

Microcanonical Partition Function

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Abstract

The canonical partition function, which represents exponential energy decay between the canonical ensemble states, is a cornerstone of the mechanical statistics. All the thermodynamic state-functions derived from it. The canonical partition function yields correctly many statistical phenomena but it fails to explain the long-tail distribution. The canonical ensemble conserves material and volume, and it has a constant temperature – but it does exchange energy with an external bath. Hereafter it is claimed that this model is incorrect. Here we claim that the canonical ensemble is the quantum limit approximation of a microcanonical ensemble that conserves material, volume, and energy. Since it conserves energy, its temperature is constant. In addition, according to the second law, in equilibrium, all its states and all its microstates have equal energy. The partition function of this microcanonical ensemble converges to the canonical partition function in the quantum limit, and to the power-law energy distribution in the classical limit. Therefore, the canonical ensemble is a private case of the microcanonical ensemble.

Introduction

Traditionally, statistical mechanics distinguishes between three kinds of systems: the microcanonical ensemble, the canonical ensemble, and the grand-canonical ensemble. The differences between them are described as follows [1]:

“The microcanonical ensemble does not transact energy with the surroundings; nor does it transact matter. Hence, its energy remains constant. The canonical ensemble is a system that does not exchange material with the surroundings. However, it does exchange energy. It is in thermal contact with the surroundings (heat bath). Thus, a closed system in thermal equilibrium is characterized by temperature, volume and the number of particles. The system is not isolated; hence, its microstates are not all equiprobable. Thus, $S = -\sum_{i=1}^N p_i \ln p_i$ provides a natural formula for the entropy of a system whose microstates are not equiprobable. The third is the macro-canonical ensembles that can exchange both energy and particles.”

This quotation, with minor changes, from the textbook of Murthy [1], is widely accepted by the community and appears in many textbooks [i.e.2] as well as in Wikipedia. The unequal probabilities of the microstates are the reason why many authors start their analysis with the unequal energy distribution between the microstates, represented by the canonical partition function Z_C , namely,

$$Z_C = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right). \quad (1)$$

Where ε_i is the energy of the microstate i , and $k_B T$ is the average energy of the microstates. The summation is over all the microstates of the ensemble.

A common use of Z_C is the calculation of the probability p_i to find a particle having energy ε_i , namely,

$$p_i = \frac{1}{Z_C} \exp\left(-\frac{\varepsilon_i}{k_B T}\right). \quad (2)$$

Here T is the temperature of the canonical ensemble (the bath temperature) and k_B is Boltzmann constant. Similarly, the energy of the ensemble $\langle E \rangle$ is given by,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z_C}{\partial T} = \frac{1}{Z_C} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right). \quad (3)$$

Since it was shown that every thermodynamic state function could be derived from the canonical partition function, it is considered a starting point in statistical mechanics. However, the canonical statistical mechanics based on the canonical partition function fails to explain the power-law distributions [2]. In order to overcome this problem, some authors suggested “entropies” that violate the second law of thermodynamics. A notable one is the Tsallis “nonextensive” entropy [3]. Nonextensive entropy means a system, not in equilibrium, which means that temperature cannot be defined and MaxEnt formalism is not applicable [4].

There are some more problems with the canonical ensemble:

Ideal gas that can be confined in an isolated vessel, and therefore according to the definition above is a microcanonical ensemble, is a typical example of a canonical ensemble.

In contradistinction, a constant temperature blackbody which must absorb energy from an external bath in order to keep its temperature constant suppose to be canonical. Nevertheless in the Rayleigh-Jeans regime, it cannot be described by the canonical partition function.

Moreover, what is the meaning of unequal energy distribution in the microstates? A microstate is a distinguishable distribution of the energy of a system among its states. Every instance the system exists only in one microstate, however, the system constantly moves from one microstate to another. Our lack of knowledge in what microstate the system exists is the meaning of its entropy. Therefore, in equilibrium, all the microstates have, per definition, an identical number of states and an identical amount of energy.

