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ON THE FEATURES OF IDEAL BOSE-GAS THERMODYNAMIC PROPERTIES AT A FINITE PARTICLE NUMBER

The paper is devoted to the theory of an ideal Bose-gas with a finite number N of particles. The exact expressions for the partition functions and occupation numbers of the model in the grand canonical, canonical, and microcanonical ensembles are found. From the calculations, it is followed that, oppositely to the accepted opinion that the chemical potential μ of an ideal Bose-gas is only negative, it can take values in the range $-\infty < \mu < \infty$. The asymptotic expressions (in the case $N \gg 1$) for the partition functions and occupation numbers for all above-mentioned thermodynamic ensembles are also evaluated.

K e y w o r d s: ideal Bose-gas, Bose-distribution, canonical ensembles.

1. Introduction

The theory of ideal Bose-gas is referred to the old and well-studied field of statistical physics [1–4], where practically all observables are calculated in the thermodynamic limit. Nevertheless, the real experiments aimed at its verification are often performed with the systems consisting of a finite number of particles N. For example, in the experiments with atomic Bose-gases [5–8] whose results are interpreted as the experimental confirmation of the phenomenon of Bose-condensation, the number of particles is at most $\sim 10^4$ or does not attain the Avogadro number which is of macroscopic value. Based on this, the corresponding calculations for the finite number particle ideal Bose-gas were presented in [9–11], where the model of a magnetic trap with the harmonic potential was considered.

Below, an attempt will also make to consider the system with a finite number of free bosons, but to

calculate the averaged number of particles in each quantum state explicitly taking into account that its initial occupation number is restricted by N. It was shown that, due to this seemingly evident condition of the physical nature, not all well-known results can be confirmed by exact and rather simple calculations. In doing so, we calculate the observables for all basic statistical ensembles, namely, the grand canonical (GCE), canonical (CE), and microcanonical (MCE) ones which are defined below.

2. Ideal Bose-gas

A quantum particle located in the vessel of volume V has the discrete energy spectrum ε_k, where the index k runs the values $0, 1, ..., \infty$, as the energy ε_k of the state increases.

Consider the model system consisting of N bosons non-interacting with one another that are placed into this vessel with impenetrable walls. Then the system is characterized by a configuration $[n]$, i.e., by a collection of the occupation numbers $\mathbf{n}_k$. Each of these

quantities indicates the number of particles in the k-th state with the energy ε_k. It is naturally to suppose that $\mathbf{n}_k$ *cannot exceed* the number of particles N in the system. In this case, the total number of particles and the total energy of such a model system can be given by the simple equalities:

$$N = \sum_{k=0}^{\infty} \mathbf{n}_k, \quad E = \sum_{k=0}^{\infty} \mathbf{n}_k \varepsilon_k. \tag{1}$$

Let us place the vessel into a thermostat with the temperature T. Under the action of thermal fluctuations on the vessel walls, the configuration $[n]$ will vary (stochastically) with the time, but the number N is preserved by the task condition. As is known, we obtain the time-averaged values of the observable quantities from experiments. In their calculations, the ergodic hypothesis is usually accepted in statistical physics. According to it, the mean over the time coincides with the mean over the ensemble.

Note that the ensemble is a collection of systems with all possible configurations or, in other words, with different distributions of particles over the states. The ensembles can be very different. Each specific ensemble is determined by the own distribution function $f[n]$, and the most popular among them are, as mentioned above, GCE, CE, and MCE.

3. Grand Canonical Ensemble

Let us define the distribution function for GCE in the form

$$f[n] = \mathrm{e}^{-\beta(E-\mu N)} = \prod_k \mathrm{e}^{-\mathbf{n}_k \beta(\varepsilon_k - \mu)}, \tag{2}$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$ stands for the reciprocal temperature, and μ is the chemical potential. It should be noted that the distribution function determined in this way does not formally contain any restrictions on the number N. So, it should be attributed to GCE ones.

Since $f[n]$ (2) is factorized, the partition function of such a system can be easily calculated [12]:

$$Z = \sum_{[n]} f[n] = \sum_{\mathbf{n}_0=0}^{N} \mathrm{e}^{-\mathbf{n}_0 \beta(\varepsilon_0 - \mu)} \times$$

$$\times \sum_{\mathbf{n}_1=0}^{N} \mathrm{e}^{-\mathbf{n}_1 \beta(\varepsilon_1 - \mu)} \dots \sum_{\mathbf{n}_k=0}^{N} \mathrm{e}^{-\mathbf{n}_k \beta(\varepsilon_k - \mu)} \dots =$$

$$= \prod_k \frac{1 - \mathrm{e}^{-\beta(\varepsilon_k - \mu)(N+1)}}{1 - \mathrm{e}^{-\beta(\varepsilon_k - \mu)}}. \tag{3}$$

