J Stat Phys (2008) 131: 597–611
DOI 10.1007/s10955-008-9513-3

# Two Hard Spheres in a Spherical Pore: Exact Analytic Results in Two and Three Dimensions

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Received: 3 August 2007 / Accepted: 27 February 2008 / Published online: 19 March 2008

**Abstract** The partition function and the one- and two-body distribution functions are evaluated for two hard spheres with different sizes constrained into a spherical pore. The equivalent problem for hard disks is addressed too. We establish a relation valid for any dimension between these partition functions, second virial coefficient for inhomogeneous systems in a spherical pore, and third virial coefficients for polydisperse hard spheres mixtures. Using the established relation we were able to evaluate the cluster integral $b_2(V)$ related with the second virial coefficient for the Hard Disc system into a circular pore. Finally, we analyse the behaviour of the obtained expressions near the maximum density.

**Keywords** Hard spheres · Configuration integral · Exact results · Confined fluids · Small systems · Inhomogeneous fluids · Spherical interfaces · Spherical wall

## 1 Introduction

The Hard Spheres (HS) and Hard Disks (HD) systems have attracted the interest of many physicists owing to they constitute prototypical simple fluids. Hard-core models, such as HD and HS are paradigmatic entropy driven systems. The search of their accurate equation of state is a long-standing problem of great importance in statistical mechanics [1–14]. The evaluation of virial coefficients [1–4, 15–23] and the analysis of phase transitions [14, 24, 25] are some of the principal subjects. The monodisperse systems as well as bidisperse and polydisperse ones have been extensively studied.

Recently special attention was paid to systems of few HS and HD confined in small vessels. The study of these inhomogeneous systems has shed light on aspects of loss of ergodicity [26], freezing and glass transitions [27, 28], thermodynamic second law [29], and other fundamental questions of statistical mechanics and thermodynamic [30, 31].

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Exact and approximate analytic properties of hard spherical bodies at different dimensions have been very important in the evolution of Free Energy Density Functional Theories for HS [32, 33]. Besides its own relevance the HS system is the starting point of several approximate theories of liquids [34, 35], therefore exact analytical results become still more interesting. Even though the apparent simplicity of HS and HD fluids, a few exact analytical results are known at present. For homogeneous systems the third and fourth virial coefficients for HS and HD have been calculated on the monodisperse [22, 36–39] and polydisperse systems [40–42], numerical results for higher order terms have also been obtained [43–45]. In addition, for inhomogeneous systems of HS into a spherical pore the analytic expression for the second virial coefficient is known [46]. Until present the exact canonical partition function of few bodies in a pore has been solved for two HD [47] and recently for two HS [48], in a rectangular box. Such results for equal sized particles were compared with dynamical simulation approaches [31, 49, 50]. The three HD in a rectangular box problem was analyzed [51] but the complete integration of its configuration integral (CI) could not be performed. Exact analytic results exist for the zero-dimensional limit, which corresponds to a so narrow cavity that is able to contain one particle at most. Also, several exact results have been obtained for the Hard Rod system (HR) the 1D version of HS [15, 52–54] which actually may be considered completely solved.

The aim of the present work is to evaluate the canonical partition function for two spherical particles in a spherical pore at two and three dimensions. Expressions for the free energy and one particle density are also derived. In Sect. 2 of this work we show that in the canonical ensemble a spherical pore containing HS or HD can be seen as another particle. We establish a relation between the CI of the canonical partition function for $N$ polydisperse hard spherical particles and the respective CI for $N-1$ particles inside a spherical vessel. In Sect. 3 we evaluate the canonical partition and density distribution functions for two HD and HS into a spherical pore. The obtained expressions apply to the non additive system of unequal sized particles in a pore, which includes the more usual and restrictive additive system. The analysis of the CI expressions and the thermodynamic properties of the system are shown in Sect. 4. Finally in Sect. 5 we present our conclusions.

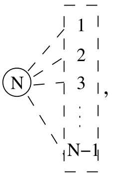
## 2 The In–Out Diagram Relation

In this section we will refer to non additive HS, but the discussion also applies to HD and to the equivalent system in any dimension. We are interested in a system with fixed number of particles ($N$) and temperature, then we will consider the canonical ensemble. In such ensemble the partition function factorizes into CI and a trivial kinetic terms. The CI of the system is characterized by the set of hard repulsion distances between each pair of particles $\{d_{ij}\}$. The system is additive only if the repulsion distances are $d_{ij} = R_i + R_j$ for positive radii of particles $\{R_i\}$. When the above relation is not fulfilled or any other particular assumption is made on the set $\{d_{ij}\}$ the system is non additive. We will analyze the CI for a $N$-HS system in an open (and virtually infinite) volume ($Q_N$). In order to obtain a non-null contribution to the integral, each pair of particles $ij$ must fulfill $r_{ij} > d_{ij}$, where $r_{ij}$ is the distance between particles $ij$. The above relation between $r_{ij}$ and $d_{ij}$ is a consequence of the exponential Boltzmann's factor. Then we have

$$Q_N = \int \dots \int \prod_{\langle ij \rangle} e_{ij}\, dr_1 \dots dr_N, \tag{1}$$

$$e_{ij} = \exp(-\phi_{ij}(r_{ij})) = \begin{cases} 0 & \text{if } r_{ij} \le d_{ij} \quad \text{(overlap)}, \\ 1 & \text{if } r_{ij} > d_{ij} \quad \text{(no overlap)}, \end{cases} \tag{2}$$

where $\phi_{ij}(r_{ij})$ is the hard core spherical potential for the pair of particles $ij$. In virial series and related subjects this factor is usually named $\widetilde{f}$, however in the framework of canonical partition function it appears naturally as an exponential function. Then we prefer to name it $e$ or $e_{ij}$ function or simply an $e$-bond, which will be plotted as a dashed segment. Such a $Q_N$ can be expressed as a Ree-Hoover's graph (also called modified star graph) [22, 36]

