Quantum Distribution Functions in Systems with an Arbitrary Number of Particles

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Expressions for the entropy and equations for the quantum distribution functions for systems of non-interacting fermions and bosons with an arbitrary, including small, number of particles are obtained.

Одержано вирази для ентропії та рівняння для квантових функцій розподілу в системах невзаємодійних ферміонів і бозонів із довільним, у тому числі малим, числом частинок.

Key words: fermions, bosons, distribution function, entropy, quantum dot, factorial, gamma function, Bose–Einstein condensation.

Ключові слова: ферміони, бозони, функція розподілу, ентропія, квантова точка, факторіял, гама-функція, конденсація Бозе–Айнштайна.

1. INTRODUCTION

Currently, much attention is paid to the study of quantum properties of systems with a small number of particles, such as quantum dots, other mesoscopic objects and nanostructures. In this regard, the problem of describing such objects with taking into account their interaction with the external environment is of current importance.

Statistical description is usually used to study systems with very large numbers of particles. Nevertheless, statistical methods of description can be also used in the study of equilibrium states of systems with a small number of particles and even one particle. When

considering a system within the grand canonical ensemble, it is assumed that it is a part of a very large system, a thermostat, with which it can exchange energy and particles. The thermostat itself is characterized by such statistical quantities as temperature T and chemical potential μ. Assuming that the subsystem under consideration is in thermodynamic equilibrium with the thermostat, the subsystem itself is characterized by the same values, even if it consists of a small number of particles. For example, we can consider the thermodynamics of an individual quantum oscillator [1]. In the case, when an exchange of particles with a thermostat is possible, the time-averaged number of particles of a small subsystem may be not an integer and, in particular, even less than unity.

In statistical physics, the entropy and distribution functions of particles over quantum states are calculated under the assumption that the number of particles is very large. This consideration for fermions leads to the Fermi−Dirac distribution, and for bosons, it leads to the Bose−Einstein distribution [1].

In this work, the entropy and distribution functions of non-interacting particles are calculated in the case when no restrictions are imposed on their number in a system being in thermodynamic equilibrium with the environment. In particular, the number of particles can be small, and not an integer and even less than unity. Equations determining the distribution functions of fermions and bosons are obtained, and their differences from the standard Fermi−Dirac and Bose−Einstein distributions are analysed. A feature of the obtained exact distribution functions, in comparison with the distributions found in the limit of a large number of particles, is the presence of energy boundaries, beyond which the average number of particles at all levels turns to zero or unity.

2. ENTROPY AND DISTRIBUTION FUNCTION OF FERMIONS

Let us consider a quantum system of fermions whose energy levels ε_j have the multiplicity of degeneracy z_j. If at each level j there are $N_j \leq z_j$ particles, then, the statistical weight of such a state in the case of Fermi−Dirac statistics is given by the well-known formula [1]:

$$\Delta\Gamma_j = \frac{z_j!}{N_j!(z_j - N_j)!}. \tag{1}$$

The entropy is defined as the logarithm of the total statistical weight by the relation:

$$S = \ln(\Delta\Gamma) = \sum_j \ln(\Delta\Gamma_j) = \sum_j \left[\ln(z_j!) - \ln(N_j!) - \ln\big((z_j - N_j)!\big) \right]. \tag{2}$$

To calculate all factorials under assumption $N \gg 1$ and $z \gg 1$, the Stirling's formula [2] is usually used in the form

$$\ln(N!) \approx N \ln(N/e) . \tag{3}$$

When studying systems with small N, the accuracy of this formula is insufficient. Therefore, for example, with $N = 16$, its accuracy is 7.5%. For $N = 1,\ 2$, there are negative numbers on the right in (3). For small N, one can use a more accurate formula:

$$\ln(N!) \approx N \ln\left(\frac{N}{e}\right) + \ln \sqrt{2\pi N} . \tag{4}$$

For $N = 16$, its accuracy is already 0.017%; for $\ln(2!) \approx 0.693$, this formula gives a value of 0.652. Taking into account the more accurate formula (4), for the entropy $S = \sum_j S_j$, we obtain the expressions:

$$S_j = -z_j \left(n_j \ln(n_j) + (1 - n_j) \ln(1 - n_j) \right) - \frac{1}{2} \ln\left(2\pi z_j n_j (1 - n_j) \right) . \tag{5}$$