It can be seen that an essential and distinguishing factor of this calculation is the upper limit of each sum in the state occupation numbers, which forbids any distributions with at least one occupation number, greater than N. As noted, this physical (as well as mathematical) constraint does not preclude the direct calculation of the mean occupation number for every state. As a result, this number can be easily determined and takes the form

$$\overline{n}_k = Z^{-1} \sum_{[\mathbf{n}]} \mathbf{n}_k f[\mathbf{n}] = n_k - (N+1)m_k, \tag{4}$$

where n_k and m_k are defined as follows:

$$n_k = \frac{1}{\mathrm{e}^{\beta(\varepsilon_k - \mu)} - 1}, \quad m_k = \frac{1}{\mathrm{e}^{\beta(\varepsilon_k - \mu)(N+1)} - 1}.$$

It is seen that the first term on the right-hand side of (4) is the ordinary Bose-distribution, and the second one introduces the dependence on the Bose-particle number of the system into the average over the ensemble.

This point is worth to be noted, since the mean number of occupation following from expressions (3) and (4) coincides formally with that for the parastatistics [3] under the condition $p = N$, though it is quite obvious that the order p of the parastatistics and the number N are the very different physical quantities without any connection with each other. In addition, the derivation of the corresponding formula in [3] seems not to be quite proper, because the Stirling factorial formula is used in it for the quantities less than 1. Nevertheless, the final result turns out proper and coincides with formula (4) which is obtained with the help of exact calculations. It is easy to be convinced that, in the case when $p < N$ (in the limit $p = 1$, one deals, in fact, with Fermi-particles), the calculations should be done separately, but when the parastatistics parameter $p > N$ (including macroscopically large, but hardly achievable value $p \gg N$), all obtained formulas and conclusions are preserved.

It should be also noted that, in the case $p < N$, the mean number of paraparticles in the state will be describe by formula (4) with the substitution $p \to N$, but the obtaining of various thermodynamic quantities is not a trivial task and, for systems with given, but arbitrary numbers N and $p(< N)$, demands special calculations. At the same time, the case $p > N$ has no physical sense because of the same reason –

the particle number in each quantum state cannot be larger than N, and expression (4) stays to be valid.

The last expression testifies that, namely due to its second term, the number $\bar{n}_k$ has a finite value for

$$-\infty < \mu < \infty,$$

rather than only for $\mu < 0$. This means that this well-known assertion is not absolutely true. Indeed, if it is restricted by the first term of this expression (Bose-distribution), then one has

$$\varepsilon_0 - \mu = \frac{1}{\beta} \ln\left(1 + \frac{1}{n_0}\right),$$

and it is seen that the chemical potential cannot exceed the lowest state energy. Otherwise, its occupation number $\bar{n}_0$ may become equal to non-physical value – infinity.

At the same time, the exact formula is

$$\bar{n}_0 = \frac{1}{e^{\beta(\varepsilon_0 - \mu)} - 1} - \frac{N + 1}{e^{\beta(\varepsilon_0 - \mu)(N+1)} - 1}, \quad (5)$$

and one cannot obtain the similar expression for μ analytically. But it is not difficult to present its several typical examples: so, if $\bar{n}_0 = N$, then $\mu \to \infty$; if $\bar{n}_0 = N/2$, then $\mu \to \varepsilon_0$; and, eventually, if $\bar{n}_0 = 0$, then $\mu \to -\infty$. For the chosen values of the chemical potential, the calculated ground-state occupation numbers turn out to be valid regardless of the temperature. Thus, for all real values of μ, the occupation number of the ground particle quantum state remains finite. It can be assumed that the found corrections in the mean occupation numbers of the ground and excited states should affect thermodynamic properties of the Bose-systems, although the first one – to the ground state – is the most significant.

In the end of this Section, it is worth to note that, in the general situation, the different GCE thermodynamic parameters β (or T) and μ can be presented in terms of fixed N and E by means of the system of equations [cf. (1)]

$$N = \sum_{k=0}^{\infty} \bar{n}_k, \quad E = \sum_{k=0}^{\infty} \bar{n}_k \varepsilon_k. \quad (6)$$

4. Canonical Ensemble

By definition, the distribution function for CE takes the form

$$f_{\mathrm{CE}}[n] = f[n]\delta\left(N - \sum_k \mathbf{n}_k\right). \quad (7)$$

In other words, the restriction on the total Bose-particle number is introduced and contained in the very distribution function. In accordance with the generally accepted definition, such a restriction is a necessary condition of CE existence.