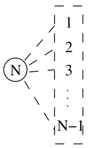
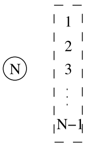
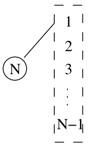
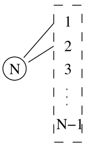
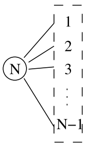
$Q_N =$  , (3)

where the $N$-th particle at (3) was drawn separately and its $e$-bond appears explicitly. The remaining $(N-1)$-particle system with $e$-bonds between pairs is outlined as a rectangular box. The relation between the Mayer $f$ function (or $f$-bond) and $e$ is given by

$$e_{ij} = 1 + f_{ij}, \tag{4}$$

$$f_{ij} = \begin{cases} -1 & \text{if } r_{ij} \le d_{ij} \quad \text{(overlap)}, \\ 0 & \text{if } r_{ij} > d_{ij} \quad \text{(no overlap)}. \end{cases} \tag{5}$$

We can transform each $e$-bond that links the pairs $Ni$ $(i : 1, \ldots, N-1)$ through the usual bond relation (4) performing the decomposition over particle $N$

$Q_N =$  $=$  $+$  $+$  $+ \cdots +$  . (6)

In this representation all the equivalent graphs on the left of (6) that takes into account permutations of the $N-1$ particles were omitted for clarity. It is possible to map this general problem to the $N$-HS additive system defined by the set of particle radii $\{R_i\}$ through the assignment $d_{ij} = R_i + R_j$. We define the additive/subtractive generalization of the additive system by the assignment $d_{ij} = |R_i \pm R_j|$, and specifying which set of pairs assume the minus sign. If we are interested in a system of additive spheres contained in a spherical vessel, as is our case, the exclusion distances between the center of the pore (which is the $N$-particle) and the center of each $i$-particle is $d_{iN} = (P - R_i)$, where $P$ is the radio of the spherical pore. We name to this specific additive/subtractive $\{d_{ij}\}$ as an additive-in-pore system.

Through the assignment of $\{d_{ij}\}$ for an additive-in-pore system, the last graph of (6) may be interpreted as the CI of $(N-1)$ additive HS in a pore $(Q^P_{(N-1)})$, due to the condition $r_{iN} \le d_{iN}$ with $1 \le i \le N-1$ imposed by the $f$-bonds in (5). Therefore $\{d_{iN}\}$ in that graph should be named inclusion (and not exclusion) distances. More precisely, last graph is $V_\infty$

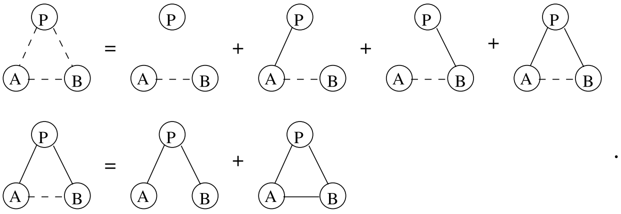
times $Q^P_{(N-1)}$, being $V_\infty$ the volume of the infinite space,

$$Q^P_{(N-1)} = V_\infty^{-1} \int \dots \int \prod_{\langle iN \rangle} f_{iN} \prod_{\langle ij \rangle} e_{ij}\, dr_1 \dots dr_{N-1} dr_N,$$
$$= \int_P \cdots \int \prod_{\langle ij \rangle} e_{ij}\, dr_1 \dots dr_{N-1}, \tag{7}$$

where the integration domains depend on pore size $P$. From now on, last graph of (6) will be called the $(N-1)$-in-pore graph, even in the more general framework of non additive systems. If we have $N-1$ equal (and additive) hard spheres of radio $\sigma/2$ into a pore of radio $P$, on the additive-in-pore picture we assign $d_{iN} = (P - \sigma/2)$. The same system can be analyzed as an entirely additive system with $d_{iN} = (P - \sigma) + \sigma/2$, if $P > \sigma$. We can obtain a Mayer type decomposition by transforming iteratively each $e$-bond in (3, 7) by an $f$-bond.

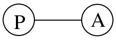
## 3 Two Bodies in a Pore

In this section we will apply the in–out relation for three bodies. In (8) we perform the simple decomposition over the particle $P$ and show the relation between the 2-particles-in-pore graph and the Mayer type graph

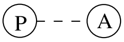


(8)

All the integrals in (8) may be directly evaluated, the easiest are the simply connected graphs that become factorable [55]. In the evaluation of different graphs we will use the notation of [42]. The exclusion/inclusion distances between pair of spheres are $AB$, $PA$, $PB$. Being that $\{AB, PA, PB\}$ are completely independent we deal with a non-additive system. Now we will briefly analyze the two bodies or one body in a pore problem. Assuming that $PA$ is the exclusion/inclusion distance between $A$ and $P$, we have for HS



$$= Sp(PA), \tag{9}$$

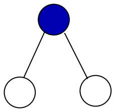
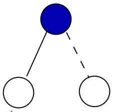
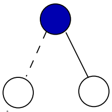
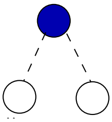


$$= V_\infty - Sp(PA), \tag{10}$$

$$Sp(R) = \frac{4\pi}{3} R^3, \tag{11}$$

where $Sp(R)$ is the volume of the sphere of radio $R$. Equation (9) is the accessible volume for a particle in a pore with inclusion distance $PA$ (eventually $PA = P - A$), which is related to the second coefficient of the pressure virial series [42] for a mixture of two HS gases. The CI of two spheres with a repulsion distance $PA$ (eventually $PA = P + A$) is given by (10), where $V_\infty$ is the volume of the total space. These obviously are not novel results.

