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# BOSE-EINSTEIN CONDENSATION AS A DEPOSITION PHASE TRANSITION OF QUANTUM HARD SPHERES AND NEW RELATIONS BETWEEN BOSONIC AND FERMIONIC PRESSURES

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We investigate the phase transition of Bose–Einstein particles with the hard-core repulsion in the grand canonical ensemble within the Van der Waals approximation. It is shown that the pressure of non-relativistic Bose–Einstein particles is mathematically equivalent to the pressure of simplified version of the statistical multifragmentation model of nuclei with the vanishing surface tension coefficient and the Fisher exponent  $\tau_{\rm F}=\frac{5}{2}$ , which for such parameters has the 1-st order phase transition. The found similarity of these equations of state allows us to show that within the present approach the high density phase of Bose-Einstein particles is a classical macro-cluster with vanishing entropy at any temperature which, similarly to the system of classical hard spheres, is a kind of solid state. To show this we establish new relations which allow us to identically represent the pressure of Fermi–Dirac particles in terms of pressures of Bose–Einstein particles of two sorts.

 $\mathit{Keywords}$ : quantum gases, Van der Waals, equation of state, statistical multifragmentation model, Bose–Einstein condensation, deposition phase transition.

## 1. Introduction

The phenomenon of Bose–Einstein (BE) condensation is, probably, one of the most striking manifestation of collective quantum effects [1, 2]. Due to its great importance the phase transition (PT) of BE condensation in the ideal gas is discussed in all textbooks on statistical mechanics. However, it seems that even the BE condensation in an ideal gas itself has a number of weak points which are discussed in details in [3]. Thus, in the wast majority of the textbooks it is written that the BE condensation of ideal gas is the 3-rd order phase transition (see, for instance, [1]), although in the famous book [2] (see the section 12.3 for details) it is argued that the BE condensation is the 1-st order PT between liquid and gas. The main question we answer here is what kind

In what follows we demonstrate that the pressure of the non-relativistic BE particles with the hard-core interaction taken in the Van der Waals (VdW) approximation can be identically reduced to the one of the simplified version of statistical multifragmentation model (sSMM) [4] with a vanishing surface tension of the constituents (see below). This exactly solvable model was formulated in [5] and solved exactly in [6–9], while its new and more realistic generalization can be found in [10]. Although the sSMM [5–10] lacks the Coulomb interaction between the nuclei and the asymmetry energy of nuclei, its exact analytical solution established both in the thermodynamic limit

of PT is the BE condensation in the quantum system with the simplest interaction, namely with the hard-core repulsion? In all textbooks it is written that the BE condensate is the group of particles with zero momentum. However, the question is what is it? Is it a liquid or a solid?

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[6, 7, 10] and for finite volumes [8, 9] is able to qualitatively describe the main properties of the nuclear liquid-gas PT.

The mathematical similarity between the VdW equation of state (EoS) of BE hard spheres and the sSMM allows us to show that the high density phase of BE particles with hard-core repulsion is a classical macro-cluster which, similarly to the system of classical hard-spheres, is a solid state [11, 12] and not a liquid as it was argued in K. Huang book [2]. In our analysis we also analyzed the pressure of Fermi-Dirac (FD) particles with the hard-core repulsion which in many respects is similar to the one of sSMM, although it does not have the 1-st order PT. This analysis allows us to find out some new relations between the pressures of BE and FD particles with the hardcore repulsion, which help us to demonstrate that the macro-cluster of BE particles is, indeed, a classical object. The found relations allow us to clearly demonstrate under what conditions the FD particles with the hard-core repulsion can have the first order phase transition.

The work is organized as follows. In Sect. II we analyze the pressure of BE and FD particles with the hard-core repulsion in the VdW approximation in a form convenient for the grand canonical ensemble. Sect. III is devoted to discussion of the properties of the macro-cluster with the help of the BE-FD decomposition identities which identically represent the pressure of FD particles in terms of two BE pressures. Our conclusions are given in Sect. IV.

## 2. BE Condensation as the 1-st Order Phase Transition

The EoS of hard-spheres with BE or FD statistics in the grand canonical ensemble variables under the Van der Waals approximation for the hard-core repulsion can be obtained either analyzing the free energy of the Van der Waals gas in canonical ensemble [13, 14] or more rigorously from the quantum partition function in the grand canonical ensemble [15]. In the grand canonical variables it has the form

$$p_{\pm} = p_{\pm}^{id}(T, \nu) \equiv$$

$$\equiv \pm Tg \int \frac{d^3k}{(2\pi\hbar)^3} \ln\left[1 \pm \exp\left[\frac{\nu - e(k)}{T}\right]\right], \tag{1}$$

where  $\nu \equiv \mu - 4V_0 p_{\pm}$ . In Eq. (1) the lower sign is for the BE statistics, while the upper sign is for the

FD one. Here T is temperature of the system,  $\mu$  is its chemical potential,  $\nu$  is an effective chemical potential, g is the number of spin-isospin states (degeneracy factor), m is the mass of particle,  $V_0 = \frac{4}{3}\pi R^3$  is the "eigen volume" of particle, and R is the half of the minimal interaction range of the hard-core potential U(r) of a one component system (with a single hard-core radius)

$$U(r) = \begin{cases} 0, & |r| > 2R, \\ \infty, & |r| \le 2R. \end{cases}$$
 (2)

More sophisticated interaction between the BE particles is considered in [3].

