Self-consistent Treatment of Quantum Gases of D-dimensional Hard Spheres Beyond the Van der Waals Approximation

K. A. Bugaev$^{1,2}$

$^1$Bogolyubov Institute for Theoretical Physics, Metrologichna str. 14/8, Kiev 03680, Ukraine and $^2$Department of Physics, Taras Shevchenko National University of Kiev, 03022 Kiev, Ukraine

The necessary conditions to derive the quantum VdW EoS with hard-core repulsion from the quantum partition are discussed. On a plausible example it is shown that an alternative way to account correctly for the 3-rd virial coefficient of classical hard spheres leads to inconsistencies. The multicomponent formulation of the quantum VdW EoS with hard-core repulsion is derived within a self-consisting approximation. For practical applications it is simplified, extended to higher densities and generalized to the case of hard convex bodies of any dimension $D \geq 2$.

Keywords: quantum gases, Van der Waals, equation of state, multicomponent mixture

I. INTRODUCTION

The concept of hard-core repulsion plays an important role in the statistical mechanics of classical systems since it allows one to correctly account for the basic properties of real gases at short distances despite of its simplicity. Furthermore, the systems of hard spheres and hard discs have played the role of test sites to demonstrate the power of novel mathematical methods and new ideas in physics for decades. Since the invention of the Van der Waals (VdW) equation of state (EoS) $^1$ a great progress in extending the hard spheres EoS to the high packing fractions has been achieved $^2,^3$.

Unfortunately, this is not the case for quantum systems, since the rigorous quantum statistical treatment of dense systems is extremely difficult. Moreover, even for a single sort of particles the quantum VdW EoS with the hard-core repulsion was never obtained from the quantum grand canonical partition and the conditions that are necessary for such a derivation were never clearly stated and discussed. However, the intensive experimental studies of nuclear $^4,^5$ and hadronic $^6,^7$ systems and other phases of strongly interacting matter $^9$ require the quantum EoS with multicomponent hard-core repulsion, i.e. with many different hard-core radii of particles. Besides, the realistic quantum EoS are absolutely necessary to model the properties of dense quantum systems which can be nowadays studied in atomic traps.

Recenty the situation is improving, since presently there exist two quantum EoS which, in principle, allow one to go beyond the second virial coefficient, but none of them was, so far, obtained from the quantum partition function. The first of these quantum EoS suggested in Ref. $^10$ is a generalization of a famous one-component Carnahan-Starling EoS $^11$. However, it was obtained in the canonical ensemble by replacing the total volume of the system by the volume $V_{nc}$ that is available for the motion of $N$ particles in a free energy of some abstract system. Despite its thermodynamic consistency, in the grand canonical ensemble the generalization of Carnahan-Starling EoS suggested in Ref. $^10$ looks somewhat unnatural, since it contains not only the native variables of this ensemble, i.e. the temperature $T$ and chemical potential $\mu$, but also the particle number density. Moreover, below it will be shown that without additional assumptions it cannot be derived from the quantum partition.

Another quantum EoS of such type is based on the concept of induced surface tension (IST) $^5,^12$ which allows one to account for the second, third and fourth virial coefficients of classical hard spheres $^6$. In contrast to the quantum generalization of Carnahan-Starling EoS of Ref. $^10$, the IST one is formulated solely in the grand canonical variables and from the very beginning it is written for a mixture of an arbitrary number of sorts of particles $^4,^12$. The IST EoS can be derived in two ways (compare the derivations of Refs. $^4$ and $^7$), but both of them are heuristic. In particular, in Ref. $^7$ the IST EoS was derived in the grand canonical ensemble using the generalization of a popular trick to replace the chemical potential $\mu$ by a shifted one $\mu \rightarrow \mu - bp$ $^13$, where $b$ is the excluded volume of a pair of particles and $p$ is the system pressure.

Unfortunately, the absence of a rigorous mathematical procedure on how to generalize the classical EoS to the quantum system leads to the appearance of the statements that the usual VdW procedure by replacing the total volume of the system by the available one (and its equivalent in the grand canonical ensemble $\mu \rightarrow \mu - bp$ suggested in $^12$ and generalized in $^5,^12$) is not a unique one $^14$. Although there was a strong critique of such claims $^12$, it is mathematically involved and, therefore not widely available. Thus, a rigorous derivation of the quantum VdW EoS and its multicomponent generalizations like the quantum IST EoS $^5,^12$ are absolutely necessary, since these are the basic tasks of the quantum statistics of interacting particles. Moreover, due to the fast development of atomic traps and the corresponding possibilities to study the EoS of dense quantum systems such analysis is highly desirable.

The work is organized as follows. In Sect. 2 the quantum VdW EoS is obtained by the Laplace transform method from quantum grand canonical partition. The pitfalls of the alternative “derivation” to account for the third virial coefficient of classical hard spheres in a quantum EoS are closely discussed in Sect. 3. The de-
tailed analysis of the excluded volume of the mixture of hard spheres of different radii and the corresponding EoS of hard spheres and hard convex particles are given in Sect. 4, while Sect. 5 is devoted to conclusions.

II. 2. BRIEF DERIVATION OF QUANTUM VDW EOS FOR HARD SPHERES

In all textbooks on statistical mechanics it is written that the VdW EoS for Boltzmann statistics cannot be rigorously derived, since it is an extrapolation of the low density expansion to high densities. Therefore, it is of great interest and importance to derive the quantum VdW EoS for a gas with hard-core repulsion. In contrast to the heuristic treatment of the quantum VdW EoS of Refs. [13, 15] here, for simplicity, we consider only the hard-core repulsion and start the discussion with the energy spectrum of the system of one sort of particles. The particles with a hard-core repulsion, classical or quantum, behave as an ideal gas since the particles that do not touch each other have zero potential energy, whereas in the case when they touch each other their potential energy is infinite, but such states cannot contribute into the partition. Hence, we neglect the effects of Lorentz contraction of the eigen volume \( V_0 \) of the particles \([17, 18]\) and consider the dilute systems and low temperatures compared to the particle mass \( m \).