The origin of the common misconception that there is “unequal energy distribution of the microstates” is the confusion between microstates and states. A microstate is a “state” of the whole ensemble that comprises all its states and their energies. Since the entropy is a measure of our lack of knowledge in what microstate the ensemble is, only their number contributes to entropy or, in the words of Gibbs, “the whole is simpler than its parts”. The origin of the exponential decay of the probability p_i to find a particle or a radiation mode with energy ε_i as in Eq.(1) is the second law of thermodynamics, namely, the propensity of entropy to grow to its maximum. The equilibrium distribution of energy between its particles is the distribution that maximizes the number of microstates. The maximum entropy is reached where no change can increase the number of microstates of a system, and therefore it is stable, namely, in equilibrium. The equilibrium is the point where the entropy’s expression reaches its maximum value under the system’s constraints.

Statistical entropy is defined in two ways: the Boltzmann entropy,

$$S = k_B \ln W,$$

where W is the number of microstates and the Gibbs entropy,

$$S = -k_B \sum_{j=1}^W p_j \ln p_j,$$

Here p_j is the probability of the microstate j , and the summation is over their number. If all the microstates have the same probability, namely, $p_j = 1/W$, then $S = -k_B \sum_{j=1}^W p_j \ln p_j = k_B W \left(\frac{1}{W}\right) \ln W = k_B \ln W$. Therefore, the equal probability of all the microstates is the maximum entropy solution which is the Boltzmann entropy. Gibbs entropy should not be confused with the canonical “entropy” $S = -k_B \sum_{i=1}^N p_i \ln p_i$ in which the summation is over the states, and as we will see usually $W > N$.

Definitions

To demonstrate this point, we consider a theoretical ensemble of B distinguishable boxes and P indistinguishable balls and calculate for it the equivalents of the energy distribution, entropy, and temperature. We consider each ball as a quant of energy and a box as a particle. We follow Planck's microcanonical derivation to calculate the equilibrium distribution of the balls in the boxes of our ensemble [5]. The probabilities are calculated by maximizing the dimensionless entropy, subject to the constraint of conservation of the number of balls P . We show that this ensemble is analogous to the distribution of energy in the particles of an ideal gas and to the distribution of photons in the radiation modes of a blackbody.

Hereafter, it is shown that the canonical partition function yields erroneous results where the number of balls is greater than the number of boxes, namely the energy of the quanta is smaller than the average energy as in the classical limit. Therefore, the canonical ensemble formalism is correct only for systems in which the energy of the quanta is greater than $k_B T$, which is the quantum limit.

We propose a microcanonical partition function that yields identical results to the canonical partition function in the quantum limit and the power-law energy distribution in the classical limit. This partition function is also applicable to the intermediate zone in which the energy of the quanta is similar to the average energy.

First, we define for this ensemble the basic statistical mechanics' quantities, namely, a microstate, a state, and equilibrium.

A microstate is a distinguishable configuration of the balls in the boxes. I.e. if we have 2 balls and 2 boxes there are $W = 3$ microstates (2,0) (1,1) (0,2). However, we should remember the balls constantly change places between the boxes and we do not know in what microstate the system is. Nevertheless, for the entropy, we need to know only their number, namely, the entropy of this ensemble is $\ln 3$.

A state is the group of all the boxes with the same amount of balls. In the example above, there are 2 states (we do not count the empty boxes as will be explained later) State 1 which comprises of 2 boxes of 1 ball and state 2 of 1 box with 2 balls. This definition is analogous to a blackbody, in which all its particles that emit their photons in the same frequency at the same time in the same direction are coherent namely they are in a single mode. Please note that each state has the same amount of balls. As we will see later not only all the microstates have the same energy but all the states have equal energy.

Equilibrium is achieved when the probability of all the microstates is equal and the number of balls in all the states is also equal.