The potential U(r) in Eq. (2) acts in a simplest possible way: (i) if two particles 1 and 2, for definiteness, do not interact, i.e. the distance between them is larger, than two hard-core radii R, |r| > 2R. then U(r) = 0 and, therefore, their total energy is the sum of their single-particle (kinetic) energies  $e_1$  and  $e_2$ ; (ii) if these two particles interact, then |r|=2Rand  $U(|r|=2R)=\infty$ , but such configurations do not contribute to partition (and all thermodynamic functions), since they are suppressed by the statistical operator  $\exp\left[-\frac{\hat{H}_{hc}}{T}\right]$  due to an infinite potential energy (here  $\hat{H}_{hc}$  denotes the Hamiltonian of the system). As a result, the total energy of the particles with the hard-core repulsion equals to the sum of their single-particle (kinetic) energies and this allows one to find the pressure (1) directly from the quantum partition function. In other words, the particles with the hard-core interaction behave similarly to an ideal quantum gas.

This is a important property of this EoS which leads to a well-known practical consequence, namely that the energy per particle coincides with the one of the ideal gas. Due to this property the sophisticated equations of state with the hard-core repulsion, known as the hadron resonance gas model, are very successfully used to describe the multiplicities of hadrons [16–18] and light (anti-, hyper)nuclei [19, 20] which are measured in the high energy nuclear collisions and to get a reliable thermodynamic information about next to the last stage of such collisions.

For further analysis it is convenient to introduce the auxiliary functions

$$\mathcal{F}_{\pm}(p) \equiv T \sum_{l=1}^{K_{\text{max}}} \frac{(\mp 1)^{(l+1)}}{l} n_0^{id} \left[ \frac{T}{l}, \nu(p) \right], \tag{3}$$

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and, hence, Eq. (1) becomes  $p_{\pm} = \mathcal{F}_{\pm}(p_{\pm})$ , where

$$\begin{split} n_0^{id} \left[ \frac{T}{l}, \nu \right] &= \int \frac{g \, d^3 k}{(2\pi\hbar)^3} \, e^{\frac{l\left[\nu - \sqrt{m^2 + \mathbf{k}^2}\right]}{T}} \simeq \\ &\simeq \int \frac{g \, d^3 k}{(2\pi\hbar)^3} \, e^{\frac{l\left[\nu - m - \frac{k^2}{2m}\right]}{T}} = g \left[ \frac{m \, T}{2\pi \, l \, \hbar^2} \right]^{\frac{3}{2}} e^{\frac{l\left[\nu - m\right]}{T}}, \quad (4) \end{split}$$

where the particle number density of Boltzmann point-like particles with temperature T and chemical potential  $\nu$  is denoted as  $n_0^{id} [T, \nu]$  and the upper limit of sum in Eq. (3) is  $K_{\text{max}} \to \infty$ . To avoid the unnecessary complexity in our derivations through out this work we regard the limit  $K_{\text{max}} = 2K + 1 \to \infty$  strictly in this sense. For the BE statistics (sign – in Eqs. (3)) it is not important, but it is very important for the case of FD statistics (sign + in Eqs. (3)).

The function  $\mathcal{F}_{\pm}$  in (3) is, apparently, obtained by expanding the ln-function in Eq. (1). For large values of  $l\gg 1$  the inequality  $lm\gg T$  is valid for any nonvanishing mass m and, therefore, in this case one can use the non-relativistic approximation in the left hand side momentum integral in Eq. (4) and get the right hand side expression (4). However, for convenience we will use such an approximation for any  $l\geq 1$ , assuming that considered temperatures are very low compared to the particle mass, i.e.  $m\gg T$ . Moreover, in what follows we will always use the non-relativistic approximation for particle energy, unless it is specified explicitly.

To make a direct comparison with the sSMM [5–9] we explicitly write Eq. (1) for the BE statistics (a=-1)

$$p_{-} = T g \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \times \times \sum_{k=1}^{K_{\text{max}}} \frac{(-a)^{(k+1)}}{k^{\frac{5}{2}}} \exp\left[ \frac{k(\mu - m - 4V_{0} p_{-})}{T} \right],$$
 (5)

using Eq. (3) and the right hand side of Eq. (4). Comparing Eq. (5) with Eq. (15) from Ref. [6], one can see that the pressure of BE hard spheres is mathematically absolutely equivalent to the sSMM with the "volume"  $4kV_0$  of k-nucleon nuclei, with the vanishing surface tension of all nuclei and with the Fisher exponent  $\tau_{\rm F} = \frac{5}{2}$  (or for the index  $\tau \equiv \tau_{\rm F} + \frac{3}{2} = 4$  in terms of Refs. [6,7]). After an invention of the famous Fisher droplet model [21] it became clear that all real gases consist of the clusters of all possible size that

are made by the molecules, and the right hand side of Eq. (5) demonstrates this for the BE particles.