Suppose that \( \{e_k\} \) is a set of all possible energies of a single particle. Then the total energy of an ideal gas with a hard-core repulsion is \( E = \sum_k n_k e_k \) and the total number of particles of the system of volume \( V \) is \( N = \sum_k n_k \), where the primed summations denote the sum not over the energy levels, but over the different states of a particle. Hence, if the level with energy \( e_k \) has a degeneracy \( g_k \), then in the primed summations such a level, corresponding to the energy \( e_k \), is taken into account exactly \( g_k \) times. Now we can write the quantum partition of such a system as

\[
Q(T, \mu, V) = \sum_{N=0}^{\infty} \sum_{n_1+n_2+\ldots=N} \sum_{\{n\}} e^{\left[\sum_{n \in \{n\}} n e_k \right]} \Theta (V - bN) = \sum_{N=0}^{\infty} \sum_{n_1+n_2+\ldots=N} e^{\left[\sum_{n \in \{n\}} n e_k \right]} \Theta (V - bN) \cdot \tag{1}
\]

Here \( \mu \) is the chemical potential of the system, while \( T \) is its temperature and \( b = 4 V_0 \) denotes the excluded volume per pair of particles (classical second virial coefficient), while \( V_0 \) is an eigen volume. The \( \Theta \)-function in Eq. (1) allows one to formally extend the summation over \( N \) to infinity, but in fact it restricts such a sum to a finite value of \( \max\{N\} = \lfloor V/b \rfloor \). This is the first simplification of the VdW approximation, since the dense packing of particles corresponds to a larger number \( N_{\text{dens}} \approx 0.741 V/V_0 \) \( \sim 3 \max\{N\} \), but if we use the correct number \( N_{\text{dens}} \) the low density limit will be wrong (see below). In order to find the correct thermodynamic limit of the partition \([19]\) we use the technique of the Laplace transform with respect to \( V \) to the isobaric partition \([19]\)

\[
Q(T, \mu, \lambda) = \int_0^\infty dV e^{-\lambda V} Q(T, \mu, V) = \int_0^\infty dV e^{-\lambda V} \times \sum_{n_1+n_2+\ldots=N} \sum_{\{n\}} e^{\left[\sum_{n \in \{n\}} n e_k \right]} \Theta (V - b(n_1 + n_2 + \ldots)) = \int_0^\infty dV e^{-\lambda V} \sum_{n_1+n_2+\ldots=N} \sum_{\{n\}} e^{\left[\sum_{n \in \{n\}} n e_k \right]} \Theta (V) \cdot \tag{2}
\]

where in the last equation above we changed the variable \( V \) to the available volume \( \tilde{V} = V - b(n_1 + n_2 + \ldots) \) and accounted for the extra terms in the exponential functions with a corresponding value of \( n_k \). This change of variable allows us to sum over the values of \( n_k \) to get rid of the \( \Theta \)-function and to express the partition as a product over all levels of energy

\[
Q(T, \mu, \lambda) = \int_0^\infty d\tilde{V} \exp \left[ \sum_k \ln \left( \sum_{n_k} e^{\left[\sum_{n \in \{n\}} n e_k - \tilde{\lambda} n_k \right]} \right) - \lambda \tilde{V} \right] \cdot \tag{3}
\]

Henceforth, for definiteness’ sake, we will mainly analyse the systems with the Fermi-Dirac statistics (FD), but we will also give the answers for the Bose-Einstein (BE) one in the appropriate places. Hence, the sum over \( n_k \) under the logarithm symbol can be written as

\[
\sum_{n_k=0}^{n_k} e^{\left[\sum_{n \in \{n\}} n e_k - \tilde{\lambda} n_k \right]} = \sum_{n_k=0}^{n_k} \omega(k, \lambda)^{n_k} = \begin{cases} 1 + \omega(k, \lambda), & \text{for FD,} \\ [1 - \omega(k, \lambda)]^{-1}, & \text{for BE.} \end{cases} \cdot \tag{4}
\]

In order to make the integration over \( \tilde{V} \) we have to make the usual Thomas–Fermi approximation for the density of discrete levels of energy (density of states) \([20]\)

\[
\sum_k \ln [1 \pm \omega(k, \lambda)] \to \tilde{V} \int d^3 k g_k (2\pi \hbar)^3 \ln [1 \pm \omega(k, \lambda)] \cdot \tag{5}
\]

Note, however, that compared to the ideal gas case considered in textbooks the volume of the system in Eq. (5) has to be replaced by the available volume \( V \). A word of caution has to be said here with respect to the degeneracy: for low densities the prescription \([5]\) with \( g_k = g = \text{const} \) is reasonable, but for high densities it is possible that one has to assume an energy dependence of \( g_k \). Actually, one of a few principle purposes to make this analysis was a necessity to motivate the experimental work to study the hard-core repulsion in quantum systems at high densities in order to clarify the possible energy dependence of \( g_k \).

Assuming in this work that \( g_k = g = \text{const} \) is the spin-isospin degeneracy of considered particles we can make integration in Eq. (5) and get the isobaric partition

\[
Q(T, \mu, \lambda) = \lambda g \int \frac{d^3 k}{(2\pi \hbar)^3} \ln [1 \pm \omega(k, \lambda)] \cdot \tag{6}
\]
for the model one (M1, hereafter). In what follows the upper (lower) sign will be for FD (BE) statistics. Similarly to the analysis of Ref. [13], it is easy to show that in the thermodynamic limit $V \to \infty$ the rightmost singularity of the partition function $Q$ is the simple pole $\lambda_0$ defined as

$$\lambda_0 = \pm g \int \frac{d^3 k}{(2\pi \hbar)^3} \ln [1 \pm \omega(k, \lambda_0)],$$

(7)

which is located on the real axis in the complex plane of $\lambda$. Then after making the inverse Laplace transform

$$Q(T, \mu, V) = \frac{1}{2\pi i} \int_{x-i\infty}^{x+i\infty} d\lambda Q(T, \mu, \lambda) \exp(\lambda V) \bigg|_{V \to \infty} = \exp(\lambda_0 V) \left[ 1 - b g \int \frac{d^3 k}{(2\pi \hbar)^3} \frac{1}{[\omega(k, \lambda_0)]^{-1} \pm 1} \right]^{-1},$$

