The Van der Waals excluded volume procedure for the HG gas is proposed. The derivation is based on the grand canonical partition function for the system of particles of several species interacting by hard core potentials. The obtained formulae for thermodynamical quantities are consistent with underlying principles of statistical mechanics as well as with thermodynamical identities. The model can be applied to the analysis of experimental data for particle number ratios in relativistic nucleus-nucleus collisions.
Here we use the notation
\[
\phi(T; m) = \frac{1}{2\pi^2} \int_0^\infty p^2 dp \ \exp \left( -\frac{\sqrt{p^2 + m^2}}{T} \right) = \frac{m^2}{2\pi^2} K_2 \left( \frac{m}{T} \right),
\]
where \( K_2 \) is the modified Bessel function. The asymptotic behavior of \( \phi(T; m) \) in the non-relativistic limit, \( m >> T \), has the form
\[
\phi(T; m) \approx \left( \frac{mT}{2\pi} \right)^{3/2} \exp( -m/T ) .
\]

By means of the Mayer functions
\[
f_{ij} \equiv \exp \left( -\frac{u(\|\vec{r}_i - \vec{r}_j\|)}{T} \right) - 1 ,
\]
one can rewrite the integrand of Eq. (3) in the following form
\[
\exp \left( -\frac{U}{T} \right) = \prod_{i=1}^{N-1} \prod_{j=i+1}^N \left[ 1 + f_{ij} \right] \approx \prod_{i=1}^{N-1} \left[ 1 + \sum_{j=i+1}^N f_{ij} \right]
\]
The approximate equality in the last expressions is based on the assumption that the gas is rarefied and, therefore, the terms containing products \( f_{ij} f_{im} \) can be dropped.

Let us introduce the notations
\[
\int d^3 r_i f_{ij} = -2b(T, \vec{r}_j) .
\]
Now we shall use the rigid ball model, i.e. we assume the hard-core interaction between the particles:
\[
u(\|\vec{r}_i - \vec{r}_j\|) = \begin{cases} \infty & \text{if } \|\vec{r}_i - \vec{r}_j\| \leq 2R \\ 0 & \text{if } \|\vec{r}_i - \vec{r}_j\| > 2R , \end{cases}
\]
\((R \text{ is the particle radius})\). In this case \( b \) defined by Eq. (8) does not depend on temperature. For \( V^{1/3} \gg R \) the dependence of \( b \) on \( \vec{r}_j \) is negligible and the integral in Eq. (8) can be easily calculated:
\[
b = \frac{16}{3} \pi R^3 .
\]
Substituting Eqs. (7-8) into Eq. (3) one gets
\[
Z(V, T, N) = \frac{1}{N!} [\phi(T; m)]^N \prod_{i=1}^N (V - 2(N - i)b)
\]
\[
= \frac{1}{N!} [\phi(T; m)]^N V^N \exp \left[ \sum_{i=1}^N \log \left( 1 - 2(N - i) \frac{b}{V} \right) \right] .
\]
In a rarefied gas the value of \( 2bN \) is much smaller then the total volume \( V \). In this case one can approximate \( \log(1 - x) \approx -x \) in Eq. (11). This yields
\[
Z(V, T, N) \approx \frac{1}{N!} [\phi(T; m) V]^N \exp \left( -\sum_{i=1}^N 2(N - i) \frac{b}{V} \right) .
\]
Performing the summation in the exponential and using approximate relation \( \exp(-Nb/V) \approx 1 - Nb/V \) one gets CPF of one component rigid ball gas:
\[
Z(V, T, N) \approx \frac{1}{N!} [\phi(T; m) V]^N \exp \left( -N(N - 1) \frac{b}{V} \right)
\]
\[
\approx \frac{1}{N!} [\phi(T; m)]^N (V - Nb)^N .
\]
\[\]
Substituting the expression (13) into the formula for pressure one finds the well known VdW equation for rigid ball gas:

\[ p(V, T, N) \equiv T \frac{\partial \log Z(V, T, N)}{\partial V} = \frac{NT}{V - bN}. \]  

(14)

Note that \( b \) (10) is equal to 4\( v \), where \( v = 4\pi R^3/3 \) is the particle volume. The VdW equation of state (14) is obtained from the statistical mechanics of rigid balls within a rarefied gas approximation, \( vN << V \). For a dense gas the VDW equation (14) should be considered as a phenomenological extrapolation.

