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Krzysztof Redlich and Kacper Zalewski

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# Thermodynamics of the low density excluded volume hadron gas

Krzysztof Redlich<sup>1,2,3</sup> and Kacper Zalewski<sup>4,5</sup>

<sup>1</sup>*Institute of Theoretical Physics, University of Wrocław, PL-50-204 Wrocław, Poland*

<sup>2</sup>*EMMI, GSI Helmholtzzentrum fuer Schwerionenforschung, 64291 Darmstadt, Germany*

<sup>3</sup>*Department of Physics, Duke University, Durham, North Carolina 27708, USA*

<sup>4</sup>*Institute of Nuclear Physics, Polish Academy of Sciences, PL-31-342 Kraków, Poland*

<sup>5</sup>*Institute of Physics, Jagiellonian University, PL-30-059 Kraków, Poland*

We consider thermodynamics of the excluded volume particles at finite temperature and chemical potential, in the low density approximation. We assume Boltzmann statistics and study the influence of the excluded volume on an ideal gas thermodynamics at the same temperature, pressure and numbers of particles. We show, that considering the change of the free enthalpy due to the excluded volume, and using the Maxwell identities, one can derive relevant thermodynamic functions and parameters of multi-component gases. The derivation is quite general as particles may have different sizes and shapes which can also depend on their momenta. Besides its simplicity and generality, our approach has the advantage of eliminating the transcendental equations occurring in earlier studies. A representative example of the excluded volume thermodynamics is the single-component gas of hard spheres. For this case, using the virial expansion, the validity limits of the low-density approximation are also discussed.

## I. INTRODUCTION

A detailed analysis of secondary hadrons produced in heavy ion collisions (HIC) in a very broad energy range from SIS to LHC has shown that they are of thermal origin [1–4]. Particle yields are excellently described as the Hadron Resonance Gas (HRG), an uncorrelated gas composed of all known hadrons and resonances constrained by the conservation laws [1]. The HRG is also very successful to quantify the equation of state (EoS) of the hadronic phase of QCD at finite temperature and density, as was shown recently by comparing the EoS obtained in lattice gauge theory with the predictions of the HRG model [5–8]. These results indicate that HRG is a remarkably good approximation to QCD thermodynamics in the confined phase, and that HIC experiments are indeed probing the thermal QCD medium.

The statistical partition function for HRG is constructed for a mixture of ideal gases, nevertheless, according to the arguments by Dashen, Ma and Bernstein [9] and Hagedorn [10], it includes attractive interactions through resonance contributions.

Different extensions of the HRG model have been proposed, including not only the attractive, but also the repulsive interactions between hadrons. The later are experimentally known to be important at short distances. Clearly, the effect of both interactions on the thermodynamics can be introduced in a model independent way, using the S-matrix approach [9]. In the low density approximation the resulting expression for the partition sum of the hadron gas reduces to the Beth-Uhlenbeck form [11], where the interaction contribution is linked to the experimental phase shifts [12]. However, due to far incomplete data on phase shifts, this approach can be systematically used only in selected sectors of hadron interactions [12–14].

A transparent phenomenological way to account for repulsions in a hadron gas is to abandon the point-like

nature of particles and introduce for them finite sizes. In this way the repulsive interactions in the hadron gas are implemented via the excluded volumes. Exact formulae for the thermodynamic functions of the excluded volume gas are not known, but low density approximations have been developed [15–25]. The hard core hadron resonance gas models were also successfully applied in heavy ion phenomenology [1–3] and in the interpretation of recent lattice data [26–29].

In the following, we focus on the implementation of the repulsive interactions in a hadron gas via excluded volumes, as introduced in Refs. [20, 21]. We propose a new method, which is based on the Maxwell identities, to calculate the thermodynamic functions and parameters of the low density excluded volume gas, subject to Boltzmann statistics. They are expressed in terms of the excluded volumes for pairs of particles, and the thermodynamic functions and parameters of the ideal gas at the same temperature, pressure and number of particles of each kind. The derivation is quite general, as particles may have different sizes and shapes, which may also depend on their momenta. Besides its simplicity and generality, our approach has the advantage of eliminating the transcendental equations occurring in earlier studies. The results from Refs. [20–23] follow as special cases from our analysis, except for the partial pressures in an  $r$ -component gas of hard spheres presented in Ref. [23], where some additional assumptions, or the higher order corrections, are needed.

A system of hard spheres with all particle volumes being equal, is a special example of the excluded volume gas. For this case we use the known results concerning the virial expansion, to find the validity limits of the low density approximation to the thermodynamics of the excluded volume gas.

