log p_i$ is the Gibbs-Shannon entropy.
The above logic shows that
\[ \left( \begin{array}{c}
\text{Thermodynamic first law} \\
\text{(Boltzmann distribution)}
\end{array} \right) \Rightarrow \left( \begin{array}{c}
\text{Thermodynamic entropy is} \\
\text{Gibbs-Shannon entropy}
\end{array} \right) \]
while we show the opposite direction:
\[ \left( \begin{array}{c}
\text{Thermodynamic first law} \\
\text{(thermodynamic entropy is)} \\
\text{Gibbs-Shannon entropy}
\end{array} \right) \Rightarrow \left( \begin{array}{c}
\text{Boltzmann distribution}
\end{array} \right) \]

The contribution of this paper is therefore two fold: (1) shows that Boltzmann distribution is the only distribution that Gibbs-Shannon entropy is the thermodynamic entropy, and (2) gives a new way of deriving the Boltzmann distribution.

**II. MAIN RESULT**

We consider thermodynamic systems with \( m + n \) generalized forces and displacements. The thermodynamic first law can then be written as
\[ dU = TdS + \sum_{\eta=1}^{n} X_\eta d\chi_\eta + \sum_{\eta=1}^{m} Y_\eta dy_\eta \]

We intentionally use \( U \) instead of \( E \) and Greek letter \( \chi \) instead \( x \) to distinguish thermodynamic quantities and random variables. \( U, \chi_1, \ldots, \chi_n \) are thermodynamic quantities and \( E, x_1, \ldots, x_n \) are random variables. We also intentionally choose different letters for generalized forces \( (X_i \text{ vs } Y_i) \) and displacements \( (\chi_i \text{ vs } y_i) \) to emphasize that the ensemble we are going to study is parameterized by \( T \), generalized forces \( X_1, \ldots, X_n \), and generalized displacements \( y_1, \ldots, y_m \); that is, \( E, x_1, \ldots, x_n, Y_1, \ldots, Y_m \) are random variables, while \( T, X_1, \ldots, X_n, y_1, \ldots, y_m \) are parameters. In other word, we are studying a \((T, X_1, \ldots, X_n, y_1, \ldots, y_m)\) ensemble.

The above notation is a general framework for all thermodynamic systems. For example, for an \((\mu, V, T)\)-ensemble (one component grand canonical ensemble), we have \( m = n = 1, y_1 = V, Y_1 = -p, \chi_1 = N, X_1 = \mu \).

The main result is the following theorem:

**Theorem 1.** Consider thermodynamic systems whose first law reads
\[ dU = TdS + \sum_{\eta=1}^{n} X_\eta d\chi_\eta + \sum_{\eta=1}^{m} Y_\eta dy_\eta \]

Any \((T, X_1, \ldots, X_n, y_1, \ldots, y_m)\) ensemble that has:
- Probability density function proportional to some function of \( T, E, x_1, x_2, \ldots, x_n \)
- \( \langle E \rangle = U, \langle x_\eta \rangle = \chi_\eta \) for all \( \eta = 1, \ldots, n \)
- Thermodynamic entropy \( S \) and Gibbs-Shannon entropy \( H \) has relationship \( S = k_B H \)

the probability density function of micro-state \( \omega \) must have the form
\[ \Pr(\omega) \propto \exp \left[ \frac{\sum_{\eta=1}^{n} X_\eta y_\eta - E(\omega)}{k_B T} \right] \]

where \( E(\omega), x_1(\omega), \ldots, x_n(\omega) \) are macroscopic states that \( \omega \) has.