**Table 1** Relation between the set of zeta functions $\{Z, Z'_{\mathrm{I}}, Z'_{\mathrm{II}}, Z''\}$ and the integration of one dark particle linked with two other white particles. Note that in $Z'_{\mathrm{I}}$ and $Z'_{\mathrm{II}}$, $R_1$ is the repulsion distance with the left white sphere, while $R_2$ corresponds to the right one, with $R_1 \geq R_2$

| | <br>$Z \equiv Z(r, R_1, R_2)$ | <br>$Z'_{\mathrm{I}}(r, R_1, R_2)$ | <br>$Z'_{\mathrm{II}}(r, R_1, R_2)$ | <br>$Z''(r, R_1, R_2)$ |
|---|---|---|---|---|
| HS | | $Sp(R_1) - Z$ | $Sp(R_2) - Z$ | $V_\infty - Sp(R_1) - Sp(R_2) + Z$ |
| HD | | $Cr(R_1) - Z$ | $Cr(R_2) - Z$ | $V_\infty - Cr(R_1) - Cr(R_2) + Z$ |

### 3.1 Two Spheres in a Pore

Now we focus on the two spheres in a pore problem and then we need to integrate the 2-in-pore graph (left-hand side graph on second row of (8)). Before integral evaluation we may state that some set of values $\{AB, PB, PA\}$ produce a zero sized graph, since $A$ and $B$ spheres may not enter into the pore $P$. If $AB > PA + PB$, then (2) and (5) imply that $r_{AB} > r_{PA} + r_{PB}$ thus avoiding the triangular relation and therefore the 2-in-pore graph becomes zero. From now on we will assume $AB \leq PB + PA$ and $PB \geq PA$, which is compatible with a pore of radius $P$ that contains two particles of radius $A$ and $B$ ($P \geq A + B$) with $A \geq B$.

For the calculus of density distribution it is useful introducing the function $Z(r, R_1, R_2)$ [42], which represents the volume of intersection of two spheres of radius $R_1$ and $R_2$ separated by a distance $r$ (assuming $R_1 \geq R_2$)

$$Z(r, R_1, R_2) = \begin{cases} Sp(R_2) & \text{for } r \leq R_1 - R_2, \\ I_2(r, R_1, R_2) & \text{otherwise}, \\ 0 & \text{for } r > R_1 + R_2, \end{cases} \tag{12}$$

$$I_2(r, R_1, R_2) = \frac{\pi}{12\,r}(R_1 + R_2 - r)^2\big(r^2 - 3(R_1 - R_2)^2 + 2r\,(R_1 + R_2)\big). \tag{13}$$

The function $I_2(r, R_1, R_2)$ is the volume in the partially overlapping configuration, and is symmetric through the permutation $R_1 \leftrightarrow R_2$. Other functions related with $Z(r, R_1, R_2)$ are summarized in Table 1 (the extended form definition of $Z$ functions is displayed in Appendix A). This set of functions is related with the integration of one spherical body linked with other two. As we have two types of bonds $e$ and $f$ there are four different Zeta functions. The use of these functions accounts us to write down two relevant distribution functions in a simple way: the pair distribution function $g_2(r_{AB})$ (in which the position of the pore center was integrated) and the one body distribution function of one particle $\rho_1(r_A)$. Both, $r_A$ and $r_B$ have their origin in the center of the pore

$$g_2(r_{AB}) = \left(Q_2^P\right)^{-1} e_{AB} Z(r_{AB}, PB, PA), \tag{14}$$

$$\rho_1(r_A) = \left(Q_2^P\right)^{-1}(-f_{PA}) \times \begin{cases} Z'_{\mathrm{I}}(r_A, PB, AB) & \text{for } AB \leq PB, \\ Z'_{\mathrm{II}}(r_A, AB, PB) & \text{for } AB > PB, \end{cases} \tag{15}$$

$$\rho_1(r_B) = \left(Q_2^P\right)^{-1}(-f_{PB}) \times \begin{cases} Z'_{\mathrm{I}}(r_B, PA, AB) & \text{for } AB \le PA, \\ Z'_{\mathrm{II}}(r_B, AB, PA) & \text{for } AB > PA, \end{cases} \tag{16}$$

where $\rho_1(r_B)$ is equivalent to $\rho_1(r_A)$ through the transformation $A \leftrightarrow B$ in (15). Performing the complete integration (for example, in (14)), we found the CI for two HS in a pore

$$Q_2^P = \int_{AB}^{PA+PB} 4\pi r_{AB}^2 Z(r_{AB}, PB, PA) dr_{AB}, \tag{17}$$

$$Q_2^P = \begin{cases} \frac{\pi^2}{18}(PA + PB - AB)^3(AB^3 + 3AB^2(PA + PB) \\ \quad - (PA + PB + 3AB)((PA - PB)^2 - 2PA\,PB)) & \text{for } AB \ge PB - PA, \\ \frac{16\pi^2}{9} PA^3(PB^3 - AB^3) & \text{for } AB < PB - PA, \end{cases} \tag{18}$$

which is valid as long as $AB \le PA + PB$, whereas $Q_2^P = 0$ if $AB > PA + PB$. There are explicit relations between the non additive, the additive, and the additive-in-pore systems. These are expressed in (19) and (20) respectively, which allow the map from one to other system when the triangular relation is fulfilled

$$\begin{aligned} AB &= A + B, & 2A &= AB + PA - PB, \\ PB &= P + B, & 2B &= AB - PA + PB, \\ PA &= P + A, & 2P &= -AB + PA + PB, \end{aligned} \tag{19}$$

$$\begin{aligned} AB &= A + B, & 2A &= AB - PA + PB, \\ PB &= P - B, & 2B &= AB + PA - PB, \\ PA &= P - A, & 2P &= AB + PA + PB. \end{aligned} \tag{20}$$