## II. THERMODYNAMICS OF THE EXCLUDED VOLUME GAS

When modeling thermodynamics of the extended particles, a dimensional scale is the size of the excluded volumes in coordinate space, which is the input in the phenomenological approach, whereas a basic variable is the configuration integral,

$$C = \int d^{3N} x e^{-\sum_{\{i,j\}}^N U_{ij}(\mathbf{x}_i - \mathbf{x}_j)}, \quad (1)$$

where the summation is taken over all pairs of particles. A pair-wise potential in the exponent, is introduced such that,  $U_{ij}(\mathbf{x}_i - \mathbf{x}_j) = \infty$  when particles  $i$  and  $j$  overlap, and  $U_{ij}(\mathbf{x}_i - \mathbf{x}_j) = 0$  otherwise. The occurrence of particle overlap may depend on more variables than written explicitly in Eq. (1), e.g. it can depend on the orientations of the volumes associated with the particles. Then it is understood, that in Eq. (1), the integrations over these additional variables are also included.

The definition given in Eq. (1) is very general, as it is applicable for any shapes of the particles, which are not necessarily the same for all of them. The only requirement is, that the pair-wise potential must be define when two given particles overlap and when they do not.

Introducing the Mayer functions,

$$f_{ij}(\mathbf{x}_i - \mathbf{x}_j) = e^{-U_{ij}(\mathbf{x}_i - \mathbf{x}_j)} - 1, \quad (2)$$

in Eq. (1), expanding the integrand of  $C$  in powers of  $f_{ij}$  up to leading order, and performing the integrations, one finds, that

$$C = V^N \left( 1 - \frac{1}{V} \sum_{\{i,j\}} v_{i,j}(T) \right), \quad (3)$$

where

$$v_{i,j}(T) = - \int d^3 x f_{i,j}(x) \quad (4)$$

are the excluded volumes for pairs of particles, which in general, may depend on temperature.

The evaluation of the integrals over Mayer functions in Eq. (4) can be elementary, like e.g. for the gas of hard spheres, or may be more advanced, like for the gas of Lorentz contracted hard spheres [22]. In the following, we will not introduce any particular form of  $f_{ij}$ , and assume, that the integration in Eq. (4) has been done.

For further applications we consider the expression,  $T \log C$ . From Eq. (3), one finds, that to leading order in  $v_{ij}$ ,

$$T \log C = NT \log V - \frac{T}{V} \sum_{\{i,j\}} v_{i,j}(T). \quad (5)$$

This yields, in particular, the equation of state

$$\frac{pV}{NT} = \frac{V}{N} \frac{\partial \log C}{\partial V} \Big|_{N,T} = 1 + \frac{1}{VN} \sum_{\{i,j\}}^N v_{i,j}(T). \quad (6)$$

For the case of  $N$  identical particles with the unique two-particle excluded volume  $2v(T)$ , one finds,<sup>#1</sup> that in the large  $N$ -limit

$$T \log C = NT \left( \log \frac{V}{N} - \frac{N}{V} v(T) + 1 \right), \quad (7)$$

and

$$\frac{pV}{NT} = \frac{V}{N} \frac{\partial \log C}{\partial V} \Big|_{N,T} = 1 + v(T)n, \quad (8)$$

where  $n=N/V$ , is the particle density. Note, that when the particles are not identical, but all  $v_{i,j}(T)$  are equal, then only the combinatorial factor in the configuration integral changes, so that the equation of state remains unchanged.

In some approaches, the excluded volume depends on the momenta of the particles (cf. e.g. [22]). Then, the Mayer function for particles  $i$  and  $j$  depends on their momenta and it is necessary to average it over the Boltzmann distribution. As a result, the coefficients  $v_{i,j}$  become temperature dependent. Having made this change, the terms of first order in the excluded volumes are correctly reproduced. However, since the average of the square of the excluded volume is not equal to the square of its average, this simple method works only up to first order. This is enough for the low density approximation, however not for the more precise calculations needed when discussing its validity limits.

Let us consider an  $r$ -component gas and denote by  $N_i$  the number of particles of species  $i$ , with the total number of particles  $\sum_{i=1}^r N_i = N$ . Then, including the combinatorial factor,  $\prod_{i=1}^r N_i!$ , in the configuration integral (1), one finds, that in the large  $N_i$ -limit for all  $i = 1, \dots, r$ ,

$$T \log C = NT \log V - \frac{T}{2V} \sum_{i,j} N_i N_j v_{i,j}(T) - T \sum_i N_i (\log N_i - 1), \quad (9)$$

and

$$\frac{pV}{NT} = 1 + \frac{1}{2NV} \sum_{i,j} N_i N_j v_{i,j}(T). \quad (10)$$

The above result agrees with that obtained in Ref. [23]. However, contrary to the earlier approaches, there is no need to solve any transcendental equations to describe relevant thermodynamic functions. The reason is that we use a different set of parameters as independent variables. For the description of a state of the system any complete set of parameters is equally acceptable. E.g.