Due to the mathematical similarly to the sSMM, using the exact solution of sSMM [6,7,9] one can immediately conclude that Eq. (5) describes two phases: the gaseous phase  $p_g = p_-(T,)$  for the low densities defined by the inequality  $\mu < \mu_c(T)$ , and high density phase pressure  $p_s = \frac{(\mu - m)}{4V_0}$  for  $\mu > \mu_c(T)$ . According to the Gibbs criterion the PT occurs, if the pressures of two phases are equal, i.e.  $p_g(T,\mu_c) = p_s(T,\mu_c)$ . This equation defines the phase equilibrium curve  $\mu = \mu_c(T)$  of the 1-st order PT.

At the PT curve  $\mu = \mu_c(T)$  the effective chemical potential becomes

$$\nu_c = \mu_c - 4V_0 \, p_g(T, \mu_c) =$$

$$= \mu_c - 4V_0 \, p_s(T, \mu_c) \equiv m. \tag{6}$$

Using this result one can identically rewrite the pressure at PT curve as

$$p_{c-} = T g \left[ \frac{m T}{2\pi\hbar^2} \right]^{\frac{3}{2}} \sum_{k=1}^{K_{\text{max}}} \frac{1}{k^{\frac{5}{2}}} \underset{K_{\text{max}} \to \infty}{=}$$

$$= \frac{T g}{\Gamma \left[ \frac{5}{2} \right]} \left[ \frac{m T}{2\pi\hbar^2} \right]^{\frac{3}{2}} \int_{0}^{\infty} \frac{t^{\frac{3}{2}}}{e^t - 1} dt, \tag{7}$$

where we used the integral representation of the Riemann  $\zeta\left[\frac{5}{2}\right]$ -function [22]. Here  $\Gamma(z)$  is the usual gamma-function which for the natural numbers n is defined as  $\Gamma(n+1)=n!$ . Taking  $t=\frac{\omega}{T}$  in the integral in Eq. (7), one finds the usual representation of pressure as an integral over the particle energy  $\omega$  [1].

Although the critical pressure (7) coincides with the one obtained usually for the point-like particles [1], the particle number density of gas  $n_{-}$  is modified due to the presence of hard-core interaction. Using the particle number density of the gas of point-like particles  $n_{-}^{id}(T, \nu)$  one can write

$$n_{-}^{id}(T,\nu) \equiv \frac{\partial p_{-}^{id}(T,\nu)}{\partial \nu} =$$

$$= g \left[ \frac{mT}{2\pi\hbar^2} \right]^{\frac{3}{2}} \sum_{k=1}^{K_{\text{max}}} \frac{1}{k^{\frac{3}{2}}} \exp\left[ \frac{k(\nu-m)}{T} \right], \tag{8}$$

$$n_{-}(T,\nu) \equiv \frac{\partial p_{-}^{id}(T,\nu)}{\partial \mu} = \frac{n_{-}^{id}(T,\nu)}{1 + 4V_0 n_{-}^{id}(T,\nu)}.$$
 (9)

From Eq. (9) one can see that at the PT curve the particle number density of the gas is smaller than the particle number density of the dense phase, since

$$n_{-}(T,\nu_c) < n_s \equiv \frac{\partial p_s}{\partial \mu} = \frac{1}{4V_0},\tag{10}$$

and, hence, for any finite temperature T the particle number density of point-like particles  $n_{-}^{id}(T,\nu_c)$  is finite too. Therefore, the particle number density of gaseous phase is smaller than the one of the high density phase as indicated by the inequality (10). As a result, the BE PT is of the 1-st order.

Substituting into Eqs. (8) and (9) the value  $\nu = \nu_c$  one can get the temperature of BE condensation as

$$T_c^{\text{BE}} = \frac{2\pi\hbar^2}{m} \left[ \frac{1}{g\zeta \left[ \frac{3}{2} \right]} \frac{n_-}{1 - 4V_0 n_-} \right]^{\frac{2}{3}}.$$
 (11)

Note that for large values of the excluded volume  $V_0$  and high particle number densities  $n \to \frac{1}{4V_0}$  the hard-core repulsion may essentially increase the value of the PT temperature and make it more realistic compared to the traditional estimate obtained for the point-like particles [1], i.e. if one takes the limit  $V_0 \to 0$  on the right hand side of Eq. (11).

It is necessary to stress that the above results are generic in a sense that one can consider the effective values of degeneracy factor  $g \to g^{\rm eff}$  and the one of excluded volume  $4V_0 \to V_0^{\rm eff}$  which correspond to a more realistic EoS than the VdW EoS and which is able to reproduce the pressure of quantum particles beyond the second virial coefficient approximation at least in some (even in a narrow) range of thermodynamic parameters.

Since we are also interested in analyzing the case of FD particles, we would like to obtain the above result using a different approach, namely without referring to the sSMM results of Refs. [6–8]. First we consider the limit  $\mu \to \infty$  in Eq. (5) for very large, but finite values of  $K_{\rm max}$ . Apparently, this limit should correspond to the dense phase of our EoS. Then in this limit  $V_0 p_s/T \gg 1$  and for  $\mu > m + 4 V_0 p_s$  the leading terms of Eq. (5) for a = -1 can be cast as

$$\ln\left[\frac{p_s K_{\text{max}}^{\frac{5}{2}}}{T\phi(T)}\right] \simeq K_{\text{max}} \left[\mu - (m + 4V_0 p_s)\right]. \tag{12}$$

Here the thermal density of the gas of classical hard spheres is denoted as  $\phi(T) = g \left[ \frac{mT}{2\pi\hbar^2} \right]^{\frac{3}{2}}$ . In deriving

Eq. (5) we have chosen the large values of chemical potential  $\mu > \mu_c$ , which are not allowed in the thermodynamic limit, but for finite systems they can be used [8, 9]. Now from Eq. (12) one can see that for  $K_{\text{max}} \to \infty$  the logarithmic correction disappears and the pressure of dense phase  $p_s = \frac{\mu - m}{4V_0}$  acquires a familiar form.

