On the thermodynamics of two-level Fermi and Bose nanosystems

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Equations are obtained for the quantum distribution functions over discrete states in systems of non-interacting fermions and bosons with an arbitrary, including small, number of particles. The case of systems with two levels is considered in detail. The temperature dependences of entropy, heat capacities and pressure in two-level Fermi and Bose systems are calculated for various multiplicities of degeneracy of levels.
Key words: distribution function, fermions, bosons, entropy, thermodynamic functions, two-level systems, quantum dot, factorial, gamma function

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I. INTRODUCTION

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

Statistical description is usually used to study systems with a very large number of particles N in a large volume V with a subsequent transition to the thermodynamic limit $N \to \infty, V \to \infty$ at $n = N/V = const$. However, statistical methods can also be applied to the study of equilibrium states of systems with a small number of particles and even one particle in a finite volume. When considering a many-particle system within the framework of a 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 quantities, even one consisting 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 may even be less than unity. For this case, the equations that determine the average number of particles in each state for the Fermi-Dirac and Bose-Einstein statistics were obtained by the authors in [2]. In this work, based on the theory proposed in [2], the temperature dependences of entropy, heat capacities and pressure in systems with two levels are calculated.

The model of quantum objects with two states is used to describe a wide range of phenomena [3,4]. The concept of two-level systems was initiated by the phenomena of magnetic resonance and was further developed in connection with the advent of lasers. Issues related to the equilibrium thermodynamics of two-level systems turned out to be less studied [4]. The two-level model is also applicable for describing multilevel systems at temperatures lower than the energy difference between the second and the next after it energy level.

The second section of the article presents general relations for entropy, distribution functions of particles and thermodynamic quantities of an arbitrary number of fermions and bosons for a system with an arbitrary number of levels. In the third and fourth sections the two-level systems of bosons and fermions are studied in detail, the temperature dependences of their entropy, heat capacities, pressure and populations of levels are calculated. In conclusion the obtained results are discussed.

II. ENTROPY AND DISTRIBUTION FUNCTIONS OF FERMIONS AND BOSONS

In this section we present a brief derivation of equations for the average numbers of particles in quantum states and formulas for thermodynamic quantities for an arbitrary number of levels and number of particles, which are valid for both Bose-Einstein and Fermi-Dirac statistics [2]. Let us consider a quantum system of non-interacting particles, the energy levels ε_j of which have the multiplicities of degeneracy z_j. If there are N_j particles at each level j, then

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$n_j = N_j/z_j$ is the average number of particles at level j or the population of the level. In the case when for fermions $n_j \neq 0, 1$ and for bosons $n_j \neq 0$, the average number of particles in each state is found from the condition of an extremum of the entropy $S = \sum_j S_j$

$$\frac{\partial}{\partial n_j}\big(S - \alpha N - \beta E\big) = 0, \tag{1}$$

where the total number of particles N and the total energy E are determined by the formulas

$$N = \sum_j N_j = \sum_j n_j z_j, \tag{2}$$

$$E = \sum_j \varepsilon_j N_j = \sum_j \varepsilon_j n_j z_j. \tag{3}$$

In (1) α, β are the Lagrange multipliers, which are found from a comparison with thermodynamic relations, wherefrom it follows $\alpha = -\mu/T$, $\beta = 1/T$, T – temperature, μ – chemical potential [1]. Let us introduce the notation for the derivative of entropy:

$$\frac{\partial S_j}{\partial n_j} \equiv z_j\, \theta_j(n_j). \tag{4}$$

The expression for entropy S_j and the form of functions $\theta_j(n_j)$ are different for fermions and bosons, and will be obtained in the following sections. From (1) – (4) we find the equations that determine the population of levels

$$\theta_j(n_j) = \frac{(\varepsilon_j - \mu)}{T}. \tag{5}$$

For a fixed total number of particles, due to condition (2), these equations are not independent.

When constructing the thermodynamics of systems located in a limited volume, the dependence of the level energy on volume should be taken into account. This dependence arises as a consequence of the boundary condition for the wave function at the boundary of the volume V. For both the sphere and the cube $\varepsilon_j \sim V^{-2/3}$. Therefore, we will assume that $\varepsilon_j = \xi_j V^{-\alpha}$, where $\alpha > 0$, so that $d\varepsilon_j/dV = -\alpha\big(\varepsilon_j/V\big)$, $d^2\varepsilon_j/dV^2 = \alpha(\alpha+1)\big(\varepsilon_j/V^2\big)$. In numerical calculations we always assume $\alpha = 2/3$. For the thermodynamic potential $\Omega = E - TS - \mu N$ the known relation $d\Omega = -SdT - Nd\mu - pdV$ is valid, therefore the pressure is determined from the condition

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = -\sum_j z_j n_j \frac{d\varepsilon_j}{dV} = \frac{\alpha}{V}\sum_j z_j n_j \varepsilon_j. \tag{6}$$

To calculate heat capacities and thermodynamic coefficients it is necessary to use the expression for the differential of population, which follows from (5):

$$z_j \theta_j^{(1)}(n_j)\, dn_j = -\theta_j(n_j)\frac{dT}{T} - \frac{d\mu}{T} + \frac{1}{T}\frac{d\varepsilon_j}{dV}\, dV, \tag{7}$$

where

$$\frac{\partial \theta_j(n_j)}{\partial n_j} \equiv z_j\, \theta_j^{(1)}(n_j). \tag{8}$$

With taking into account (7), (8) we find the differentials of the number of particles N, entropy S and pressure p:

$$dN = -A_1\frac{dT}{T} - A\frac{d\mu}{T} + B\frac{dV}{T}, \tag{9}$$

$$dS = -A_2\frac{dT}{T} - A_1\frac{d\mu}{T} + B_1\frac{dV}{T}, \tag{10}$$

$$dp = B_1\frac{dT}{T} + B\frac{d\mu}{T} - DdV. \tag{11}$$

In (9) – (11) the following notations are used:

$$A \equiv \sum_j \frac{1}{\theta_j^{(1)}}, \quad A_1 \equiv \sum_j \frac{\theta_j}{\theta_j^{(1)}}, \quad A_2 \equiv \sum_j \frac{\theta_j^2}{\theta_j^{(1)}},$$

$$B \equiv \sum_j \frac{1}{\theta_j^{(1)}} \frac{d\varepsilon_j}{dV} = -\frac{\alpha}{V} \sum_j \frac{\varepsilon_j}{\theta_j^{(1)}}, \quad B_1 \equiv \sum_j \frac{\theta_j}{\theta_j^{(1)}} \frac{d\varepsilon_j}{dV} = -\frac{\alpha}{V} \sum_j \frac{\theta_j \varepsilon_j}{\theta_j^{(1)}}, \tag{12}$$

$$D \equiv \sum_j \left[z_j n_j \frac{d^2\varepsilon_j}{dV^2} + \frac{1}{T\theta_j^{(1)}} \left(\frac{d\varepsilon_j}{dV} \right)^2 \right] = \frac{\alpha}{V^2} \sum_j \left[(1+\alpha) z_j n_j \varepsilon_j + \frac{\alpha \varepsilon_j^2}{T\theta_j^{(1)}} \right].$$