**Proof.** Let’s begin by assuming the probability density of micro-state \( \omega \) satisfies
\[ \Pr(\omega) \propto f \left( E(\omega), x_1(\omega), \ldots, x_n(\omega), T \right) \]

the normalization constant is
\[ Z = \sum_\omega f_\omega \]

where the sum is over all microscopic states, \( f_\omega \) is short for \( f \left( E(\omega), x_1(\omega), \ldots, x_n(\omega), T \right) \). In the above formula, the temperature \( T \) appears as a parameter, and micro-states \( \omega \) and its macro-states \( E(\omega), x_1(\omega), \ldots, x_n(\omega) \) do not depend on \( T \). Note that if \( S = k_B H \), then the thermodynamic entropy
\[ S = -k_B \sum_\omega \frac{f_\omega}{Z} \log \left( \frac{f_\omega}{Z} \right) \]
\[ = -k_B \left\{ \sum_\omega f_\omega \log f_\omega \left( \frac{f_\omega}{Z} \right) - \log Z \right\} \quad (2) \]

If we keep the other parameters \((X_1, \ldots, X_n, y_1, \ldots, y_m)\) fixed and perturb the temperature \( T \) by \( dT \), then the change of entropy
\[ dS = \left( \frac{\partial S}{\partial T} \right)_{X_1,\ldots,X_n,y_1,\ldots,y_m} dT \quad (3) \]

where
\[ \left( \frac{\partial S}{\partial T} \right)_{X_1,\ldots,X_n,y_1,\ldots,y_m} = -k_B \left\{ \sum_\omega \frac{Z \cdot f_\omega}{Z^2} \cdot \log f_\omega - \frac{\partial Z}{\partial T} \cdot f_\omega \log f_\omega \right\} \]
\[ = -k_B \sum_\omega \left( \frac{\partial f_\omega}{\partial T} \right) \left( \frac{f_\omega}{Z} \right) \cdot \log (f_\omega) \quad (4) \]
Also
\[
\langle E \rangle = \sum_{\omega} \frac{f_{\omega}}{Z} \cdot E^{(\omega)}
\]

and therefore
\[
d\langle E \rangle = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{X_1, \ldots, X_n, y_1, \ldots, y_m} dT = \sum_{\omega} \frac{\partial}{\partial T} \left( \frac{f_{\omega}}{Z} \right) \cdot E^{(\omega)} \cdot dT
\]

(5)

Same argument applies for \( \langle x_\eta \rangle \), we therefore have
\[
d\langle x_\eta \rangle = \left( \frac{\partial \langle x_\eta \rangle}{\partial T} \right)_{X_1, \ldots, X_n, y_1, \ldots, y_m} dT = \sum_{\omega} \frac{\partial}{\partial T} \left( \frac{f_{\omega}}{Z} \right) \cdot x^{(\omega)}_\eta \cdot dT
\]

(6)

III. DISCUSSION

The word “ensemble” is quite uninformative, we can basically construct an arbitrary set and build a \( \sigma \)-algebra and probability measure on it and call it “ensemble”. The things that are really interesting to physicists are those ensembles that describe thermodynamic systems. For an ensemble to be able to describe a thermodynamic system, it needs to be clear that those thermodynamic quantities are described by which quantity of the ensemble. These ensemble quantities might be a parameter of the ensemble (such as total energy for microcanonical ensemble and temperature for canonical ensemble), or statistics of some random variable on the ensemble (such the internal energy \( U \) is described by the expected value of microstate energies of the ensemble \( \langle E \rangle \) for canonical ensemble).

Our main result is purely mathematical, it does not assume any physical picture on what kind of system the ensemble describe, but just which ensemble quantity describe which thermodynamic quantity. But when the Boltzmann like distribution emerge from those mathematics as a conclusion, we showed that, when an ensemble describe a thermodynamic system in a way that the thermodynamic quantity \( T, y, \chi \) are described by the parameters, \( \chi \) described by expected values, and the thermodynamic entropy described by Shannon entropy, it necessarily describes a system contacting with a reservoir. Or on the other hand, for an ensemble that \( T, y, \chi \) are described in the same way, if it does not obey Boltzmann like distribution, then thermodynamic entropy could not be described by Shannon entropy.

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