

# Revision of Boltzmann statistics for a finite number of particles

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The Stirling approximation,  $\ln(N!) \approx N \ln(N) - N$ , is used in the literature to derive the exponential Boltzmann distribution. We generalize the latter for a finite number of particles by applying the more exact Stirling formula and the exact function  $\ln(N!)$ . A more accurate and analytical formulation of Boltzmann statistics is found in terms of the Lambert W-function. The Lambert-Boltzmann distribution is shown to be a very good approximation to the exact result calculated by numerical inversion of the Digamma-function. For a finite number of particles  $N$  the exact distribution yields results that differ from the usual exponential Boltzmann distribution. As an example, the exact Digamma-Boltzmann distribution predicts that the constant-volume heat capacity of an Einstein solid decreases with decreasing  $N$ . The exact Digamma-Boltzmann distribution imposes a constraint on the maximum energy of the highest populated state, consistent with the finite total energy of the microcanonical ensemble. © 2009 American Association of Physics Teachers.

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## I. INTRODUCTION

The usual exponential Boltzmann distribution describes the populations of (non-degenerate) energy states  $\varepsilon_i$ ,  $i = 0, 1, \dots, m$ , for non-interacting particles in an isolated system.<sup>1</sup> A crucial step in the derivation is the application of Stirling's approximation:<sup>2,3</sup>

$$\ln(n!) \approx n \ln(n) - n \quad (\text{Stirling's approximation}). \quad (1)$$

For small values of  $n$  Eq. (1) is very crude because it does not contain the leading term,  $(1/2)\ln(n)$ , of the Stirling series:<sup>4</sup>

$$\begin{aligned} \ln(n!) = & \left(n + \frac{1}{2}\right) \ln(n) - n + \frac{1}{2} \ln(2\pi) + \frac{1}{12n} - \frac{1}{360n^3} \\ & + \dots \quad (\text{Stirling series}). \end{aligned} \quad (2)$$

The Stirling formula gives a much better approximation to  $\ln(n!)$  because it includes all the leading terms in Eq. (2):<sup>3</sup>

$$\begin{aligned} \ln(n!) \approx & \left(n + \frac{1}{2}\right) \ln(n) - n \\ & + \frac{1}{2} \ln(2\pi) \quad (\text{Stirling formula}). \end{aligned} \quad (3)$$

The reciprocal terms  $1/(12n) - 1/(360n^3) + \dots$  in Eq. (2) are not essential if  $n > 2$  (see Fig. 1). Generally, the occupation number  $n_i$  of the highest energy states  $\varepsilon_i$  is very small if  $\varepsilon_i \rightarrow \infty$ . However, the range of applicability of Eq. (1) is limited to very large values of  $n_i$ , where the condition  $\ln(n_i)/2 \ll n_i \ln(n_i) - n_i$  is satisfied. If  $n_i$  is small, say  $n_i = 1$  or 2, Eq. (1) yields negative values (see Fig. 1). Therefore, the exponential Boltzmann distribution is limited strictly to  $n_i \gg 1$  and applies only for  $\varepsilon_i$  not too large. However, the distribution is used in the literature even for  $\varepsilon_i \rightarrow \infty$  and  $n_i \rightarrow 0$ , where Eq. (1) does not apply. It is interesting that Stirling's approximation, Eq. (1), fails and the more accurate Stirling formula, Eq. (3), is required to derive the Gaussian distribution from the binomial distribution.<sup>5</sup>

It is natural to ask if the use of the more exact Stirling formula, Eq. (3), and the exact Stirling series, Eq. (2), leads to a more accurate formulation of the Boltzmann variational problem of the calculation of the most probable population of energy states of the microcanonical ensemble, and if the exact distribution is different from the exponential Boltzmann distribution. The solution of the Boltzmann variational problem using Eq. (3) leads to a transcendental equation. We show that this equation can be solved in closed form by using the Lambert W-function, also known as the Product-Log function or omega function.<sup>6</sup> The Lambert W-function  $W(x)$  is defined as the solution of the equation  $W(x)\exp(W(x)) = x$ . Several symbolic computation packages contain routines for the Lambert W-function and recent articles discuss problems that can be solved analytically using this function.<sup>6</sup> The solution of the Boltzmann variational problem using the exact function  $\ln(n!)$  leads to a complicated transcendental equation, which must be solved numerically. In any case, it is worthwhile to obtain a more exact and physically tractable solution of the Boltzmann variational problem.

## II. REVISED BOLTZMANN DISTRIBUTION

### A. Formulation of the variational problem

We consider an isolated system of  $N$  indistinguishable non-interacting particles with total constant energy  $E$ .<sup>2</sup> Each particle may exist in any of the energy states  $\varepsilon_0 < \varepsilon_1 < \dots < \varepsilon_m$ , where  $m$  is the total number of states. The population is characterized by the set of numbers  $n_0, n_1, \dots, n_m$  of the particles in the energy states  $\varepsilon_0, \varepsilon_1, \dots, \varepsilon_m$ , respectively. The probability of finding  $n_i$  distinguishable particles in each of the  $m$  states is given by  $p_i^{n_i}$ , where  $p_i$  is the probability of the occupation of energy state  $\varepsilon_i$ . The total probability of a configuration  $(n_0, \varepsilon_0), (n_1, \varepsilon_1), \dots, (n_m, \varepsilon_m)$  is given by the product  $p_0^{n_0} p_1^{n_1} \dots p_m^{n_m}$ . For indistinguishable particles the statistical weight of the same configuration is given by<sup>1</sup>