Thereby, the calculation of the partition function $f_{\mathrm{CE}}[n]$ becomes harder due to the presence of the δ-function in (7), but the exact analytic calculation can be carried out for this ensemble as well.

Let us write down $\delta(N - \sum_k \mathbf{n}_k)$ as an integral:

$$\delta\left(N - \sum_k \mathbf{n}_k\right) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx\, e^{ixN} \prod_k e^{-ix\mathbf{n}_k}. \quad (8)$$

Then the partition function of CE takes the form

$$Z_{\mathrm{CE}} = \sum_{[n]} f_{\mathrm{CE}}[n] = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx\, e^{-w(x)}, \quad (9)$$

where

$$w(x) = -ixN - \sum_k \ln \frac{1 - e^{-[\beta(\varepsilon_k - \mu) + ix](N+1)}}{1 - e^{-[\beta(\varepsilon_k - \mu) + ix]}}, \quad (10)$$

$$\bar{n}_k^{\mathrm{CE}} = \frac{Z_{\mathrm{CE}}^{-1}}{2\pi} \int_{-\pi}^{\pi} dx\, e^{-w(x)} \times$$

$$\times \left(\frac{1}{e^{\beta(\varepsilon_k - \mu) + ix} - 1} - \frac{N + 1}{e^{[\beta(\varepsilon_k - \mu) + ix](N+1)} - 1}\right). \quad (11)$$

For the case $N \gg 1$, integrals (9) and (11) can be calculated with the help of the saddle-point method. The point is determined from the equation

$$\frac{\partial w(x)}{\partial x} = 0 = -i\left(N - \sum_k \left(\frac{1}{e^{\beta(\varepsilon_k - \mu) + ix} - 1} - \right.\right.$$

$$\left.\left. - \frac{N + 1}{e^{[\beta(\varepsilon_k - \mu) + ix](N+1)} - 1}\right)\right),$$

which holds, due to Eqs. (6), for $x = 0$. The second derivative at the saddle point takes the form

$$w_{xx} = \left.\frac{\partial^2 w(x)}{\partial x^2}\right|_{x=0} = \sum_k \left(\frac{e^{\beta(\varepsilon_k - \mu)}}{(e^{\beta(\varepsilon_k - \mu)} - 1)^2} - \right.$$

$$\left. - \frac{(N + 1)^2 e^{\beta(\varepsilon_k - \mu)(N+1)}}{(e^{\beta(\varepsilon_k - \mu)(N+1)} - 1)^2}\right). \quad (12)$$

As a result, if the condition $N \gg 1$ holds, we obtain

$$Z_{\mathrm{CE}} = \frac{Z}{\sqrt{2\pi w_{xx}}}. \tag{13}$$

The mean value of the occupation number for CE for $N \gg 1$ is

$$\bar{n}_k^{\mathrm{CE}} = -\beta^{-1} \frac{\partial \ln Z_{\mathrm{CE}}}{\partial \varepsilon_k} = \bar{n}_k - m_k^{\mathrm{CE}}, \tag{14}$$

where

$$m_k^{\mathrm{CE}} = \frac{1}{2w_{xx}} \big(n_k(n_k+1)(2n_k+1) - $$

$$- (N+1)^3 m_k(m_k+1)(2m_k+1) \big), \tag{15}$$

and the quantities n_k and m_k are defined in (4). The direct verification shows that the numbers (11) of occupation in the ground state and in the excited ones in CE are, respectively, larger and less than in in the case of GCE.

5. Microcanonical Ensemble

The distribution function for MCE is easily set and takes the form

$$f_{\mathrm{MCE}}[n] = f[n]\delta(N - \sum_k \mathbf{n}_k)\delta(E - \sum_k \mathbf{n}_k \varepsilon_k). \tag{16}$$

This generalization follows from the well-known definition of a microcanonical ensemble, in which not only the number of particles is fixed, but the energy as well. For the corresponding δ-function, we again use the integral representation analogous to (8):

$$\delta\big(E - \sum_k \mathbf{n}_k \varepsilon_k\big) = \frac{1}{2\pi} \int\limits_{-\pi}^{\pi} dy \mathrm{e}^{iyE} \prod_k \mathrm{e}^{-iy\mathbf{n}_k \varepsilon_k}, \tag{17}$$

and it can be easily sumed over the configurations. Then, for the partition function in MCE, we get [cf. (9)]

$$Z_{\mathrm{MCE}} = \sum_{[n]} f_{\mathrm{MCE}}[n] = \frac{1}{(2\pi)^2} \int\limits_{-\pi}^{\pi} dxdy \, \mathrm{e}^{-w(x,y)}, \tag{18}$$

where [cf. (10)]

$$w(x,y) = -iNx - iEy - $$

$$- \sum_k \ln \frac{1 - \mathrm{e}^{-[\beta(\varepsilon_k-\mu)+ix+iy\varepsilon_k](N+1)}}{1 - \mathrm{e}^{-[\beta(\varepsilon_k-\mu)+ix+iy\varepsilon_k]}}. \tag{19}$$