Thus, using (20) we may evaluate the *CI* of two additive spheres in a pore

$$Q_2^P = \left(\frac{4\pi}{3}\right)^2 (P - A - B)^3 \left(P^3 + 3PAB - A^3 - B^3\right), \tag{21}$$

above expression is valid for $P \ge A + B$, whereas $Q_2^P = 0$ if $P < A + B$. With the aim of check, using (8, 18, 19) we have obtained the third virial coefficient in the additive polydisperse system [41, 42] the right-hand side graph on second row of (8). In addition, in the case of equal sized spheres with radii $A$ we obtain

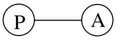
$$Q_2^P = \left(\frac{4\pi}{3}\right)^2 (P - 2A)^3 \left(P^3 + 3\,A^2 P - 2A^3\right), \tag{22}$$

$$Q_2^P = \left(\frac{4\pi}{3}\right)^2 (P - A)^6 - \left(\frac{4\pi}{3}\right)^2 (2A)^3 (P - A)^3 + \pi^2 (2A)^4 (P - A)^2 - \frac{\pi^2}{18}(2A)^6. \tag{23}$$

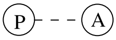
These two equations are equivalent. In (22) it seems clear the existence of a root on $Q_2^P$ at $P = 2A$. On the other hand, (23) shows the volume and area dependence, being $V = (4\pi/3)(P - A)^3$ and $Ar = 4\pi(P - A)^2$. A simple relation connects $Q_2^P$ with the second cluster integral $b_2(V)$ (which was stated in the second row of (8)); due to $b_2(V)$ has been analytically evaluated in previous works [46] we were able to check the validity of our result. Distribution functions for two additive spheres in a pore are shown in Appendix B.

### 3.2 Two Disks in a Pore

The two-dimensional problem of two HD in a circular pore is very similar to the problem of two HS in a spherical pore in three dimensions. Therefore we will briefly outline the aforementioned analysis concerning HD. In the two particle system or one disk in a pore, we obtain



$$= Cr(PA), \tag{24}$$



$$= V_\infty - Cr(PA), \tag{25}$$

$$Cr(R) = \pi R^2, \tag{26}$$

where $Cr(R)$ is the surface area of the circle with radio $R$. To maintain an unified point of view for both systems, HD and HS, we name the measure of the total space $V_\infty$ (although it is actually an area). Equation (24) is the accessible area for a particle in a pore with an inclusion distance $PA$ (eventually $PA = P - A$), which is related to the second coefficient of the pressure virial series on a mixture [42]. The configuration integral of two disks with repulsion distance $PA$ (eventually $PA = P + A$) is given by (25). For the two disk in a pore problem we have

$$Z(r, R_1, R_2) = \begin{cases} Cr(R_2) & \text{for } r \le R_1 - R_2, \\ I_2(r, R_1, R_2) & \text{otherwise}, \\ 0 & \text{for } r > R_1 + R_2, \end{cases} \tag{27}$$

$$\begin{aligned} I_2(r, R_1, R_2) = {} & R_1^2 \arccos\left[\frac{r^2 + R_1^2 - R_2^2}{2rR_1}\right] + R_2^2 \arccos\left[\frac{r^2 - R_1^2 + R_2^2}{2rR_2}\right] \\ & - \frac{1}{2}\sqrt{(r + R_1 + R_2)(-r + R_1 + R_2)(r - R_1 + R_2)(r + R_1 - R_2)}. \end{aligned} \tag{28}$$

The function $I_2(r, R_1, R_2)$ is the surface area in the partially overlapping configuration. The set of functions related with $Z(r, R_1, R_2)$ for disks are summarized in Table 1 (see the full extended form in Appendix A). On terms of the set of $Z$ functions it is possible to write down the pair distribution function $g_2(r_{AB})$, and the one body distribution function $\rho_1(r_A)$

$$g_2(r_{AB}) = \left(Q_2^P\right)^{-1} e_{AB} Z(r_{AB}, PB, PA), \tag{29}$$

$$\rho_1(r_A) = \left(Q_2^P\right)^{-1} (-f_{PA}) \times \begin{cases} Z'_{\mathrm{I}}(r_A, PB, AB) & \text{for } AB \le PB, \\ Z'_{\mathrm{II}}(r_A, AB, PB) & \text{for } AB > PB, \end{cases} \tag{30}$$

where $\rho_1(r_B)$ is equal to $\rho_1(r_A)$ under the transformation $A \leftrightarrow B$ in (30). Both, $r_A$ and $r_B$, have their origin in the center of the pore. Performing the complete integration of (29), for example, we find the partition function for two disks in a pore