Systems with a fixed number of particles are usually considered. In this case $dN = 0$, and the differential of the chemical potential can be excluded from (9) – (11). As a result, we arrive at the following formulas for the isochoric and isobaric heat capacities:

$$C_{V,N} = \frac{\left(A_1^2 - AA_2\right)}{A}, \tag{13}$$

$$C_{p,N} = \frac{\left(A_1^2 - AA_2\right)}{A} - \frac{\left(AB_1 - A_1 B\right)^2}{A\left(B^2 - ADT\right)}. \tag{14}$$

We also present formulas for the coefficient of volumetric expansion

$$\alpha_{pN} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} = -\frac{\left(AB_1 - A_1 B\right)}{V\left(B^2 - ADT\right)}, \tag{15}$$

the isothermal compressibility

$$\gamma_{TN} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = -\frac{AT}{V\left(B^2 - ADT\right)} \tag{16}$$

and the isochoric thermal pressure coefficient

$$\beta_{VN} = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_{V,N} = \frac{\left(AB_1 - A_1 B\right)}{pTA}. \tag{17}$$

The remaining thermodynamic coefficients can be found from the above coefficients and the heat capacities [6]. The conditions for thermodynamic stability of a system are the inequalities $\left(\partial p/\partial V\right)_T < 0$ and $C_{V,N} > 0$ [1]. We also note that the general thermodynamic relation $C_p - C_V = TV\left(\alpha_p^2/\gamma_T\right)$ turns out to be valid.

III. TWO-LEVEL BOSON SYSTEM

Using the general formulas given in the previous section, we consider a special case of a system of bosons which can exist only in two states with energies $\varepsilon_2 > \varepsilon_1$ and multiplicities of degeneracy z_1 and z_2. If in a system of bosons at each level 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]

$$\Delta\Gamma_j = \frac{(z_j + N_j - 1)!}{N_j!\,(z_j - 1)!}. \tag{18}$$

In the general case, when the number of particles can be small and take fractional values, the factorials in (18) should be determined through the gamma function $N! = \Gamma\left(N+1\right)$ [2], so that the statistical weight (18) will be written in the form

$$\Delta\Gamma_j = \frac{\Gamma(z_j + N_j)}{\Gamma(N_j + 1)\,\Gamma(z_j)}. \tag{19}$$

This implies the formula for the nonequilibrium entropy $S = \sum_j S_j = \sum_j \ln \Delta\Gamma_j$, where

$$S_j \equiv S_{Bj} = \ln\Gamma\big(z_j n_j + z_j\big) - \ln\Gamma\big(z_j n_j + 1\big) - \ln\Gamma\big(z_j\big). \tag{20}$$

In this case, in the equations of the previous section that determine the population of levels and thermodynamic quantities, one should use the formulas

$$\theta_j(n_j) \equiv \theta_{Bj}(n_j) \equiv \psi\big(z_j n_j + z_j\big) - \psi\big(z_j n_j + 1\big), \tag{21}$$

$$\theta_j^{(1)}(n_j) \equiv \theta_{Bj}^{(1)}(n_j) \equiv \psi^{(1)}\big(z_j n_j + z_j\big) - \psi^{(1)}\big(z_j n_j + 1\big), \tag{22}$$

where $\psi(x) \equiv d\ln\Gamma(x)/dx$, $\psi^{(1)}(x) \equiv d^2\ln\Gamma(x)/dx^2$ are the logarithmic derivatives of the gamma function [5]. Functions (21), (22) can be calculated using the formulas

$$\theta_{Bj}(n_j) = \int_0^\infty \frac{e^{-z_j n_j t}\big(1 - e^{-(z_j-1)t}\big)}{e^t - 1}\,dt, \quad \theta_{Bj}^{(1)}(n_j) = -\int_0^\infty t\,\frac{e^{-z_j n_j t}\big(1 - e^{-(z_j-1)t}\big)}{e^t - 1}\,dt. \tag{23}$$

At zero temperature all bosons are located at the ground level, so that in this case $\mu = \varepsilon_1$ and the total number of particles, energy and pressure are given by formulas $N = z_1 n_1$, $E = \varepsilon_1 N$ and $p = \alpha\big(N/V\big)\varepsilon_1$. The entropy, when taking into account the discreteness of levels, at $T = 0$ turns out to be different from zero

$$S_{B0} = \ln\Gamma\big(N + z_1\big) - \ln\Gamma\big(N + 1\big) - \ln\Gamma\big(z_1\big). \tag{24}$$

Thus, the third law of thermodynamics is satisfied in the Nernst formulation, according to which all processes at zero temperature occur at a constant entropy, but not in the Planck formulation which requires turning of the entropy to zero.

In the two-level Bose system, two characteristic temperatures can be defined. At one of them the transition of particles from the lower level to the upper level begins

$$T_{B1} = \frac{\Delta\varepsilon}{\Phi_B\big(0, N/z_1\big)}, \tag{25}$$

and at the second characteristic temperature all particles transit from the lower level to the upper level

$$T_{B2} = \frac{\Delta\varepsilon}{\Phi_B\big(N/z_2, 0\big)}, \tag{26}$$

where $\Delta\varepsilon \equiv \varepsilon_2 - \varepsilon_1 > 0$. In (25), (26) the notation is also used $\Phi_B(n_2, n_1) \equiv \theta_{B2}(n_2) - \theta_{B1}(n_1)$. Obviously, the condition of the existence of these temperatures is the positivity of denominators in (25), (26). These requirements

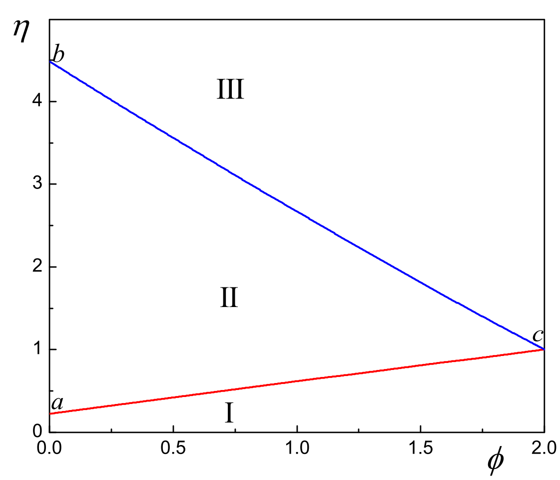

Figure 1: Regions of existence of the characteristic temperatures (25), (26) on the plane $\big(\phi, \eta\big)$, for $N = 2$: I – T_{B1}, T_{B2} do not exist; II – only T_{B1} exists; III – both temperatures T_{B1}, T_{B2} exist. On the curve ac $\Phi_B(0, \phi) = 0$, on the curve bc $\Phi_B(\phi/\eta, 0) = 0$. Coordinates of points: a – $(0, 0.22)$; b – $(0, 4.5)$; c – $(2, 1)$.