In order to show that the EoS (5) for a=-1 has the 1-st order PT we examine the derivative  $D^1p_- \equiv T \frac{\partial p_-}{\partial \rho^{id}}$ . Hereafter to avoid a confusion we will distinguish the particle number density of point-like particles as the function given by the right hand side of Eq. (8) and the same quantity as the independent variable  $\rho^{id}_-$ . The derivative  $D^1p_-$  is more convenient to employ for the spinodal instability point of the gas than the derivative  $\frac{\partial p_-}{\partial n_-}$ , since its expression is simpler. Note that appearance of the spinodal instability point of the gas taken at the given isotherm signals about the 1-st order PT [1]. Indeed, the expression for  $D^1p_-$ 

$$D^{1}p_{-} \equiv T \frac{\partial p_{-}}{\partial \nu} \frac{\partial \nu}{\partial \rho_{-}^{id}} = \left[ \sum_{k=1}^{K_{\text{max}}} \frac{1}{k^{\frac{3}{2}}} \exp\left[ \frac{k(\nu - m)}{T} \right] \right] \times \left[ \sum_{k=1}^{K_{\text{max}}} \frac{1}{k^{\frac{1}{2}}} \exp\left[ \frac{k(\nu - m)}{T} \right] \right]^{-1}, \tag{13}$$

shows that, if the effective chemical potential  $\nu=\mu-4V_0\,p_-$  approaches the value  $\nu=m$ , then the derivative  $\frac{\partial \rho_-^{id}}{\partial \nu}\equiv \frac{\partial n_-^{id}}{\partial \nu}\to \infty$  diverges for  $K_{\rm max}\to \infty$  and, hence, in this limit  $D^1p_-=0$ . Thus, we have found that the spinodal instability point of the gas of BE hard spheres coincides with the PT curve.

Now we turn to the analysis of the FD particles with the hard-core repulsion. For  $\nu \leq m$  the pressure of such particles  $p_+$  and its  $\nu$ -derivative can be explicitly written as

$$p_{+} = T g \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \times$$

$$\times \sum_{k=1}^{K_{\text{max}}} \frac{(-1)^{(k+1)}}{k^{\frac{5}{2}}} \exp \left[ \frac{k(\nu - m)}{T} \right] \Big|_{\nu = \mu - 4V_{0} p_{+}}, \quad (14)$$

$$n_{+}^{id} \equiv \frac{\partial p_{+}}{\partial \nu} = g \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \times$$

$$\times \sum_{k=1}^{K_{\text{max}}} \frac{(-1)^{(k+1)}}{k^{\frac{3}{2}}} \exp \left[ \frac{k(\nu - m)}{T} \right] \Big|_{\nu = \mu - 4V_{0} p_{+}}. \quad (15)$$

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A similarity with the sSMM can be more clearly seen for  $\nu = \mu - 4V_0 p_+ \rightarrow m$ , if in the sum (14) one adds the even terms to the preceding odd ones

$$p_{+} = T g \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \left[ \sum_{k \in \text{odd}}^{K_{\text{max}} - 2} \frac{\exp\left[\frac{k(\nu - m)}{T}\right]}{k^{\frac{5}{2}}} \times \right]$$

$$\times \left[ 1 - \frac{k^{\frac{5}{2}}}{(k+1)k^{\frac{5}{2}}} \exp\left[\frac{(\nu - m)}{T}\right] + \right] + \frac{\exp\left[\frac{K_{\text{max}}(\nu - m)}{T}\right]}{K_{\text{max}}^{\frac{5}{2}}} \simeq$$

$$\simeq T g \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \left[ \sum_{k \in \text{odd}}^{K_{\text{max}} - 2} \frac{5}{2k^{\frac{7}{2}}} \times \right]$$

$$\times \exp\left[\frac{k(\nu - m)}{T} - \frac{5}{2k}\right] + \frac{\exp\left[\frac{K_{\text{max}}(\nu - m)}{T}\right]}{K_{\text{max}}^{\frac{5}{2}}},$$

$$(17)$$

where we expanded the binomial  $(k+1)^{\frac{5}{2}}$  keeping two leading terms and approximated the ratio  $k^{\frac{5}{2}}/(k+1)^{\frac{5}{2}} \simeq \exp[-\frac{5}{2k}]$ . Evidently, this approximation is suited for  $k \gg 1$ , but for qualitative analysis it is very convenient, since in the vicinity of PT the main role is played by the largest cluster. Eq. (17) shows that, apart from the term with  $k=K_{\max}$ , in the left vicinity of the point  $\nu \to m-0$  the EoS for FD particles with the hard-core repulsion is similar to the sSMM for the clusters of the odd number of constituents which have the Fisher exponent  $\tau_{\rm F}=\frac{7}{2}$  and a vanishing value of surface tension coefficient.