Here, $n_j = N_j / z_j$ is the average number of particles at level j (or the population of the level). This formula differs from the usual formula for the entropy of a Fermi gas [1] by the last term. Taking into account that the total number of particles N and the total energy E are determined by the formulae:

$$N = \sum_j N_j = \sum_j n_j z_j , \tag{6}$$

$$E = \sum_j \varepsilon_j N_j = \sum_j \varepsilon_j n_j z_j , \tag{7}$$

the average number of particles in each state is found from the condition:

$$\frac{\partial}{\partial n_j} \left(S - \alpha N - \beta E \right) = 0 , \tag{8}$$

where α, β are the Lagrange multipliers. From here, we find the equation determining the average number of particles in a state j:

$$\ln\left(\frac{1 - n_j}{n_j} \right) + \frac{1}{2 z_j} \left(\frac{1}{1 - n_j} - \frac{1}{n_j} \right) = \alpha + \beta \varepsilon_j . \tag{9}$$

Neglecting the second term on the left side, we obtain the usual Fermi−Dirac distribution:

$$n_j^{(0)} = \left(e^{\alpha+\beta\varepsilon_j} + 1\right)^{-1}. \qquad (10)$$

From comparison with thermodynamic relations, it follows that $\alpha = -\mu/T$, $\beta = 1/T$ (T—temperature, μ—chemical potential), so that $\theta_j = (\varepsilon_j - \mu)/T$. In the absence of a magnetic field, for particles with spin $1/2$, the smallest multiplicity of degeneracy only in the spin projection is equal to two. With $z_i \gg 1$, the second term on the left in Eq. (9) can be taken into account as a small correction, so that, in this approximation, the distribution function will take the form:

$$n_j = n_j^{(0)} - \frac{1 - 2n_j^{(0)}}{2z_j}. \qquad (11)$$

For an arbitrary, including small and non-integer, number of particles N, the factorial should be determined through the gamma function $\Gamma(x)$:

$$N! = \Gamma(N+1). \qquad (12)$$

In this case, the statistical weight (1) is also expressed through the gamma function:

$$\Delta\Gamma_j = \frac{\Gamma(z_j + 1)}{\Gamma(N_j + 1)\Gamma(z_j - N_j + 1)}. \qquad (13)$$

Some formulae for the gamma function as well as formulae related to it are given in the Appendix. With allowance for Eq. (13), for the nonequilibrium entropy $S = \sum_j S_j$, there follows the formula:

$$S_j = -\ln\left(\Gamma(z_j n_j + 1)\right) - \ln\left(\Gamma\left(z_j(1 - n_j) + 1\right)\right) + \ln\left(\Gamma(z_j + 1)\right). \quad (14)$$

It is obvious that the contribution to the total entropy comes only from partially occupied levels, for which $0 < n_j < 1$. In this case, when $n_j \neq 0,\ 1$, from the condition (8), we find the equation that determines the average number of particles in each state:

$$\psi\left(z_j(1 - n_j) + 1\right) - \psi(z_j n_j + 1) \equiv \theta_j(n_j) = \frac{\varepsilon_j - \mu}{T}, \qquad (15)$$

where $\psi(z)$ is the logarithmic derivative of the gamma function (the psi function) (A4). If we use the asymptotic formulae (A3) and (A6) given in the Appendix, then, formula (14) will turn into (5), and formula (15) will turn into (9). Using formula (A11), Eqs. (15) can be written in the form

$$z_j(1 - 2n_j)\sum_{k=1}^{\infty} \frac{1}{\big(k + z_j(1 - n_j)\big)(k + z_j n_j)} = \frac{\varepsilon_j - \mu}{T}.\qquad(16)$$

Note that, here, the series converges rather slowly and the rate of its convergence decreases with increasing z_j; so, for calculations, it is more convenient to use formulae (15).