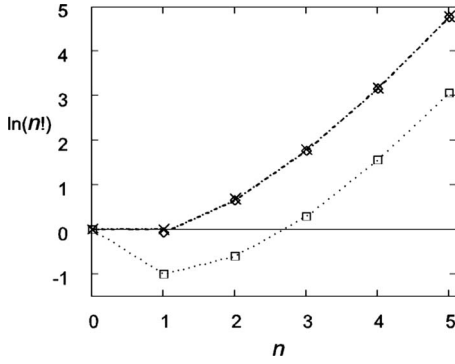


Fig. 1. Comparison of Stirling's approximation, Eq. (1) ( $\square$ ), and the Stirling formula, Eq. (3) ( $\diamond$ ), with the exact function  $\ln(n!)$  ( $\times$ ) up to  $n=5$ .

$$w(n_0, n_1, \dots, n_m) = \frac{N!}{n_0! n_1! \dots n_m!}. \quad (4)$$

The total probability of the configuration  $(n_0, \varepsilon_0), (n_1, \varepsilon_1), \dots, (n_m, \varepsilon_m)$  takes the form

$$P(n_0, n_1, \dots, n_m) = w(n_0, n_1, \dots, n_m) p_0^{n_0} p_1^{n_1} \dots p_m^{n_m}, \quad (5)$$

where  $w(n_0, n_1, \dots, n_m)$  is given by Eq. (4). We adopt the principle of equal *a priori* probabilities  $p_0 = p_1 = \dots = p_m = p$ , so that the product  $p_0^{n_0} p_1^{n_1} \dots p_m^{n_m}$  in Eq. (5) reduces to the constant  $p^{n_0 + n_1 + \dots + n_m} = p^N$ , where

$$N = \sum_{i=0}^m n_i. \quad (6)$$

The most probable configuration, corresponding to the maximum of the probability in Eq. (5), is calculated given the constraint of the fixed total number of particles, Eq. (6), and the total energy:

$$E = \sum_{i=0}^m n_i \varepsilon_i. \quad (7)$$

Because of the two constraints, two of the  $m$  variables in Eq. (5) are dependent. One way to find the extremum is the Lagrange method of undetermined multipliers using two multipliers,  $\alpha$  and  $\beta$ , in the form<sup>7</sup>

$$F(n_0, n_1, \dots, n_m) = P(n_0, n_1, \dots, n_m) + \alpha \left( N - \sum_{i=0}^m n_i \right) + \beta \left( E - \sum_{i=0}^m n_i \varepsilon_i \right). \quad (8)$$

At this stage of the analysis all the  $n_i$  are free variables, so that  $N \neq \sum_{i=0}^m n_i$  and  $E \neq \sum_{i=0}^m n_i \varepsilon_i$ . The values  $n_i^*$  of an extremum of  $F$  can be calculated from the equation

$$dF = \sum_{i=0}^m \left( \frac{\partial F}{\partial n_i} \right) \Big|_{n_i^*} = 0, \quad (9)$$

where  $\partial F / \partial n_i$  is the partial derivative of  $F$  with respect to  $n_i$  provided that all other variables  $n_j$  with  $j \neq i$  are kept constant. Because all  $\partial F / \partial n_i \leq 0$ , the only way to satisfy Eq. (9) is to require that

$$\left( \frac{\partial F}{\partial n_0} \right)_{n_0^*} = \left( \frac{\partial F}{\partial n_1} \right)_{n_1^*} = \dots = \left( \frac{\partial F}{\partial n_m} \right)_{n_m^*} = 0. \quad (10)$$

We also have  $\partial N / \partial n_i = \partial E / \partial n_i = 0$  so Eq. (10) can be expressed as

$$\frac{\partial F}{\partial n_i} \Big|_{n_i^*} = \frac{\partial P}{\partial n_i} \Big|_{n_i^*} - \alpha - \beta \varepsilon_i = 0 \quad \text{for } i = 0, 1, \dots, m. \quad (11)$$

The derivative  $\partial P / \partial n_i$  in Eq. (11) contains the derivative  $d(1/n_i!) / dn_i$ . In this form,  $d(1/n_i!) / dn_i$  cannot be used to solve Eq. (11) analytically. The usual approach is to replace the function  $P$  in Eq. (11) by  $\ln(P)$ . Because  $P > 0$  and  $\ln(P)$  is a monotonic function of  $P$ , both  $\ln(P)$  and  $P$  have extremum for the same  $n_i^*$ . Hence the function

$$\Phi(n_0, n_1, \dots, n_m) = \ln(P(n_0, n_1, \dots, n_m)) + \alpha \left( N - \sum_{i=0}^m n_i \right) + \beta \left( E - \sum_{i=0}^m n_i \varepsilon_i \right) \quad (12)$$

also has an extremum at  $n_i^*$ . Because  $\partial \ln(n_j!) / \partial n_i = 0$  for  $j \neq i$ , the derivative of  $\ln(P)$  can be written as

$$\frac{\partial \ln(P)}{\partial n_i} = \frac{\partial}{\partial n_i} \left( \ln(N! p^N) - \sum_{j=0}^m \ln(n_j!) \right) = - \frac{\partial}{\partial n_i} \ln(n_i!). \quad (13)$$

We use Eq. (13) and obtain the condition for an extremum of  $\Phi$  in Eq. (12) in the form

$$- \frac{\partial}{\partial n_i} \ln(n_i!) \Big|_{n_i^*} - \alpha - \beta \varepsilon_i = 0. \quad (14)$$

It remains to solve Eq. (14).