<sup>#1</sup> For  $N$  identical particles, one needs to introduce the combinatorial factor,  $1/N!$ , into the configurational integral (1).

for the single-component gas, one can use the parameters  $(T, p, N)$  or  $(T, V, \mu)$ . The fact, that in some process  $N$  changes at constant  $\mu$ , or the other way round, is irrelevant here. Indeed, the pressure, temperature and chemical potential are related by the following equation [23],

$$p = a(T)e^{-b(T)p+\mu/T}. \quad (11)$$

In Ref. [23] this equation is used to find  $p(T, \mu)$ , which requires the solution of a transcendental equation. The calculation of  $\mu(p, T)$ , from Eq. (11) is, on the other hand, elementary.

### III. MAXWELL IDENTITIES AND THEIR IMPLICATIONS

Elementary phenomenological thermodynamics will now be used to find the thermodynamic functions and parameters of the excluded volume gas at low density, in terms of the excluded volumes  $v_{i,j}(T)$ , and the parameters and thermodynamic functions of an ideal gas at the same temperature, pressure and numbers of particles. The parameters and thermodynamic functions of the ideal gas will be denoted with the superscript, *id*.

Let us consider first a single-component gas of particles with the excluded volume for a pair of particles,  $2v(T)$ . In this case, the parameter  $v(T)$  may be interpreted as the single-particle excluded volume. Now we introduce the excluded volume  $2\lambda v(T)$ . Then for  $\lambda = 0$ , we have an ideal gas, and for  $\lambda = 1$ , the gas we are interested in. The point is to find, how the thermodynamic functions and parameters change, when  $\lambda$  increases from zero, where the familiar relations for an ideal gas hold, to one. The changes are calculated at constant temperature, pressure and number of particles.

We consider the differential of the free enthalpy

$$dG = -SdT + Vdp + \mu dN + pNv(T)d\lambda, \quad (12)$$

where the last term on the right-hand side is the work done on the system when the excluded volume of each particle grows. This work is done against the pressure in the surrounding of the particle, which is equal to the external pressure  $p$ . The low density approximation is implied by the form of this term. In the exact theory, the excluded volumes can overlap and, therefore, the increase of the total excluded volume is slower than linear in  $N$ . For a low density gas, however, these overlaps can be neglected and formula (12) holds.

Since free enthalpy is a well-defined function of state, the following Maxwell identities are valid

$$\frac{\partial \mu}{\partial \lambda}|_{N,T,p} = \frac{\partial pNv(T)}{\partial N}|_{T,p,v} = pv(T), \quad (13)$$

$$\frac{\partial V}{\partial \lambda}|_{N,T,p} = \frac{\partial pNv(T)}{\partial p}|_{T,N,v} = Nv(T), \quad (14)$$

$$-\frac{\partial S}{\partial \lambda}|_{N,T,p} = \frac{\partial pNv(T)}{\partial T}|_{N,p,v} = pN \frac{dv(T)}{dT}. \quad (15)$$

Integrating the above equations at constant temperature, pressure and number of particles from  $\lambda = 0$  to  $\lambda = 1$ , one gets

$$\mu(T, p) = \mu^{id}(T, p) + pv(T) \quad (16)$$

$$V(T, p, N) = V^{id}(T, p, N) + Nv(T), \quad (17)$$

$$S(T, p, N) = S^{id}(T, p, N) - Np \frac{dv(T)}{dT}. \quad (18)$$

For the energy, this implies

$$E(T, p, N) = E^{id}(T, p, N) - TNp \frac{dv(T)}{dT}. \quad (19)$$

Equivalent expressions for thermodynamic functions have been obtained in Ref. [22], with the substitution,  $NT = pV$ , in the correction term in Eq. (19), which is legitimate at first order in  $v(T)$ .

For a Bose gas the well-known condition,  $\mu^{id}(T, p) < m$ , where  $m$  is the mass of a particle, implies that

$$\mu(T, p) < m + pv. \quad (20)$$

This upper bound is equal to the minimum free enthalpy needed to introduce one more particle into the system. It consists of the rest energy of the particle  $m$  and of the work  $pv(T)$ , at constant temperature and pressure, necessary to create the single particle excluded volume. This observation implies, that when  $v(T)$  decreases, the abundance of particles is enhanced.