The forms of distribution functions for a system of Fermi particles at $z = 2$, $z = 10$ and arbitrary j are shown in Fig. 1. The dependence $n(\theta)$ obtained from Eq. (9) with

$$\theta_j = \ln\big((1 - n_j)/n_j\big) + (1/2z_j)\big((1 - n_j)^{-1} - n_j^{-1}\big)$$

(curves *2* in Fig. 1) turns out to be multiple-valued and leads to a significant discrepancy with the calculation performed using the exact formulae (15) (curves *1* in Fig. 1), so that Eq. (9) turns out to be inapplicable for calculating average occupation numbers. In the standard Fermi−Dirac distribution (10) (curves *4* in Fig. 1), for an arbitrary value of the parameter θ ($-\infty < \theta < \infty$), the distribution function does not turn exactly to zero or unity. At $\theta \to \infty$, the distribution function exponentially tends to zero: $n(\theta) \simeq e^{-\theta}$, and at $\theta \to -\infty$, it tends to unity: $n(\theta) \simeq (1 - e^{\theta})$.

A feature of the exact distribution function defined by Eqs. (15), (16) is the limited range of values of the parameter θ_j, in which the
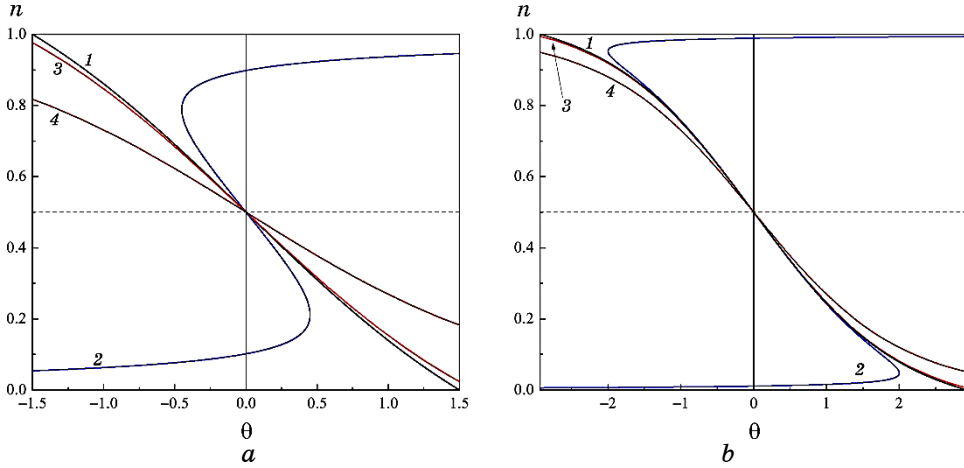

Fig. 1. Distribution function of Fermi particles, $n(\theta)$, over states in various approximations with multiplicities of level degeneracy: (*a*) $z = 2$, (*b*) $z = 10$. *1*—distribution function (DF) calculated using the exact formula (15); *2*—DF calculated using approximate Eq. (9); *3*—DF calculated using formula (11); *4*—conventional Fermi−Dirac DF (10).

function is different from 0 or 1. In this case, $\theta_{j\min} < \theta_j < \theta_{j\max}$, where

$$\theta_{j\max} = -\theta_{j\min} = \psi(z_j + 1) - \psi(1) = \sum_{k=1}^{z_j} k^{-1} . \qquad (17)$$

At $\theta_j \geq \theta_{j\max}$, the average number of particles at level j becomes zero ($n_j = 0$), and at $\theta_j \leq \theta_{j\min}$, it is equal to unity ($n_j = 1$). Thus, for given values of T and μ, the population of level j is different from zero and unity, when there is fulfilled the inequality

$$-\theta_{j\max} < (\varepsilon_j - \mu)/T < \theta_{j\max} . \qquad (18)$$

All the other levels remain either empty or completely occupied, so that there is only a finite number of partially occupied levels, and their number increases with increasing temperature.