The grand canonical partition function (GCPF) is expressed through the CPF in the following way:

\[ Z(V, T, \mu) = \sum_{N=0}^{\infty} \exp\left(\frac{\mu N}{T}\right) Z(V, T, N), \]  

(15)

where \( \mu \) is the chemical potential. In the case of rigid ball gas, the upper limit of the sum is in fact not infinite. The CPF (3) becomes equal to zero if \( N \) exceeds \( N_0 \sim V/v \).

Let \( \exp\left(\frac{\mu N^*}{T}\right) Z(V, T, N^*) \) is the maximal term in the sum (15). The rest of terms are also positive, hence the following inequalities are satisfied

\[ \exp\left(\frac{\mu N^*}{T}\right) Z(V, T, N^*) < Z(V, T, \mu) < N_0 \times \exp\left(\frac{\mu N^*}{T}\right) Z(V, T, N^*). \]  

(16)

The pressure can be expressed via GCPF by the formula

\[ p(T, \mu) = T \lim_{V \to \infty} \frac{\log Z(V, T, \mu)}{V}. \]  

(17)

Taking Eq. (16) into account one gets

\[ p(T, \mu) \geq \lim_{V \to \infty} \frac{\mu N^* + T \log Z(V, T, N^*)}{V}, \]

\[ p(T, \mu) \leq \lim_{V \to \infty} \frac{\mu N^* + T \log Z(V, T, N^*)}{V} + T \lim_{V \to \infty} \frac{\log N_0}{V}. \]

Since \( V^{-1} \log N_0 \to 0 \) in the thermodynamical limit, \( V \to \infty \), the pressure \( p(T, \mu) \) (17) is defined by the largest term, with \( N = N^* \), of the GCPF (15). \( N^* \) is also the average number of particles in the grand canonical formulation. Using the VdW approximation (13) for the CPF one finds

\[ p(T, \mu) = T \lim_{V \to \infty} \frac{1}{V} \log \left[ \frac{A^{N^*}(V - N^*b)^{N^*}}{N^*!} \right], \]  

(18)

where \( A = \exp(\mu/T)\phi(T; m) \), and \( N^* = N^*(V, T, \mu) \) corresponds to the maximum of the expression in the square brackets.

Let us show that Eq. (18) leads to the result

\[ p(T, \mu) = T \xi, \]  

(19)

where \( \xi \) is defined by the transcendental equation

\[ \xi = A \exp(-b\xi). \]  

(20)

Using the asymptotic representation for the \( \Gamma \)-function logarithm at \( N \to \infty \)

\[ \log \Gamma(N + 1) \approx N(\log N - 1) \]  

(21)

it is easy to check that the value of \( N^* \) satisfying the maximum condition of logarithm argument in Eq. (18) is given by the formula

\[ N^* \approx Vn, \]  

(22)
where \( n = n(T, \mu) \) is related to \( \xi \) via equation
\[
 n = \frac{\xi}{1 + b \xi}. \tag{23}
\]
Substitution of Eq. (22) into Eq. (18) with account for Eqs. (20, 23) yields the formula (19). The quantity \( n = n(T, \mu) \) is a particle number density in the grand canonical formulation. One can readily check that the definition of the \( Eq. (19) \) can be therefore written in the form [3]:
\[
p^{id}(T, \mu) = T \exp(\mu/T) \phi(T; m) = T \ n^{id}(T, \mu). \tag{24}
\]
Eq. (19) can be therefore written in the form [3]:
\[
p(T, \mu) = p^{id} \left( T, \mu - \frac{bp(T, \mu)}{T} \right). \tag{25}
\]
It can be also presented in the form of Eq. (14) with \( N = N^*(V, T, \mu) \), which demonstrates explicitly the equivalence between canonical and grand canonical formulations at \( V \to \infty \).