In order to calculate the entropy of a system of P balls in N states, we calculate the number of its microstates [5], namely,

$$W = \frac{(N+P-1)!}{(N-1)!P!} . \quad (4)$$

Designating $n = P/N$ and applying Stirling formula $\ln n! \cong n \ln n - n$, we obtain for $S = \ln W$,

$$S \cong N[(n+1) \ln(n+1) - n \ln n] \text{ or,} \\ S \cong \sum_{i=1}^N [(n_i+1) \ln(n_i+1) - n_i \ln n_i]. \quad (5)$$

n_i is the number of balls in a box in the state i , and $i = 1, 2, \dots, (N-1), N$ boxes. If all the states have the same number of balls $\langle n \rangle = \frac{P}{N} = n_i$ where i is the number of boxes in the state, a high n_i means that there are many balls in a state, thus we can add or remove energy in small amounts as compared to the average energy – this is the classical limit.

The canonical approximation

In the quantum limit $n_i \ll 1$. The number of balls in a state is negligible, therefore, $1 + n_i \cong 1$, and the first term of Eq. (5) vanishes and the entropy expression become canonical, namely,

$$S = \ln W \cong - \sum_{i=1}^N n_i \ln n_i. \quad (6)$$

To find n_i , namely, the number of balls in a box of the state i , that maximizes the entropy of Eq.(6), we derive S by n_i , subject to the constraint of conservation of the number of balls $P = \sum_i n_i i$. Using the Lagrange multiplier technique, we solve,

$$\frac{\partial}{\partial n_i} \sum_{i=1}^N [-n_i \ln n_i + \beta(P/N - n_i i)] = 0, \text{ where } \beta \text{ is a Lagrange multiplier.}$$

We obtain that, $\ln n_i + 1 + \beta i = 0$, or,

$$n_i = e^{-\beta i - 1}. \quad (7)$$

Since all the states are equiprobable, all $n_i i$ are equal and,

$$\beta^{-1} = P/N \text{ or } \beta = 1/\langle n \rangle.$$

To obtain the probability p_i , n_i of Eq. (7) is normalized with respect to the sum of all the n_i 's. Since the total number of the n_i 's in the canonical approximation is $\sum_{i=1}^N n_i = \sum_{i=1}^N e^{-\beta i - 1} = Z_C/e$, where,

$Z_C = \sum_{i=1}^N e^{-\beta i}$, is the canonical partition function. The probability to find a box with n_i balls is,

$$p_i = \frac{n_i}{\sum_{i=1}^N n_i} = \frac{e^{-\beta i}}{Z_C}. \quad (8)$$

Eq. (8) is the basis of the probability theory. Example: suppose that $\beta = 10^4$, which means that we have one ball for 10^4 boxes. The probability to find two balls in a box is negligible (about 10^{-8}); therefore, we expect that all the boxes will have the same small probability $p_i = 10^{-4}$ to find a ball. This result is obtained from Eq. (8), namely, $\int_0^\infty e^{-\beta i} di = \frac{1}{\beta}$. The assumption that each state has the same probability to have a ball as the other states is the default assumption in probability calculation (in the canonical

approximation a state is a single box). In the case of $\beta i \ll 1$, which means more balls than boxes, the probabilities of Eq.(8) are meaningless, as Z_C does not converge.

The general solution

Now we calculate n_i more accurately from the general microcanonical entropy of Eq.(5). The analogous derivation of Eq.(7) yields,

$$\frac{\partial}{\partial n_i} \sum_i [(n_i + 1) \ln(n_i + 1) - n_i \ln n_i + \beta(P/N - n_i i)] = 0, \text{ and obtain that,}$$

$$\ln(n_i + 1) - \ln n_i - \beta i = 0, \text{ namely,}$$

$$n_i = \frac{1}{\exp(\beta i) - 1}. \quad (9)$$

We see that the expression for $n_i = \frac{1}{\exp(\beta i + 1)}$ of Eq. (7) was replaced by $n_i = \frac{1}{\exp(\beta i) - 1}$, and the partition function Z_C is changed accordantly to,

$$Z_{MC} = \sum_i (\exp(\beta i) - 1)^{-1}. \quad (10)$$

Where Z_{MC} is the microcanonical partition function. The probability of Eq. (8) is replaced by,

$$p_i = \frac{n_i}{\sum_{i=1}^N n_i} = \frac{n_i}{Z_{MC}} = \frac{(\exp(\beta i) - 1)^{-1}}{\sum_{i=1}^N (\exp(\beta i) - 1)^{-1}} \quad (11)$$