The approximate expression for the distribution function (11) (curves *3* in Fig. 1) following from formula (9) gives a good approximation to the exact dependence (curves *1* in Fig. 1). However, at points where the exact distribution function becomes zero and unity, the approximate function (11) is different from these values and exists for all values of the parameter θ. The difference between the exact distribution (15) (curves *1* in Fig. 1) and the usual Fermi–Dirac distribution (10) (curves *4* in Fig. 1) is more significant: the larger the absolute value of the parameter θ and the smaller the degeneracy factor z.

Equation (15) and approximate formula (11) determine the average number of particles in a state j as a function of temperature and chemical potential: $n_j = n_j(T, \mu)$. A substitution of these functions into Eqs. (6), (7), (14) gives equilibrium values of the entropy $S = S(T, \mu)$, the energy $E = E(T, \mu)$, and the number of particles $N = N(T, \mu)$ as functions of temperature and chemical potential. These quantities are natural variables for the large thermodynamic potential, which can be defined by the usual expression

$$\Omega(T, \mu) = E(T, \mu) - TS(T, \mu) - \mu N(T, \mu) ; \qquad (19)$$

so, at a constant volume, there holds the well-known identity $d\Omega = -SdT - Nd\mu$.

For a fixed total number of particles N, Eqs. (15) are not independent, since the populations of the levels are linked by the relation (6). If the total number of particles is such that they can completely occupy the lower j levels, and the level $j+1$ turns out to be occupied partially, so that $N = \sum_{k=1}^{j} z_k + N_{j+1}$ and $0 < N_{j+1} < z_{j+1}$, then, at $T \to 0$ K, the chemical potential takes the value $\mu = \varepsilon_{j+1}$.

Near zero temperature, $\mu \cong \varepsilon_{j+1} - T\theta_{j+1}(N_{j+1}/z_{j+1})$.

The entropy at zero temperature turns to zero only in the case when all levels are completely occupied or empty. In the presence of an unoccupied level, the entropy at $T = 0\,\text{K}$ is different from zero. Thus, the third law of thermodynamics is always satisfied in the Nernst formulation, according to which all processes at zero temperature occur at constant entropy. Moreover, in the Planck formulation, which requires turning of the entropy to zero, the third law is satisfied only in the case of completely occupied levels.

3. ENTROPY AND DISTRIBUTION FUNCTION OF BOSONS

If at each level of a boson system with the multiplicity of degeneracy z_j there are N_j particles, then, the statistical weight of such a state in the Bose−Einstein statistics [1] is as follows:

$$\Delta\Gamma_j = \frac{(z_j + N_j - 1)!}{N_j!(z_j - 1)!}. \tag{20}$$

The entropy is defined by the relation

$$S = \ln(\Delta\Gamma) =$$
$$= \sum_j S_j = \sum_j \ln(\Delta\Gamma_j) = \sum_j \left[\ln\big((z_j + N_j - 1)!\big) - \ln(N_j!) - \ln\big((z_j - 1)!\big) \right]. \tag{21}$$

It should be noted that, if the level is not degenerate ($z_j = 1$) or not occupied ($N_j = 0$), then, as in the above considered case of Fermi−Dirac statistics (1), $\Delta\Gamma_j = 1$, and it does not contribute to the total entropy. Using the Stirling's formula (4), we have

$$S_j = (z_j + z_j n_j - 1)\ln(z_j + z_j n_j - 1) - z_j n_j \ln(z_j n_j) - (z_j - 1)\ln(z_j - 1) +$$
$$+ \frac{1}{2}\ln\big(2\pi(z_j + z_j n_j - 1)\big) - \frac{1}{2}\ln(2\pi z_j n_j) - \frac{1}{2}\ln\big(2\pi(z_j - 1)\big). \tag{22}$$