$$Q_2^P = \int_{AB}^{PA+PB} 2\pi r_{AB} Z(r_{AB}, PB, PA)\, dr_{AB}, \tag{31}$$

$$Q_2^P = \begin{cases} \pi\kappa(PB^2+PA^2+AB^2)+\pi PB^2 PA^2\big(\pi -\ \arccos\big[\frac{PB^2+PA^2-AB^2}{2PBPA}\big]\big) \\ \quad -\pi PB^2 AB^2 \arccos\big[\frac{PB^2-PA^2+AB^2}{2PBAB}\big] \\ \quad -\pi PA^2 AB^2 \arccos\big[\frac{-PB^2+PA^2+AB^2}{2PAAB}\big] & \text{for } AB \geq PB-PA \\ \pi^2 PA^2(2PB^2-AB^2) & \text{for } AB < PB-PA, \end{cases} \tag{32}$$

$$\kappa = \frac{1}{4}\sqrt{(PB+PA+AB)(-PB+PA+AB)(PB-PA+AB)(PB+PA-AB)}, \tag{33}$$

where $\kappa$ represents the area of the triangle with sides $PB$, $PA$, $AB$. The arguments of the arccosine function in (32) are the internal angles of this triangle and their sum is $\pi$. In particular, for the additive in pore system with different sized disks, the previous equation can be simplified

$$\begin{aligned} Q_2^P &= 2\pi\kappa\left(P^2+A^2+B^2-P\,(A+B)+AB\right) \\ &\quad +\pi(P-B)^2(P-A)^2\left(\pi -\ \arccos\left[\frac{P^2-P(A+B)-AB}{(P-B)(P-A)}\right]\right) \\ &\quad -\pi(P-B)^2(A+B)^2 \arccos\left[\frac{P(A-B)+B^2+A\,B}{(P-B)(A+B)}\right] \\ &\quad -\pi(P-A)^2(A+B)^2 \arccos\left[\frac{-P(A-B)+A^2+A\,B}{(P-A)(A+B)}\right], \end{aligned} \tag{34}$$

$$\kappa = \sqrt{PBA(P-A-B)}. \tag{35}$$

Equation (34) applies in the case $P \geq A+B$, whereas $Q_2^P = 0$ if $P < A+B$. Using (8, 19) and (34) the third virial coefficient is correctly obtained in the additive polydisperse system [40]. By evaluating the above expressions for two disks with equal radii, we find

$$\begin{aligned} Q_2^P &= 2\pi A\sqrt{P(P-2A)}\left((P-A)^2+2A^2\right) \\ &\quad +2\pi(P-A)^2\left((P-A)^2-(2A)^2\right)\arccos\left[\frac{A}{P-A}\right], \end{aligned} \tag{36}$$

or

$$\begin{aligned} Q_2^P &= \left(\frac{128}{15}\sqrt{2}\pi A^{3/2}\right)(P-2A)^{5/2} \\ &\quad \times\left(1+\frac{19}{28A}(P-2A)+\frac{9}{224A^2}(P-2A)^2+O_3(P-2A)\right). \end{aligned} \tag{37}$$

Equation (36) has a root at $P = 2A$. Thus, in (37) we study the local behaviour of (36) near its root. Distribution functions for two additive disks in a pore is discussed in Appendix B.

## 4 Results

Let us make a few remarks on the new results obtained in this work. The configuration integral in (18, 32) are analytical functions of the system parameters in the domain

$AB, PA, PB > 0$ except when we focus on the non additive regime for $AB = PB - PA$. From here on we will restrict ourselves to $AB \le PA + PB$. For HS the configuration integral is polynomial, although it is not true for HD. In the two additive bodies in a pore system, the CI (21, 34) become null at close packing pore size $P_{CP} = A + B$, even though systems do not lose the rigid rotation degrees of freedom. Over all density range $P \in (P_{CP}, +\infty)$ CIs are monotonic analytic functions, therefore, none ergodic/non-ergodic transition happens and no van der Waals loop is expected [47, 51].

As we are interested in thermodynamic properties we analyze the Free energy of the system. Taken into account the kinetic factor, which contains the temperature dependence and usual thermodynamic relations we obtain the entropy $S$

$$S/k = -\beta F + \beta U = \ln\bigl(Q_2^P\bigr), \tag{38}$$

where $U$ is the energy of the ideal gas ($\beta U = 2, 3$ for two HD and HS, respectively). An important result derived from (21, 34) is that the Free Energy diverges logarithmically at $P_{CP}$. In order to obtain the pressure we need to define the system volume $V_{\text{sys}}$, both magnitudes are related by

$$\beta P_W = \left.\frac{d\ln(Q_2^P)}{dV_{\text{sys}}}\right|_{\beta} = \left.\frac{d\ln(Q_2^P)}{dP}(V'_{\text{sys}})^{-1}\right|_{\beta}, \tag{39}$$

where $V'_{\text{sys}}$ is the area of the surface enclosing $V_{\text{sys}}$. A particular volume definition implicitly induce a surface definition and then only modifies the surface area in (39). Although we are considering a small and very simple system composed by solely two hard spherical particles in a pore, it is not obvious which is the system volume. In principle, three different volumes may be considered, the volume accessible to the particle $A$, that is $V_A$; the same for the $B$ particle i.e. $V_B$ (see (9, 24)); and the volume of the free space in the pore. The later may be interpreted as the accessible volume for a particle with a vanishing radio and does not depend on the size of the chosen particle. We propose that $V_A$ and $V_B$ are the relevant volumes. In such a case the pressure on the wall became

$$\beta P_W = \left.\frac{d\ln(Q_2^P)}{dV_A}\right|_{\beta, V_B} + \left.\frac{d\ln(Q_2^P)}{dV_B}\right|_{\beta, V_A}, \tag{40}$$

$$\beta P_W = \rho_1(r_A = P - A) + \rho_1(r_B = P - B), \tag{41}$$

where (40, 41) are generalizations of Dalton's Law, and the equivalence between them is trivial.