Using the expressions for the parameters  $V, S, E$  of the excluded volume gas in terms of the parameters of the ideal gas from Eqs. [17,18,19], one finds the relations between the volume densities,

$$n = \frac{n^{id}}{1 + vn^{id}} \quad (21)$$

$$s = \frac{s^{id} - n^{id}p \frac{dv(T)}{dT}}{1 + vn^{id}} \quad (22)$$

$$\epsilon = \frac{\epsilon^{id} - n^{id}Tp \frac{dv(T)}{dT}}{1 + vn^{id}}, \quad (23)$$

of particle number, entropy and energy, respectively. The arguments  $(T, p, N)$ , have been skipped in these equations.

The above relations, which link the thermodynamics of the point-like and the excluded volume particle gases, are consistent with previous studies in Ref. [20], and are also very successful in the applications to thermal description of particle production yields in HIC [1–3].

The method introduced above, for the single-component gas, can be generalized to multi-component system. For an  $r$ -component gas the differential of the free enthalpy reads,

$$dG = -SdT + Vdp + \sum_i^r \mu_i dN_i \quad (24)$$

$$+ \frac{1}{2} \sum_{ij} p_i N_j v_{i,j}(T) d\lambda,$$

where we have introduced,  $p_i = \frac{N_i}{N}p$ , the relation which is valid for ideal gases, and is also legitimate, in the correction term due to excluded volumes.

The last term in Eq. (24), which describes the work done when the excluded volumes increase, can be interpreted as the sum of works done around all particles. The work done around a particle of type  $i$  is a sum of  $r$  terms: the work needed to free the volume  $v_{i,1}(T)d\lambda$  from particles of type one against the partial pressure  $p_1$ , the work needed to free the volume  $v_{i,2}(T)d\lambda$  from particles of type two against the partial pressure  $p_2$ , and so on, up to particles of type  $r$ . Thus, for the multi-component gas the one-particle excluded volume can be defined, but it does not have a simple geometric meaning.

Moreover, there is some ambiguity in dividing the work associated with the increase of the excluded volumes among the surroundings of the particles. Clearly, the term  $p_1 N_2 v_{12} d\lambda = p_2 N_1 v_{12} d\lambda$ , contributes to the work done in the surroundings of the particles of types 1 and 2. Following the interpretation presented above, for each particle of type 1 this work is  $\frac{p_2}{2} v_{12} d\lambda$ , and for each particle of type 2, it is  $\frac{p_1}{2} v_{12} d\lambda$ . According to Ref. [23], however, for  $r = 2$  and for the second kind of particles being point-like, the contribution of this term to the work done around a particle of type 1 is zero, and around a particle of type 2 it is  $p_1 v_{12}(T) d\lambda$ . Both these interpretations are consistent with our leading order expression for the differential of free enthalpy.

For an  $r$ -component gas, the Maxwell identities are generalized as

$$\frac{\partial \mu_i}{\partial \lambda} \Big|_{N,T,p} = \frac{\partial \left( \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N} v_{i,j} \right)}{\partial N_i} \Big|_{T,p,\lambda} \quad (25)$$

$$= p \sum_j \frac{N_j}{N} v_{i,j} - \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N^2} v_{i,j},$$

$$\frac{\partial V}{\partial \lambda} \Big|_{N,T,p} = \frac{\partial \left( \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N} v_{i,j}(T) \right)}{\partial p} \Big|_{N,T,\lambda} \quad (26)$$

$$= \frac{1}{2} \sum_{i,j} \frac{N_i N_j}{N} v_{i,j}(T),$$

$$-\frac{\partial S}{\partial \lambda} \Big|_{N,T,p} = \frac{\partial \left( \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N} v_{i,j}(T) \right)}{\partial T} \Big|_{N,p,\lambda} \quad (27)$$

$$= \frac{1}{2} \sum_{i,j} \frac{N_i N_j}{N} \frac{d v_{i,j}(T)}{dT},$$

where the subscript  $N$  indicates that all the multiplicities  $N_1, \dots, N_r$  are fixed. Integrating the above equations over  $\lambda$  from zero to one, at fixed temperature, pressure

and numbers of particles, one finds

$$\mu = \mu^{id} + p \sum_j \frac{N_j}{N} v_{i,j} - \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N^2} v_{i,j}, \quad (28)$$

$$V = V^{id} + \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N} v_{i,j}, \quad (29)$$

$$S = S^{id} - \frac{1}{2} p \sum_{i,j} \frac{N_i N_j}{N} \frac{d v_{i,j}}{dT}, \quad (30)$$

where the arguments in each case are  $(T, p, N_1, \dots, N_r)$ . Following, the discussion of the single-component gas, the generalization of Eqs. (21), (22) and (23), to the  $r$ -component gas, is rather transparent.