### III. APPLICATION OF STIRLING'S APPROXIMATIONS

#### A. Crude Stirling's approximation

If we apply Stirling's approximation, Eq. (1), or the Stirling formula, Eq. (3), to Eq. (14), we find

$$- \ln(n_i^*) - \frac{\mu}{2n_i^*} - \alpha - \beta \varepsilon_i = 0, \quad (15)$$

where  $\mu=0$  or 1 represents the solution for Eq. (1) or Eq. (3), respectively. If  $\mu=0$ , the solution of Eq. (15) yields the exponential Boltzmann distribution:<sup>7</sup>

$$n_i^* = \exp(-\alpha - \beta \varepsilon_i), \quad (16)$$

where  $\beta=1/(kT)$ ,  $k$  is Boltzmann's constant, and  $T$  is the thermodynamic temperature. The ratio  $P_i = n_i^* / N$  is the usual exponential Boltzmann probability. The partition function is given by

$$Z = \sum_{i=0}^m \exp(-\beta \varepsilon_i). \quad (17)$$

The Lagrange multiplier  $\alpha$  can be written as

$$\alpha = -\ln(N/Z). \quad (18)$$

## B. The more accurate Stirling formula

For  $\mu=1$  the solution of Eq. (15) is obtained in terms of the Lambert W-function  $W(x)$ :<sup>6</sup>

$$n_{i,W}^* = \frac{-1}{2W\left(-\frac{1}{2}\exp(\alpha_W + \beta\varepsilon_i)\right)}, \quad (19)$$

where the subscript  $W$  refers to the values calculated with the function  $W(x)$ . Because the second derivative of  $\Phi$  is negative,

$$\left. \frac{\partial^2 \Phi}{\partial n_i^2} \right|_{n_{i,W}^*} = -\frac{1}{n_{i,W}^*} + \frac{1}{2(n_{i,W}^*)^2} < 0, \quad (20)$$

the solution  $n_{i,W}^*$  is a maximum, and the ratio  $P_{i,W} = n_{i,W}^*/N_W$  is the Lambert-Boltzmann probability, where  $N_W = \sum_{i=0}^m n_{i,W}^*$ . In analogy to Eq. (17) we calculate the Lambert W-partition function  $Z_W$  in the form

$$Z_W = \sum_{i=0}^m \frac{n_{i,W}^*(\varepsilon_i)}{n_{i=0,W}^*(\varepsilon_0=0)} = -2N_W W\left(-\frac{1}{2}\exp(\alpha_W)\right). \quad (21)$$

The solution of Eq. (21) for the Lagrange multiplier  $\alpha_W$  yields the form

$$\alpha_W = -\ln\left(\frac{N_W}{Z_W}\right) - \frac{Z_W}{2N_W}. \quad (22)$$

In contrast to Eq. (18) the value of  $\alpha_W$  is limited to a certain range as is discussed in Sec. III C.

## C. Range of $\alpha_W$

For the real and positive numbers  $n_{i,W}^*$  the range of the argument  $x = -\exp(\alpha_W + \beta\varepsilon_i)/2$  of  $W(x)$  in Eq. (19) is limited to  $0 \geq x \geq -1/e$ . In the range  $0 \geq x \geq -1/e$ ,  $W(x)$  is the  $W_0^-$ -branch of the Lambert W-function,  $-1 \leq W_0^- \leq 0$ .<sup>6</sup> Therefore the function  $W$  in Eqs. (19) and (21) has to be replaced by  $W_0^-$ . The range of validity of  $x$  imposes a constraint on the parameters  $\alpha_W$  and  $\varepsilon_i$ :

$$0 \leq \exp(\alpha_W + \beta\varepsilon_i) \leq 2/e. \quad (23)$$

Equation (23) implies that  $\alpha_W$  is related to the value  $\varepsilon_{Wm}$  of the highest energy state by

$$\alpha_W = \ln(2/e) - \beta\varepsilon_{Wm}. \quad (24)$$

For a given  $\alpha_W$  Eq. (23) requires that

$$0 \leq \varepsilon_0 < \dots < \varepsilon_i < \dots \leq \varepsilon_{Wm} = (\ln(2/e) - \alpha_W)/\beta. \quad (25)$$

Equation (25) suggests that the Lambert-Boltzmann distribution, Eq. (19), applies only up to the maximum energy  $\varepsilon_{Wm}$  (inclusive of the  $\varepsilon_{Wm}$ -value). If we substitute Eq. (22) into Eq. (25), we can calculate  $\varepsilon_{Wm}$  explicitly,

$$\varepsilon_{Wm} = \frac{1}{\beta} \left[ \ln\left(\frac{2N_W}{eZ_W}\right) + \frac{Z_W}{2N_W} \right], \quad (26)$$

or

$$Z_W = -2N_W W_0^-(\exp(-\beta\varepsilon_{Wm} - 1)). \quad (27)$$

The constraints in Eqs. (26) and (27) define the functional dependence of the parameters  $\varepsilon_{Wm}$ ,  $N_W$ , and  $Z_W$  for which the Lambert-Boltzmann distribution in Eq. (19) applies.