For the sake of clarity from here on we will analyze the system of two equal sized particles, i.e. $B = A$ and $P_{CP} = 2A$. An interesting point about (23) for two HS, is the fact that it has the simplest possible shape. Indeed, each term has a very simple mean. The first term refers to the ideal gas, while the second term is clearly related to the first virial series correction (due to the interaction between particles) both of them appear in the homogeneous two body system. The third term is the product between the area of the system and the second surface virial coefficient at a planar hard wall $W_2$ [56–60]. Finally the fourth term forces the root of CI at $P = P_{CP}$. From (22) and (37) the CI goes to zero at $P_{CP}$ with multiplicity 3 and $5/2$ for HS and HD, respectively, and its value for two HD in a square box is 4 [47]. The mean of such values are probably related to the number of degrees of freedom lost at the *ultimate solid* or *CP* density. The logarithmic divergence of the Free Energy and (40) induce an order one pole at the maximum density. The equations of state for HS and HD are, respectively,

$$\beta P_W = \frac{1}{4\pi(P-1)^2}\left(\frac{3}{(P-2)} + \frac{5}{4} - \frac{9}{16}(P-2) + O_2(P-2)\right), \tag{42}$$

and

$$\beta P_W = \frac{1}{2\pi(P-1)}\left(\frac{5/2}{(P-2)} + \frac{19}{28} - \frac{149}{392}(P-2) + O_2(P-2)\right). \tag{43}$$

Here, we choose $A$ as the unit length. Note that (42) and (43) are truncated forms of the equation of state but the exact complete expressions can be easily derived from (22, 36, 40). It seems that some of the afore analyzed properties about the *ultimate solid* are valid for any finite number of particles $N$. That is, the CI must go to zero at some $P = P_{CP}(N)$ value with a multiplicity $\alpha_{-1}(N)$, which is a positive real number. This characteristic implies the logarithmic divergence of the Free Energy and induces an order one pole on $P_W$ at the maximum density. Then we conjecture that the equation of state near the *ultimate solid* density, takes the form

$$\beta P_W = \frac{1}{\Omega_D\,(P-1)^{D-1}}\left(\frac{\alpha_{-1}}{(P-P_{CP})} + \alpha_0 + \alpha_1(P-P_{CP}) + O_2(P-P_{CP})\right), \tag{44}$$

where $D$ is the dimensionality of the system and $\Omega_D$ is the solid angle integral. This last equation can be rewritten in the following way

$$\begin{aligned}\beta P_W \frac{V}{N} = {} & \frac{\alpha_{-1}}{ND}\left(1-(V_o/V)^{1/D}\right)^{-1} + \frac{\alpha_0(P_{CP}-1)}{ND} \\ & + \frac{\alpha_0+\alpha_1(P_{CP}-1)}{ND}(P-P_{CP}) + O_2(P-P_{CP}),\end{aligned} \tag{45}$$

where $V = \Omega_D\,(P-1)^D/D$ and $V_o = \Omega_D\,(P_{CP}-1)^D/D$. It is interesting to mention that first term of (45) is equal to the equation of state for the bulk solid phase of HS and HD systems at the highest density limit [61–64].

As was mentioned before, CIs are monotonic analytic functions, then the pressure is a monotonic analytic function of $P \in (2, +\infty)$ and does not develop a van der Waals loop. This is not the case for two and three HD in a rectangular box [31, 47, 51]. In Fig. 1 we display the equations of state (42, 43) as a function of pore size, both of them diverge at $P = 2$. For comparison, the equation of state for two HD system confined in a square box pore is also plotted, being the size parameter $P$ one half side of the square. The equation of state for two HD in a square box has two branches that are joined on a non analytic point at $P = 2$, while the divergence appears at $P = P_{CP} = 1 + 1/\sqrt{2}$ and takes place when the discs are fitted on the two opposite vertices of the box. These two equations of state for two HD on different shaped pores converge as the pore size grows. Present results of $\beta P_W$ for HS perfectly agree with the Monte Carlo results [65] (extracted from Fig. 1 on that work) which were obtained by numerical integration of the same equations.

The density distribution of one HS particle corresponding to a system with two equal sized HS (see (56) in Appendix B) has been plotted on Fig. 2. Density profiles for several radii of the pore $P$ are shown in this figure by a solid line, each curve has a maximum at $r = P - 1$ and fall off to zero discontinuously for $r > P - 1$. Density distributions change gradually from the complete radial localization, when $P = P_{CP} = 2$ to the quasi-uniform

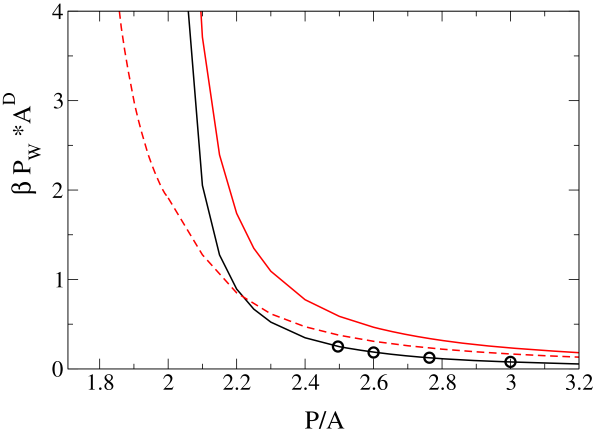


**Fig. 1** (Color online) Equation of state for two HD and HS. *Continuous curves* correspond to HD (*up*) and HS (*down*) calculated in the present work. For comparison, we also include the results for: two HD in a square box [47] (*dashed line*), and Monte Carlo simulation for two HS in a spherical pore [65] (*circles*)