#### IV. VALIDITY OF THE LOW DENSITY APPROXIMATION

In the previous sections, we have derived the thermodynamic observables of a gas of extended particles, under the low density approximation. In order to determine reliably the validity limits of this approximation, it is necessary to compare our results with the exact solution, or with its good approximation. In the excluded volume gas problem, such comparison is possible for the gas of hard spheres of the same radius  $R$ , i.e. with the volume

$$v_0 = \frac{4}{3} \pi R^3. \quad (31)$$

The corresponding single-particle excluded volume is then,  $v = 4v_0$ . For  $R = 0$ , the gas reduces to the ideal gas, and the low density approximation yields the exact result. With increasing  $R$  the approximation deteriorates. The task is to find, up to what values of  $R$ , the low density approximation is reliable, within a given error margin.

The equation of state of the gas of hard spheres can be written in the form of a virial expansion,

$$\frac{p}{nT} = \sum_{i=1}^{\infty} b_i z^{i-1}; \quad z = nv. \quad (32)$$

The virial coefficients  $b_i$  are known explicitly [32, 33] for  $i = 1, \dots, 12$ , and they are quoted in Table 1.

$b_1$	1	$b_4$	0.286949	$b_7$	0.0130235	$b_{10}$	0.0004035
$b_2$	1	$b_5$	0.11025	$b_8$	0.004183	$b_{11}$	0.000123
$b_3$	0.625	$b_6$	0.0388819	$b_9$	0.001309	$b_{12}$	0.000037

Table 1. Virial coefficients for the gas of hard spheres from Refs. [32, 33].

Comparing Eqs. (8) and (32), it is clear, that the low density approximation is obtained when only the first two terms of the virial expansion are taken into account. The convergence of the virial expansion deteriorates when the



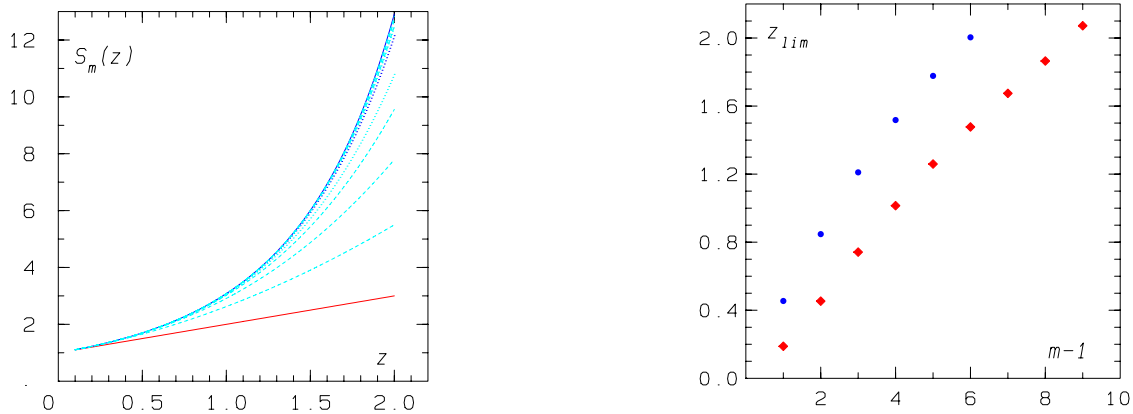


FIG. 1: Left-hand figure: The virial series from Eq. (38) truncated at  $m = 2, \dots, 12$ . The term  $m = 2$  corresponds to the lowest line. Right-hand figure: The limiting values  $z_{lim}$  of  $z$  for which the accuracy of  $S_m(z)$  from Eq. (38) with  $m=2, \dots, 10$ , relative to  $S_{12}(z)$ , is 2% (diamonds) and 10% (dotes).

parameter  $z$  increases. In order to find how good the convergence is, we must define the relevant range of  $z$ .