In the quantum limit in which $\beta i \gg 1$, $\exp(\beta i) - 1 \cong \exp(\beta i)$, and we obtain that the partition function of Eq.(10) and the probability of Eq.(11) becomes canonical.

In the classical limit, when $\beta i \ll 1$, then $\exp(\beta i) - 1 \cong \beta i$, thus $n_i = 1/\beta i$ and the new partition function is,

$$Z_{MC} = \frac{1}{\beta} \sum_{i=1}^N \frac{1}{i} = \frac{1}{\beta} H_N,$$

where $H_N = \sum_{i=1}^N \frac{1}{i}$ is the harmonic number and the probability to find a box with n_i balls become,

$$p_i = 1/\beta i Z_{MC} = \frac{\frac{1}{i}}{\sum_{i=1}^N \frac{1}{i}} = \frac{1}{i H_N}, \quad (12)$$

which is the empirical Zipf law (Usually Zipf law is written as $p_i = 1/i^s H_N$ where s is an empirical slope parameter. Here we obtain that $s = 1$). Please note that in the classical limit the general expression of the probability $p_i = \frac{n_i}{\sum_{i=1}^N n_i}$ is replaced by $p_i =$

$$\frac{\frac{1}{i}}{\sum_{i=1}^N \frac{1}{i}}. \text{ This is a direct outcome of the fact } n_i i = 1/\beta.$$

The empirical Zipf law appears in several different ways and hereafter we derive a few of them,

Using Riemann sum, namely treating $\frac{1}{i}$ as a continuous function and replacing the box by the area below its curve, we can write, $\int_i^{i+\Delta} \frac{di'}{i'} = \ln(i + \Delta) - \ln(i) = \ln\left(1 + \frac{\Delta}{i}\right)$

where Δ is the integration increment that is, in our case, $\Delta=1$. The harmonic number will become,

$$H_N = \int_1^{N+1} \frac{di'}{i'} = \ln(N+1) \text{ and we obtain that,}$$

$$p_i = \frac{1}{iH_N} \cong \frac{\ln(1+\frac{1}{i})}{\ln(N+1)} = \log_{N+1}(1 + \frac{1}{i}). \quad (13)$$

Eq. (13) is called Planck-Benford law [8, 11] and is a different expression of Zipf law.

Example: For $N = 9$, Eq.(13) yields the Benford law of the unequal distribution of digits in random files, namely, $p_i = \log_{10}(1 + \frac{1}{i})$. Here p_i is the probability to find a box with n_i balls. Newcomb found this law empirically in the 19th century in logarithmic tables [6]. It is worth noting that that Eq. (9) can be written as, $i = \frac{1}{\beta} \ln(1 + \frac{1}{n})$. When this equation is normalized, we obtain that $p_n = \log_{N+1}(1 + \frac{1}{n}) = \frac{1}{nH_N}$ where p_n is the relative number of boxes with n balls. We see that Zipf law is applicable both to i and to n . The reason for this phenomenon is that $n_i = \langle n \rangle / i$ and $i = \langle n \rangle / n_i$ this symmetry is responsible for this effect. In fact, Zipf law is valid for any pair $xy = \text{constant}$, in the classical limit.

To demonstrate the application of Zipf law consider $B = 3$ distinguishable boxes and $P = 3$ identical balls: Therefore, $N = 3$. From Eq.(13), we obtain:

$$p_1 = \ln 2 / \ln 4 = 0.5; \quad p_2 = \ln(3/2) / \ln 4 = 0.29; \quad p_3 = \ln(4/3) / \ln 4 = 0.21.$$

Namely, there is a probability of 50% to find a box with a single ball, 29% to find a box with 2 balls, and 21% to find a box with 3 balls. Empty boxes do not have balls (or energy) and therefore do not have entropy and cannot be calculated by entropy maximization. This is the reason why Benford law is sometimes called “the first digit law” since the first digit of a number is never zero.