Apparently, from Eqs. (14) and (17) one can also derive Eq. (12) and establish the pressure of dense phase  $p_s = \frac{\mu - m}{4V_0}$  similarly to the case of BE particles. However, the derivative

$$\frac{\partial \rho_{+}^{id}}{\partial \nu} \equiv \frac{\partial^{2} p_{+}}{\partial \nu^{2}} = \frac{g}{T} \left[ \frac{m T}{2\pi \hbar^{2}} \right]^{\frac{3}{2}} \times \times \sum_{k=1}^{K_{\text{max}}} \frac{(-1)^{(k+1)}}{k^{\frac{1}{2}}} \exp\left[ \frac{k(\nu - m)}{T} \right], \tag{18}$$

with respect to the effective chemical potential  $\nu = \mu - 4V_0 p_+$  is finite for  $\nu = m$ , since, in contrast to the case of BE particles, the sum staying

in Eq. (18) converges in the limit  $K_{\text{max}} \to \infty$ . Indeed, with the help of integral representation of the Riemann  $\zeta$ -function [22] for  $\nu = m$  one finds

$$\sum_{k=1}^{\infty} \frac{(-1)^{(k+1)}}{k^{\frac{1}{2}}} = \frac{1}{\Gamma\left[\frac{1}{2}\right]} \int_{0}^{\infty} \frac{t^{-\frac{1}{2}}}{e^t + 1} dt \simeq 0.6049, \quad (19)$$

and, therefore, the derivative  $D^1p_+ \equiv T \frac{\partial p_+}{\partial \rho_+^{id}}$  does not vanish for  $\nu = m$  and, hence, there is no 1-st order PT in this case.

In our opinion this is a very simple and good example that the presence of a macro-cluster with the finite probability in a finite system is a necessary, but not a sufficient condition of the 1-st order PT existence in such a system. We believe this is an important message to be taken into account by the authors of Refs. [23,24] who consider the presence and gradual disappearance of the macro-cluster as a signal of the 1-st order nuclear liquid-gas PT in finite systems. The whole point is that in finite systems the macro-cluster of maximal size can appear as the metastable state of finite probability not only for the 1-st order PT, but also for the 2-nd order PT or even for the cross-over [8, 9]. The present analysis once more shows one that for vanishing surface tension coefficient the value of the Fisher exponent  $\tau_{\rm F}$  defines the PT order [9].

One can readily check that all the results on PT existence remain valid, if one uses the relativistic expression for particle energy, i.e. if one makes a replacement  $m+\frac{k^2}{2m}\to \sqrt{m^2+k^2}$ . However, in this case the BE condensation does not look mathematically identical to the sSMM and, hence, the corresponding analysis is not made here.

### 3. Decomposition Identity between Bosonic and Fermionic Pressures

Apart from the formal difference between the EoS of the BE and FD particles we would like to understand (i) whether our interpretation of the appearance of classical macro-clusters is correct, and (ii) under what circumstances the appearance of macro-cluster can be associated with the 1-st order PT in the system of FD particles. Indeed, an absence of the 1-st order PT in the EoS of FD particles with the hard-core repulsion may question the validity of our hypothesis about the existence of classical macro-clusters and, therefore, one may think that BE condensation leads to an appearance of quantum macro-cluster with BE statis-

tics, while the quantum macro-cluster with FD statistics cannot be formed due to some reason, namely due to the Pauli blocking principle.

To demonstrate the validity of our hypothesis we consider a peculiar mathematical identity between the BE and FD pressures which we call a BE-FD decomposition identity

$$\underbrace{-Tg \int \frac{d^3k}{(2\pi\hbar)^3} \ln\left[1 - \exp\left[\frac{\nu - \sqrt{m^2 + k^2}}{T}\right]\right]}_{p_B\left(\frac{\nu}{T}, m, g\right)} \equiv$$

$$\equiv Tg \int \frac{d^3k}{(2\pi\hbar)^3} \left\{ \underbrace{\ln\left[1 + \exp\left[\frac{\nu - \sqrt{m^2 + k^2}}{T}\right]\right]}_{p_F\left(\frac{\nu}{T}, m, g\right)} - \underbrace{-\frac{1}{8} \ln\left[1 - \exp\left[\frac{2\nu - \sqrt{4m^2 + k^2}}{T}\right]\right]}_{p_B\left(\frac{2\nu}{T}, 2m, 2^{-3}g\right)} \right\}, \tag{20}$$

which will help us to understand the appearance of a classical macro-cluster for BE and FD statistics. The fact that now we do not use the non-relativistic approximation to the particle energy is not important.