Obviously, the total volume of the spheres  $Nv_0$  must be smaller than the total volume of the gas. This implies, that

$$z < 4. \quad (33)$$

Moreover, it is not possible to pack hard spheres into a volume without leaving free spaces. Consequently for the closest packing

$$nv_0 = \frac{\pi}{3\sqrt{2}}. \quad (34)$$

An equivalent formula was conjectured by Kepler in 1611, then Gauss in 1831 demonstrated, that this is the closest packing possible, if the spheres form a lattice. The general proof is difficult, however can be handled by using computers. Its completion was announced by T.C. Hales in 2014. From this limit, one gets

$$z < 2.96. \quad (35)$$

Finally, it is plausible, that the hadrons form a fluid rather than a condensed phase. The condition for the freezing of the gas of hard spheres is,  $nv_0 = 0.494$  [32], which yields the limit,

$$z < 1.976. \quad (36)$$

Above this limit, the virial expansion for the gaseous phase of hard spheres system diverges. Consequently, one concludes, that the relevant region of  $z$ , is as follows

$$0 \leq z < 2. \quad (37)$$

We introduce the partial sum,

$$S_m(z) = \sum_{i=1}^m b_i z^{i-1}, \quad (38)$$

for  $m \geq 2$ . Knowing the values of virial coefficients, one can quantify, how good is the low density approximation for different values of  $0 \leq z \leq 2$ .

In Fig. 1-left, we show the sum  $S_m(z)$  for  $0 \leq z \leq 2$ , and for different  $m = 2, \dots, 12$ . The low density approximation is seen in this figure to describe the equation of state within less than few percent, for  $z < 0.5$ . With increasing  $z$  up to unity, the series is known to converge and the deviations are up to 30%, whereas for  $z > 1$  a large corrections to the low density approximation are to be expected. For  $z$  close to two, the virial expansion in Eq. (32) diverges.

In Fig. 1-right, we show for  $m = 2, \dots, 9$  the limiting values of  $z$  for which the accuracy of approximation of  $S_{12}(z)$  series by  $S_m(z)$  is two and ten percent, respectively. Since only the values of  $z < 2$  are of interest, the limits significantly exceeding  $z = 2$ , are not shown in this figure.

The Hadron Resonance Gas (HRG) formulated with excluded volume from Eq. (31), was applied to describe particle production in heavy ion collisions in a very broad energy range from SIS up to LHC [1]. All particle yields in heavy ion collisions were successfully quantified by the model along a common freezeout line in the temperature and baryon-chemical potential plane [1, 30]. This finding allows to quantify the conditions for the applicability of the low density approximation in the HRG of excluded volume particles, for the phenomenologically relevant system, along the freezeout line.

In applications, the total density of particles at chemical freezeout is temperature and chemical potential dependent, and consequently, changes with the collision energy  $\sqrt{s}$ . Thus,  $z$  in Eq. (32) is a function of  $\sqrt{s}$ , and of the chosen value of  $R$ . Let us introduce the function

$$z(\sqrt{s}, R) = \frac{16\pi}{3} n(\sqrt{s}) R^3, \quad (39)$$

where  $R$  is expressed in fermis.

In Fig. 2-left, we show the energy dependence of

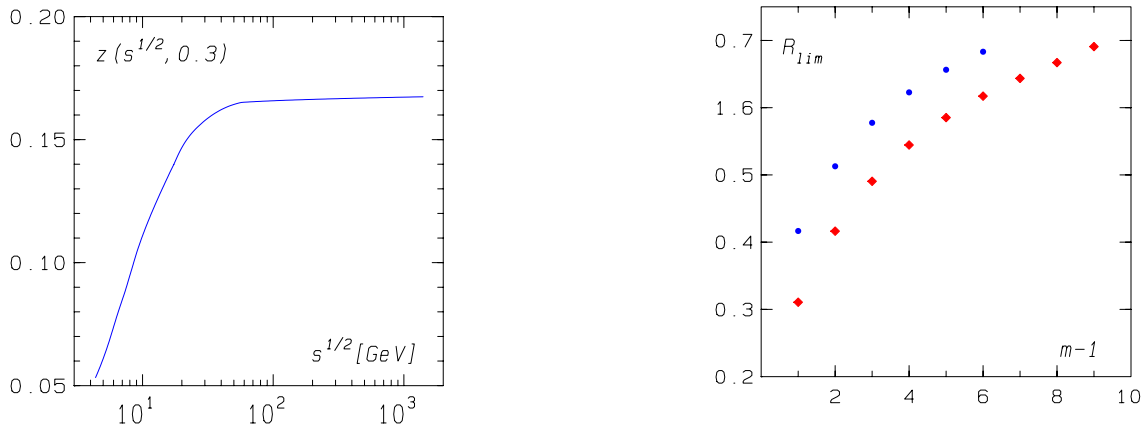


FIG. 2: Left-hand figure: Function  $z(\sqrt{s}, 0.3)$  from Eq. (39) along the chemical freezeout line extracted from particle yields data taken in central nucleus-nucleus collisions at different collision energies [1, 31]. Right-hand figure: The limiting values of  $R$  from Eq. (39) at  $n = 0.375 \text{ fm}^{-3}$ , for which the accuracy of the truncated series  $S_m(z)$  for  $m=2, \dots, 10$ , relative to  $S_{12}(z)$ , is 2% (diamonds) and 10% (dots).