Then, from condition (8), it follows the equation for the distribution function over states:

$$\ln\left(\frac{z_j + z_j n_j - 1}{z_j n_j}\right) + \frac{1}{2z_j}\left(\frac{z_j}{z_j + z_j n_j - 1} - \frac{1}{n_j}\right) = \alpha + \beta\varepsilon_j, \tag{23}$$

and for $z_j \to \infty$, we obtain the usual Bose−Einstein distribution:

$$n_j^{(0)} = \left(e^{\alpha + \beta\varepsilon_j} - 1\right)^{-1}. \tag{24}$$

Taking into account the correction of order $1/z_j$, we have

$$n_j = n_j^{(0)} - \frac{1 + 2n_j^{(0)}}{2z_j} . \tag{25}$$

When determining factorials through the gamma function, the statistical weight (20) will be written in the following form:

$$\Delta\Gamma_j = \frac{\Gamma(z_j + N_j)}{\Gamma(N_j + 1)\Gamma(z_j)} . \tag{26}$$

This implies the formula for nonequilibrium entropy $S = \sum_j S_j$:

$$S_j = \ln\left(\Gamma(z_j n_j + z_j)\right) - \ln\left(\Gamma(z_j n_j + 1)\right) - \ln\left(\Gamma(z_j)\right). \tag{27}$$

As noted, unoccupied levels ($n_j = 0$) do not give a contribution to the total entropy. For $n_j \neq 0$, from condition (8), we find the equation for the average number of particles in each state:

$$\psi(z_j n_j + z_j) - \psi(z_j n_j + 1) \equiv \theta_j(n_j) = (\varepsilon_j - \mu)/T . \tag{28}$$

If one uses asymptotic formulae (A3) and (A6), formula (27) will turn into Eq. (22), and formula (28) will turn into Eq. (23).

By using formula (A8), Eq. (28) can be represented as

$$\sum_{k=1}^{z_j - 1} 1/(z_j n_j) + z_j - k = (\varepsilon_j - \mu)/T . \tag{29}$$

The form of distribution functions for a system of Bose particles at $z = 2$, $z = 10$ and arbitrary j is shown in Fig. 2.

In the standard Bose–Einstein distribution (24), the parameter θ can take arbitrary positive values ($0 < \theta < \infty$). At $\theta \to \infty$, the distribution function exponentially tends to zero: $n(\theta) \simeq e^{-\theta}$, and at $\theta \to 0$, it increases according to the law $n(\theta) \simeq 1/\theta$.

The dependence $n(\theta)$ obtained from Eq. (23) with

$$\theta_j = \ln\left((z_j + z_j n_j - 1)/z_j n_j\right) + (1/2z_j)\left(z_j/(z_j + z_j n_j - 1) - 1/n_j\right)$$