(8)

where the integration contour in the complex $\lambda$-plane is chosen to the right-hand side of the rightmost singularity, i.e. $\chi > \lambda_0$ (see [13] for more details). From Eq. (8) in the thermodynamic limit $V \to \infty$ one finds the system pressure as $p = T \lambda_0$, since $Q(T, \mu, V \to \infty) \sim \exp(\lambda_0 V)$ by definition [20]. Equation for $p$ in this limit becomes

$$p(T, \nu) = \pm T g \int \frac{d^3 k}{(2\pi \hbar)^3} \ln \left[ 1 \pm \exp \left( \frac{\mu - b p - e(k)}{T} \right) \right],$$

(9)

where $e(k) \equiv \sqrt{k^2 + \nu^2}$ is the relativistic energy of a particle of mass $m$ and $\nu \equiv \mu - b p$ is the shifted chemical potential. Thus, Eq. (9) justifies the shift of the chemical potential $\mu$ suggested in Ref. [13] to introduce the quantum hard-core repulsion in the grand canonical ensemble.

In order to show that the pressure (9) is, indeed, similar to the VdW EoS at low densities one has to find out the particle number density $n$, to write the quantum virial expansion and substitute in it the expression for density. Although this is a known subject, see, for instance, [20] and a detailed analysis of quantum virial expansion made in Ref. [12], for our purposes it is sufficient to consider the low density limit, i.e. if $\max \{\omega(k, p/T)\} \ll 1$. Then for the particle number density $n$ one finds

$$n \equiv \frac{\partial p}{\partial \mu} = \frac{n_{id}(T, \nu)}{1 + bn_{id}(T, \nu)} \Rightarrow n_{id}(T, \nu) = \frac{n}{1 - bn},$$

(10)

$$n_{id}(T, \nu) \equiv \frac{\partial p}{\partial \nu} = g \int \frac{d^3 k}{(2\pi \hbar)^3} \frac{\omega(k, p/T)}{1 \pm \omega(k, \nu)} \simeq g \int \frac{d^3 k \omega(k, p/T)}{(2\pi \hbar)^3} \left[ 1 \mp \omega(k, \nu) + \omega(k, p/T)^2 \ldots \right] \simeq \frac{g}{2\pi \hbar^3} \int \frac{d^3 k \omega(k, p/T)}{(2\pi \hbar)^3} \left( 1 \pm \omega(k, \nu) - \omega(k, p/T) \right) \ldots$$

(11)

where the particle number density of point-like particles $n_{id}(T, \nu)$ is expanded in powers of the Boltzmann exponential $\omega(k, p/T)$. Similarly expanding the $\ln(1 \pm \omega(k, \nu))$ function in this limit, one obtains

$$p^{M1}(T, \nu) \equiv p_{id}(T, \nu) \simeq T g \int \frac{d^3 k \omega(k, p/T)}{(2\pi \hbar)^3} \times \left[ 1 \mp \omega(k, p/T) + \frac{\omega(k, p/T)^2}{2} + \frac{\omega(k, p/T)^3}{3} \ldots \right] \simeq T n_{id}(T, \nu) \left[ 1 + a_2^{(0)} n_{id}(T, \nu) + a_3^{(0)} n_{id}(T, \nu)^2 \ldots \right],$$

(12)

where the quantum virial expansion of $p_{id}(T, \nu)$ for point-like particles (ideal gas) in terms of quantum virial coefficients $a_j^{(0)}$ and powers of $n_{id}(T, \nu)$ is used. The explicit formulas for $a_j^{(0)}$ can be found in [12, 20]. However, for our purpose it is important that such an expansion can be obtained from Eqs. (9) and (13). Substituting the right Eq. (10) into expression for pressure (13), one finally gets

$$p^{M1} \simeq \frac{T n}{1 - bn} \left[ 1 + a_2^{(0)} \frac{n}{1 - bn} + a_3^{(0)} \frac{n^2}{(1 - bn)^2} + \ldots \right],$$

(14)

where the first term on the right-hand side of Eq. (14) is the Boltzmann gas pressure, while the other terms are the quantum corrections. Since the coefficients $a_j^{(0)}$ do not depend on $\nu$, but only on the temperature $T$ [12, 20], Eq. (14) is the quantum VdW EoS in the canonical ensemble variables $T$ and $n$.

### III. 3. GOING BEYOND THE VDW APPROXIMATION

Above we have seen that in contrast to the claims of Ref. [14] there is no ambiguity in deriving the quantum gas pressure with the hard-core repulsion. Nevertheless, now we modify the derivation of the preceding section in order to demonstrate how dangerous the outcome of the suggestion of Ref. [14] to modify the system volume via the effective degrees of freedom may be. For pedagogical reasons, we consider only an inclusion of the third classical virial coefficient into the quantum partition. Here we follow the suggestion of Ref. [14] to modify the number of degrees of freedom, or degeneracy factor $g$. Hence instead of Eq. (9) we write

$$\sum_k \ln [1 \pm \omega(k, \lambda)] \to \tilde{V} G(\lambda) \int \frac{d^3 k g}{(2\pi \hbar)^3} \ln [1 \pm \omega(k, \lambda)] \left( 1 \pm \omega(k, \lambda) \right),$$

(15)

where the additional factor $G(\lambda)$ is introduced. Note that one could, of course, introduce some complicated function $\tilde{n}(T, \mu)$ by hand and consider the dependence $G(\tilde{n}(T, \mu))$ instead of $G(\lambda)$. At the end of the derivation one could of course choose the former function $G$ in such a way that $\tilde{n}(T, \mu)$ would coincide with the particle number density $n$ of the system. Such a trick is employed in Ref. [10] to generalize the Carnahan-Starling EoS to the quantum case. One should, however, remember that at this stage of the derivation neither the pressure of the
system $\rho$ nor its derivatives (including $n$) are defined yet. Hence, if the factor $G(\lambda)$ is introduced into Eq. \[15\], then in the absence of additional assumptions, i.e. in the simplest case, a mathematical consistency requires that $G(\lambda)$ must depend on $\lambda$ only. The practical reason for such a choice is that for dilute systems that are analysed in this section the quantity $p/T$ is the particle number density of point-like particles (see Eq. \[19\] for M1 and below for this model).