### III. TWO COMPONENT VDW GAS

In the case of two particle species CPF has the following form:
\[
Z(V, T, N_1, N_2) = \frac{1}{N_1!N_2!} \int \prod_{i=1}^{N_1} d^3 p_i^{(1)} d^3 r_i^{(1)} (2\pi)^3 \exp \left( -\frac{m_1^2 + (p_i^{(1)})^2}{T} \right) \nonumber
\]
\[
\times \prod_{k=1}^{N_2} d^3 p_k^{(2)} d^3 r_k^{(2)} (2\pi)^3 \exp \left( -\frac{m_2^2 + (p_k^{(2)})^2}{T} \right) \exp \left( -\frac{U^{(1,2)}}{T} \right),
\]
where \( m_1, N_1 (m_2, N_2) \) are the mass and number of particles of the 1-st (2-nd) species,
\[
U^{(1,2)} = \sum_{1 \leq i < j \leq N_1} u_{11}(|\vec{r}_i^{(1)} - \vec{r}_j^{(1)}|) + \sum_{1 \leq k < l \leq N_2} u_{22}(|\vec{r}_k^{(2)} - \vec{r}_l^{(2)}|) + \sum_{i=1}^{N_1} \sum_{k=1}^{N_2} u_{12}(|\vec{r}_i^{(1)} - \vec{r}_k^{(2)}|).
\]

It should be mentioned that in the case of two particle species \( U^{(1,2)} \) contains three types of two-particle potentials. While the potentials \( u_{11} \) and \( u_{22} \) describe interactions between particles of the same species and can be handled similarly to the potential \( u \) of one-component case, the potential \( u_{12} \) describing interactions between particles of different species requires an special treatment and prevents a straightforward generalization of the one-component VDW equation to the two-component gas.

The integration of (26) over the particle momenta gives the following expression for the CPF
\[
Z(V, T, N_1, N_2) = \frac{\phi(T; m)}{N_1!N_2!} \int \prod_{i=1}^{N_1} d^3 r_i^{(1)} \prod_{k=1}^{N_2} d^3 r_k^{(2)} \exp \left( -\frac{U^{(1,2)}}{T} \right). \tag{28}
\]

The next step, however, involves the Mayer functions of three types \((p, q=1,1; 2,2; 1,2)\):
\[
f_{ik}^{(pq)} = \exp \left( -\frac{u_{pq}(|\vec{r}_i^{(p)} - \vec{r}_k^{(q)}|)}{T} \right) - 1, \quad p, q = 1, 2
\]
(note that \( f_{il}^{12} = f_{il}^{21} \)). The integrand of (28) can be rewritten as
\[
\exp\left(-\frac{U}{T}\right) = \prod_{k=1}^{N_v} \prod_{l=k+1}^{N_w} \left[ 1 + f^{(w)}_{kl} \right] \prod_{i=1}^{N_v} \prod_{j=i+1}^{N_v} \left[ 1 + f^{(vv)}_{ij} \right] \prod_{m=1}^{N_w} \left[ 1 + f^{(vw)}_{im} \right]
\]
\[
\simeq \prod_{k=1}^{N_v} \left[ 1 + \sum_{l=k+1}^{N_w} f^{(w)}_{kl} \right] \prod_{i=1}^{N_v} \left[ 1 + \sum_{j=i+1}^{N_v} f^{(vv)}_{ij} \right] \prod_{m=1}^{N_w} f^{(vw)}_{im},
\]

where \( v, w = 1, 2 \) and \( N_v \geq N_w \).

For each type of Mayer function we introduce the notation

\[
\int d^3r_i^{(p)} f^{(pq)}_{ij} = -2b_{pq}(T, r_j^0).
\]

For the rigid ball model at \( V^{1/3} \gg \max(R_1, R_2) \) \( (R_p \text{ is the radius of a particle of p-th species, } p = 1, 2) \) it yields

\[
b_{pq} = \frac{2}{3} \pi (R_p + R_q)^3.
\]