(curves *2* in Fig. 2) turns out to be multiple-valued and leads to a significant discrepancy with the calculation performed using the exact formula (28) (curves *1* in Fig. 2). Therefore, Eq. (23) is not applicable for calculating average occupation numbers. However, the approximate formula for the distribution function (25) following from Eq. (23) gives a good approximation, almost coinciding with the exact dependence (curves *1* in Fig. 2). The essential difference consists in that, at some boundary value $\theta = \theta_{max}$, the exact
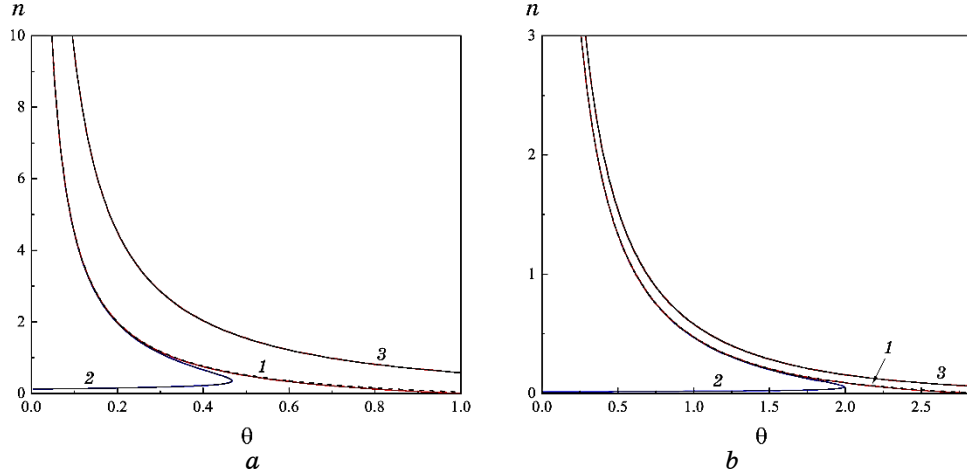
Fig. 2. Distribution function of Bose particles, $n(\theta)$, over states in various approximations with multiplicities of level degeneracy: (*a*) $z = 2$, (*b*) $z = 10$. *1*—distribution function (DF) calculated using the exact formula (28); *2*—DF calculated using approximate Eq. (23); *3*—conventional Bose–Einstein DF (24). The calculation using the approximate formula (25) gives a dependence that practically coincides with curve *1* (dotted line).

function (28) turns to zero, while the approximate function (25) remains finite, although exponentially small.

Thus, for the exact DF (28) with values $n_j \neq 0$, the parameter θ_j changes in the finite region $0 < \theta_j < \theta_{i\max}$, where:

$$\theta_{j\max} = \psi(z_j) - \psi(1) = \sum_{k=1}^{z_j-1} k^{-1} \qquad (30)$$

and $n_j(\theta_{j\max}) = 0$. At $\theta_j \to 0$, the exact DF increases according to the law $n_j(\theta_j) \simeq (z_j - 1)/(z_j\theta_j)$. Thus, at given T and μ, the population of level j is different from zero, when there holds the inequality

$$0 < \frac{\varepsilon_j - \mu}{T} < \theta_{j\max}. \qquad (31)$$

All the other levels remain empty; so, there are only a finite number of partially occupied levels, and their number increases with increasing temperature.

At zero temperature and a fixed number of Bose particles, only the lower level is occupied, and the chemical potential takes the value $\mu = \varepsilon_1$. The entropy $S_1 = \ln\big(\Gamma(N + z_1)\big) - \ln\big(\Gamma(N + 1)\big) - \ln\big(\Gamma(z_1)\big)$ remains nonzero in this case, so that the third law of thermodynamics is satisfied only in the Nernst formulation. With a slight in-

crease in temperature, the lower level continues to remain occupied with other levels being empty in a certain temperature range, and the chemical potential changes linearly with temperature $\mu \cong \varepsilon_1 - T\theta_1(N/z_1)$. At the temperature T_1 determined by the condition

$$\varepsilon_2 - \varepsilon_1/T_1 = \theta_2(0) - \theta_1(N/z_1) , \qquad (32)$$

there begins filling of the second level, and the number of particles at the lower level decreases. At further increase of temperature, there begins filling of higher levels. At a certain temperature T_B, the number of particles at the ground level will turn to zero. This temperature is determined by the equations for partially occupied levels:

$$\theta_2\left(n_2(T_B)\right) - \theta_{1\max} = \frac{\varepsilon_2 - \varepsilon_1}{T_B} , \ \ \theta_3\left(n_3(T_B)\right) - \theta_{1\max} = \frac{\varepsilon_3 - \varepsilon_1}{T_B} , \ \ \dots, \ (33)$$

where $\theta_{1\max} = \psi(z_1) - \psi(1)$, provided that

$$z_2 n_2(T_B) + z_3 n_3(T_B) + \dots = N , \ \ \mu_B = \varepsilon_1 - T_B\theta_{1\max} .$$

If one goes down in temperature, then, T_B corresponds to the temperature, at which the filling of the lower level begins, and therefore, it can be considered as an analogue of the temperature of Bose–Einstein condensation in macroscopic systems [1].