Assuming that the factor $G(\lambda)$ does not generate the rightmost singularity of the isobaric partition $Q(T, \mu, \lambda)$, one can repeat the steps of deriving Eqs. \[6\]–\[8\] for the hypothesis \[15\] and obtain the following result for the system pressure in the thermodynamic limit

$$
\frac{p(T, \nu)}{T} = \pm G' \left( \frac{p}{T} \right) \frac{d^3k}{(2\pi)^3} \ln \left[ 1 \pm \exp \frac{\nu - e(k)}{T} \right],
$$

(16)

where at the end of the calculations we used the explicit form of the function $\omega(k, p/T)$ and the same notation for the shifted chemical potential $\nu \equiv \mu - bp$, as above. Comparing Eqs. \[10\] and \[16\] for the system pressure, one concludes that the degeneracy factor is, indeed, modified by the function $G \left( \frac{p}{T} \right)$. It is convenient to represent Eq. \[16\] for an auxiliary density $\rho \equiv p/T$ in a compact form

$$
p = \frac{G(\rho)}{T} p_{id}(T, \nu), \quad \Rightarrow \quad n_{id}(T, \nu) = \frac{\partial p_{id}(T, \nu)}{\partial \nu},
$$

(17)

where the pressure of point-like particles $p_{id}(T, \nu)$ with the shifted chemical potential $\nu$ is given by the right-hand side of Eq. \[9\], since the pressure of M1 is indeed the pressure of an ideal gas with the shifted value for the chemical potential $\nu$. Hence, the definition of the particle number density of such particles $n_{id}(T, \nu)$ coincides with the right-hand side of Eq. \[11\]. Then the particle number density of the present model (M2 hereafter) is

$$
n \equiv \frac{\partial p}{\partial \mu} = \frac{n_{id}(T, \nu)}{G(\rho)^{-1} + bn_{id}(T, \nu) - \frac{G'(\rho)}{G(\rho)} p_{id}(T, \nu)},
$$

(18)

where the notation $G'(\rho) = \frac{dG(\rho)}{d\rho}$ is introduced.

For dilute systems one can substitute the virial expansion \[12\] for $p_{id}(T, \nu)$ into Eq. \[15\] and express the density of point-like particles as

$$
n_{id} \approx \frac{G(\rho)^{-1} n}{1 - bn + \frac{G'(\rho)}{G(\rho)} n[1 + a_2 n_{id} + a_3 n_{id}^2 + \ldots]}.
$$

(19)

Expansion of $p_{id}(T, \nu)$ in Eq. \[17\] according to Eq. \[19\] with the simultaneous substitution of \[19\] into \[17\] allows one to write the pressure of M2 as

$$
p^{M2} \approx \frac{nT[1 + a_2 n_{id} + a_3 n_{id}^2 + \ldots]}{1 - bn + \frac{G'(\rho)}{G(\rho)} n[1 + a_2 n_{id} + a_3 n_{id}^2 + \ldots]}. \quad (20)
$$

In order to reveal the effect of modifying the degeneracy factor on the quantum virial expansion of M2 let us consider one of the simplest choices for the function $G(\rho)$

$$
dG \rho \quad \Rightarrow \quad G = \exp \left[ \frac{c_3}{c_4} \ln \left[ 1 + c_4 \rho \right] - \frac{c_3}{c_4} \rho \right]. \quad (21)
$$

which contains two constants $c_3$ and $c_4$ whose meaning will be clear in a moment. This example allows us to get the quantum third virial coefficient for a dilute system, by writing $G'(\rho) \approx -c_3 \rho \approx -c_3 n \Rightarrow G(\rho)^{-1} \approx 1 + \frac{c_3}{c_4} \rho^2 \approx 1$, where in the last step we approximated the M2 pressure by the ideal gas one $nT$. Furthermore, expanding the denominator of Eq. \[20\] with respect to the powers of $G'(\rho)/G(\rho)$, one gets

$$
\frac{1}{1 - bn} \left\{ 1 + c_3 n^2[1 + \ldots] \right. \left. + \frac{c_3^2 n^4[1 + \ldots]^2}{[1 - b n]^2} + \ldots \right\}, \quad (22)
$$

where the shorthand notation $[1 + \ldots] \equiv [1 + (0) a_{id} + a_2 (0) n_{id}^2 + \ldots] \approx 1$ is introduced. With the help of this result and Eq. \[14\] one can establish the following relation for the M2 pressure \[20\]

$$
p^{M2} \approx \frac{p^{M1}}{1 + c_3 n^2[1 + \ldots] + \frac{c_3^2 n^4[1 + \ldots]^2}{[1 - b n]^2} + \ldots}, \quad (23)
$$

which allows us to easily find the relation between the quantum third virial coefficients of M1 and M2. Indeed, since the virial expansion for any pressure is defined as $p = nT[1 + a_2 n + a_3 n^2 + \ldots]$, from Eq. \[23\] one concludes that the term $c_3 n^2$ in the brackets of \[23\] cannot modify the second virial coefficient $a_{id}^{M1}$ of M1, but will shift $a_{id}^{M1}$ and all higher order coefficients. Hence, one can write

$$
a_{id}^{M2} = a_{id}^{M1} + c_3 = a_{id}^{(0)} + 2a_{2}(0) b + b^2 + c_3,
$$

(24)

where for $a_{id}^{M1}$ the result of Ref. \[12\] is used. It is well known that the classical VdW EoS provides the wrong value for the third virial coefficient of hard spheres $b^2 = 16V_0^2$ instead of $10V_0^2$ \[20\]. Hence, one can use the parameter $c_3$ to cure this problem. If one chooses $c_3 = -6V_0^2 = -\frac{b}{a} b^2$, then the M2 third virial coefficient \[24\] will have the correct classical limit, when the quantum corrections proportional to $a_{id}^{(0)}$ and $a_{id}^{(0)}$ are negligible, i.e. at high values of $T$ \[12\] \[21\]. Such a choice, however, would lead to a huge enhancement of the degeneracy factor, if in Eq. \[21\] the coefficient $c_4 = 0$ is negligible.