The BE-FD decomposition identity (20) can be obtained in the following sequence of steps: first we note that

$$\ln\left[1 - \exp\left[\frac{2\nu - \sqrt{4m^2 + 4k^2}}{T}\right]\right] \equiv$$

$$\equiv \ln\left[1 + \exp\left[\frac{\nu - \sqrt{m^2 + k^2}}{T}\right]\right] +$$

$$+ \ln\left[1 - \exp\left[\frac{\nu - \sqrt{m^2 + k^2}}{T}\right]\right]. \tag{21}$$

Next one can integrate Eq. (21) over  $d^3k$  with the degeneracy factor g and change a particle momentum on the left hand side of Eq. (21) as  $2k \to k$  and in the momentum integral to get a multiplier  $\frac{1}{8}$ . Finally, interchanging the positions of integrals for lighter and heavier bosons one arrives at Eq. (20).

Eq. (20) shows one that for the given values of T and  $\nu$  the pressure of ideal gas of bosons (the upper line of Eq. (20)) of mass m and degeneracy g can be identically decomposed into the sum of two terms. The first pressure corresponds to the ideal gas

of fermions with same mass and degeneracy (the first term on the right hand side of Eq. (20)), while the second pressure describes the bosons with the double mass and double charge (and the double excluded volume  $V_0$ , if  $\nu = \mu - 4V_0p$  accounts for the effects of hard-core repulsion as above), but with the reduced degeneracy  $\frac{g}{8}$ . Then the heavy bosons may be interpreted as "pairs" of fermions.

Applying the BE-FD decomposition identity (20) (n-1) times to the pressure  $p_B\left(\frac{2\nu_B}{T}, 2m, 2^{-3}g\right)$  of "pairs", one can identically extract the contribution of bosonic macro-cluster  $(n \gg 1)$  with the mass  $2^n m$ , the charge  $2^n$  and the degeneracy  $2^{-3n}g$  from the pressure of bosons of mass m, charge 1 and degeneracy g and get the following useful relation

$$p_{B}\left(\frac{\nu_{B}}{T}, m, g\right) \equiv p_{B}\left(\frac{2^{n}\nu_{B}}{T}, 2^{n}m, 2^{-3n}g\right) + \sum_{k=0}^{n-1} p_{F}\left(\frac{2^{k}\nu_{B}}{T}, 2^{k}m, 2^{-3k}g\right), \tag{22}$$

where  $p_{\rm F}\left(\frac{2^k\nu_B}{T}, 2^km, 2^{-3k}g\right)$  denotes the pressure of auxiliary fermions with the mass  $2^k m$ , the charge  $2^k$ and degeneracy  $2^{-3k}g$ . For low temperatures  $T \ll m$ one can safely use the non-relativistic approximation for the energy of particle. Applying the identity (22) to the gas pressure of bosons  $p_{-}$  of the EoS considered in the preceding section, i.e. for  $\nu_B \leq \nu_c$ , one can immediately conclude that for  $\nu_B < m$  the effective chemical potential of the bosonic macro-cluster on the right hand side of Eq. (22) is  $(\nu_B - m)2^n \to -\infty$  for  $n \gg 1$  and, hence, such a macro-cluster does not exist for  $\nu_B < m$ . It is evident, that the bosonic macrocluster on the right hand side of Eq. (22) does not exist for  $\nu_B = m$  as well, since for  $n \gg 1$  its degeneracy  $2^{-3n}g \to 0$  vanishes. Apparently, this argument is valid for the case  $\nu_B < m$  as well. Therefore, in the whole gaseous phase and at the condensation curve of the EoS of BE particles with the hard-core repulsion considered in the preceding section the bosonic macro-cluster is absent, i.e. for  $\nu_B \leq m$  one finds

$$p_B\left(\frac{\nu_B}{T}, m, g\right) = \sum_{k=0}^{\infty} p_F\left(\frac{2^k \nu_B}{T}, 2^k m, 2^{-3k} g\right),$$
 (23)

that the pressure of BE particles can be identically written as an infinite sum of the pressures of FD particles with certain masses, charges and degeneracies. In the preceding section it was shown that the pressure of FD particles with the hard-core repulsion does not have the 1-st order PT and, thus, in the thermodynamic limit there is no fermionic macro-cluster for each pressure staying on the right hand side of Eq. (23). However, the pressure of BE particles staying on the left hand side of Eq. (23) demonstrates the 1-st order PT of the BE condensation. Therefore, the only possible explanation out of this apparent contradiction is that the BE condensation leads to an appearance of the classical macro-cluster which is the sum of individual classical macro-clusters generated by the set of fermionic pressures that are staying on the right hand side of Eq. (23).

Now it is appropriate to discuss the properties of the dense phase of BE hard spheres within the VdW approximation. Since the pressure of dense phase  $p_s=\frac{\mu-m}{4V_0}$  does not depend on the temperature explicitly, then the entropy density of dense phase  $s_s=\frac{\partial p_s}{\partial T}=0$  is zero at any temperature, while the particle number density of this phase is  $n_s=\frac{\partial p_s}{\partial \mu}=\frac{1}{4V_0}$ . Furthermore, from the thermodynamic identity

$$\varepsilon_s = Ts_s + \mu n_s - p_s = \frac{m}{4V_0} \tag{24}$$

one can see that the energy density  $\varepsilon_s$  of the dense phase, indeed, corresponds to the particles at rest which have the highest possible density within the adopted approximation. Therefore, similarly to the case of classical hard spheres it is more appropriate to call this phase as the solid state [11,12] (since there is not attraction between the particles and the surface tension coefficient is zero). Furthermore, it seems it is more appropriate to consider the BE condensation of particles with the hard-core repulsion as the deposition PT from a gas to a solid. Of course, one has to remember that, on the other hand, it is a condensate of hard spheres with a vanishing momentum.