are satisfied not for all values of the quantities z_1, z_2, N. There are three possibilities: I) the existence condition is not satisfied in both cases, and the temperatures T_{B1}, T_{B2} do not exist; II) the existence condition is satisfied for (25), but it is not satisfied for (26), so only the temperature T_{B1} exists and the temperature T_{B2} is missing; III) both temperatures T_{B1}, T_{B2} exist. It is convenient to introduce variables:

$$\eta \equiv \frac{z_2}{z_1}, \qquad \phi \equiv \frac{N}{z_1}. \tag{27}$$

The regions I, II, III on the plane (ϕ, η) are shown in Fig. 1. In the figures, for convenience, we assume that η and ϕ can take arbitrary positive values. Only those values of η and ϕ correspond to the physical parameters, for which conditions (27) are satisfied. In the notation (27) $T_{B1} = \Delta\varepsilon / \Phi_B(0,\phi)$ and $T_{B2} = \Delta\varepsilon / \Phi_B(\phi\eta^{-1}, 0)$. Note that functions $\Phi_B(0,\phi)$ and $\Phi_B(\phi\eta^{-1}, 0)$ depend also on the number of particles N as on a parameter.

The dependences of the dimensionless temperatures $\tau_{B1} = T_{B1}/\Delta\varepsilon$ and $\tau_{B2} = T_{B2}/\Delta\varepsilon$ on η for a fixed parameter ϕ are shown in Fig. 2. In the region I (Fig. 1) the temperatures T_{B1}, T_{B2} do not exist. Physically, this means that in the case when the multiplicity of degeneracy of the upper level is considerably less than the multiplicity of degeneracy of the ground level ($\eta < \eta_1$ in Fig. 2), all particles remain locked at the ground level at arbitrary permissible temperatures, and $n_2 = 0$, so that energy cannot be transferred to the system and it remains adiabatically isolated from the thermostat. In this case the pressure and entropy remain constant, and the heat capacities are equal to zero.

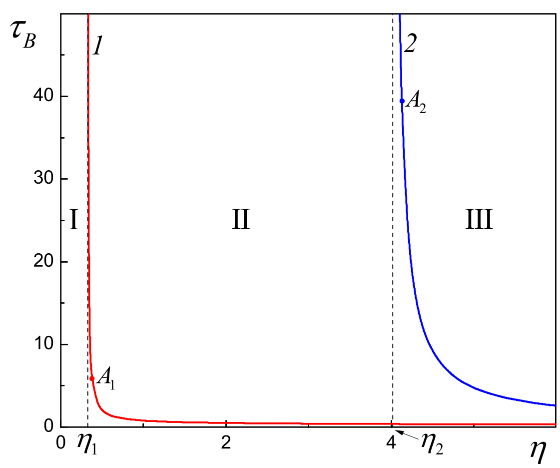

Figure 2: Dependences of the temperatures τ_{B1} (*1*) and τ_{B2} (*2*) on η for $z_1 = 8$, $N = 2$, $\phi = 0.25$; the point $A_1 = (0.38,\ 5.85)$ for $z_2 = 3$, the point $A_2 = (4.13,\ 39.44)$ for $z_2 = 33$; $\eta_1 = 0.33$, $\eta_2 = 4.02$.

In the region II (Fig. 1) there is the temperature T_{B1} ($\eta_1 < \eta < \eta_2$ in Fig. 2) at which the transition of particles from the lower to the upper level begins, and the dependence of populations on temperature at $T > T_{B1}$ is determined by the system of equations

$$\theta_{B1}(n_1) = \frac{(\varepsilon_1 - \mu)}{T}, \qquad \theta_{B2}(n_2) = \frac{(\varepsilon_2 - \mu)}{T}, \qquad N = z_1 n_1 + z_2 n_2. \tag{28}$$

In the limit of high temperatures $T \to \infty$ the populations of levels tend to constant values $n_{1\infty}$ and $n_{2\infty}$, which are determined by the conditions $\theta_{B1}(n_{1\infty}) = \theta_{B2}(n_{2\infty})$ and $N = z_1 n_{1\infty} + z_2 n_{2\infty}$. The temperature dependences of the entropy and heat capacities for this case are shown in Fig. 3*a*. At temperatures $T < T_{B1}$ the entropy S_{B1} and pressure are constant, and the heat capacities are zero. At temperature T_{B1} the entropy and pressure begin to increase monotonically, and the heat capacities take on by jumps finite values. Initially, the heat capacities increase reaching their maxima, and with a further increase in temperature they decrease monotonically. In the limit $T \to \infty$ the entropy tends to a finite value $S_{B\infty}$, and the heat capacities tend to zero.

In the region III (Fig. 1) there exist two temperatures T_{B1}, T_{B2} ($\eta > \eta_2$ in Fig. 2). In this case at T_{B1} the transition of particles from the lower to the upper level begins, and at $T = T_{B2}$ all particles transit to the upper level, so that the lower level proves to be empty $n_1 = 0$. In the temperature range $T_{B1} < T < T_{B2}$ the temperature dependence of populations is determined by equations (28). The temperature dependences of the entropy and heat capacities for this case are shown in Fig. 3*b*. Here also at temperatures $T < T_{B1}$ the entropy S_{B1} is constant and the heat capacities are zero. At temperature T_{B1} the entropy begins to increase monotonically up to a maximum value S_{B2} at T_{B2}, and the heat capacities take on by jumps finite values. With an increase in temperature the heat capacities first increase, and then they begin to decrease down to finite values at temperature T_{B2}. At $T > T_{B2}$ the entropy S_{B2} and pressure