Now we compare the result of Eq. (13) to the results obtained by actual counting of the boxes with the balls. From Eq.(4) we obtain $W = 10$ microstates. Each microstate has an equal number of balls $P = 3$. The microstates are (3,0,0) (0,3,0) (0,0,3) (2,1,0) (2,0,1) (0,2,1) (0,1,2) (1,2,0) (1,0,2) (1,1,1). The total “number” of boxes in all the microstates is $BW = 30$. From them 12 are empty, 9 have 1 ball, 6 have 2 balls and 3 have 3 balls. The normalized ratios of the occupied boxes $p_1:p_2:p_3$ are about 50: 33: 17. From Eq.(13) we obtained that the ratios are 50: 29: 21. These differences are originated at the inaccuracy of Stirling approximation for small numbers.

We saw that for this system in which $W = 10$ there are $N = 3$ states: $n = 1$ with $i = 9$ boxes: $n = 2$ with $i = 6$ boxes: $n = 3$ with $i = 3$ boxes. We expect that each state will have in equilibrium equal amount of balls (10 balls per state). Here we obtained 9: 12: 9 this ratio is with a good agreement for such a small ensemble in a regime that is neither quantal nor classical.

To summarize, we consider an ensemble of balls and boxes and derive its statistical mechanic's quantities by maximizing Boltzmann entropy subject to a constraint of

conservation of the number of balls. We suggest a microcanonical partition function $Z_{MC} = \sum_i (\exp(\beta i) - 1)^{-1}$, which yields in the quantum limit $\beta i \rightarrow \infty$ the canonic partition function, and in the classical limit $\beta i \rightarrow 0$ yields the harmonic number.

$$Z_{\text{quantum}} = \lim_{\beta i \rightarrow \infty} \sum_i (\exp(\beta i) - 1)^{-1} = \sum_{i=1}^{\infty} \exp(-\beta i)$$

$$Z_{\text{classical}} = \lim_{\beta i \rightarrow 0} \sum_i (\exp(\beta i) - 1)^{-1} = \sum_{i=1}^N \frac{1}{\beta i}$$

Similarly, the probability to find n_i balls yield Maxwell-Boltzmann's distribution in the quantum limit and Zipfian power-law distribution in the classical limit.

Application to physics

Zipf law and Benford law are considered as a branch of probability. It has been applied in the economy, sociology, and finance [6, 9, 10, 11]. However, the probability p_i to find a box as a function $\beta i = \frac{1}{n_i}$ is a cornerstone of physics. Zipf law is applied for the population of cities (where the cities are the boxes and the citizens are the balls). Benford law is applied to the distribution of digits in financial reports (where the digits are the boxes and their values are the numbers of balls). In Economy, the boxes may be the deciles or percentile and the income is the number of balls. The quantity $i = \langle n \rangle / n_i$, which is of interest to physicists, is not so intuitive. Assuming that a radiation mode is in a thermal bath (a blackbody) of a temperature T ; the average number $\langle n \rangle$ of balls-photons in a radiation mode (a state) have energy $k_B T$. The energy of a photon is $\frac{k_B T}{n_i} = i = h\nu_i = \varepsilon_i$. Therefore i is the energy of a quant $h\nu_i$ and $\beta i = \frac{h\nu_i}{k_B T}$. Please note that in the partition function ε_i is the energy of a quant and not the energy of a state. In the quantum limit, all the energy is in one quant and there are many empty boxes therefore ε_i is also the detected energy of a state but this is not the case in the classical limit. In Planck distribution, it is written explicitly $\frac{h\nu_i}{k_B T}$.