## D. Exact solution of the Boltzmann problem in terms of the inverse Digamma-function

The exact derivative of  $\ln(n!)$  is given by the Digamma-function  $\psi_0$ :  $d \ln(n!)/dn = \psi_0(n+1)$ , where the argument  $n$  in  $\psi_0$  can be any real number. Equation (15) acquires the form

$$-\psi_0(n_{i,\psi}^* + 1) - \alpha_\psi - \beta\varepsilon_i = 0, \quad (28)$$

where the subscript  $\psi$  refers to the values calculated with the Digamma-function. The solution of Eq. (28) is obtained in terms of the inverse Digamma-function,  $\psi_0^{-1}$ :

$$n_{i,\psi}^* = \psi_0^{-1}(-\alpha_\psi - \beta\varepsilon_i) - 1. \quad (29)$$

In contrast to  $W_0^-$ ,  $\psi_0^{-1}$  is not included in the generally available software packages and must be calculated numerically. The Digamma-partition function  $Z_\psi$  which is analogous to Eq. (21) has the form

$$Z_\psi = \frac{N_\psi}{\psi_0^{-1}(-\alpha_\psi) - 1}. \quad (30)$$

The correct range of the argument  $\alpha_\psi$  of  $\psi_0^{-1}$  is found by requiring that  $n_{i,\psi}^*$  be non-negative. For  $n_{i,\psi}^* \geq 0$  Eq. (28) suggests that  $-\alpha_\psi - \beta\varepsilon_i \geq \psi_0(1) = -\gamma$ , where  $\gamma = 0.577\dots$  is the Euler-Mascheroni constant. Because  $\beta\varepsilon_i \geq 0$ , we find that  $\alpha_\psi$  is related to the maximum value  $\varepsilon_{\psi m}$  by

$$0 \leq \varepsilon_{\psi m} = (\gamma - \alpha_\psi)/\beta. \quad (31)$$

The constraint in Eq. (31) is similar to Eq. (25) of the Lambert-Boltzmann distribution, except for the constant  $\gamma$ , which replaces  $\ln(2/e) \approx -0.307$ . The exact value of the maximum energy  $\varepsilon_{\psi m}$  is larger by the quantity of  $(\gamma - \ln(2/e))/\beta \approx 0.884kT$  than the approximate value  $\varepsilon_{Wm}$  given in Eq. (25). For large energies,  $\varepsilon_{\psi m}, \varepsilon_{Wm} \gg kT$ , the difference  $\varepsilon_{\psi m} - \varepsilon_{Wm}$  is not important.

If we apply Eq. (31) to Eq. (30), we can express the exact Digamma-partition function  $Z_\psi$  as

$$Z_\psi = \frac{N_\psi}{\psi_0^{-1}(\beta\varepsilon_{\psi m} - \gamma) - 1}. \quad (32)$$

As in Eq. (27) the exact partition function  $Z_\psi$  in Eq. (32) can be expressed in closed form in terms of the  $N_\psi$  and  $\varepsilon_{\psi m}$ . Note that the usual partition sum  $Z$  in Eq. (17) is independent of  $N$ .

## IV. RESULTS AND DISCUSSION

### A. Exponential Boltzmann versus the Lambert- and the exact Boltzmann distribution

As an example, we consider a system with  $n_0^* = 600$  particles in the ground state with  $\varepsilon_0 = 0$ . Equation (15) with  $\mu = 0$  yields  $\alpha = -\ln(n_0^*) = -6.397$ ; Eq. (15) with  $\mu = 1$  and the exact  $\psi_0$ -Boltzmann equation, Eq. (28), yield  $\alpha_W = -\ln(n_0^*) - 1/(2n_0^*) = \alpha_\psi = -\psi_0(n_0^* + 1) = -6.398$ . If we use Eqs. (25) and (31), we find  $\beta\varepsilon_{Wm} = \ln(2/e) - \alpha_W = 6.091$  and  $\beta\varepsilon_{\psi m} = \gamma - \alpha_\psi = 6.975$ , respectively. Within the range of applicability, the Lambert-Boltzmann distribution in Eq. (19) and the exact

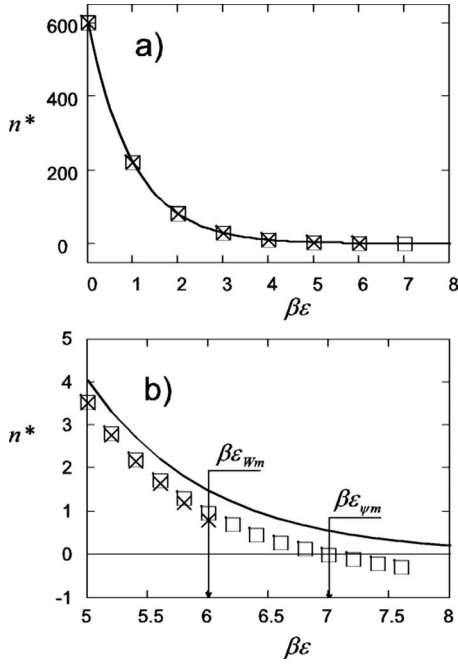


Fig. 2. (a) The solid curve is the exponential Boltzmann distribution  $n^*$ , Eq. (16);  $\times$ , the Lambert-Boltzmann distribution  $n_{W}^*$ , Eq. (19); and  $\square$ , the exact Digamma-Boltzmann distribution  $n_{\psi}^*$ , Eq. (29) as a function of  $\beta\varepsilon$ , where  $\varepsilon$  is the energy of the states and  $\beta=1/kT$ . The arrows show the maximum energies  $\beta\varepsilon_{Wm}=\ln(2/e)-\alpha_W\approx 6.1$  and  $\beta\varepsilon_{\psi m}=\gamma-\alpha_{\psi}\approx 7.0$  of  $n_{W}^*$  and  $n_{\psi}^*$ . Note that  $n_i^*$  in Eq. (16) disagrees with  $n_{W}^*$  and  $n_{\psi}^*$ . The distributions shown are for  $n_0^*=n_{0,W}^*=n_{0,\psi}^*=600$  for the ground state of the zero energy  $\varepsilon_0=0$  and  $T=300$  K. (b) The same as in (a) in the range  $5\leq\beta\varepsilon\leq 7$ , where the discrepancies between  $n^*$ ,  $n_{W}^*$ , and  $n_{\psi}^*$  are most pronounced;  $n_{W}^*$  and  $n_{\psi}^*$  were calculated using Mathematica.