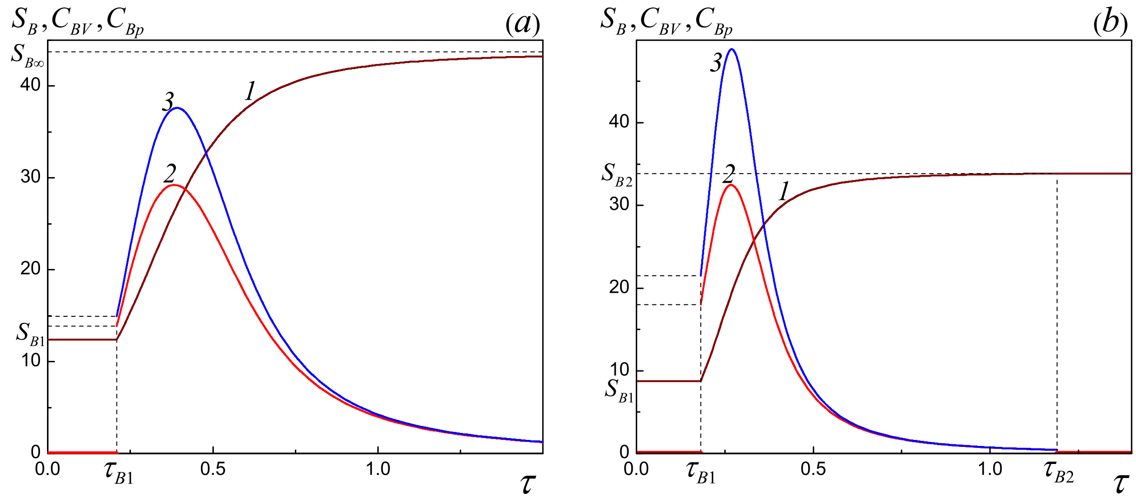

Figure 3: Dependences of the entropy $S_B(\tau)$ (*1*), the heat capacities $C_{BV}(\tau)$ (*2*) and $C_{Bp}(\tau)$ (*3*) on the dimensionless temperature $\tau = T/\Delta\varepsilon$ for the two-level boson system. (*a*) Region II. Jumps of heat capacities at τ_{B1}: $\Delta C_{BV} = 13.84$, $\Delta C_{Bp} = 14.92$. Entropy values: $S_{B1} = 12.41$, $S_{B\infty} = 43.74$. Parameters: $z_1 = 8, z_2 = 96, N = 16$; $\tau_{B1} = 0.21$, $n_{1\infty} = 0.08$, $n_{2\infty} = 0.16$. (*b*) Region III. Jumps of heat capacities at τ_{B1}: $\Delta C_{BV} = 17.99$, $\Delta C_{Bp} = 21.49$; jumps at τ_{B2}: $\Delta C_{BV} = -0.43$, $\Delta C_{Bp} = -0.44$. Entropy values: $S_{B1} = 8.77$, $S_{B2} = 33.87$. Parameters: $z_1 = 8$, $z_2 = 256$, $N = 8$; $\tau_{B1} = 0.18$, $\tau_{B2} = 1.2$.

remain constant, and the heat capacities turn to zero by jumps. In this region of high temperatures the energy of the system reaches its maximally possible value and no longer increases with increasing the thermostat temperature.

IV. TWO-LEVEL FERMION SYSTEM

Let us consider a system of fermions which can exist in two states with energies $\varepsilon_2 > \varepsilon_1$ and multiplicities of degeneracy z_1 and z_2. Such a system can contain no more than $z_1 + z_2$ particles. If there are $N_j \le z_j$ particles at each level j, then the statistical weight of such a state in the case of Fermi-Dirac statistics is given by the well-known formula [1]

$$\Delta\Gamma_j = \frac{z_j!}{N_j!(z_j - N_j)!}\,. \tag{29}$$

In the general case, when the number of particles can be small and take fractional values, the factorials in (29) should be determined through the gamma function [2], so that the statistical weight (29) will be written in the form

$$\Delta\Gamma_j = \frac{\Gamma(z_j+1)}{\Gamma(N_j+1)\Gamma(z_j - N_j + 1)}. \tag{30}$$

This implies the formula for nonequilibrium entropy $S = \sum_j S_j = \sum_j \ln\Delta\Gamma_j$, where

$$S_j \equiv S_{Fj} = \ln\Gamma(z_j+1) - \ln\Gamma(z_j n_j + 1) - \ln\Gamma\big[z_j(1-n_j)+1\big]. \tag{31}$$

For a system of fermions in the equations of Section II, which determine the population of levels and thermodynamic quantities in the general case, it should be taken

$$\theta_j(n_j) \equiv \theta_{Fj}(n_j) \equiv \psi\big[z_j\big(1-n_j\big)+1\big] - \psi\big(z_j n_j + 1\big), \tag{32}$$

$$\theta_j^{(1)}(n_j) \equiv \theta_{Fj}^{(1)}(n_j) \equiv -\,\psi^{(1)}\big[z_j\big(1-n_j\big)+1\big] - \psi^{(1)}\big(z_j n_j + 1\big). \tag{33}$$

To calculate these functions one can use the formulas

$$\theta_{Fj}(n_j) = \int_0^\infty \frac{e^{-z_j n_j t} - e^{-z_j(1-n_j)t}}{e^t - 1}\,dt, \quad \theta_{Fj}^{(1)}(n_j) = -\int_0^\infty t\,\frac{e^{-z_j n_j t} + e^{-z_j(1-n_j)t}}{e^t - 1}\,dt. \tag{34}$$

In the two-level fermion system two cases must be distinguished: A) the number of particles is less than or equal to the multiplicity of degeneracy of the lower level $0 < N \le z_1$, B) the number of particles is greater than the multiplicity of degeneracy of the lower level $z_1 < N \le z_1 + z_2$. In the case A), at zero temperature all particles are at the ground level $n_1 \le 1, n_2 = 0$, so that the number of particles, energy and pressure are determined by the formulas $N = z_1 n_1$, $E = \varepsilon_1 N$ and $p = \alpha\big(N/V\big)\varepsilon_1$, and the chemical potential $\mu = \varepsilon_1$. The entropy is given by the formula

$$S_{FA} = \ln\Gamma(z_1+1) - \ln\Gamma(N+1) - \ln\Gamma\big[z_1+1-N\big]. \tag{35}$$

If the level is not filled $N < z_1$, then the entropy (35) at $T = 0$ is nonzero and the third law of thermodynamics is satisfied in the Nernst formulation. Only when the level is completely filled $N = z_1$ the entropy turns to zero, and then the third law of thermodynamics turns out to be valid in the Planck formulation. In the case B) at zero temperature the lower level is filled, and $N - z_1$ particles are located on the upper level. Only particles of the upper level contribute to the entropy, so that

$$S_{FB} = \ln\Gamma(z_2+1) - \ln\Gamma(N+1-z_1) - \ln\Gamma(z_1+z_2+1-N). \tag{36}$$

It turns to zero only if both levels are completely occupied $N = z_1 + z_2$. The energy and pressure in this case are given by the formulas $E = \varepsilon_1 z_1 + \varepsilon_2(N - z_1)$, $p = \big(\alpha/V\big)\big[\varepsilon_1 z_1 + \varepsilon_2(N - z_1)\big]$, and the chemical potential $\mu = \varepsilon_2$.