In this case, the mean value of the number of occupation is presented in terms of the integral

$$\bar{n}_k^{\mathrm{MCE}} = \frac{Z_{\mathrm{MCE}}^{-1}}{(2\pi)^2} \int\limits_{-\pi}^{\pi} dxdy \, \mathrm{e}^{-w(x,y)} \times$$

$$\times \Bigg(\frac{1}{\mathrm{e}^{\beta(\varepsilon_k-\mu)+ix+iy\varepsilon_k} - 1} - $$

$$- \frac{N+1}{\mathrm{e}^{[\beta(\varepsilon_k-\mu)+ix+iy\varepsilon_k](N+1)} - 1} \Bigg), \tag{20}$$

which can be considered as a generalization of integral (11). In the analytic calculation of the partition function (18), we take, as above, $N \gg 1$ and again use the saddle-point method whose point has the coordinates $x = y = 0$. As a result, we obtain

$$Z_{\mathrm{MCE}} = \frac{1}{2\pi} \frac{Z}{\sqrt{d}}, \tag{21}$$

where

$$d = w_{xx} w_{yy} - w_{xy}^2, \tag{22}$$

$$w_{xx} = \frac{\partial^2 w(x,y)}{\partial x^2}\bigg|_{x=y=0}, \quad w_{xy} = \frac{\partial^2 w(x,y)}{\partial x \partial y}\bigg|_{x=y=0},$$

$$w_{yy} = \frac{\partial^2 w(x,y)}{\partial y^2}\bigg|_{x=y=0},$$

$$\bar{n}_k^{\mathrm{MCE}} = \bar{n}_k - m_k^{\mathrm{MCE}}, \tag{23}$$

and

$$m_k^{\mathrm{MCE}} = \frac{1}{2d} \Big((w_{yy} + \varepsilon_k^2 w_{xx})b_k - (2\varepsilon_k w_{xx} - w_{xy})\frac{a_k}{\beta} \Big), \tag{24}$$

$$a_k = n_k(n_k+1) - (N+1)^2 m_k(m_k+1),$$

$$b_k = n_k(n_k+1)(2n_k+1) - (N+1)^3 m_k(m_k+1)(2m_k+1).$$

As is seen from formulas (22) and (23), the mean values of the numbers of occupation of the ground state and of the excited ones in MCE are, respectively, larger and less, than in the above-considered GCE and CE.

6. Conclusions

The obtained results are in a sense different from the commonly known ones (see, e.g., [1–4]) and supplement them. In our opinion, the cause lies in that the previous investigations (at least, the studies of systems in which the number of particles (bosons, in this case) is strictly specified) neglected some physically obvious fact, namely: the limitation imposed on the numbers of occupation $\mathbf{n}_k \leq N$, which requires the special discussion and consideration.

Nevertheless, even for a sufficiently large number of bosons that usually corresponds to the experiments on the Bose–Einstein condensation of cold atomic gases, their thermodynamic quantities (in particular, the condensate density) should depend, as is shown above, on the particle number N. Therefore, we believe that the presented results can be useful for the thermodynamics and statistical physics of Bose-systems with finite numbers of particles.

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ПРО ОСОБЛИВОСТІ ТЕРМОДИНАМІЧНИХ
ВЛАСТИВОСТЕЙ ІДЕАЛЬНОГО БОЗЕ-ГАЗУ
ПРИ СКІНЧЕННОМУ ЧИСЛІ ЧАСТИНОК

Стаття присвячена теорії ідеального бозе-газу зі скінченною кількістю N частинок. Знайдено точні вирази для функцій розподілу та чисел заповнення для даної моделі у великому канонічному, канонічному та мікроканонічному ансамблях. З розрахунків випливає, що на відміну від загальноприйнятої думки, що хімічний потенціал μ ідеального бозе-газу лише негативний, він може приймати значення в діапазоні $-\infty < \mu < \infty$. Також оцінено асимптотичні вирази (у випадку $N \gg 1$) для функцій розподілу і чисел заповнення для всіх вищезгаданих термодинамічних ансамблів.

К л ю ч о в і с л о в а: ідеальний бозе-газ, бозе-розподіл, канонічні ансамблі.