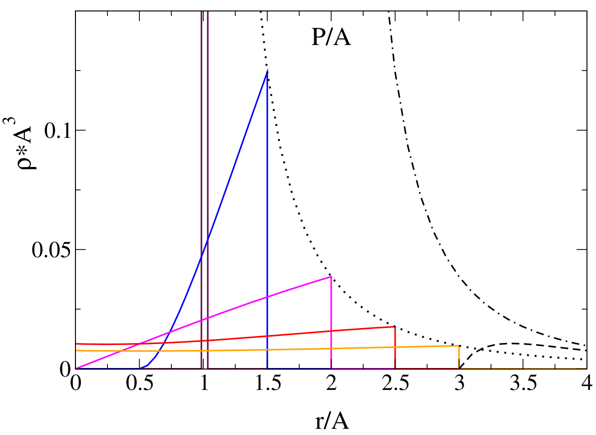


**Fig. 2** (Color online) Density profiles for two HS system as a function of $r$ for various $P$ values. Both, $P$ and $r$ are in units of $A$. *Continuous lines* indicate results for pore radii $P = 2.01, 2.5, 3, 3.5, 4$. *Other curves* are referred to top abscissa axis. *Dashed curve* shows density at central point $\rho(P, r = 0)$, whereas *dot-dashed curve* corresponds to density at contact $\rho(P, r = P - 1)$. The *dotted curve* is the shifted *dot-dashed* one (see text)

distribution at $P = 4$. For a pore size $P > 3$ the density at $r = 0$ becomes non null and a constant density plateau develops for $0 < r < P - 3$. The dashed and dot-dashed curves show the evolution of the minimum (at $r = 0$) and the maximum (at $r = P - 1$) values of the density profiles as a function of pore radio $P$. The dotted curve indicates once again the contact density $\rho(P, r = P - 1)$, which is related to the pressure of the system by (41), but now as a function of $P - 1$. These three lines are functions of pore size, and refer to the top abscissa axis. We find that all these properties are also exhibited by the two HD in a circular pore system. We can mention that at $P = 3.4069$ the central density reaches its maximum value, which is close but greater than half of the density at contact.

The complete dependence of the second cluster integral $b_2(V)$ for a system of particles contained into a spherical vessel is related to the second virial coefficient by $B(V) = -b_2(V)$. From (8) we obtain

$$V b_2(V) = \frac{1}{2}\left(Q_2^P - V^2\right). \tag{46}$$

Using (22) we derived $b_2(V)$ for two equal HS in a spherical pore,

$$Vb_2(V) = b_2 V + 2\pi A^4 Ar - \left(\frac{4}{3}\pi\right)^2 A^6, \tag{47}$$

where $V = (\frac{4\pi}{3})(P-A)^3$, $b_2 = -\frac{2\pi}{3}(2A)^3$, and $Ar = 4\pi(P-A)^2$. As was discussed before (in Sect. 3.1) this expression was previously calculated in literature [46]. For the first time, we present the complete dependence of $b_2(V)$ for a HD system into a circular vessel. Then, using (36) and (46)

$$Vb_2(V) = b_2 V + \frac{1}{3}(2A)^3 Ar - \frac{1}{60}\pi(2A)^5 \frac{1}{(P-A)} + O_3\left(\frac{1}{P-A}\right), \tag{48}$$

where $V = \pi(P-A)^2$, $b_2 = -\frac{1}{2}\pi(2A)^2$, and $Ar = 2\pi(P-A)$. Actually $V$ is the accessible area (see (26)) and $Ar$ is its perimeter. Although in (48) we choose express $b_2(V)$ as a truncated series expansion of the complete expression, the exact form of $b_2(V)$ (for two HD and HS with equal or unequal size) may be obtained with the same procedure. The factor multiplying $Ar$ is the second virial coefficient of the surface tension (in fact the linear tension) $W_2$ [56–60], as far as we know it was not previously evaluated. The third term is the first finite size-curvature correction and it has a minus one power on $(P-A)$, which is two units smaller than the former term as happens in HS at (47). All the forthcoming terms of the series (not shown in (48)) are negatives with odd degree in $(P-A)^{-1}$. The expansion of (48) converges so quickly that, if we truncate at fifth order, the deviation is smaller than one percent in the worst case for $P = 2A$, when the system attains its highest density.

We can mention that CI of two Hard Rod system confined into a segment (the one dimensional equivalent of two HD and HS in a spherical pore) is easy to evaluate analytically [15, 52–54]. Then, this work provides a set of analytic properties for dimensions $D = 1, 2$ and 3, and any general approximate theory for inhomogeneous confined liquid phase [33] may be compared with these exact results.

## 5 Conclusions

We have established a deep relation between CI of a $N$-polydisperse system of hard spheres, CI of a $(N-1)$-polydisperse system in a spherical shaped pore, and Mayer type diagrams [35, 55]. The relation valid in any dimension was used in the present work only for checking purposes. A similar relation was stated previously in the Gran Canonical Ensemble [46].