For the case of two-level fermion system four characteristic temperatures can be determined. At the temperature

$$T_{F1} = \frac{\Delta\varepsilon}{\Phi_F\big(0,\phi\big)} \tag{37}$$

particles from the lower level begin to transit to the upper empty level. At the temperature

$$T_{F2} = \frac{\Delta\varepsilon}{\Phi_F\big(\phi\eta^{-1},0\big)} \tag{38}$$

all particles from the lower level, which becomes empty, transit to the upper level. At the temperature

$$T_{F3} = \frac{\Delta\varepsilon}{\Phi_F\big((\phi-1)\eta^{-1},1\big)} \tag{39}$$

particles from the lower, completely filled level, begin to transit to the upper, partially filled level. Finally, at the temperature

$$T_{F4} = \frac{\Delta\varepsilon}{\Phi_F\big(1,\phi-\eta\big)} \tag{40}$$

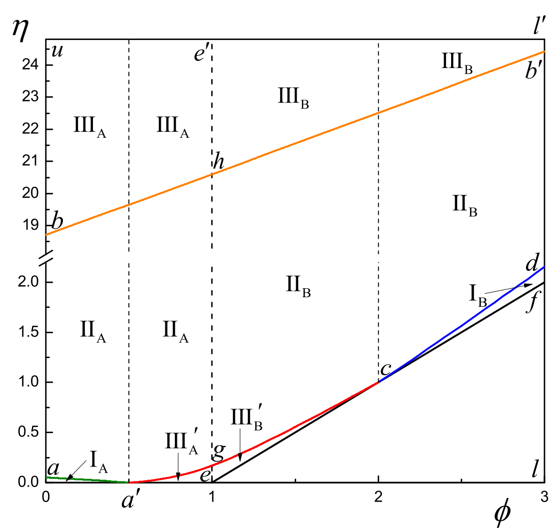

Figure 4: Regions of existence of the characteristic temperatures (37) – (40): $\mathrm{I_A}$ $(0aa')$, $\mathrm{I_B}$ (cdf) – none of these temperatures exist, $\mathrm{II_A}$ $(aa'ghb)$ – only T_{F1} (37) exists, $\mathrm{II_B}$ $(gcdb'h)$ – only T_{F3} (39) exists, $\mathrm{III_A}$ $(bhe'u)$ – T_{F1} (37) and T_{F2} (38) exist, $\mathrm{III_B}$ $(hb'l'e')$ – T_{F2} (38) and T_{F3} (39) exist, $\mathrm{III'_A}$ $(a'eg)$ – T_{F1} (37) and T_{F4} (40) exist, $\mathrm{III'_B}$ (ecg) – T_{F3} (39) and T_{F4} (40) exist. Region (efl) is forbidden, because the condition $N \le z_1 + z_2$ is not satisfied here.

particles completely fill the upper level, while some part of them remains at the lower level. In formulas (37) – (40) we use the notation $\Phi_F(n_2, n_1) \equiv \theta_{F2}(n_2) - \theta_{F1}(n_1)$. Note that the functions in the denominators of formulas (37) – (40), written in the variables (ϕ, η), depend also on N as on a parameter. Obviously, the condition of the existence of these temperatures is the positivity of denominators in (37) – (40). These requirements are satisfied not for all values of the quantities z_1, z_2, N. The regions where these temperatures may exist on the plane (ϕ, η), (27) are shown in Fig. 4.

The dependences of the dimensionless temperatures $\tau_F = T_F/\Delta\varepsilon$ on the parameter η at a fixed parameter ϕ in different cases are shown in Fig. 5. There are four regions of variation of the parameter ϕ, where characteristic temperatures depend differently on the parameter η: *a*) $0 < \phi < 1/2$ (Fig. 5*a*), *b*) $1/2 < \phi < 1$ (Fig. 5*b*), *c*) $1 < \phi < 2$ (Fig. 5*c*), *d*) $\phi > 2$ (Fig. 5*d*).