Substituting (30) and (31) into (28) one gets

\[
Z(V, T, N_1, N_2) = \frac{1}{N_1!N_2!} [\phi(T; m_1)]^{N_1} [\phi(T; m_2)]^{N_2} \prod_{k=1}^{N_v} (V - 2(N_w - k)b_{vw})
\]
\[
\times \prod_{i=1}^{N_v} (V - 2(N_v - i)b_{vw} - 2N_w b_{vw}) = \frac{1}{N_1!N_2!} [\phi(T; m_1)]^{N_1} [\phi(T; m_2)]^{N_2} V^{N_1 + N_2}
\]
\[
\times \exp \left[ \sum_{k=1}^{N_v} \log \left( 1 - 2(N_w - k)\frac{b_{vw}}{V} \right) + \sum_{i=1}^{N_v} \log \left( 1 - 2(N_v - i)\frac{b_{vw}}{V} - 2N_w \frac{b_{vw}}{V} \right) \right].
\]

We again assume that the gas is rarefied and the total proper volume of all particles is much smaller than the total volume of the system. Then it follows from Eq. (33):

\[
Z(V, T, N_1, N_2) \simeq \frac{1}{N_1!N_2!} [\phi(T; m_1)]^{N_1} [\phi(T; m_2)]^{N_2} V^{N_1 + N_2}
\]
\[
\times \exp \left[ - \sum_{k=1}^{N_v} 2(N_w - k)\frac{b_{vw}}{V} - \sum_{i=1}^{N_v} \left( 2(N_v - i)\frac{b_{vw}}{V} + 2N_w \frac{b_{vw}}{V} \right) \right].
\]

Performing the summation in the exponential

\[
Z(V, T, N_1, N_2) \simeq \frac{1}{N_1!N_2!} [\phi(T; m_1)]^{N_1} [\phi(T; m_2)]^{N_2} V^{N_1 + N_2}
\]
\[
\times \exp \left( -N_2(N_2 - 1)\frac{b_{22}}{V} - N_1(N_1 - 1)\frac{b_{11}}{V} - 2N_1N_2 \frac{b_{12}}{V} \right)
\]
\[
\text{and introducing quantities } \tilde{b}_{12} \text{ and } \tilde{b}_{21} \text{ constrained by the condition}
\]
\[
\tilde{b}_{12} + \tilde{b}_{21} = 2b_{12},
\]

we can rewrite the CPF in the form

\[
Z(V, T, N_1, N_2) \simeq \frac{1}{N_1!N_2!} [\phi(T; m_1)]^{N_1} [\phi(T; m_2)]^{N_2} V^{N_1 + N_2} \left[ \exp \left( -N_1 \frac{b_{11}}{V} - N_2 \frac{b_{21}}{V} \right) \right]^{N_1}
\]
\[
\times \left[ \exp \left( -N_2 \frac{b_{22}}{V} - N_1 \frac{\tilde{b}_{12}}{V} \right) \right]^{N_2}.
\]

Imposing the additional constraints \( 2N_v \tilde{b}_{vw}/V \ll 1 \) we obtain the final expression for the partition function of the two-component VdW gas.
\[ Z(V,T,N_1,N_2) \cong \frac{1}{N_1!N_2!} [\phi(T;m_1)]^{N_1} [\phi(T;m_2)]^{N_2} \times (V - N_1b_{11} - N_2\tilde{b}_{21})^{N_1} (V - N_2b_{22} - N_1\tilde{b}_{12})^{N_2} . \]  

Substituting expression (38) into the formula for the pressure one obtains
\[ p(V,T,N_1,N_2) \equiv T \frac{\partial \log Z(V,T,N_1,N_2)}{\partial V} = \frac{N_1T}{V - b_{11}N_1 - \tilde{b}_{21}N_2} + \frac{N_2T}{V - b_{22}N_2 - \tilde{b}_{12}N_1} . \]  

The equation of state (39) is consistent with the virial expansion up to second order and can be considered as a generalization of the VdW equation for the two-component system. We define \( \tilde{b}_{12} \) and \( \tilde{b}_{21} \) as the following:
\[ \tilde{b}_{12} = 2 \frac{b_{11}b_{12}}{b_{11} + b_{22}} , \quad \tilde{b}_{21} = 2 \frac{b_{22}b_{12}}{b_{11} + b_{22}} . \]  

Eq. (40) satisfies the constraints (36) and leads to the correct physical behavior in the limiting cases when both particle radii are equal to each other or when one of the particle radius is equal to zero. If two species have equal radii, \( R_1 = R_2 \), equation (39) is reduced to the one-component VdW equation (14) with \( N = N_1 + N_2 \) and \( \mu = b_{11} = b_{22} = \tilde{b}_{12} = \tilde{b}_{21} \). Note that in a general case, \( R_1 \neq R_2 \), the VdW excluded volumes in Eq. (39) are different for different particle species.