$z(\sqrt{s}, 0.3)$  for the HRG, which includes all particles and resonances, listed by the Particle data Group. For simplicity, the radius  $R$  in Eq. (39) was assumed to be common for all particles and antiparticles with the value,  $R \simeq 0.3 \text{ fm}$ .

The function  $z(\sqrt{s}, 0.3)$  is small at low energies below AGS, increases monotonically with increasing energy, and at high energies beyond SPS, it saturates at the value slightly below 0.17. In our further estimates we will use the approximation  $z(\sqrt{s}, 0.3) = 0.17$ , or equivalently,  $n = 0.375 \text{ fm}^{-3}$ .

The upper bound of  $z$ , established in Eq. (36) implies, in general, the restriction on the radius of the hard core repulsion,

$$R < 0.680 \text{ fm}, \quad (40)$$

for density  $n = 0.375 \text{ fm}^{-3}$ . One could go beyond this limit, speculating that the virial series is asymptotic, in the sense that the sum of the first terms gives a reasonable approximation, in spite of the divergence of the series, but this is rather risky.

In Fig. 2-right, we show, for  $m = 2, \dots, 9$ , the limiting values of  $R$  for which the accuracy of the truncated series is two and ten percent, respectively. For  $R = 0.3 \text{ fm}$ , the low density approximation is good enough to get two percent accuracy. For  $R = 0.5 \text{ fm}$ , in order to get this accuracy, one would need to include two more terms in the virial expansion, while for ten percent accuracy, still one more term is needed.

To further improve the equation of state of a gas with hard core repulsion, it was proposed [20], to consider the equation of state in the following form

$$\frac{p}{nT} = \frac{1}{1 - nv(T)}. \quad (41)$$

This is equivalent to putting  $b_k = 1$  for all  $k$ , instead of neglecting them for  $k > 2$ , in the virial expansion (32). Since  $b_3 = 0.625$ , the error in the  $O(z^2)$  term is reduced

by almost a factor of two. The errors on the higher order terms are greatly increased, but for sufficiently small values of  $z$  this is unimportant. Comparing with the partial sum  $S_{12}(z)$ , one finds, that the improved low density approximation is better than the standard one for  $z < 0.312$ , i.e. for  $R < 0.37 \text{ fm}$ .

## V. SUMMARY AND CONCLUSIONS

We have discussed thermodynamics of the excluded volume particles at finite temperature and chemical potential, in the low density approximation. Assuming Boltzmann statistics, the influence of the excluded volume on an ideal gas thermodynamics has been derived from the change of the free enthalpy and by using the Maxwell identities.

The calculation of the relevant thermodynamic functions and parameters of the excluded volume gas, in terms of the two-particle excluded volumes and of the thermodynamic functions and parameters of the ideal gas, splits into two steps:

At the first step, it requires calculating the two-particle excluded volumes, which is rather standard, but one should keep in mind, that the conversion of the momentum dependence of the two-particle excluded volumes into their temperature dependence, works only in the low density approximation and under Boltzmann statistics. The single particle exclusive volume is a natural concept for the single-component gas. For multi-component systems, analogous excluded volumes appear, but there are ambiguities in their definitions and they have no simple geometrical meaning.

The thermodynamical calculation proposed here, which is the second step, is valid in the low density approximation. In order to go beyond this limit, it would be necessary to correct for possible overlaps of excluded volumes.

The physical picture behind the thermodynamic calculation, introduced here, is based on the observation, that by increasing excluded volume  $v(T)$  of particles, the work done on the system at constant temperature ( $T$ ), pressure ( $p$ ) and particles number ( $N$ ), equals the increase of the free enthalpy. Thus e.g., for the single-component gas, the free enthalpy stored in the excluded volumes is  $Npv$ . Its differential, yields the corrections to the entropy, volume and chemical potential of the gas, and through Maxwell identities, provides the relation between thermodynamics of the extended and point-like particle gases. This new approach, is also valid for the multi-component systems.

A problem of phenomenological importance is that of the validity limits for the low density approximation in heavy ion collisions. Assuming that all particles are hard spheres with the same radius  $R$ , we have shown, based on the virial expansion of the equation of state, that for

$R = 0.3$  fm the approximation, for the relevant range of parameters, is very good. For  $R = 0.5$  fm it introduces a significant error, and for  $R = 1$  fm, it is doubtful.