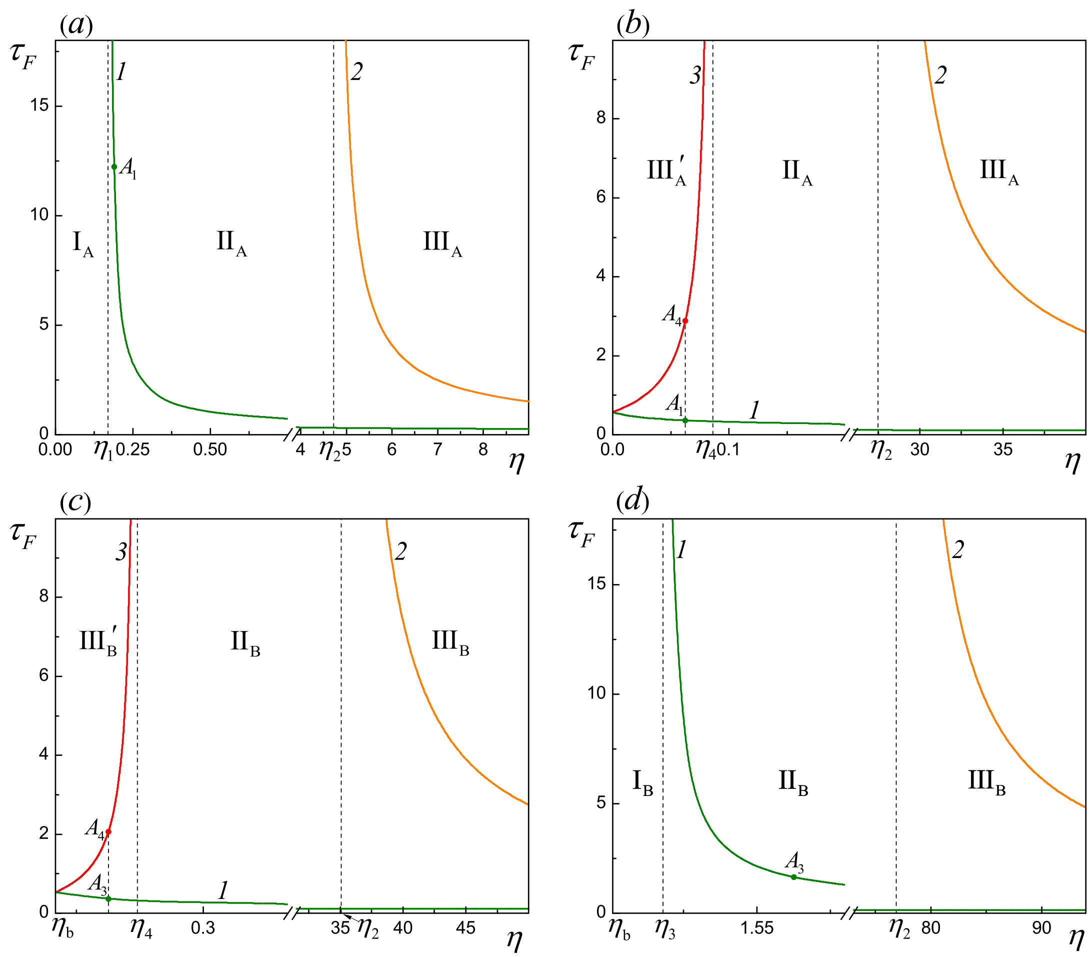

Figure 5: Dependences of the dimensionless temperatures on the parameter η, characterizing the ratio of the degeneracy factors of the upper and lower levels.
(*a*) τ_{F1} (37) – *1*, τ_{F2} (38) – *2* for $z_1 = 16$, $N = 2$ and $\phi = 0.125$; $\eta_1 = 0.17$, $\eta_2 = 4.72$; $A_1 = (0.188, 12.2)$ – matches to $z_2 = 3$, $A_2 = (4.75, 137.1)$ – matches to $z_2 = 76$ (not shown).
(*b*) τ_{F1} – *1*, τ_{F2} – *2*, τ_{F4} (40) – *3* for $z_1 = 16$, $N = 14$ and $\phi = 0.875$; $\eta_4 = 0.086$, $\eta_2 = 27.5$; $A_1 = (0.063, 0.36)$, $A_4 = (0.063, 2.88)$ – match to $z_2 = 1$, $A_2 = (27.5, 1862.4)$ – matches to $z_2 = 440$ (not shown).
(*c*) τ_{F3} (39) – *1*, τ_{F2} – *2*, τ_{F4} – *3* for $z_1 = 16$, $N = 18$ and $\phi = 1.125$; $\eta_b = 0.125$, $\eta_4 = 0.22$, $\eta_2 = 35.1$; $A_3 = (0.186, 0.35)$, $A_4 = (0.186, 2.06)$ – match to $z_2 = 3$, $A_2 = (35.13, 802.1)$ – matches to $z_2 = 562$ (not shown).
(*d*) τ_{F3} – *1*, τ_{F2} – *2* for $z_1 = 16$, $N = 40$ and $\phi = 2.5$; $\eta_b = 1.5$, $\eta_3 = 1.52$, $\eta_2 = 76.9$; $A_3 = (1.56, 1.65)$ – matches to $z_2 = 25$, $A_2 = (76.9, 13825.9)$ – matches to $z_2 = 1230$ (not shown).

The temperature dependences of the entropy and heat capacities for the cases *b*) $1/2 < \phi < 1$ and *d*) $\phi > 2$ are shown in Figures 6 and 7.

In the range of the parameter values *b*) $1/2 < \phi < 1$ (Fig. 6) in the region $\mathrm{III_A}$ (Fig. 6*c*), at temperatures $\tau < \tau_{F1}$ the entropy S_{F1} is constant and the heat capacities are equal to zero. At $\tau = \tau_{F1}$ the heat capacities take on by jumps finite values, then with increasing temperature they reach maximums and begin to decrease. At temperature $\tau = \tau_{F2}$ the heat capacities turn to zero by jumps. The entropy on the interval $\tau_{F1} < \tau < \tau_{F2}$ increases monotonically from S_{F1} to S_{F2}. The pressure increases monotonically with increasing temperature. In the temperature region with