4. SUMMARY AND CONCLUSIONS

In connection with the intensive study of quantum systems of small sizes, the problem of theoretical description of such objects with taking into account their interaction with the environment is becoming actual increasingly. Methods of statistical mechanics can be also used to describe such systems with a small number of particles, which are in thermodynamic equilibrium with a thermostat.

In this work, the equations are obtained for the distribution functions of fermions and bosons over quantum states for systems with an arbitrary, including a small, number of particles; in the limiting case, when the number of particles and the multiplicity of degeneracy of levels in the system are large, these distributions transform into the well-known Fermi–Dirac and Bose–Einstein distributions, respectively. For systems with a small number of particles and at low temperatures, the average number of particles at a given level can differ significantly from the values predicted by the Fermi–Dirac and Bose–Einstein distributions. It is of interest to

test experimentally the applicability of the obtained distributions for structures with a small number of particles.

APPENDIX. Some Properties of the Gamma Function and Its Logarithmic Derivative (The Psi Function)

The definition of the gamma function is as follows:

$$\Gamma(x) = \int_0^\infty e^{-t} t^{x-1} dt = \int_0^1 \left(\ln\left(\frac{1}{t}\right) \right)^{x-1} dt \,. \tag{A1}$$

For the logarithm of the gamma function, there holds the integral representation:

$$\ln\left(\Gamma(x)\right) = \int_0^\infty \left[(x-1)e^{-t} - \frac{e^{-t} - e^{-xt}}{1 - e^{-t}} \right] \frac{dt}{t} \,, \tag{A2}$$

and the asymptotics at $x \to \infty$ is as follows:

$$\ln\left(\Gamma(x)\right) \simeq \left(x - \frac{1}{2} \right) \ln(x) - x + \frac{1}{2} \ln(2\pi) \,. \tag{A3}$$

The logarithmic derivative of the gamma function (the psi function) is defined by the formula

$$\psi(x) \equiv \frac{d}{dx} \ln\left(\Gamma(x)\right) = \frac{1}{\Gamma(x)} \frac{d\Gamma(x)}{dx} \,. \tag{A4}$$

The integral representation is valid for it as follows:

$$\psi(x) = \int_0^\infty \left[\frac{e^{-t}}{t} - \frac{e^{-xt}}{1 - e^{-t}} \right] dt \,, \tag{A5}$$

and the asymptotics at $x \to \infty$ is as follows:

$$\psi(x) \simeq \ln(x) - \frac{1}{2x} \,. \tag{A6}$$

There are useful formulas:

$$\psi(x + 1) = \psi(x) + \frac{1}{x} \,, \tag{A7}$$

$$\psi(x + n) = \sum_{k=1}^{n-1} \frac{1}{(n-k) + x} + \psi(x+1) \ (n \geq 2) \,, \tag{A8}$$

$$\psi(1 - x) = \psi(x) + \pi \operatorname{ctg}(\pi x) \,, \tag{A9}$$

$$\psi(1) = -\gamma, \ \psi(n) = -\gamma + \sum_{k=1}^{n-1} k^{-1} \ (n \geq 2), \qquad (A10)$$

$$\psi(1 + x) = -\gamma + \sum_{k=1}^{\infty} \frac{x}{k(k + x)}, \qquad (A11)$$

where $\gamma = 0.5772$ is Euler's constant.

REFERENCES

1. L. D. Landau and E. M. Lifshitz, *Statistical Physics. Part 1. Volume 5 of Course of Theoretical Physics* (Oxford: Elsevier–Butterworth-Heinemann: 1980).

2. *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables* (Eds. M. Abramowitz and I. A. Stegun). Nat'l Bureau of Standards. Appl. Math. Ser. Vol. **55** (Washington, D.C.: U.S. Govt. Printing Office: 1964).