A double extrema form of the calculus of variations is put forward in which only the smallest one of the finite differences is physically meaningful to represent the variational derivatives defined on the discrete points. The most probable distribution for the Boltzmann system is then reproduced without the Stirling’s approximation, and free from other theoretical problems.

Keywords: Boltzmann distribution, most probable distribution, finite difference, Discrete calculus of variations

I. INTRODUCTION

Boltzmann distribution lies in the heart of statistics physics with applications in mathematics, chemistry and engineering, and it was first given more than 100 years ago [1]. However, seldom feels comfortable with its derivation with use of the Stirling’s approximation [2–6]. A more puzzling point is that, if one uses more accurate expression of the Stirling’s approximation, or attempts to exact the derivation of the Boltzmann distribution without invoking the Stirling’s approximation, he always runs into the a surplus ∼ −1/2 term [5, 6] in the distribution. One can find the relevant derivation in most standard statistical physics or physical chemistry textbooks, for instance, [7, 8]. The key steps are outlined in the following.

Considering a gaseous system of $N$ noninteracting, indistinguishable particles confined to a space of volume $V$ and sharing a given energy $E$. Let $\varepsilon_i$ denote the energy of $i$-th level and $\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \ldots$, and $g_i$ denote the degeneracy of the level. In a particular situation, we may have $n_1$ particles in the first level $\varepsilon_1$, $n_2$ particles in the second level $\varepsilon_2$, and so on, defining a distribution set $\{n_i\}$ [7]. The number of the distinct microstates in set $\{n_i\}$ is then given by,

$$\Omega \{n_i\} = \prod_i \left( \frac{(g_i)^{n_i}}{n_i!} \right).$$

(1)

The distribution set $\{n_i\}$ must conform to two macroscopic conditions,

$$\sum_i n_i = N, \sum_i n_i \varepsilon_i = E.$$ 

(2)

The entropy of the system is $S = S(N, V, E) = k_B \ln \Omega \{n_i^*\}$ where $k_B$ is the Boltzmann constant, and $\{n_i^*\}$ is the most probable distribution, determined by maximizing the following variational,

$$f = k_B \ln \Omega \{n_i\} - \alpha \left( \sum_i n_i - N \right) - \beta \left( \sum_i n_i \varepsilon_i - E \right),$$

(3)

where $\alpha$ and $\beta$ are two Lagrangian multipliers. The variational calculation gives with the discrete indices $i = 1, 2, 3, \ldots$ [5–8],

$$\delta f = \sum_i (\delta n_i (\ln g_i - \alpha - \beta \varepsilon_i) - \delta \ln n_i! \cdot \delta n_i^*).$$

(4)

The most probable distribution $\{n_i^*\}$ satisfies [5–8],

$$\frac{\delta f}{\delta n_i^*} = (\ln g_i - \alpha - \beta \varepsilon_i) - \frac{\delta \ln n_i^*!}{\delta n_i^*} = 0, \text{ i.e., } \psi(1 + n_i^*) = \ln g_i - \alpha - \beta \varepsilon_i,$$

(5)

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where
\[ \psi(1 + x) = \frac{d \ln x!}{dx} \] (6)
is the so-called Digamma function of variable \( x \), and \( \Gamma(1 + x) \equiv x! \) is the Gamma function.

When \( x \gg 1 \), utilizing the usual form of the Stirling’s approximation \( \ln x! \approx x \ln x - x \), we have,
\[ \psi(1 + x) \approx \ln x. \] (7)

In the limit \( x \gg 1 \), the standard expression for the Boltzmann statistics is recovered \[8\].
\[ n_i^* \approx g_i e^{-\alpha - \beta \varepsilon_i} \] (8)

However, it is not satisfactory. We can use grand ensemble statistics to prove that the approximately-equal-to symbol \( \approx \) is in fact the identical-to one \( = \) \[8\], and a more convenient and detailed derivation is available from a website lecture note \[9\].

The Stirling’s approximation \( \ln x! \approx x \ln x - x \) holds only when \( x \) is large. When \( x \) is small, a slight deviation from the distribution \( n_i^* \approx g_i e^{-\alpha - \beta \varepsilon_i} \) as \( i \to \infty \) may cause a ”long tail” contribution. How about a more accurate approximation of \( \ln x! \) is used? In the following section II, we will show the continuous calculus of variations in step \[4\] is questionable. In section III, with the proper use of the discrete calculus of variations, the relevant difficulty in approximating \( \ln x! \) is removed, and the approximate relation \[7\] turns out to be an exact result. In section IV, some further comments on the derivatives in the discrete calculus of variations are added. The final section V is a brief conclusion.