From the right Eq. \[21\] one can see that for a positive value of the coefficient $c_4$ the resulting EoS has a structure that is similar to the hard-core repulsion for large values of $\rho$, i.e. $G(\rho) \approx \exp \left[ -\frac{c_4}{c_4} \rho \right]$, but for $c_3 = -6V_0^2 < 0$ and $c_4 > 0$ instead of a repulsion one has an attraction. Hence, in the limit of Boltzmann statistics (high temperatures) the coefficient $c_4$ can be fixed to reduce the value of the excluded volume of particles from $b = 4V_0$ to their total volume $V_0$. In other words, writing $b + c_4 = 4V_0 - \frac{b}{a} b^2 = V_0$, one finds $c_4 = 2V_0 = 0.5b$.

At first glance such a model looks better than the VdW EoS, but, in fact, it leads to the limiting temperature $T_{lim}(\nu)$ as a function of the shifted chemical potential $\nu$. The reason for such a behaviour can be seen from the left Eq. \[17\]. It is evident that for a large value of $p_{id}(T, \nu)/T$ the right-hand side of this equation at $\rho = 0$ can be so
large, i.e. \( G(0) p_{sd}(T, \nu) / T \gg 1 \), that the monotonically growing function \( G(\rho) p_{sd}(T, \nu) / T \) of \( \rho \) would never cross or be tangential to the straight line \( \rho \) and hence there would be no solution of the left Eq. (17). The critical value of the variable \( p_{sd}(T, \nu) / T \) for which such a solution exists can be found from the condition that the functions \( G(\rho) p_{sd}(T, \nu) / T \) and \( \rho \) are tangential to each other at the point \( \rho = \rho_1 \equiv [2c_3]^{-1}[c_1 + \sqrt{c_3^2 - 4c_3}] \), which for the coefficients \( c_1 = -6V_0^2 \) and \( c_4 = 2V_0 \) discussed above is \( \rho_1 \approx 0.6067V_0^{-1} \). Solving the left Eq. (17) for \( \rho = \rho_1 \), one obtains the following inequality for the M2 parameters

\[
p_{sd}(T, \nu) \leq 0.3237TV_0^{-1}.
\]

Since the ideal gas pressure \( p_{sd}(T, \nu) \) is a monotonically increasing function of the variables \( T \) and \( \nu \), then the solution of inequality (25) is \( T \leq T_{lim}(\nu) \), where it is assumed that for \( T = T_{lim}(\nu) \) the inequality (26) is obeyed as equality. Apparently, the same conclusion is valid for a zero value of the coefficient \( c_3 \), since for \( c_3 = -6V_0^2 < 0 \) there is a strong enhancement of pressure due to \( G(\rho) \).

Note that the existence of limiting temperature for the quantum VdW EoS of pion gas with both the hard-core repulsion and attraction was recently found in Ref. [21]. Here, however, we consider only the limiting temperature of quantum systems that uses a trick to modify the degeneracy factor \( \mu_K \) and hard-core radii \( R_K \). Assume that the total particle number of \( K \)-th sort is \( N_K = n_{K,1} + n_{K,2} + \ldots \) and they have energy \( E_K = \epsilon_{K,1}n_{K,1} + \epsilon_{K,2}n_{K,2} + \epsilon_{K,3}n_{K,3} + \ldots \), while the total number of particles is \( N_{tot} = \sum_K N_K \). Here \( n_{K,i} \) is the number of particles of sort \( K \) occupying the energy level \( \epsilon_{K,i} \). Assuming that the hard-core repulsion can be taken into account via the excluded volume \( V_{excl} \), one can write a multicomponent analog of partition (11) as

\[
Q(T, \{\mu_K\}, V) = \sum_K \sum_{N_K=0}^{\infty} \sum_{l} e^{\left[\mu_K N_K - E_K\right]} \Theta (V - V_{excl}).
\]

here the excluded volume of all pairs taken per particle is

\[
V_{excl} = \frac{1}{N_{tot}} \sum_{K,L} N_K \frac{2}{3} \pi (R_K + R_L)^3 N_L.
\]

Since an exact evaluation of the partition (20) is very complicated, we are going to simplify Eq. (27) by introducing statistical average quantities. Writing explicitly the binomial in Eq. (27) and regrouping the terms with powers of \( R_K \) one finds

\[
V_{excl} = \sum_K N_K \left[ v_K^* + \frac{s_K}{2} \cdot \overline{R} + \frac{c_K}{2} \cdot \overline{R^2} \right] = \frac{s_K}{2} \sum_K R_K N_K = \overline{V_{excl}} = \frac{1}{N_{tot}} \sum_K n_{K,i} N_K \sum_L R_L^3 N_L.
\]

In the second equality above we introduced the eigen volume \( v_K^* = \frac{4}{3} \pi R_K^3 \), eigen surface \( s_K = 4 \pi R_K^2 \) and eigen (double) perimeter \( c_K = 4 \pi R_K \) of \( K \)-th sort of spheres and the powers of hard-core radii \( \overline{P_{excl}} = \frac{1}{N_{tot}} \sum_K R_K N_K \). In the second equality above we introduced the closest packing volume of each sort of sphere \( v_K^* \equiv v_K^* / q \) with \( q = \frac{2}{\sqrt{6}} \approx 0.741 \) and the compensative “mean-field” term which is proportional to \( u_K = 1 - 1 / q \approx -0.35 \). With these notations Eq. (29) is exact, but now we introduce the self-consistent approximation for it by replacing the exact averaging in the excluded volume expression (29) with the statistical ones (for \( n = 1, 2, 3 \))

\[
\overline{V_{excl}} = \frac{1}{N_{tot}} \sum_K R_K N_K \to \frac{1}{\sum_L} \frac{\langle N_L \rangle}{N_L}. \tag{30}
\]
where $\langle N_k \rangle \equiv T \frac{\partial}{\partial \mu_k} \ln Q(T, \{\mu_k\}, V)$ is the mean number of particles of $L$-th sort found from the partition \[20\]. Assuming that the partition \[20\] under approximation \[30\] is known, then the quantity $R^n$ can be found from it as

$$R^n = \frac{\sum_{L=1}^{2} R^n_1 \frac{\partial}{\partial \mu_1} \ln Q(T, \{\mu_1\}, V)}{\sum_{L=1}^{2} \frac{\partial}{\partial \mu_1} \ln Q(T, \{\mu_1\}, V)},$$ \[31\]