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- [1] For reviews see e.g., P. Braun-Munzinger, K. Redlich and J. Stachel, In \*Hwa, R.C. (ed.) et al.: Quark gluon plasma\* 491-599 (2003). A. Andronic, Int. J. Mod. Phys. A **29**, 1430047 (2014).
  - [2] J. Stachel, A. Andronic, P. Braun-Munzinger and K. Redlich, J. Phys. Conf. Ser. **509**, 012019 (2014).
  - [3] A. Andronic, P. Braun-Munzinger, K. Redlich and J. Stachel, J. Phys. G **38**, 124081 (2011).
  - [4] F. Becattini, P. Castorina, A. Milov and H. Satz, Eur. Phys. J. C **66**, 377 (2010).
  - [5] F. Karsch, K. Redlich and A. Tawfik, Phys. Lett. B **571**, 67 (2003).
  - [6] S. Ejiri, *et al.*, Nucl. Phys. A **774**, 837 (2006).
  - [7] A. Bazavov *et al.*, [HotQCD Collaboration], Phys. Rev. D **86**, 034509 (2012).
  - [8] S. Borsanyi, Z. Fodor, S. D. Katz, S. Krieg, C. Ratti and K. Szabo, JHEP **1201**, 138 (2012).
  - [9] R. Dashen, S. K. Ma and H. J. Bernstein, Phys. Rev. **187**, 345 (1969).
  - [10] R. Hagedorn, CERN yellow report 71-12, (1971).
  - [11] E. Beth and G. Uhlenbeck, Physica **4**, 915 (1937).
  - [12] W. Weinhold, B. Friman and W. Nörenberg, Phys. Lett. B **433**, 236 (1998).
  - [13] W. Broniowski, F. Giacosa and V. Begun, Phys. Rev. C **92**, no. 3, 034905 (2015).
  - [14] B. Friman, P. M. Lo, M. Marczenko, K. Redlich and C. Sasaki, Phys. Rev. D **92**, no. 7, 074003 (2015).
  - [15] F. Karsch and H. Satz, Phys. Rev. D **21**, 1168 (1980).
  - [16] R. Hagedorn and J. Rafelski, Phys. Lett. B **97**, 136 (1980).
  - [17] R. Hagedorn, Z. Phys. C **17**, 265 (1983).
  - [18] M. I. Gorenstein, V. K. Petrov, and G. M. Zinovjev, Phys. Lett. B **106**, 327 (1981).
  - [19] J. Cleymans, M. I. Gorenstein, J. Staltnacke, and E. Suhonen, Physica Scripta **48**, 277 (1993).
  - [20] D. H. Rischke, M. I. Gorenstein, H. Stöcker, and W. Greiner, Z. Phys. C **51**, 485 (1991).
  - [21] G. D. Yen, M. I. Gorenstein, W. Greiner, and S. N. Yang, Phys. Rev. **C56**, 2210 (1997).
  - [22] K.A. Bugaev et al., Phys. Lett. B **485**, 121 (2000).
  - [23] M.I. Gorenstein, A.P. Kostyuk and Ya.D. Krivenko, J. Phys. G **25**, L75 (1999).
  - [24] V. Vovchenko, D. V. Anchishkin and M. I. Gorenstein, J. Phys. A **48**, no. 30, 305001 (2015).
  - [25] J. I. Kapusta and K. A. Olive, Nucl. Phys. A **408**, 478 (1983).
  - [26] A. Andronic, P. Braun-Munzinger, J. Stachel and M. Winn, Phys. Lett. B **718**, 80 (2012).
  - [27] M. Albright, J. Kapusta and C. Young, Phys. Rev. C **90**, no. 2, 024915 (2014).
  - [28] M. Albright, J. Kapusta and C. Young, Phys. Rev. C **90**, no. 2, 024915 (2014).
  - [29] V. Vovchenko, D. V. Anchishkin and M. I. Gorenstein, Phys. Rev. C **91**, no. 2, 024905 (2015).
  - [30] J. Cleymans and K. Redlich, Phys. Rev. Lett. **81**, 5284 (1998).
  - [31] J. Cleymans, H. Oeschler, K. Redlich and S. Wheaton, Phys. Rev. C **73**, 034905 (2006).
  - [32] N. Clisby and B.N. McCoy, J. Stat. Phys. **bf 122** 15 (2006).
  - [33] L.V. Woodcock, Ar. Xiv cond-mat/0801-1559 (2008).