A mathematical similarity with the exact solution of sSMM allows one to reliably interpret the BE condensation of hard spheres as the 1-st order PT in which the gas condenses into a classical macrocluster of the size  $4V_0K_{\rm max}$  with  $K_{\rm max} \to \infty$  in the thermodynamic limit. Hence, at the PT curve there should exist the phase boundary. As it was shown above, formally, a macro-cluster corresponds to the term  $k=K_{\rm max}$  in the expression for pressure  $p_-$  in Eq. (5). Therefore, formally a macro-cluster can be considered as a single classical particle which is at rest. From Eq. (5) one can see that its statistical

weight is the Boltzmann one. Such an interpretation is similar to the sSMM [6,7] with the difference that in the sSMM a macro-cluster is a droplet of liquid which has the non-vanishing surface tension below the critical temperature [4,6,7,10] and a finite entropy which vanishes at T=0 only.

Moreover, considering the EoS (5) with the effective values of  $g \to g^{\rm eff}$  and  $4V_0 \to V_0^{\rm eff}$  which allow one at least in the narrow range of thermodynamic parameters to reproduce the realistic EoS of quantum particles at high densities close  $0.45/V_0 - 0.55/V_0$  and sufficiently high temperature T for which the effects of quantum statistics are not important, one should still have the BE condensation PT on the one hand. On the other hand, this should be the region of the deposition phase transitions for the classical hard spheres [11, 12]. Thus, we again should conclude that at high temperature T the BE condensation of quantum hard spheres should match with the deposition PT of the classical hard spheres.

Coming back to the ideal gas of BE particles one should consider the limit  $V_0 \rightarrow 0$  in all formulas above. In this limit the high density state has infinite particle number density and, hence, it is inaccessible. However, for any infinitesimally small eigenvolume  $V_0$  our conclusions about the deposition PT remain valid and, therefore, the whole argumentation of K. Huang in Ref. [2] about the BE condensation as the 1-st order PT is correct. Only the K. Huang interpretation of this PT as a gas-liquid one seems to be inconsistent with the modern interpretation of the PT of hard spheres.

At the moment it is not clear, if it is just a coincidence that at low pressures the real gases of monoand diatomic molecules with BE statistics, except for the helium-4 for pressures below 25 atm., indeed, demonstrate the deposition PT under cooling. Maybe a more realistic EoS of quantum particles can resolve this problem.

It is remarkable that the BE-FD decomposition identity (20) allows one to establish another important interpretation. The right hand side of the identity (20) corresponds to pressure of a mixture of the ideal gases of fermions and their pairs (which are the bosons) with the same degeneracy, but with the double mass and double charge, which are taken with the wight 1/8. The left hand side of the identity (20) shows that such a mixture should experience the 1-st order PT of BE condensation. From the famous

work of L.N. Cooper [25] it is known that the pairing of fermions can, indeed, happen under not very restrictive conditions leading to the BE condensation of fermionic pairs and the BE-FD decomposition identity (20) illustrates such a possibility for a mixture discussed above. However, for the appearing of Cooper pairs the fermions must have an attraction, which is absent in the EoS discussed here.

It is evident that the identity (21) is valid for any dimension  $D=1,2,3,\ldots$  Introducing the pressures of BE particles (sign –) and FD particles (sign +) of mass m that have the chemical potential  $\nu$  and temperature T one can write

$$p_{D\pm}(T,\nu,m) \equiv$$

$$\equiv \pm Tg \int \frac{d^D k}{(2\pi\hbar)^D} \ln \left[ 1 \pm \exp \left[ \frac{\nu - e_m(k)}{T} \right] \right], \qquad (25)$$

where  $e_m(k) \equiv \sqrt{m^2 + k^2}$ . Using the expression (25) one can generalize the BE-FD decomposition identity (20) to the dimension D for the fractional mass and charge values as

$$p_{D-}(T,\nu,m) \equiv \equiv 2^{D} p_{D-} \left( T, \frac{\nu}{2}, \frac{m}{2} \right) - 2^{D} p_{D+} \left( T, \frac{\nu}{2}, \frac{m}{2} \right).$$
 (26)

For the chargeless and massless particles, i.e. for  $\nu = 0$  and m = 0, the BE-FD decomposition identity (26) gives us the following relation between the BE and FD momentum integrals

$$p_{D-}(T,0,0) \equiv \frac{2^D}{2^D - 1} p_{D+}(T,0,0) \Rightarrow$$
 (27)

$$\Rightarrow \int_{0}^{\infty} \frac{x^{D} dx}{e^{x} - 1} = \frac{2^{D}}{2^{D} - 1} \int_{0}^{\infty} \frac{x^{D} dx}{e^{x} + 1},$$
 (28)

which for D=3 leads to a well-known identity

$$\int_{0}^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{8}{7} \int_{0}^{\infty} \frac{x^3 dx}{e^x + 1} = \frac{\pi^4}{15}.$$
 (29)

Note, however, that Eq. (28) follows from Eq. (27) after integrating the pressures of massless and chargeless particles over the angles, first, and, then, after integrating them over  $dk^D$  by parts.