Under approximation \[30\] the excluded volume \[20\] becomes a linear function of $N_K$ and, therefore, the partition \[20\] can be found by repeating the formal steps of deriving Eqs. \[22\]. Moreover, in the thermodynamic limit the formal expression for the approximated partition $\{20\}$ coincides with Eq. \[3\], i.e. $Q(T, \{\mu_k\}, V \to \infty) \sim \exp \left[ \frac{\mu}{T} \right]$, where the pressure is

$$p^{M3} = T \sum_k g_K \frac{\alpha_K d^3k}{(2\pi\hbar)^3} \ln \left[ 1 + \frac{\exp \left[ \frac{\mu^0 - \epsilon(k)}{T} \right]}{\alpha_K} \right],$$ \[32\]

$$\nu^0_{K} = \mu_{K} - \left[ \nu^0_{K} + \frac{8K}{2R} + \frac{c_k}{3} \frac{R^2}{2} + \frac{4}{3} \pi u_{K} R^3 \right] p^{M3}. \[33\]$$

In Eq. \[32\] the shifted chemical potential \[33\] is set for each sort of particle, $\epsilon_K(k) = \sqrt{k^2 + m^2}$ denotes the energy of $K$-th sort of particle and the parameter $\alpha_K = -1$ should be taken for the BE statistics, while for the FD one it must be set to $\alpha_K = 1$. Calculating the partial derivative $\frac{\partial p^{M3}}{\partial \nu^0_{K}}$ from Eq. \[32\] as a derivative of the implicit function $p^{M3}$, one can write the quantity $R^n$ \[31\] as

$$R^n = \sum_k K \frac{R^n K \nu^0_{K}(T, \nu^0_{K})}{\nu^0_{K}(T, \nu^0_{K})},$$ \[34\] for

$$\nu^0_{K}(T, \nu^0_{K}) = \frac{\partial p^{M3}}{\partial \nu^0_{K}} \bigg|_{\nu^0_{K}} \bigg(34\bigg),$$

where we introduced the density of point-like particles $\nu^0_{K}(T, \nu^0_{K})$, of sort $K$ which is just Eq. \[11\] with the following replacements $g \to g_K, m \to m_K$ and $\nu \to \nu^0_0$. Eqs. \[32\] \[33\] of model 3 (M3) form a closed system of equations for the quantum VdW EOS of hard spheres. The M3 pressure \[32\] is a quantum generalization of the approach of Refs. \[22\] \[23\] but in contrast to Refs. \[22\] \[23\] and their followers, the coefficients of surface $0.5 R^3$ and curvature $0.5 R^2$ tensions are not the fitting parameters, but are defined by the system \[32\] \[33\].

Our next step is to generalize the system \[32\] \[33\] to convex particles of arbitrary shape and to extend it to higher densities. For these aims one has to not only consider the eigen volume of convex particle of $K$-th sort $\nu^0_{K}$, their eigen surface $s^0_{K}$, two mean curvature radii $\tilde{r}_{K,1}$ and $\tilde{r}_{K,2}$, their corresponding (doubled) parameters $c_{K,1} = 4\pi \tilde{r}_{K,1}$ and $c_{K,2} = 4\pi \tilde{r}_{K,2}$ (for more details see Ref. \[20\]), but also to modify their weights in the expressions for the excluded volume \[29\] and for the chemical potential $\nu^0_{K}$ in \[33\]. To demonstrate this let us consider the famous Ishihara-Hadwiger (IH) formula \[2\] \[26\] for the classical second virial coefficient of two identical convex particles

$$2V_{excl} = 2v^0_{1} + s^0_{1}(\tilde{r}_{1,1} + \tilde{r}_{1,2}), \[35\]$$

where we used the first subscript 1 for both particles. Introducing now the equivalent sphere radius as $s_1 = 4\pi R^2 = s(R_s)$, one can identically rewrite the IH formula with the help of two auxiliary constants $A, B \in [0; 1]$ as

$$2V_{excl} = \tilde{v}_1 + \tilde{v}_2 s(\tilde{r}_{1,1}) R_s + (1 - A) c_{1,1} R_s^2 \quad + \quad \tilde{v}_2 + \tilde{v}_2 s(\tilde{r}_{1,2}) R_s + (1 - A) c_{1,2} R_s^2 \[36\]$$

where the notations

$$\tilde{v}_1 = v^0_{1} - B s(\tilde{r}_{1,1}) R_s (\tilde{a}_1 - \tilde{a}_2), \quad \tilde{v}_2 = v^0_{1} + (1 + B) s(\tilde{r}_{1,1}) R_s (\tilde{a}_1 - \tilde{a}_2), \quad \tilde{a}_k \equiv A \frac{R_s}{R_{1,k}} \quad \text{with} \quad k = 1, 2, \[39\]$$

are used. This example shows us that the IH formula has a structure of the excluded volume of Eq. \[28\] for $K = 1, 2$ and $N_K = 1$, but with different numerical weights, if one identifies $R^n_1$ with $R^n$. Also this example demonstrates us the meaning of the quantities entering Eq. \[30\]: thus, the eigen surfaces $s(\tilde{r}_{1,k}) \equiv s_K$ and eigen (double) parameters $c_{1,k} \equiv c_k$ are related to the mean curvature radii, while the effective volumes $v^0_{K}$ can, in general, differ from the eigen volume $v^0_0$. Moreover, it is clear that using the quantities $v^0_{K}$, $s_K$, $c_k$, $u_k$ and their weights in Eq. \[33\] as the adjusting parameters, one has sufficient number of parameters to reproduce $V_{excl}$ of the mixture of convex particles of different shapes and sizes.