Digamma-Boltzmann distribution in Eq. (29) are close to the exponential Boltzmann distribution in Eq. (16) [see Fig. 2(a)]. However, Eq. (16) applies up to  $\beta\varepsilon_m\rightarrow\infty$ , whereas Eqs. (19) and (29) apply up to  $\beta\varepsilon_{Wm}\approx 6$  and  $\beta\varepsilon_{\psi m}\approx 7$ , respectively [see Fig. 2(b)]. For example, for a system of equidistant energy states,  $\varepsilon_i=\Delta\varepsilon i$ , where  $i=0,1,\dots,m$  and  $\Delta\varepsilon=kT$ ,  $T=300$  K, the Lambert and the exact Digamma-

Boltzmann distributions yield approximately the same total numbers  $N$  of particles:  $N_W=\sum_{i=0}^{m=6}n_{i,W}^*=945$  and  $N_{\psi}=\sum_{i=0}^{m=7}n_{i,\psi}^*=946$ . The Lambert and Digamma statistical sums are also identical:  $Z_W=-2N_W W_0(-\exp(\alpha_W)/2)=Z_{\psi}=N_{\psi}/(\psi_0^{-1}(-\alpha_{\psi})-1)=1.576$ . If we apply Eq. (15) with  $\mu=0$ , we obtain  $N=\sum_{i=0}^{\infty}n_i^*=949$  and  $Z=N\exp(\alpha)=1.582$ . The key parameters of the exponential, Lambert- and Digamma-Boltzmann statistics are summarized in Table I. It is seen that the Lambert and Digamma-Boltzmann distributions yield approximately equal results, which differ from the exponential Boltzmann statistics. Figure 2(b) shows that  $n_i^*\geq n_{i,W}^*\geq n_{i,\psi}^*$  for  $\beta\varepsilon_i>0$ . The total probability of all three statistics is equal to unity:  $\sum_{i=0}^{\infty}n_i^*/N=\sum_{i=0}^{m=6}n_{i,W}^*/N_W=\sum_{i=0}^{m=7}n_{i,\psi}^*/N_{\psi}=1$ .

## B. Population of energy states of a quantum oscillator

The effect of the constraints in Eqs. (25) and (31) on the population of the energy states can be shown, for instance, by determining the heat capacity of a system of oscillators. In the harmonic approximation the vibrational energy of a quantum oscillator is given by  $\varepsilon_i=\Delta\varepsilon(i+1/2)$ , where  $i=0,1,\dots,m$  and  $\Delta\varepsilon=h\nu_0$  is the separation between the adjacent states,  $h$  is Planck's constant, and  $\nu_0$  is the characteristic frequency. If the usual Boltzmann distribution is used to calculate the population of the energy states, the partition function is given by

$$Z(m)=\sum_{i=0}^{i=m}\exp\left(-\frac{\varepsilon_i}{kT}\right)=\frac{1-\exp\left(-\frac{\Delta\varepsilon(m+1/2)}{kT}\right)}{\exp\left(\frac{\Delta\varepsilon}{2kT}\right)-\exp\left(-\frac{\Delta\varepsilon}{2kT}\right)}. \quad (33)$$

The maximum energy of the harmonic oscillator is not bounded from above and therefore the number of levels can be infinite,  $m\rightarrow\infty$ . However, for an isolated system of  $N$  oscillators of total energy  $E$  there is a constraint on the energies:  $0<\varepsilon_0<\dots<\varepsilon_i<\dots<\varepsilon_m\leq E$ . In equilibrium and

Table I. Comparison of the key parameters of the three forms of the Boltzmann distribution for a system with  $n_0^*=n_{0,W}^*=n_{0,\psi}^*=600$  particles in the ground state with the zero energy  $\varepsilon_0=0$  and equidistant energy states:  $\varepsilon_i=\Delta\varepsilon i$ , where  $i=0,1,\dots,m$  and  $\Delta\varepsilon=kT$ ,  $T=300$  K;  $W_0^-$  is the negative branch of the Lambert W-function,  $\psi_0^-$  is the Digamma-function,  $\gamma\approx 0.577$  is the Euler-Mascheroni constant,  $\ln(2/e)\approx -0.307$ ,  $\beta=1/kT$ ,  $k$  is the Boltzmann constant, and  $N$  is the total number of particles.

Exponential Boltzmann distribution, Eq. (16)	Lambert-Boltzmann distribution, Eq. (19)	Exact Digamma-Boltzmann distribution, Eq. (29)
$\alpha=-\ln(n_0^*)=-6.397$ Eq. (15) with $\mu=0$	$\alpha_W=-\ln(n_{0,W}^*)-1/(2n_{0,W}^*)=-6.398$ Eq. (15) with $\mu=1$	$\alpha_{\psi}=-\psi_0^-(n_{0,\psi}^*+1)=-6.398$ Eq. (28)
$\beta\varepsilon_m<\infty$	$\beta\varepsilon_{Wm}=\ln(2/e)-\alpha_W=6.091$ Eq. (25)	$\beta\varepsilon_{\psi m}=\gamma-\alpha_{\psi}=6.975$ Eq. (31)
$m<\infty$	$m_W=\varepsilon_{Wm}/\Delta\varepsilon=6$	$m_{\psi}=\varepsilon_{\psi m}/\Delta\varepsilon=7$
$N=\sum_{i=0}^{\infty}n_i^*=949$	$N_W=\sum_{i=0}^6n_{i,W}^*=945$	$N_{\psi}=\sum_{i=0}^7n_{i,\psi}^*=946$
$Z=N\exp(\alpha)=1.582$ Eq. (17)	$Z_W=-2N_W W_0\left(-\frac{e^{\alpha_W}}{2}\right)=1.576$ Eq. (21)	$Z_{\psi}=\frac{N_{\psi}}{\psi_0^{-1}(-\alpha_{\psi})-1}=1.576$ Eq. (30)