II. APPEARANCE OF ADDITIONAL \(-1/2\) TERM WITH THE CONTINUOUS CALCULUS OF VARIATIONS

With more accurate expression of \( \ln x! \) as \( \ln x! \approx (x + 1/2) \ln x - x + 1/2 \ln 2\pi \), we have \( d \ln x! / dx \approx \ln x + 1 / (2x) \), and \( \exp(d \ln x! / dx) \approx x + 1/2 \). Then we come up against a worse result,
\[ n_i^* \approx - \frac{1}{2} + g_i e^{-\alpha - \beta \varepsilon_i}. \] (9)

When the energy levels are lower to the lowest, i.e., the number \( n_i^* \) of particles is large, we have approximately the Boltzmann distribution \( n_i^* \approx g_i e^{-\alpha - \beta \varepsilon_i} \). Meanwhile, the high energy levels are less likely to be populated as \( g_i e^{-\alpha - \beta \varepsilon_i} \to 0 \) when \( \varepsilon_i \to \infty \), leading to a ”long tail” distribution from \[9\],
\[ n_i^* \approx - \frac{1}{2} i \to \infty. \] (10)

This additional \(-1/2\) term presents though the ”rigorous treatment” of Eq. \[4\] is utilized. To see it, let us consider an asymptotic expression of the Digamma function \( \psi(1 + x) \) in limit \( x \to \infty \) which is, with \( O(x^{-2}) \) denoting a quantity of order \( x^{-2} \) \[14\],
\[ \psi(1 + x) \to \ln x + \frac{1}{2x} + O(x^{-2}), \quad x \to \infty. \] (11)

A surprising property of the Digamma function \( \psi(1 + x) \) is that we can numerically verify following equation which holds true for all \( x \in [0, \infty) \),
\[ e^{\psi(1+x)} \approx x + 1/2. \] (12)

The largest deviation from \( 1/2 \) occurs at the ending point \( x = 0 \) and \( e^{\psi(1)} = e^{-\gamma} \approx 0.561 \), with \( \gamma \approx 0.577 \) is the Euler–Mascheroni constant. As \( x \) increases from zero, the difference \( e^{\psi(1+x)} - x \) monotonically converges to \( 1/2 \); and at \( x = 10 \) and \( 10^2 \), it gives 0.503 and 0.500, respectively. Clearly, Eq. \[12\] turns out to be approximately valid in whole range of \( n_i^* \in [0, \infty) \). When \( x \) is large, \( x + 1/2 \approx x \); however, when \( x = 0 \), \( e^{\psi(1+x)} \approx 0.561 \approx 1/2 \) leads to the spurious ”long tail” distribution again.

The additional \(-1/2\) term has to be removed, because the energy levels can never be negatively occupied. However, one can not simply discard the \(-1/2\) term in the limit \( i \to \infty \), because this term is associated with a divergence as the number of particles is summed up over all energy levels,
\[ \sum_{i}^{\infty} n_i^* \approx - \frac{1}{2} \sum_{i=1}^{\infty} 1 + \sum_{i=1}^{\infty} g_i e^{-\alpha - \beta \varepsilon_i}, \quad \text{and} \quad \sum_{i=1}^{\infty} 1 \to \infty. \] (13)
This situation bears a resemblance to the famous divergence in quantum electrodynamics. Some feels comfortable with it but other are strongly against it. Remembering that the lattice quantum fields are helpful to eliminate the undesired divergences, we are confident that the similar and proper treatment of the discrete calculus can be used to get rid of the difficulty. To note that the discrete calculus of variations is a well-established discipline in mathematics with much wider applications, and one of the fundamental principles is clear for the derivatives should be replaced by finite differences [10–13].

### III. REMOVAL OF ADDITIONAL $-1/2$ TERM WITH DISCRETE CALCULUS OF VARIATIONS

To note that the change of the number of the particle should be integers. The application of the variational calculation to the Boltzmann system in Eq. (4) must be with care. Since the number of particle is discrete, we must thus define the Digamma function on discrete lattices $x = 0, 1, 2, 3, \ldots$ Furthermore, the smallest possible change of the particle can only be $+1$ or $-1$ and can never be an infinitesimal.