Although the system \[32\] \[33\] is derived under a self-consistent approximation, for the practical purposes it looks rather complicated and, hence, we simultaneously simplify it and extrapolate to higher densities. First, we recall that for low densities one can approximate the pressure \[32\] using the lowest density term in the virial expansion as

$$p^{M3} = T \sum_k K \frac{R^n K \nu^0_{K}(T, \nu^0_{K})}{\nu^0_{K}(T, \nu^0_{K})} \simeq T \sum_k K \frac{\partial p^{M3}}{\partial \nu^0_{K}} \bigg|_{\nu^0_{K}} \bigg(40\bigg),$$

where we introduced the partial pressure for each sort of particle $p^{K}_{id}(T, \nu^0_{K})$ and approximated it by the ideal gas one. For such an approximation the terms $R^n p^{M3}$ appearing in the expression for the shifted chemical potential \[33\] can be approximated as

$$R^n p^{M3} \simeq T \sum_k K \frac{R^n K \nu^0_{K}(T, \nu^0_{K})}{\nu^0_{K}(T, \nu^0_{K})} \simeq T \sum_k K \frac{R^n K \nu^0_{K}(T, \nu^0_{K})}{\nu^0_{K}(T, \nu^0_{K})} \bigg(41\bigg),$$

where in the second step of the derivation we reverted the approximation $T \frac{\partial p^{K}_{id}(T, \nu^0_{K})}{\partial \nu^0_{K}} \simeq p^{K}_{id}(T, \nu^0_{K})$ used before. Apparently, such an approximation does not change the second virial coefficient $p^{M3}$, since the latter ones are defined by the terms $R^n p^{M3}$ and, hence, their approximation modifies the higher order virial coefficients, which now will be modified by redefining the chemical potentials $\nu^0_{K}$ in the terms $\sum_k R^n K \nu^0_{K}(T, \nu^0_{K})$. Since for the Boltzmann statistics, i.e. for $a_K \to \infty$, the last result follows directly from Eqs. \[33\] (see also Ref. \[23\] for a rigorous derivation), we adopt it and extrapolate it to all densities in the quantum case. Taking into
account all the modifications discussed above the model four (M4) pressure is

\[ p_{\text{id}}^{M4} = \sum_{K} p_{id}^{K}(T, \nu_{K}^{0}), \]  
\[ \nu_{K}^{0} = \mu_{K} + [v_{K}^{*}p_{\text{id}}^{M4} + s_{K}f_{1} + c_{K}f_{2} + u_{K}f_{3}], \]  
\[ f_{n} = A_{n} \sum_{K} R_{n}^{K} \rho_{id}^{K}(T, \nu_{K}^{n}), \text{ for } n = 1, 2, 3, \]  
\[ \nu_{K}^{1} = \nu_{K}^{0} - \Delta_{K}s_{K}f_{1}, \quad \nu_{K}^{2} = \nu_{K}^{0} - \Delta_{K}c_{K}f_{2}, \]  
\[ \nu_{K}^{3} = \nu_{K}^{2} - \Delta_{K}u_{K}f_{3}, \]  

where the constants \( A_{n} \) (with \( A_{n}\neq 0 \)) and \( \Delta_{K}^{n} \) are, respectively, the common and individual (for \( K \)-th sort of particles) weights with which the average quantity \( R_{n}^{K}p_{\text{id}}^{M3} \) enters the expressions of chemical potentials \( \nu_{K}^{n} \).

Note that in nuclear physics the leptonidous expansion of the binding energy of large nuclei contains similar terms and, moreover, the mean-field one \( u_{K}f_{3} \) is often called the Gaussian curvature.

The positive constants \( \Delta_{K}^{n} > 0 \) are introduced in order to account for the third, fourth and higher order virial coefficients of classical hard spheres. Such an approach leads to the hierarchy of partial pressures of point-like particles

\[ p_{\text{id}}^{K}(T, n_{K}^{n-1}) > p_{\text{id}}^{K}(T, n_{K}^{n}) \quad \text{for} \quad n = 1, 2, \]  

since for a positive value of coefficient \( A_{n} \) one finds \( n^{-1} > n_{K}^{n} \). It is evident that the higher the pressure is, the higher the density is and the stronger the inequalities and \( n^{-1} > n_{K}^{n} \) are for \( n = 1, 2 \). Therefore, at high particle number densities one should expect that for properly chosen coefficients \( A_{n} \) and \( \Delta_{K}^{n} \), and for positive values of \( v_{K}^{*}, s_{K} \) and \( c_{K} \) the following set of inequalities

\[ v_{K}^{*}p_{\text{id}}^{M4} \gg s_{K}f_{1} \gg c_{K}f_{2}, \]  

should appear. Moreover, for any sign of \( A_{3} \) coefficient, the inequality \( v_{K}^{3} \gg v_{K}^{2} \) can be easily established at high densities due to a strong suppression of \( p_{\text{id}}^{K}(T, n_{K}^{3}) \), where \( n = 1, 2 \) compared to \( p_{\text{id}}^{K}(T, n_{K}^{2}) \), and, hence, in this limit the M4 EoS will reproduce the dense packing behaviour.

Therefore, choosing the coefficients \( A_{n} \) and \( \Delta_{K}^{n} \) from fitting the pressure of classical hard spheres in the whole gaseous phase, one can substitute them into the M4 equations and get the quantum EoS for multicomponent mixture of hard convex particles for a dimension \( D = 3 \). Our confidence is based on the fact that for the one-component case with a truncated system, which accounts only for the pressure \( p_{\text{id}}^{M4} \) and for \( f_{1} \), one could choose \( \Delta_{1}^{1} = 0.245 \) (\( A_{1} = 2 \) was fixed, while \( A_{n} \neq 0 \)) to simultaneously reproduce the second, third and fourth virial coefficient of classical hard spheres. Such an EoS provides a very good description of nuclear, hadronic and neutron matter properties with the minimal number of adjustable parameters. Moreover, it can be shown numerically that the standard compressibility factor \( Z = p/(\rho T) \) (here \( \rho \) denotes pressure and \( n \) is the particle number density) of one- and two-component mixtures of hard spheres and hard discs are excellently reproduced by the system (42)-(46) for the whole gaseous phase up to the transition to the solid phase.