The transformation to the grand canonical ensemble is similar to that of one-component case. The GCPF has the form
\[ Z(V,T,\mu_1,\mu_2) = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \exp \left( \frac{\mu_1N_1 + \mu_2N_2}{T} \right) Z(V,T,N_1,N_2) , \]  

where \( \mu_q \) \((q = 1, 2)\) are the chemical potentials of each particle species. The total number of terms, \( N_0 \), in double sum (41) is of the order of \( V^2 \). Since \( V^{-1} \log N_0 \rightarrow 0 \) at \( V \rightarrow \infty \) the pressure can be expressed via the maximum term in the sum (41):
\[ p(T,\mu_1,\mu_2) = \lim_{V \rightarrow \infty} \frac{T}{V} \log \left[ \exp \left( \frac{\mu_1N_1^* + \mu_2N_2^*}{T} \right) Z(V,T,N_1^*,N_2^*) \right] . \]  

In the VDW approximation (38) the last expression takes the form
\[ p(T,\mu_1,\mu_2) = \lim_{V \rightarrow \infty} \frac{T}{V} \log \left[ \frac{A_1^{N_1^*} A_2^{N_2^*} (V - N_1^*b_{11} - N_2^*\tilde{b}_{21})^{N_1^*} (V - N_2^*b_{22} - N_1^*\tilde{b}_{12})^{N_2^*}}{N_1^*!N_2^*!} \right] , \]  

where \( A_p = \exp(\mu_p/T) \phi(T,m_p) \).

Let us show that the pressure (43) can be calculated by the formula
\[ p(T,\mu_1,\mu_2) = T(\xi_1 + \xi_2) , \]  

where the values of \( \xi_q \) are found from the set of coupled transcendental equations
\[ \xi_1 = A_1 \exp(-b_{11}\xi_1 - \tilde{b}_{12}\xi_2) , \]  
\[ \xi_2 = A_2 \exp(-b_{22}\tilde{b}_{21} - \tilde{b}_{21}\xi_1) . \]

Using the asymptotic representation for the \( \Gamma \)-function logarithm it is easy to check that the values of \( N_p^* \) satisfying the maximum condition of the logarithm argument in Eq.(43) are given by the formula
\[ N_p^* \cong V n_p , \]  

where \( n_p = n_p(T,\mu_1,\mu_2) \) are related to \( \xi_p \) via the equations
\[ \xi_1 = \frac{n_1}{1 - n_1b_{11} - n_2\tilde{b}_{21}} , \]  
\[ \xi_2 = \frac{n_2}{1 - n_2b_{22} - n_1\tilde{b}_{12}} . \]
The substitution of Eq. (47) into Eq. (43) yields the formula (44).

The set of linear equations (48) and (49) can be solved for \( n_p \):

\[
\begin{align*}
    n_1 &= \frac{\xi_1 [1 + \xi_2 (b_{22} - \tilde{b}_{21})]}{1 + \xi_1 b_{11} + \xi_2 b_{22} + \xi_1 \xi_2 (b_{11} b_{22} - \tilde{b}_{12})}, \\
    n_2 &= \frac{\xi_2 [1 + \xi_1 (b_{11} - \tilde{b}_{12})]}{1 + \xi_1 b_{11} + \xi_2 b_{22} + \xi_1 \xi_2 (b_{11} b_{22} - \tilde{b}_{12})}.
\end{align*}
\]  

(50)  

(51)

Similarly to the one component case, the quantities \( n_p \) are particle number densities. One can readily check that the definition \( n_p = \frac{\partial \rho(T, \mu_1, \mu_2)}{\partial \mu_p} \) leads to Eqs. (50) and (51), provided that formulae (44–46) are taken into account.