In brief, there is an analogy between the thermodynamic physical quantities like temperature and energy and the statistical quantities of the “balls and boxes” ensemble, namely,

1. The number of boxes having n_i balls – i is equivalent to ε_i or $h\nu_i$, namely, the energy of a quant.
2. The average number of balls in a box $\langle n \rangle = \beta^{-1}$ is equivalent to $k_B T$. (or the average energy of a degree of freedom).
3. βi is equivalent to $\varepsilon_i / k_B T$. This term that is so familiar to any physicist is treated as the energy of a particle with respect to the average. However, this is true only in the quantum approximation when the whole energy of a particle is

in one photon. Actually, the term $\frac{\varepsilon_i}{k_B T} = \frac{1}{n_i}$ is the reciprocal of the number of quanta in a state. Indeed in Plack law where n_i can be bigger than 1 the energy ε_i is the quant energy namely, $n_i = \left(\exp\left(\frac{h\nu}{k_B T}\right) - 1\right)^{-1}$.

The new partition function Z_{MC} complies with the average energy of the ensemble of Eq.(3) namely,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z_{MC}}{\partial T}. \text{ Since } Z_{MC} = \sum_i (\exp(\varepsilon_i/k_B T) - 1)^{-1} \text{ then,}$$

$$\langle E \rangle = \frac{1}{Z_{MC}} \sum_i \frac{\varepsilon_i \exp(\varepsilon_i/k_B T)}{(\exp(\varepsilon_i/k_B T) - 1)^2}. \quad (13)$$

In the quantum limit when $\varepsilon_i/k_B T \gg 1$, then we obtain the canonical expression, namely,

$$\langle E \rangle = \frac{1}{Z_C} \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T).$$

In the classical limit when $\varepsilon_i/k_B T \ll 1$, then Eq.(13) becomes,

$$\langle E \rangle = \frac{1}{Z_{MC}} \sum_{i=1}^N \frac{(k_B T)^2 \exp(\varepsilon_i/k_B T)}{\varepsilon_i} \cong \frac{1}{Z_{MC}} \sum_{i=1}^N \frac{(k_B T)^2}{\varepsilon_i}. \text{ Since in this limit,}$$

$$Z_{MC} = \sum_{i=1}^N \frac{1}{\beta \varepsilon_i} = \sum_{i=1}^N \frac{k_B T}{\varepsilon_i}, \text{ we obtain that,}$$

$$\langle E \rangle = k_B T.$$

This is the Rayleigh-Jeans approximation. This result cannot be obtained from the canonical partition function.

This formalism can yield the Bose-Einstein distribution, namely the macro-canonical ensemble [8]. In the canonical and microcanonical derivations, the constraint was on the total number of balls, namely, $\sum n_i i$. However, if we add a constraint on n_i , it means that we reduce the number of possibilities to distribute the balls in the boxes. The Lagrange equation will become

$$\sum_i [(n_i + 1) \ln(n_i + 1) - n_i \ln n_i + \beta n_i i - \mu n_i] = 0. \text{ The derivation of this equation yields Bose-Einstein distribution [8], namely, } n_i = \frac{1}{\exp(\beta i - \mu) - 1}.$$

It should be noted that the derivation of Planck distribution in several textbooks is presented as a part of the canonical ensemble. It means that there is a claim that Planck law can be derived from the canonical partition function. This is done by an erroneous

$$\text{derivation, namely, } Z_C = \sum_{i=1}^{\infty} \exp\left(-\frac{h\nu_i}{k_B T}\right) = \frac{\exp\left(-\frac{h\nu_i}{k_B T}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)} = \frac{1}{\exp\left(\frac{h\nu_i}{k_B T}\right) - 1}.$$

Therefore the conclusion is that the canonical partition function yields the correct occupation number as obtained by the microcanonical ensemble of Planck. However, the canonical partition function converges only for $h\nu_i > k_B T$, and therefore beyond the canonical approximation, namely, $h\nu_i < k_B T$, this derivation is not valid. Moreover, the summation on the infinite number of states is only correct for $h\nu_i \gg k_B T$ where the probabilities of the high-energy states are negligible.