Apparently, the whole derivation of M3 and M4 pressures can be straightforwardly extended to arbitrary dimension \( D \geq 2 \) by replacing the integration measure

\[ \frac{d^{3}k}{(2\pi\hbar)^{3}} \rightarrow \frac{d^{D}k}{(2\pi\hbar)^{D}} \]  

in the corresponding expressions and by replacing the 3-dimensional eigen volume \( v_{K}^{0} \) by the \( D \)-dimensional eigen hyper-volume \( v_{K}^{0} \), the 2-dimensional eigen surface \( s_{K} \) by the \( (D - 1) \)-dimensional eigen hyper-surface and so on in them, to have at the end \( D + 1 \) equations similar to the system. Since the virial coefficients of classical hard spheres are known for higher dimensions, they can be used in the system. Having the virial coefficients for the \( D \)-dimensional classical hard convex particles one can determine their parameters \( v_{K}, s_{K}, c_{K} \) etc from the fitting pressure \( p \) or the compressibility factor and write the all necessary parameters for the system.

V. CONCLUSIONS

In this work we discussed the necessary conditions to derive the quantum VdW EoS with hard-core repulsion directly from the quantum partition. Using a plausible example it is shown that an alternative way to account for the hard-core repulsion suggested in Ref. leads to severe inconsistencies. The multicomponent formulation of the quantum VdW EoS with hard-core repulsion is derived within the self-consisting approximation. For practical applications it is simplified, extrapolated to higher densities and also generalized to the case of hard convex bodies. For the first time, the suggested approach allows one to treat the hard spheres and hard convex bodies of various dimensions \( D \geq 2 \) on the same footing. The model parameters can be determined from the best description of classical systems and then used in the quantum EoS. Since this approach is formulated solely in terms of the grand canonical variables, it can be used to model the properties of many physical systems with non-conserved number of particles. In particular, it can be used for the mixtures of constituents with very different physical properties like a mixture of hadrons, nuclei and bags of quark-gluon plasma which are hard to model within the other approaches.

Acknowledgments. The author appreciates the valuable comments of I.P. Yakimenko, V. Vovchenko, L. Bravina, B. Grinyuk, E. Zabrodin and N. Yakovenko and the partial support by the National Academy of Sciences of Ukraine (project No. 0118U003197). Also the author is grateful to the COST Action CA15213 “THOR” for supporting his networking.
[1] J. D. van der Waals, Z. Phys. Chem. 5, 133 (1889).
[2] J. P. Hansen and I. R. McDonald, Theory of Simple Fluids (Academic Press, Amsterdam, 2006).
[3] Theory and Simulation of Hard Sphere Fluids and Related Systems, Lect. Notes Phys. Vol. 753, edited by A. Mulero (Springer-Verlag, Berlin, 2008).
[4] V. V. Sagun, A. I. Ivanytskyi, K. A. Bugaev and I. N. Mishustin, Nucl. Phys. A 924, 24 (2014) and references therein.
[5] A. I. Ivanytskyi, K. A. Bugaev, V. V. Sagun, L. V. Bravina and E. E. Zabrodin, Phys. Rev. C 97, 064905 (2018).
[6] V. V. Sagun et al., Eur. Phys. J. A 54, 100 (2018).
[7] K. A. Bugaev et al., Nucl. Phys. A 970, 133 (2018).
[8] K. A. Bugaev et al., Universe 5, 0063, 1 (2019) and references therein.
[9] K. A. Bugaev et al., Phys. Part. Nucl. Lett. 15, 210 (2018).
[10] V. Vovchenko, Phys. Rev. C 96, 015206 (2017).
[11] N. F. Carnahan, K.E. Starling, J. Chem. Phys. 51, 635 (1969).
[12] K. A. Bugaev, A. I. Ivanytskyi, V. V. Sagun, E. G. Nikonov and G. M. Zinovjev, Ukr. J. Phys. 63, 863 (2018).
[13] D. H. Rischke, M. I. Gorenstein, H. Stöcker and W. Greiner, Z. Phys. C 51, 485 (1991).
[14] S. Typel, Eur. Phys. J. A 52, 16 (2016).
[15] V. Vovchenko, D. V. Anchishkin, and M. I. Gorenstein, Phys. Rev. C 91, 064314 (2015).
[16] K. Redlich and K. Zalewski, Acta Phys. Polon. B 47, 1943 (2016).
[17] K. A. Bugaev, M. I. Gorenstein, H. Stöcker and W. Greiner, Phys. Lett. B 485, 121 (2000).
[18] see K. A. Bugaev, Nucl. Phys. A 807, 251 (2008).
[19] for an appropriate review see K. A. Bugaev and P. T. Reuter, Ukr. J. Phys. 52, 489 (2007) and references therein.
[20] K. Huang, Statistical Mechanics (Wiley & Sons, 1967).
[21] R. V. Poberezhnyuk, V. Vovchenko, D. V. Anchishkin and M. I. Gorenstein, J. Phys. G 43, 095105 (2016).
[22] A. Dillmann and G. E. Meier, J. Chem. Phys. 94, 3872 (1991).
[23] A. Laaksonen, I. J. Ford, and M. Kulmala, Phys. Rev. E 49, 5517 (1994).
[24] A. Ishihara, J. Chem. Phys. 18, 1446 (1950).
[25] H. Hadwiger, Math. Math. 54, 345 (1950).
[26] A. Ishihara, Statistical physics (Academic Press, New York, 1971).
[27] N. S. Yakovenko, K. A. Bugaev, L. V. Bravina and E. E. Zabrodin, The concept of induced surface and curvature tensions and a unified description of the gas of hard discs and hard spheres (in preparation).
[28] V. V. Sagun, K. A. Bugaev and A. I. Ivanytskyi, arXiv:1904.05955v1 [nucl-th].
[29] V. V. Sagun, I. Lopes and A. I. Ivanytskyi, Astrophys. J. 871, no. 2, 157 (2019).
[30] J. G. Loeser, Zh. Zhen, S. Kais and D. R. Herschbach, J. Chem. Phys. 95, 4525 (1991).