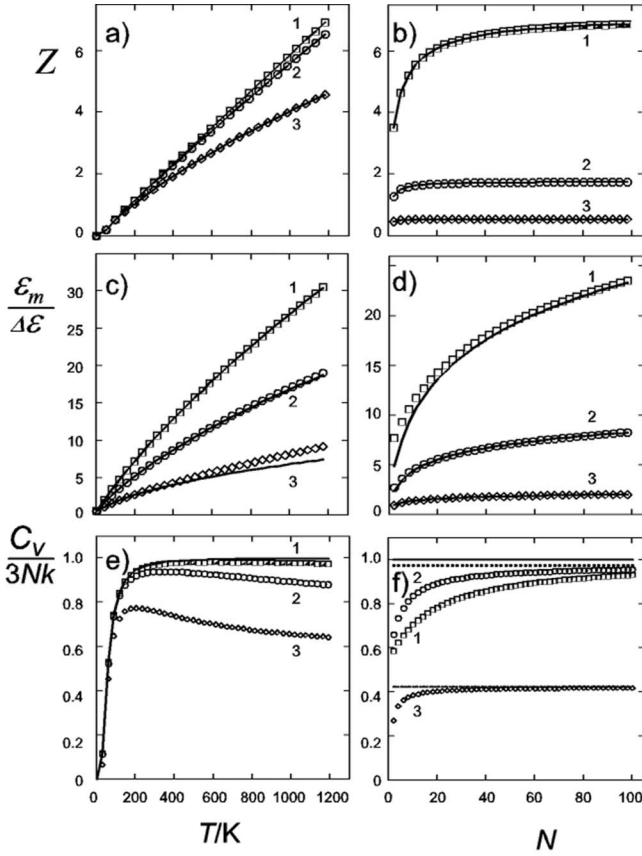


Fig. 3. The partition function  $Z$ , the maximum energy ratio  $\varepsilon_m/\Delta\varepsilon$  of the highest populated state (here  $\Delta\varepsilon=2.3\times 10^{-21}$  J), and the reduced constant-volume heat capacity  $C_V/(3Nk)$ , calculated with the exact Digamma-Boltzmann distribution for the Einstein Ag-solid as a function of the temperature  $T$  (left column) and the total number of particles  $N$  (right column). (a) The solid lines are the exact Digamma-partition function  $Z_\psi(\varepsilon_{\psi m})$ , Eq. (32), of the oscillator with energy states  $\varepsilon_i=\Delta\varepsilon(i+1/2)$ , where  $i=0,1,\dots,m$ . The points represent the conventional partition sum,  $Z(m)$ , truncated at  $m=\varepsilon_{\psi m}/\Delta\varepsilon-1/2$ , Eq. (33), at  $N=300$  (1),  $N=50$  (2), and  $N=5$  (3). (b) The solid line represents  $Z_\psi(\varepsilon_{\psi m})$ , Eq. (32); the points refer to  $Z(m)$ , Eq. (33), at  $T=1200$  K (1),  $T=300$  K (2), and  $T=100$  K (3). (c) The solid line is the exact maximum energy ratio  $\varepsilon_{\psi m}/\Delta\varepsilon$  of the oscillator, Eq. (31); the points represent the approximate values  $\varepsilon_{Wm}/\Delta\varepsilon$ , Eq. (37), corrected by  $(\gamma-\ln(2/e))kT$  at  $N=300$  (1),  $N=50$  (2), and  $N=5$  (3). (d) The solid lines are the exact energy ratio  $\varepsilon_{\psi m}/\Delta\varepsilon$ , Eq. (31), and the points are the approximate values  $\varepsilon_{Wm}/\Delta\varepsilon$ , Eq. (37), corrected by  $(\gamma-\ln(2/e))kT$  at  $T=1200$  K (1),  $T=300$  K (2), and  $T=100$  K (3). (e) The points represent the exact reduced heat capacity  $C_V/(3Nk)$  Eq. (34), versus  $T$  for  $N=300$  (1),  $N=50$  (2) (d), and  $N=5$  (3). The solid line corresponds to the usual Einstein equation, Eq. (36), for  $C_V/(3Nk)$  at  $\varepsilon_m\rightarrow\infty$ . (f) The points are the exact values of  $C_V/(3Nk)$ , Eq. (34), for  $T=1200$  K (1),  $T=300$  K (2), and  $T=100$  K (3). The lines (---), (· · ·), and (—) represent the usual Einstein equation, Eq. (36), at  $T=50$ , 300, and 1200 K, respectively. Note that the Einstein values  $C_V/(3Nk)$  are independent of  $N$ . The Dulong-Petit limiting law predicts  $C_V/(3Nk)=1$ .

for  $T<\infty$  the inequality  $N\geq n_0>\dots>n_i>\dots>n_m$  holds, so that  $\varepsilon_m\ll E$ . Nevertheless, Eq. (33) is erroneously applied in the literature without any limitation on  $\varepsilon_m$  up to  $m\rightarrow\infty$ :  $Z(\varepsilon_m\rightarrow\infty)=\exp(-\Delta\varepsilon/2kT)/(1-\exp(-\Delta\varepsilon/kT))$ .<sup>7</sup> The constraints of Eqs. (25) and (31), which arise naturally from the solvability conditions of the Boltzmann variational problem, truncate the sum in Eq. (33) at the limiting number  $m$ . Because  $m$  depends on  $N$  and  $T$ , the exact Digamma-partition function in Eq. (30) increases nonlinearly with  $N$  and  $T$  [see Figs. 3(a) and 3(b)]. Recall that the classical partition func-

tion  $Z(m\rightarrow\infty)$  is independent of  $N$ . Equations (25) and (31) define the range of validity of the exponential Boltzmann distribution and assist in the calculation of the correct values of the partition function.