Applying the identity (26) to its right hand side n times, one obtains another identity

$$p_{D-}\left(T,\nu,m\right)\equiv2^{Dn}p_{D-}\left(T,\frac{\nu}{2^{n}},\frac{m}{2^{n}}\right)-$$

$$-\sum_{k=1}^{n} 2^{Dk} p_{D+} \left( T, \frac{\nu}{2^k}, \frac{m}{2^k} \right). \tag{30}$$

For  $n \gg \ln \left[ \max \left( \frac{\nu}{T}; \frac{m}{T} \right) \right]$  with the help of identity (27) one can establish an approximative relation

$$p_{D-}(T,\nu,m) \simeq \frac{2^{D(n+1)}}{2^{D}-1} p_{D+} \left(T, \frac{\nu}{2^{n}}, \frac{m}{2^{n}}\right) - \sum_{k=1}^{n} 2^{Dk} p_{D+} \left(T, \frac{\nu}{2^{k}}, \frac{m}{2^{k}}\right), \tag{31}$$

which again relates the pressures of BE and FD particles. Note that Eqs. (25), (26), (30) and (31) are valid for the particles with the hard-core repulsion, i.e. for  $\nu = \mu - 2^{(D-1)}V_D p_{D-}(T,\nu,m)$ , where the eigenvolume of particles in the *D*-dimensional space is denoted as  $V_D$ .

#### 4. Conclusions

In this work we reconsider the VdW equation of state of BE particles with the hard-core repulsion in the grand canonical ensemble. Our analysis shows that the pressure of non-relativistic BE particles is mathematically equivalent to the one of the exactly solvable model with the 1-st order PT known as the sSMM. The EoS of BE particles corresponds to the sSMM with the vanishing surface tension coefficient and the Fisher exponent  $\tau_{\rm F} = \frac{5}{2}$ . Such a similarity allows us to show that within the present approach the high density phase of BE particles is a classical macro-cluster with vanishing entropy at any temperature which, similarly to the system of classical hard spheres and due to an absence of attraction between the particles, is a kind of solid state. Considering the limit of very small eigenvolume of BE particles we argue that the ideal gas of BE particles has the 1-st order PT as it was suggested by K. Huang in his famous textbook [2] a long time ago, but, in contrast to our conclusions, K. Huang suggested that this is the gas to liquid PT [2].

To explicitly demonstrate that a macro-cluster with the BE statistics does not exist in this EoS we investigate some peculiar relations between the pressures of BE and FD particles, the BE-FD decomposition identities, showing that under some conditions the pressure of FD particles can be identically rewritten in terms of two BE pressures. Moreover, we establish an exact representation of the pressure of BE particles of mass m, charge 1 and degeneracy g as a series

of pressures of FD particles with the masses  $2^k m$ , the charge  $2^k$  and degeneracy  $2^{-3k}g$ , where k are positive natural numbers. These new relations help us to correctly interpret the properties of a high density phase of BE particles with hard-core repulsion.

In fact, here we establish a principally new look at the problem of BE condensation. Of course, the considered model is oversimplified, but now one can use all the achievements of the SMM [4–7, 10] and introduce the surface part  $\sigma(T)k^{\frac{2}{3}}$  of the free energy of k-particle clusters (here  $\sigma(T)$  is the temperature dependent coefficient of surface tension). Such a modification will make model more realistic, since the surface part of free energy partly accounts for the short range attraction between the constituents like it is done in the full SMM. Note that in this case, however, the modified right hand side of Eq. (5) cannot be already reduced to the pressure of point-like particles  $p_-(T, \nu)$  with the shifted chemical potential  $\nu = \mu - 4V_0p_-$ .

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К.О. Бугаев, О.І. Іваницький, Б.Є. Гринюк, І.П. Якименко КОНДЕНСАЦІЯ БОЗЕ–ЕЙНШТЕЙНА КВАНТОВИХ ТВЕРДИХ СФЕР ЯК ФАЗОВИЙ ПЕРЕХІД ОСАДЖЕННЯ ТА НОВІ СПІВВІДНОШЕННЯ МІЖ ТИСКАМИ БОЗОНІВ ТА ФЕРМІОНІВ

Резюме

У великому статистичному ансамблі вивчено фазовий перехід Бозе–Ейнштейнівських частинок із відштовхуванням твердого кору у наближенні Ван дер Ваальса. Показано, що тиск нерелятивістських Бозе–Ейнштейнівських части-

нок є математично еквівалентним тиску спрощеної статистичної моделі мультифрагментації ядер із нульовим коефіцієнтом поверхневого натягу та фішерівською експонентою  $\tau_{\rm F}=\frac{5}{2}$ . Така модель має фазовий перехід 1-го роду для цих значень параметрів. Знайдена еквівалентність цих рівнянь стану дозволила нам показати, що у даному підході фаза з високою щільністю являє собою класичний макрокластер із нульовою ентропією за довільних температур, який, аналогічно системі класичних твердих сфер, є твердим тілом. Щоб з'ясувати цей факт, ми отримали нові співвідношення, які дозволили нам тотожно представити тиск ферміонів через тиск бозонів двох сортів.