The minimum finite difference for $\Delta \ln n!/\Delta n$ may take two forms. One is the so-called the forward one $\psi^+(1 + n)$, and another the backward one $\psi^+(1 + n)$,

\[
\frac{\Delta \ln n!}{\Delta n} = \frac{\ln (n+1)! - \ln (n)!}{1} = \psi^+(1 + n), \text{ and,}
\]

\[
\frac{\Delta \ln x!}{\Delta n} = \frac{\ln (n)! - \ln (n-1)!}{1} = \psi^-(1 + n).
\]

In simple forms, we have, respectively,

\[
\psi^+(1 + n) \equiv \ln(n + 1)! - \ln n! = \ln(n + 1), \quad (n \geq 0), \text{ and}
\]

\[
\psi^- (1 + n) \equiv \ln n! - \ln(n - 1)! = \ln n.
\]

Two important and somewhat trivial relations are $\ln(n + 1) \succ \ln n, \quad (n \geq 1)$, and when $n \to 0$, $\ln(n + 1) \succ \ln n$ can also be understood in the sense of $1 \approx e^{\ln(n+1)} \succ e^{\ln n} \to 0$.

The principles of the calculus of variations indicate that a variation of $\ln n!$ is to find a minimum possible amount of the changes of $\ln n!$ when $n$ is changed by a minimum possible value. Thus, $\psi^- (1 + n) = \ln n$ is singled out. I.e., the approximate result (7) happens to be an exact one. Now we have an exact relation,

\[
n^*_n = g_i e^{-\alpha - \beta \varepsilon_i}.
\]

It is right the standard form of the Boltzmann distribution applicable in the whole meaningful interval $n^*_n \in (0, n^*_0)$.

### IV. WHY THE ADDITIONAL $-1/2$ TERM OCCURS FROM THE POINT OF THE DISCRETE CALCULUS OF VARIATIONS

In above section, we stress that only a special choose of discrete derivatives among $\Delta \ln n!/\Delta n$ suffices to represent the discrete variational derivative $\delta \ln n!/\delta n$, and we single out the minimum one $\psi^- (1 + n) = \ln n$. In contrast, if including both $\psi^+(1 + n) = \ln(n + 1)$ and $\psi^- (1 + n) = \ln n$, and using the arithmetic mean of $\psi^+(1 + n)$ and $\psi^- (1 + n)$ to present the discrete variational derivative $\delta \ln n!/\delta n$ instead, we have,

\[
\psi_{\text{min}} (1 + n) \equiv \frac{1}{2} (\psi^+(1 + n) + \psi^- (1 + n)) = \left(\ln n + \ln(n + 1)\right)/2.
\]

we run across the unnecessary $-1/2$ term again, for we have,

\[
\exp (\psi_{\text{min}} (1 + n)) = \sqrt{n(n + 1)} \approx n + 1/2, \quad (n \gg 1).
\]

Such the discrete variational derivative is applicable for the definition of thermodynamic quantities for the few-particle systems in the microcanonical ensemble. Since in the ensemble both the number of particle and the energy are fixed, the temperature, for instance, can not be defined by usual derivative, but the variational derivative instead.

Following the same idea presented in above section, we must choose a minimum possible value among all possible differences. Recent treatments [15] of the definition of the temperature and other thermodynamic quantities in the microcanonical ensemble for small systems demonstrate that we must pick up the backward difference of $\Delta \ln n!/\Delta n$, based on the completely different arguments.
V. CONCLUSIONS AND DISCUSSIONS

The calculus of variations is to use a small changes in functions and functionals, to find maxima and minima of them. Once the functions and functionals are defined on the continuous intervals, the usual derivatives are sufficient. However, once they are defined on the discrete points, the variational derivatives correspond to the many finite differences. We in fact put forward a double extrema form of the calculus of variations in which only the smallest one of the finite differences is physically meaningful to represent the variational derivatives. By the double extrema form, we mean that the usual form of the calculus of variations deals with one extrema only.

The double extrema form of the variational \( \delta f = 0 \), but also \( \delta \ln n! / \delta n = \min \{ \Delta \ln n! / \Delta n \} \). The exact form the most probable distribution for the Boltzmann system is then reproduced without the Stirling’s approximation, and free from other theoretical problems. The double extrema form of the calculus of variations has in fact been used in literature on statistical mechanics for finite size systems, but based on the physical arguments.

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