### C. Exact value of the Einstein heat capacity

According to the Einstein model of the three-dimensional quantum oscillator, the constant-volume heat capacity is expressed as<sup>7</sup>

$$C_V=3kNT^2\left(\frac{\partial^2 \ln(Z(T))}{\partial T^2}\right)_{V,N}. \quad (34)$$

To calculate Eq. (34) with  $Z=Z_\psi$  we apply Eq. (33) and  $\varepsilon_{\psi m}(T)=\Delta\varepsilon(m+1/2)=kT(\gamma-\alpha_\psi)$  to Eq. (32) and obtain a transcendental equation for  $\alpha_\psi$ :

$$\alpha_\psi=\psi_0\left(N\frac{\exp(\Delta\varepsilon/(2kT))-\exp(-\Delta\varepsilon/(2kT))}{1-\exp(\alpha_\psi-\gamma)}+1\right). \quad (35)$$

Then we apply  $\alpha_\psi(T)$  to  $Z_\psi$  in Eq. (30) and calculate  $C_V$  in Eq. (34) numerically. For silver the Einstein temperature is  $\theta_E=168$  K, and hence  $\Delta\varepsilon=\theta_E k=2.32\times 10^{-21}$  J. Calculations with Eqs. (31) and (35) show that the maximum energy  $\varepsilon_{\psi m}$  increases with increasing  $T$  and  $N$  [see Figs. 3(c) and 3(d)]. For example, at  $T=293$  K and  $N=100$ , Eq. (31) yields:  $\varepsilon_m=4.7$  kT ( $0.19\times 10^{-19}$  J) and  $m=\varepsilon_{\psi m}/\Delta\varepsilon-1/2=8$ . For  $T=293$  K and  $N=6.022\times 10^{23}$  we obtain  $\varepsilon_{\psi m}=55kT$  and  $m=95$ . Because of the constraints on  $\varepsilon_{\psi m}$  and  $m$ ,  $C_V/(3Nk)$  is smaller than the Dulong-Petit limiting value  $C_V/(3Nk)=1$  even if  $T\gg\theta_E$  [see Figs. 3(e) and 3(f)]. For example, for  $N=50$  and  $T=293$  K, Eq. (34) yields  $C_V/(3Nk)=0.937$ , which is smaller by 3.7% than the value  $C_V/(3Nk)=0.973$  of the usual Einstein formula for  $\varepsilon_m\rightarrow\infty$ :<sup>7</sup>

$$C_V(\varepsilon_m\rightarrow\infty)=\frac{3N\Delta\varepsilon^2 \exp(\Delta\varepsilon/kT)}{kT^2(\exp(\Delta\varepsilon/kT)-1)^2}. \quad (36)$$

At very large values of  $N$ , say  $N=6.022\times 10^{23}$ , the exact Digamma-Einstein heat capacity, Eq. (34), approaches Eq. (36), for example, at  $T=293$  K Eqs. (34) and (36) yield the same value  $C_V/(3Nk)=0.973$ .

### D. Approximate value of the heat capacity

If we substitute Eq. (33) into Eq. (26) and solve for  $\varepsilon_{Wm}$  relative to  $\varepsilon_{Wm}=\Delta\varepsilon(m+1/2)$  for the case  $Z_W/(2N_W)\ll\ln(2N_W/(eZ_W))$ , we obtain the Lambert W maximum energy  $\varepsilon_{Wm}$  in the form

$$\varepsilon_{Wm}(T)\approx kT \ln\left[\exp\left(\frac{\Delta\varepsilon}{2kT}\right)-\frac{2N_W}{e}\left(1-\exp\left(\frac{\Delta\varepsilon}{kT}\right)\right)\right] - \frac{\Delta\varepsilon}{2}. \quad (37)$$

The sum  $\varepsilon_{Wm}+(\gamma-\ln(2/e))kT$  is close to the exact value  $\varepsilon_{\psi m}$  except for  $N_W\leq 5$  and  $T\geq 1200$  K (the melting temperature of Ag is  $T_m=1235.1$  K) [see Figs. 3(c) and 3(d)]. Recall that the quantity  $(\gamma-\ln(2/e))kT\approx 0.884kT$  corrects the discrepancy between  $\varepsilon_{Wm}$  and  $\varepsilon_{\psi m}$ . In the limiting case,  $T\rightarrow 0$ , Eq. (37) reduces to the physically reasonable value:

Table II. Three forms of the Boltzmann distribution derived using different approximations for  $\ln(n!)$ .