Summary and discussion

It is argued that both the canonical ensemble and the microcanonical ensemble have identical statistical properties: both conserve energy, their microstates are equiprobable and their states are equiprobable. While the microcanonical energy distribution is general, the canonical energy distribution is applicable only in the quantum limit when the quant's energy is greater than the average energy namely $\varepsilon_i \gg k_B T$. Therefore, the assumption that the canonical ensemble exchange energy with a bath is not necessary and is not the reason for the exponential energy decay.

From the maximum entropy principle, we derive a microcanonical partition function that replaces the canonical partition function. The new partition function yields in the quantum limit the canonical expressions, and in the classical limit, in which $\varepsilon_i \ll k_B T$, it yields the Zipfian long-tail distribution.

To derive the partition function, we define an ensemble of P balls and N states. Each state is a group of i boxes in which each box has n_i balls, such that $n_i i = \langle n \rangle = P/N$ balls. The total number of balls $P = \sum_{i=1}^N n_i i$ is conserved. We calculate the number of microstates, namely, the number of the distinguishable configurations of the balls in the boxes, $W = \frac{(N+P-1)!}{(N-1)!P!}$, and by using Stirling formula we calculate the Boltzmann entropy in which all microstates are equiprobable, to be $S = \sum_{i=1}^N [(n_i + 1) \ln(n_i + 1) - n_i \ln n_i]$. We maximize the entropy S subject to the constraint on conservation of balls and we obtain that $n_i = (\exp(\frac{i}{\langle n \rangle}) - 1)^{-1}$. When we consider a ball as a quant of energy $\varepsilon_i = i$, we obtain that $\langle n \rangle = k_B T$ and n_i is the number of quanta with energy ε_i . The obtained microcanonical partition function is,

$$Z_{MC} = \sum_i (\exp\left(\frac{\varepsilon_i}{k_B T}\right) - 1)^{-1} \text{ instead of the canonical partition function } Z_C = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right).$$

In the quantum limit both Z_{MC} and Z_C yield the same probability p_i to find a particle with energy ε_i and the same average energy $\langle E \rangle$, namely:

$$p_i = \frac{1}{Z_C} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \text{ and } \langle E \rangle = \frac{1}{Z_C} \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T).$$

In the classical limit, where $\varepsilon_i \ll k_B T$, which means that we can remove or add energy from a state in any amount (continuous energy), the canonical partition function does not converge and Z_{MC} yields,

$$p_i = \frac{\varepsilon_i^{-1}}{\sum_{i=1}^N \varepsilon_i^{-1}} \text{ and } \langle E \rangle = k_B T.$$

Namely, the probability to find a particle with energy ε_i obeys Zipf law. Both Zipf law and the canonical distribution predict that the probabilities to find high-energy particles are smaller than the probability to find low energy particles. However, in the quantum limit, the probability reduces exponentially, and in the classical limit, it reduces as a

power law. In the classical limit, the average energy is just the average energy of a classical harmonic oscillator. This result is the Rayleigh-Jeans approximation and was proved to be correct in the classical regime of blackbody radiation. What is the physical reason for the change in the probability between the quantum limit and the classical limit? In the quantum limit, the whole energy of a box is in one quant. Therefore, the energy of the excitation is the energy of the quant. In the classical regime, the energy of the quant has no straightforward connection to the energy of the particles. This is expressed in the microcanonical ensemble but cannot be expressed in the canonical one. Therefore, the canonical ensemble is a private case of the general microcanonical ensemble.

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List of symbols

B number of boxes.

P number of balls.

N number of states.

W number of microstates.

n_i the number of balls in a box: equivalent to the number of quanta.

i number of boxes with n_i boxes: equivalent to ε_i the energy of a quant.

p_i the probability of a box that appears i times.

p_n the probability of a box with n balls.

$\langle n \rangle$ The average number of balls in a state.

$\beta^{-1} = \langle n \rangle = k_B T$ Lagrange multiplier.