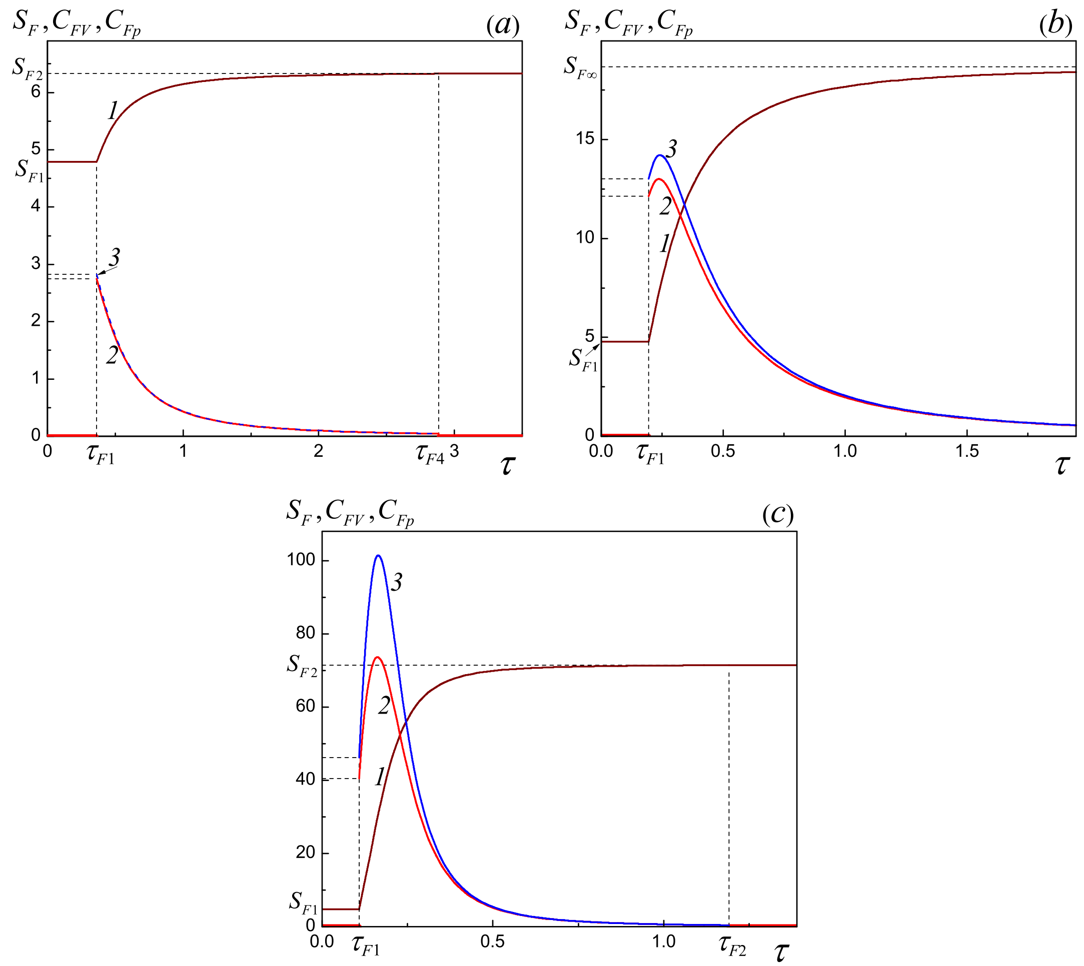

Figure 6: Dependences of the entropy $S_F(\tau)$ (*1*) and the heat capacities $C_{FV}(\tau)$ (*2*), $C_{Fp}(\tau)$ (*3*) on the interval *b*) $1/2 < \phi < 1$.
(*a*) Region $\mathrm{III}'_{\mathrm{A}}$. Jumps of heat capacities at τ_{F1}: $\Delta C_{FV} = 2.75$, $\Delta C_{Fp} = 2.83$; jumps at τ_{F4}: $\Delta C_{FV} = -0.045$, $\Delta C_{Fp} = \Delta C_{FV} - 1.6 \cdot 10^{-4}$. Entropy values: $S_{F1} = 4.8$, $S_{F2} = 6.3$. Parameters: $z_1 = 16$, $z_2 = 1$, $N = 14$; $\tau_{F1} = 0.36$, $\tau_{F4} = 2.88$.
(*b*) Region II_{A}. Jumps of heat capacities at τ_{F1}: $\Delta C_{FV} = 12.14$, $\Delta C_{Fp} = 13.02$. Entropy values: $S_{F1} = 4.8$, $S_{F\infty} = 18.7$. Parameters: $z_1 = 16$, $z_2 = 16$, $N = 14$; $\tau_{F1} = 0.19$.
(*c*) Region $\mathrm{III}_{\mathrm{A}}$. Jumps of heat capacities at τ_{F1}: $\Delta C_{FV} = 40.4$, $\Delta C_{Fp} = 46.2$; jumps at τ_{F2}: $\Delta C_{FV} = -0.397$, $\Delta C_{Fp} = -0.400$. Entropy values: $S_{F1} = 4.8$, $S_{F2} = 71.4$. Parameters: $z_1 = 16$, $z_2 = 1000$, $N = 14$; $\tau_{F1} = 0.11$, $\tau_{F2} = 1.19$.

temperature dependences, the populations are determined by the system of equations (28) with the account of the substitution $\theta_{Bj}(n_j) \to \theta_{Fj}(n_j)$. In the region II_{A} (Fig. 6*b*) there is no the limiting temperature τ_{F2}, so that at $\tau \to \infty$ the heat capacities tend to zero, and the entropy tends to the limiting value $S_{F\infty}$. In the region $\mathrm{III}'_{\mathrm{A}}$ (Fig. 6*a*), in the temperature range $\tau_{F1} < \tau < \tau_{F4}$ the heat capacities decrease monotonically, and at $\tau = \tau_{F4}$ they turn to zero by jumps. In this case, the entropy on the interval $\tau_{F1} < \tau < \tau_{F4}$ increases monotonically from S_{F1} to S_{F2}. The variation of the entropy and heat capacities with temperature in the case *c*) $1 < \phi < 2$ is similar.

In the range of the parameter values *d*) $\phi > 2$ (Fig. 7) in the region I_{B}, the state of the system does not change at arbitrary temperatures of the thermostat. In the region II_{B} (Fig. 7*a*), at temperatures $\tau < \tau_{F3}$ the entropy S_{F1} is constant and the heat capacities are equal to zero. At τ_{F3} the heat capacities take on finite values by jumps. If $z_2 > 30$, then at $\tau > \tau_{F3}$ the heat capacity curves have maxima and at $\tau \to \infty$ they tend to zero. For $z_2 < 30$ the heat capacities decrease monotonically. The entropy at $\tau > \tau_{F3}$ monotonically increases to the limiting value $S_{F\infty}$. In the region $\mathrm{III}_{\mathrm{B}}$ (Fig. 7*b*) there exists the limiting temperature τ_{F2}, at which the heat capacities turn to zero by jumps and the entropy reaches its maximum value S_{F2}. The variation of the entropy and heat capacities with temperature in the case *a*) $0 < \phi < 1/2$ is similar to the case *d*).

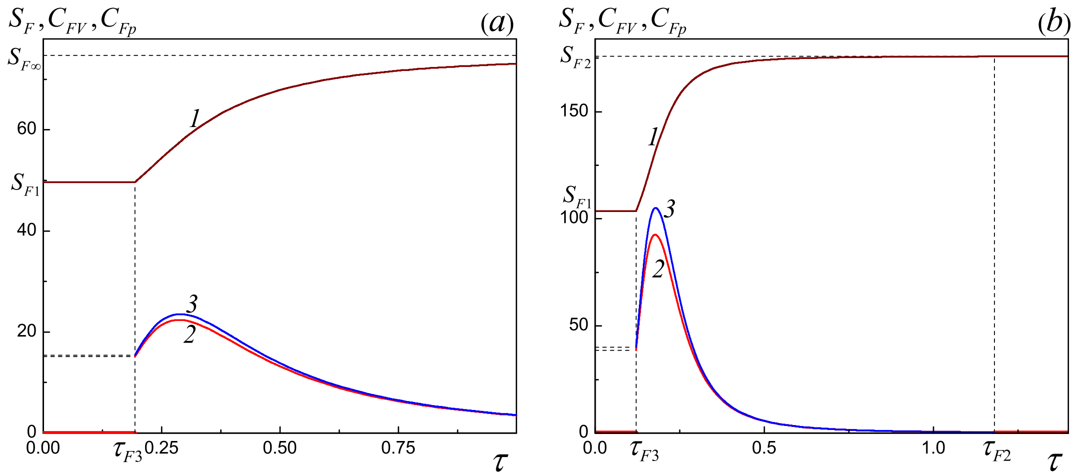

Figure 7: Dependences of the entropy $S_F(\tau)$ (*1*) and the heat capacities $C_{FV}(\tau)$ (*2*), $C_{Fp}(\tau)$ (*3*) on the interval *d*) $\phi > 2$.
(*a*) Region II_B. Jumps of heat capacities at τ_{F3}: $\Delta C_{FV} = 15.10$, $\Delta C_{Fp} = 15.45$. Entropy values: $S_{F1} = 49.7$, $S_{F\infty} = 74.7$. Parameters: $z_1 = 16$, $z_2 = 128$, $N = 34$; $\tau_{F3} = 0.19$. Maximums on the curves for heat capacities appear at $z_2 \simeq 30$.
(*b*) Region III_B. Jumps of heat capacities at τ_{F3}: $\Delta C_{FV} = 38.57$, $\Delta C_{Fp} = 40.01$; jumps at τ_{F2}: $\Delta C_{FV} = -0.414$, $\Delta C_{Fp} = -0.415$. Entropy values: $S_{F1} = 103.6$, $S_{F2} = 175.8$. Parameters: $z_1 = 16$, $z_2 = 2400$, $N = 34$; $\tau_{F3} = 0.12$, $\tau_{F2} = 1.18$.