The canonical partition and distribution functions of two HS and two HD in a spherical shaped pore were analyzed in an exact analytic framework. The analysis presented here was made assuming a very general system of two HD and HS, with different sizes and non additive potential. The obtained exact CI expression allow us to evaluate the thermodynamic observables of the system (Free Energy, Energy, Entropy, Pressure, etc.) [35, 55]. In addition, we investigate the analytic properties of CI and the equation of state at the *ultimate solid* or *cp* density, and we compare our results with the known exact result of two HD confined in a square box. Based on this study we present a general proposal for the equation of state at the *ultimate solid*, in a system of $N$ hard spherical particles contained into a pore. We also find the second virial coefficient for a HD system in a circular pore. Future works will involve the analytical evaluation of the CI for two particles in other simple shaped pores, and the analytic study of the CI for three particles in spherical pore.

**Acknowledgements** I am grateful to Dr. Leszek Szybisz and Dr. Gabriela Castelletti for all their suggestions. This work was supported in part by the Ministry of Culture and Education of Argentina through Grants CONICET PIP No. 5138/05 and UBACyT No. X298.

## Appendix A: Expanded Definition of $Z'_{\mathrm{I}}$, $Z'_{\mathrm{II}}$ and $Z''$

In this appendix it is showed the expanded form of the $Z(r, R_1, R_2)$ related set of functions for spherical bodies. We name $D$ to the dimensionality of space and we assume that $R_1 \geq R_2$. In the present notation an unified point of view for spheres and disks is chosen. The family of $Z$ functions in arbitrary dimensions reads,

$$Z(r, R_1, R_2) = \begin{cases} I_1^{(D)}(R_2) & \text{for } r \leq R_1 - R_2, \\ I_2^{(D)}(r, R_1, R_2) & \text{otherwise}, \\ 0 & \text{for } r > R_1 + R_2, \end{cases} \tag{49}$$

$$Z'_{\mathrm{I}}(r, R_1, R_2) = \begin{cases} I_1^{(D)}(R_1) - I_1^{(D)}(R_2) & \text{for } r \leq R_1 - R_2, \\ I_1^{(D)}(R_1) - I_2^{(D)}(r, R_1, R_2) & \text{otherwise}, \\ I_1^{(D)}(R_1) & \text{for } r > R_1 + R_2, \end{cases} \tag{50}$$

$$Z'_{\mathrm{II}}(r, R_1, R_2) = \begin{cases} 0 & \text{for } r \leq R_1 - R_2, \\ I_1^{(D)}(R_2) - I_2^{(D)}(r, R_1, R_2) & \text{otherwise}, \\ I_1^{(D)}(R_2) & \text{for } r > R_1 + R_2, \end{cases} \tag{51}$$

$$Z''(r, R_1, R_2) = \begin{cases} V_\infty - I_1^{(D)}(R_1) & \text{for } r \leq R_1 - R_2, \\ V_\infty - I_1^{(D)}(R_1) - I_1^{(D)}(R_2) + I_2^{(D)}(r, R_1, R_2) & \text{otherwise}, \\ V_\infty - I_1^{(D)}(R_2) - I_1^{(D)}(R_2) & \text{for } r > R_1 + R_2, \end{cases} \tag{52}$$

where $I_1^{(D)}(R_1)$ is the volume of the $D$-sphere with radio $R_1$ (the expression for $D = 3$ and $D = 2$ are in (11, 26)), and $I_2^{(D)}(r, R_1, R_2)$ is the volume of intersection of two $D$-spheres with radii $R_1$ and $R_2$, separated by a distance $r$ in the partial overlapping configuration (the expression for $D = 3$ and $D = 2$ are in (13, 28)).

## Appendix B: Distribution Functions in the Additive-in-Pore System

Assuming an additive-in-pore system, i.e. $AB = A + B$, $PA = P - A$ and $PB = P - B$, the distribution functions for two HD or HS into a spherical pore (from (14, 15) and (29, 30)) take the form

$$g_2(r_{AB}) = \left(Q_2^P\right)^{-1} \begin{cases} I_2^{(D)}(r_{AB}, P - B, P - A) & \text{for } A + B \leq r_{AB} \leq 2P - (A + B), \\ 0 & \text{otherwise}, \end{cases} \tag{53}$$

$$\rho_1(r_A) = \left(Q_2^P\right)^{-1} \begin{cases} \max[I_1^{(D)}(P - B) - I_1^{(D)}(A + B), 0] & \text{for } 0 \leq r_A \leq \mathrm{abs}[P - A - 2B], \\ I_1^{(D)}(P - B) - I_2^{(D)}(r_A, P - B, A + B) & \text{otherwise}, \\ 0 & \text{for } r_A > P - A, \end{cases} \tag{54}$$

the $\rho_1(r_B)$ function can be found by the permutation of symbols $A \leftrightarrow B$ in (54). If we have equal radii spherical particles, expressions become

$$g_2(r_{AA}) = \left(Q_2^P\right)^{-1} \begin{cases} I_2^{(D)}(r_{AA}, P-A, P-A) & \text{for } 2A \le r_{AA} \le 2(P-A), \\ 0 & \text{otherwise}, \end{cases} \tag{55}$$

$$\rho_1(r_A) = \left(Q_2^P\right)^{-1} \begin{cases} \max[I_1^{(D)}(P-A) - I_1^{(D)}(2A), 0] & \text{for } 0 \le r_A \le \text{abs}[P-3A], \\ I_1^{(D)}(P-A) - I_2^{(D)}(r_A, P-A, 2A) & \text{otherwise}, \\ 0 & \text{for } r_A > P-A. \end{cases} \tag{56}$$

Although the existence of the exact one body distribution function for two HS in a spherical pore is mentioned in [66], neither explicit expression was shown, nor further analysis was performed there.

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