Approximations for $\ln(n!)$	Stirling's approximation, Eq. (1) $\ln(n!) \approx n \ln(n) - n$	Stirling's formula, Eq. (3) $\ln(n!) \approx \left(n + \frac{1}{2}\right) \ln(n) - n + \frac{1}{2} \ln(2\pi)$	Exact function $\ln(n!)$
Most probable population numbers	$n_i^* = e^{-\alpha - \beta \varepsilon_i}$ Eq. (16)	$n_{i,W}^* = \frac{-1}{2W_0 \left(-\frac{1}{2} \exp(\alpha_W + \beta \varepsilon_i)\right)}$ Eq. (19)	$n_{i,\psi}^* = \psi_0^{-1}(-\alpha_\psi - \beta \varepsilon_i) - 1$ Eq. (29)
The partition function	$Z = \sum_{i=0}^{j \rightarrow \infty} e^{-\beta \varepsilon_i}$ Eq. (17)	$Z_W = -2N_W W_0(-\exp(-\beta \varepsilon_{Wm} - 1))$ Eq. (27)	$Z_\psi = \frac{N_\psi}{\psi_0^{-1}(\beta \varepsilon_{\psi m} - \gamma) - 1}$ Eq. (32)
The first Lagrange multiplier	$\alpha = -\ln\left(\frac{N}{Z}\right)$ Eq. (18)	$\alpha_W = -\ln\left(\frac{N_W}{Z_W}\right) - \frac{Z_W}{2N_W}$ Eq. (22)	$\alpha_\psi = -\psi_0\left(\frac{N_\psi}{Z_\psi} + 1\right)$ Eq. (30)
The maximum energy of states	$\varepsilon_i < \infty$	$\varepsilon_i \leq \varepsilon_{Wm} = (\ln(2/e) - \alpha_W) / \beta$ Eq. (25)	$\varepsilon_i \leq \varepsilon_{\psi m} = (\gamma - \alpha_\psi) / \beta$ Eq. (31)

$$\lim_{T \rightarrow 0} \varepsilon_{Wm}(T) = \frac{\Delta \varepsilon}{2}, \quad (38)$$

which implies that all particles are in the ground state. The Lagrange multipliers  $\alpha_W$  and  $\alpha_\psi$  are almost equal, for example,  $\alpha_W = \ln(2/e) - \beta \varepsilon_{Wm} = -4.086$  and  $\alpha_\psi = \gamma - \beta \varepsilon_{\psi m} = -4.081$  for  $T=293$  K and  $N_W=100$ . Equations (21) and (32) also yield equal values of the partition sums:  $Z_W = Z_\psi = 1.715$ . If we apply Eq. (37) to Eq. (34), we obtain  $C_{WV}/(3Nk) = 0.944$ , which is very close to the exact Digamma value  $C_{\psi V}/(3Nk) = 0.954$ . For  $N=5$  the discrepancy becomes larger,  $C_{WV}/(3Nk) = 0.760$  compared to  $C_{\psi V}/(3Nk) = 0.602$ , even if the condition  $Z_W/(2N_W) \ll \ln(2N_W/(eZ_W))$  for Eq. (37) is satisfied:  $0.134 \ll 1.01$ . In summary, the Lambert W approximation, Eq. (37), yields a reliable analytical estimate of the maximum energy  $\varepsilon_m$  in terms of the experimentally accessible values  $T$ ,  $N$ , and  $\Delta \varepsilon$ .

## V. CONCLUSION

If we use the Stirling formula, Eq. (3), or the exact function  $\ln(n!)$  to solve the Boltzmann variational problem, Eq. (14), we obtain the Boltzmann distribution in terms of either the Lambert W-function or the Digamma-function (see Table II). The approximate Lambert-Boltzmann distribution in Eq. (19) was shown to be a very good estimate of the exact Boltzmann statistics in Eq. (29) given in terms of the inverse Digamma-function. Because the Lambert-W function is included in most symbolic packages, the Lambert-Boltzmann distribution, Eq. (19), can be implemented more easily than the exact Digamma-Boltzmann distribution. Both the

Digamma- and the Lambert-Boltzmann distributions extend the range of applicability of the exponential Boltzmann distribution to finite values of  $N$  and  $n_i$ . The exact Boltzmann distribution naturally imposes a constraint on the maximum energy  $\varepsilon_m$  of the highest populated state, depending on  $T$  and  $N$  [see Eqs. (25), (31), and (37)]. The constraints of Eqs. (25) and (31) confine the total number  $m$  of thermally available energy states and truncate the partition sum in Eq. (17) at  $i = m$ . The smaller value of the partition sum results in a smaller value for the heat capacity compared to the usual heat capacity in Eq. (36). The discrepancy between the exact and the usual heat capacity calculated with the exponential Boltzmann distribution increases with decreasing  $N$ . Measurements of the heat capacity of nanosystems could provide experimental evidence for the exact Boltzmann statistics.

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<sup>1</sup>Sean A. C. McDowell, "A simple derivation of the Boltzmann distribution," *J. Chem. Educ.* **76**, 1393–1394 (1999).

<sup>2</sup>D. K. Russel, "The Boltzmann distribution," *J. Chem. Educ.* **73**, 299–300 (1996).

<sup>3</sup>A. S. Wallner and K. A. Brandt, "The validity of Stirling's approximation," *J. Chem. Educ.* **76**, 1395–1397 (1999).

<sup>4</sup>G. Marsaglia, and J. C. W. Marsaglia, "A new derivation of Stirling's approximation to  $n!$ ," *Am. Math. Monthly* **9**, 826–829 (1990).

<sup>5</sup>H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, 2nd ed. (Van Nostrand, New York, 1965), pp. 438–441.

<sup>6</sup>D. A. Barry, J. Y. Parange, L. Li, H. Prommer, C. J. Cunningham, and F. Stagnitti, "Analytical approximations for real values of the Lambert W-function," *Math. Comput. Simul.* **53**, 95–103 (2000).

<sup>7</sup>P. Atkins and J. De Paula, *Physical Chemistry*, 8th ed. (Oxford University Press, Oxford, 2006), pp. 560–576.