V. DISCUSSION AND CONCLUSIONS

In this work we studied the thermodynamic properties of systems of non-interacting bosons and fermions with a small number of particles. The equations for the average number of particles in each quantum state for an arbitrary number of particles were previously obtained by the authors in [2]. In the work, within the framework of theory [2], the temperature dependences of the entropy, heat capacities and pressure are calculated under the assumption that particles can be in two degenerate states.

It is shown that in the case of bosons, which at zero temperature are all at the lower level, with an increase in temperature, depending on the multiplicity of degeneracy of the upper level, three qualitatively different situations are possible. When the degeneracy factor of the upper level is low $z_2 \ll z_1$, all particles, regardless of the thermostat temperature, remain at the lower level (region I, in Fig. 1). The entropy is constant in this state. Due to the low degeneracy factor of the upper level, the system cannot receive energy from the thermostat and therefore turns out to be adiabatically isolated. With a greater degeneracy factor of the upper level, at a certain temperature T_{B1} (25), the transition of particles to the upper level becomes possible (region II, in Fig. 1). In this case the entropy and pressure begin to increase with increasing temperature, and the heat capacities at T_{B1} take on finite values by jumps. At high temperatures in the limit $T \to \infty$, particles remain distributed between two levels with finite populations, the entropy and pressure tend to constant values, and the heat capacities tend to zero (Fig. 3*a*). Finally, with a further increase of the degeneracy factor of the upper level, a case is possible when at a certain limiting temperature T_{B2} (26) all particles transit to the upper level, and the lower level becomes empty (region III, in Fig. 1). This temperature can be considered as an analogue of the Bose-Einstein condensation temperature, below which the filling of the ground level begins. At $T \geq T_{B2}$ the energy of the system reaches its maximally possible value, so that with an increase in the thermostat temperature the transfer of heat from the thermostat to the system becomes impossible. At T_{B2} the heat capacities turn to zero by jumps (Fig. 3*b*). Since the entropy at zero temperature for a system of bosons with account of discreteness of levels turns out to be finite and non-zero, the third law of thermodynamics is satisfied in the Nernst formulation.

In a gas of non-interacting fermions at zero temperature there are several qualitatively different states. If the number of particles does not exceed the degeneracy factor of the ground level $N \leq z_1$, then all particles at $T = 0$ are located at this lower level. When the degeneracy factor of the upper level is low $z_2 \ll z_1$ and $N \leq z_1/2$, all particles at any thermostat temperature, as in the case of bosons, remain at the lower level (region I_A, Fig. 4). In this state the system has a constant entropy and turns out to be adiabatically isolated. With an increase of the degeneracy factor of the upper level and for a small number of particles, at a certain temperature T_{F1} (37) the transition of particles to the upper level becomes possible (region II_A, Fig. 4). At that the entropy and pressure begin to increase, and the heat capacities take on finite values by jumps. At high temperatures in the limit $T \to \infty$, particles remain distributed between two levels with finite populations, the entropy and pressure tend to constant values, and the heat capacities tend to zero. With a further increase of the degeneracy factor of the upper level (region III_A, Fig. 4), at a certain limiting temperature T_{F2} (38) all particles transit to the upper level, and the lower level becomes empty. With an increase in temperature the state of the system does not change, its entropy and pressure remain constant, and its heat capacities are equal to zero. When the condition $N > 2z_1$ is satisfied, there is the region $\mathrm{I_B}$ similar to the region $\mathrm{I_A}$ (Fig. 4), where the system remains in the ground state at all permissible temperatures. Here, with increasing z_2 there also exist states similar to the previous case $N \leq z_1/2$ (regions $\mathrm{II_B}$ and $\mathrm{III_B}$, Fig. 4). The temperature dependences of the entropy and heat capacities for the case $N > 2z_1$ are shown in Fig. 7.

If the inequality $z_1/2 < N \leq z_1$ is satisfied, then even for a low degeneracy factor of the upper level $z_2 \ll z_1$ the region of adiabaticity of the system is absent at all temperatures, and at T_{F1} (37) the transition of particles to the upper level begins in it. At the temperature T_{F4} (40) the upper level proves to be filled, and particles continue to remain at the lower level (region $\mathrm{III'_A}$, Fig. 4). With an increase of the degeneracy factor of the upper level the system successively passes into the regions $\mathrm{II_A}$ and then $\mathrm{III_A}$, shown in Fig. 4. The temperature dependences of the entropy and heat capacities for this case $z_1/2 < N \leq z_1$ are presented in Fig. 6.

In the second qualitatively different situation, when $N > z_1$, at zero temperature the lower level is completely occupied and $N - z_1$ particles are located at the upper level. When the condition $z_1 < N \leq 2z_1$ is satisfied, in the region $\mathrm{III'_B}$ (Fig. 4) at the temperature T_{F3} (39) there begins the transition of particles to the upper level. At T_{F4} (40) the upper level proves to be filled, and a part of particles remains at the lower level. The state does not change with increasing temperature. At higher values of z_2 (region $\mathrm{II_B}$, Fig. 4) only the temperature T_{F3} exists, and in the limit $T \to \infty$ particles become distributed between two levels with finite populations. At yet more high values of z_2 (region $\mathrm{III_B}$, Fig. 4), in addition to T_{F3} there exists the limiting temperature T_{F2} (38) at which all particles transit to the upper level and the lower level becomes empty.

Note that the issue of negative and limiting temperatures in systems with a limited spectrum was considered by Yu.B. Rumer [6, 7]. In our case, by the temperature of a system with a small number of particles we mean the temperature of the thermostat with which it is in equilibrium, so that the temperature is always positive. In the above consideration, due to the finite number of levels, there exist limiting temperatures at which the energy of the system becomes maximum, so that a further increase in the temperature of the thermostat does not lead to an increase in the energy of the system.

In conclusion, we formulate the general features of the thermodynamics of two-level systems with a finite number of bosons and fermions:

1. At zero temperature the entropy can be non-zero, so that the third law of thermodynamics is satisfied in the Nernst formulation.

2. With a small degeneracy factor of the upper level particles can remain at the lower level at arbitrary temperatures.

3. As the degeneracy factor of the upper level increases, the transition of particles from the lower to the upper level becomes possible, such that in the limit of high temperatures particles are distributed between two levels with finite populations.

4. At yet greater degeneracy factor of the upper level there exists the limiting temperature at which the upper level becomes maximally filled, so that the energy reaches its greatest value. A further increase in the thermostat temperature does not change the state of the system.

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