**IV. MULTICOMPONENT VDW GAS**

The above considerations can be generalized to the multi-component VdW gas with an arbitrary number of particle species. After integration over particle momenta and simplifications similar to those of the above consideration one gets the expression for the CPF of \( K \)-component VdW gas:

\[
Z(V, T, N_1, ..., N_K) \approx \prod_{q=1}^{K} \frac{1}{N_q!} \left[ \phi(T; m_q) \right]^{N_q} \left( V - \sum_{p=1}^{K} N_p \tilde{b}_{pq} \right)^{N_q},
\]

(52)

where

\[
\tilde{b}_{pq} = \frac{2b_{pp}b_{pq}}{b_{pp} + b_{pq}},
\]

(53)

\[
b_{pq} = b_{qp} = \frac{2}{3} \pi (R_p + R_q)^3.
\]

(54)

\( R_q \) is the radius of particle of specie \( q \). \( \phi(T; m_q) \) is defined by Eq. (4). The CPF (52) yields the VDW equation of state for a \( K \)-component rigid ball gas

\[
p(V, T, N_1, ..., N_K) = \sum_{q=1}^{K} \frac{N_q T}{V - \sum_{p=1}^{K} b_{pq} N_p}.
\]

(55)

The pressure in the grand canonical ensemble is given by the formula

\[
p(T, \mu_1, ..., \mu_K) = T \sum_{p=1}^{K} \xi_p,
\]

(56)

where \( \mu_p \) are the chemical potentials (\( p = 1, ..., K \)). The functions \( \xi_p \) satisfy the set of coupled transcendental equations

\[
\xi_p = A_p \exp \left( -\sum_{q=1}^{K} b_{pq} \xi_q \right),
\]

(57)

where \( A_p = \exp(\mu_p/T)\phi(T; m_p) \). The particle densities \( n_p = n_p(T, \mu_1, ..., \mu_K) \) are obtained as the solutions of the following set of coupled linear equations

\[
\xi_p = \frac{n_p}{1 - \sum_{q=1}^{K} n_q \tilde{b}_{qp}}.
\]

(58)

In the canonical ensemble formulation of the HG model the numbers \( N_1, ..., N_K \) are not fixed. They can not be fixed because of inelastic reactions between the hadrons. The fixed values have the conserved charges: baryonic number \( B \), strangeness \( S \) (strangeness is conserved as we neglect weak decays) and electric charge \( Q \). The CPF has then the form

\[

\]

7
\[
Z(V,T,B,S,Q) \equiv \sum_{N_1,...,N_K=1}^{\infty} Z(V,T,N_1,...,N_K) \delta(B - \sum_{i=1}^{K} b_i N_i) \delta(S - \sum_{i=1}^{K} s_i N_i) \delta(Q - \sum_{i=1}^{K} q_i N_i) ,
\]

where \(b_i\), \(s_i\) and \(q_i\) are the baryonic number, strangeness and electric charge of \(i\)-th hadron species. In the application of the thermal HG models to A+A collisions, \(B\) equals the number of nucleons participating in the reaction, \(S = 0\) and \(Q = \alpha B\) with \(\alpha \approx 0.5\) for intermediate nuclei and \(\alpha \approx 0.4\) for heavy nuclei. CPF (59) can be calculated with the VdW input (52) for \(Z(V,T,N_1,...,N_K)\). The presence of the Kronecker \(\delta\)-functions in Eq. (59) makes the canonical ensemble rather complicated. In this case the system properties are defined by the pressure function (56) with the chemical potentials \(\mu_i (i = 1,...,K)\) defined as

\[
\mu_i = b_i \mu_B + s_i \mu_S + q_i \mu_Q
\]
in terms of the baryonic \(\mu_B\), strange \(\mu_S\) and electric \(\mu_Q\) chemical potentials. They are chosen, at given \(V\) and \(T\), to fix the average values \(B, S = 0\) and \(Q = \alpha B\).

V. SUMMARY

In the present paper we have proposed a generalization of the VdW excluded volume procedure for the multicomponent hadron gas. The canonical and grand canonical ensemble formulations are presented. Different hard-core radii for different hadron species have been discussed in the literature (e.g. [8-12]). The excluded volume procedure was based on the substitution \(V \rightarrow V - \sum_i b_i N_i\). This ansatz is shown to be not correct: for unequal hard-core radii the VdW excluded volumes seen by the different hadron species are different. Thermodynamical quantities in the grand canonical formulations are found to be the solution of a coupled set of the transcendental equations.

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